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Assessing denitrification in groundwater



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Betrachtungen zur Abschätzung von Denitrifikation im Grundwasser

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Table of Contents

1	INTRODUCTION	- 12 -
2	NITROGEN IN THE ENVIRONMENT	- 15 -
2.1	NITROGEN CYCLE	- 15 -
2.1.1	<i>Ammonification (mineralization)</i>	- 16 -
2.1.2	<i>Nitrification</i>	- 17 -
2.1.3	<i>Denitrification</i>	- 18 -
2.1.4	<i>Nitrate ammonification</i>	- 20 -
2.1.5	<i>Immobilisation</i>	- 20 -
2.2	NITROGEN LEACHING FROM SOILS AND ITS RELEVANCE FOR GROUNDWATER QUALITY.....	- 21 -
2.2.1	<i>Sources of nitrogen for leaching from soils</i>	- 21 -
2.2.2	<i>Seasonal aspects of nitrogen leaching</i>	- 23 -
2.2.3	<i>Runoff processes and nitrate transport</i>	- 23 -
2.2.4	<i>Nitrate transport under the aspect of heterogeneous groundwater flow pattern</i>	- 27 -
2.2.5	<i>Relevance for groundwater quality</i>	- 29 -
2.3	IDENTIFICATION OF DENITRIFICATION PROCESSES IN SUBSURFACE NATURAL ZONE	- 30 -
2.3.1	<i>Kinetics of denitrification</i>	- 30 -
2.3.2	<i>Current methods for estimation of in-situ denitrification rates</i>	- 31 -
2.3.3	<i>Denitrification in unsaturated zones</i>	- 34 -
2.3.4	<i>Denitrification in saturated zones</i>	- 42 -
2.3.5	<i>Liquid film theory for denitrification processes in subsurface zone</i>	- 48 -
2.3.6	<i>Alternative nitrate reduction processes</i>	- 50 -
2.4	CONSEQUENCES FROM KEY FACTORS INFLUENCING DENITRIFICATION ACTIVITY.....	- 51 -
2.5	DENITRIFICATION IN NITROGEN EMISSION ESTIMATION TOOLS	- 53 -
3	CHARACTERISATION OF THE CASE STUDY REGIONS	- 57 -
3.1	INTRODUCTION AND GENERAL CHARACTERISATION	- 57 -
3.2	THE YBBS CATCHMENT	- 60 -
3.2.1	<i>Catchment morphology</i>	- 60 -
3.2.2	<i>Land use characteristics</i>	- 61 -
3.2.3	<i>Geological conditions</i>	- 63 -
3.3	THE WULKA CATCHMENT	- 65 -
3.3.1	<i>Catchment morphology</i>	- 65 -
3.3.2	<i>Land use characterisation</i>	- 66 -
3.3.3	<i>Geological conditions</i>	- 68 -
4	WATER BALANCE CALCULATIONS USING THE SWAT 2000 MODEL	- 70 -
4.1	INTRODUCTION AND MOTIVATION	- 70 -
4.2	MODEL DESCRIPTION.....	- 71 -
4.3	INPUT DATA	- 72 -
4.3.1	<i>Climatic data</i>	- 72 -
4.3.2	<i>Data about waste water treatment plants (wwtp)</i>	- 73 -
4.4	MODEL CALIBRATION AND VALIDATION.....	- 73 -
4.4.1	<i>Main definitions</i>	- 73 -
4.4.2	<i>Estimation of the model performance</i>	- 74 -
4.4.3	<i>Modifications and catchment specific definitions</i>	- 74 -
4.4.4	<i>Model calibration</i>	- 75 -
4.4.5	<i>Model performance for the Ybbs catchment</i>	- 77 -
4.4.6	<i>Model performance for the Wulka catchment</i>	- 83 -
4.5	CALCULATED WATER BALANCES FOR THE YBBS AND THE WULKA CATCHMENT.....	- 89 -
4.5.1	<i>Water balance of the Ybbs catchment</i>	- 89 -
4.5.2	<i>Evaluation of the calculated water balance for the Ybbs catchment</i>	- 92 -
4.5.3	<i>Water balance of the Wulka catchment</i>	- 95 -
4.5.4	<i>Evaluation of the calculated water balance for the Wulka catchment</i>	- 99 -
4.5.5	<i>Seasonality of water balance and runoff components</i>	- 101 -
4.6	CONCLUSIONS IN TERMS OF WATER BALANCE CALCULATIONS.....	- 108 -

5	GROUNDWATER AND SURFACE WATER CHARACTERISTICS	- 109 -
5.1	MOTIVATION AND BACKGROUND	- 109 -
5.2	INDICATIONS FOR NITROGEN LOSS VIA DENITRIFICATION IN THE GROUNDWATER OF THE WULKA CATCHMENT	- 110 -
5.3	INDICATIONS FOR NITROGEN LOSS VIA DENITRIFICATION IN THE GROUNDWATER OF THE YBBS CATCHMENT- 119 -	
5.4	SUMMARY AND CONCLUSIONS	- 128 -
6	NITROGEN EMISSION ESTIMATIONS AT THE CATCHMENT SCALE.....	- 130 -
6.1	INTRODUCTION AND MOTIVATION	- 130 -
6.2	NITROGEN EMISSION ESTIMATIONS USING THE SWAT 2000 MODEL	- 131 -
6.2.1	<i>Definitions in SWAT 2000 model.....</i>	- 131 -
6.2.2	<i>Results from nitrogen emission calculations.....</i>	- 133 -
6.2.3	<i>Conclusions.....</i>	- 139 -
6.3	NITROGEN EMISSION CALCULATIONS USING THE MONERIS MODEL.....	- 140 -
6.3.1	<i>Model description.....</i>	- 140 -
6.3.2	<i>Model definitions for runoff components.....</i>	- 141 -
6.3.3	<i>Consideration of nitrogen losses via denitrification in groundwater.....</i>	- 142 -
6.3.4	<i>Estimation of nitrogen emissions for the Ybbs and the Wulka catchment.....</i>	- 144 -
6.4	DISCUSSION AND CONCLUSIONS FOR ESTIMATING NITROGEN EMISSIONS.....	- 149 -
7	QUANTIFICATION OF GROUNDWATER RESIDENCE TIMES AND THE INFLUENCE ON NITROGEN EMISSIONS FROM GROUNDWATER TO SURFACE WATERS	- 153 -
7.1	MOTIVATION.....	- 153 -
7.2	ESTIMATION OF GROUNDWATER RESIDENCE TIMES USING TRITIUM ANALYSES.....	- 153 -
7.2.1	<i>Wulka catchment.....</i>	- 153 -
7.2.2	<i>Ybbs catchment.....</i>	- 154 -
7.2.3	<i>Conclusions.....</i>	- 155 -
7.3	CALCULATION OF SPATIAL DISTRIBUTIONS OF THE GROUNDWATER RESIDENCE TIME USING GROUNDWATER TABLE OBSERVATIONS.....	- 156 -
7.3.1	<i>Development of the approach.....</i>	- 156 -
7.3.2	<i>Application for the Wulka catchment.....</i>	- 161 -
7.3.3	<i>Application for the Ybbs catchment.....</i>	- 169 -
7.4	CONCLUSIONS	- 178 -
8	SUMMARY AND CONCLUSIONS.....	- 181 -
9	REFERENCES	- 189 -
10	APPENDIX	- 198 -
10.1	GROUNDWATER RESIDENCE TIME CALCULATIONS FOR THE WULKA CATCHMENT	- 198 -
10.2	GROUNDWATER RESIDENCE TIME CALCULATIONS FOR THE YBBS CATCHMENT.....	- 202 -

Table of Figures

FIGURE 1: NITROGEN CYCLE IN SOILS (FROM NEITSCH ET AL. 2001)	- 15 -
FIGURE 2: SCHEMATIC RELATIONSHIP BETWEEN SPATIAL AND TEMPORAL PROCESS SCALES FOR A NUMBER OF HYDROLOGIC PROCESSES (FROM GRAYSON ET AL. 2001, REPRODUCED FROM BLÖSCHL ET AL. 1995)	- 24 -
FIGURE 3: VISUALISATION OF THE CONCEPT ON RUNOFF COMPONENTS AND THEIR TIME DELAY IN TERMS OF CONTRIBUTION TO SURFACE WATERS (FROM HEINECKE 2004, MODIFIED)	- 26 -
FIGURE 4: CONNECTION BETWEEN DISTANCES OF CATCHMENT AREAS TO SURFACE WATERS AND GROUNDWATER RESIDENCE TIME (FROM QUAST ET AL. 2001, MODIFIED).....	- 27 -
FIGURE 5: REASONS FOR SCALE-RELATED DISPERSION EFFECTS (MICRO SCALE DISPERSION BY GRANULAR STRUCTURE – LEFT; SMALL SCALE MACRO DISPERSION – MIDDLE; BIG SCALE MACRO DISPERSION – RIGHT) (FROM OHLENBUSCH 2000, MODIFIED)	- 28 -
FIGURE 6: RELATION BETWEEN REACTION RATE AND LIMITING SUBSTRATE CONCENTRATION OF AN ENZYME REACTION OF A FIRST ORDER KINETIC (FROM KREUZINGER 2005).....	- 30 -
FIGURE 7: DEPENDENCE BETWEEN NITROGEN ISOTOPE RATIO IN THE RESIDUAL NITRATE ($\delta^{15}N$) AND THE FRACTION OF THE UNREACTED RESIDUAL NITRATE ($LN(F_{NO3})$) IN DENITRIFICATION IN THE GROUNDWATER OF THE ‘FUHRENBERGER FELD’ (FROM BÖTTCHER ET AL. 1990)	- 32 -
FIGURE 8: CHANGES IN VERTICAL NITRATE PROFILE IN GROUNDWATER DUE TO DENITRIFICATION PROCESSES IN SUBSURFACE ZONE (FROM ROHMANN ET AL. 1985, MODIFIED)	- 43 -
FIGURE 9: GENERAL RELATION BETWEEN THE COMPLEXITY OF MODELS, MODEL TYPE AND THE GENERAL OUTPUT (FROM SCHOUMANS ET AL. 2003).....	- 54 -
FIGURE 10: LOCATION OF THE CASE STUDY REGIONS IN AUSTRIA	- 57 -
FIGURE 11: ELEVATION CHARACTERISTICS AND OVERVIEW ON THE LOCATION OF THE GROUNDWATER AND SURFACE WATER OBSERVATION STATIONS FOR THE YBBS CATCHMENT	- 60 -
FIGURE 12: LAND USE CHARACTERISTICS OF YBBS CATCHMENT	- 61 -
FIGURE 13: DEVELOPMENT OF ANIMAL UNITS AND MINERAL FERTILIZER PER HECTARE OF AGRICULTURAL AREA APPLICATION IN THE YBBS CATCHMENT (FROM ZESSNER ET AL. 2004).....	- 62 -
FIGURE 14: REGIONAL DISTRIBUTION OF NITROGEN SURPLUSES IN THE YBBS CATCHMENT FOR THE YEAR 1999 (FROM ZESSNER ET AL. 2004).....	- 63 -
FIGURE 15: GROUNDWATER THICKNESS AND ISOLINES OF POROUS AQUIFER IN DANUBE RIVER VALLEY IN RELATION TO BOUNDARIES OF THE YBBS CATCHMENT.....	- 64 -
FIGURE 16: FRACTION OF THE GEOLOGICAL FORMATION IN THE YBBS CATCHMENT	- 64 -
FIGURE 17: ELEVATION CHARACTERISTICS AND OVERVIEW ON THE LOCATION OF THE GROUNDWATER AND SURFACE WATER MEASUREMENT STATIONS FOR THE WULKA CATCHMENT.....	- 65 -
FIGURE 18: LAND USE CHARACTERISTICS OF THE WULKA CATCHMENT	- 66 -
FIGURE 19: DEVELOPMENT OF ANIMAL UNITS AND MINERAL FERTILIZER PER HECTARE OF AGRICULTURAL AREA APPLICATION IN THE WULKA CATCHMENT (FROM ZESSNER ET AL. 2004)	- 67 -
FIGURE 20: REGIONAL DISTRIBUTION OF NITROGEN SURPLUSES IN THE WULKA CATCHMENT FOR THE YEAR 1999 (FROM ZESSNER ET AL. 2004).....	- 68 -
FIGURE 21: FRACTION OF THE GEOLOGICAL FORMATION IN THE WULKA CATCHMENT.....	- 69 -
FIGURE 22: NUMBER OF SOIL CLASSES LIMITING HRU DEFINITIONS IN THE SWAT 2000 MODEL FOR SWAT PROJECT WITH 205 HRU’S FOR THE YBBS CATCHMENT	- 77 -
FIGURE 23: NUMBER OF SOIL CLASSES LIMITING HRU DEFINITIONS IN THE SWAT 2000 MODEL FOR SWAT PROJECT WITH 428 HRU’S FOR THE YBBS CATCHMENT	- 78 -
FIGURE 24: WATERSHED DELINEATION FOR THE YBBS CATCHMENT WITHIN THE SWAT 2000 MODEL WITH LOCATION OF PRECIPITATION, TEMPERATURE AND CLIMATE (SOLAR RADIATION, WIND SPEED, RELATIVE HUMIDITY) STATIONS WITH THE ADEQUATE INTERVAL OF DATA AVAILABILITY	- 79 -
FIGURE 25: COMPARISON OF OBSERVED AND SIMULATED RIVER DISCHARGE FOR THE YBBS CATCHMENT USING THE SWAT 2000 MODEL FOR THE MOST UPSTREAM LUNZ AM SEE SUBCATCHMENT IN RELATION TO SIMULATED SNOWFALL, SNOWMELT AND TO OBSERVED PRECIPITATION FOR THE PERIOD 1992-1994.....	- 80 -
FIGURE 26: COMPARISON OF SIMULATED AGAINST OBSERVED DISCHARGES FOR THE WATERSHED OUTLET GREIMPERSDORF (VERSION WITH 205 HRU’S) WITH CONSIDERATION OF LOW FLOW CONDITIONS ($Q < 0.5 * Q_M$), MODERATE FLOW CONDITIONS ($0.5 * Q_M \leq Q < 1.5 * Q_M$) AND HIGH FLOW CONDITIONS ($Q \geq 1.5 * Q_M$) RELATED TO THE MEAN DISCHARGE Q_M	- 81 -
FIGURE 27: COMPARISON OF OBSERVED AND SIMULATED RIVER DISCHARGE FOR THE YBBS CATCHMENT (VERSIONS WITH 205 HRU’S AND 428 HRU’S) USING THE SWAT 2000 MODEL FOR THE SUBCATCHMENTS OPPONITZ, KRENSTETTEN AND THE MAIN WATERSHED OUTLET GREIMPERSDORF FOR THE CALIBRATION PERIOD 1995-1997	- 83 -
FIGURE 28: NUMBER OF SOIL CLASSES LIMITING HRU DEFINITIONS IN THE SWAT 2000 MODEL FOR SWAT PROJECT WITH 106 HRU’S FOR THE WULKA CATCHMENT	- 84 -

FIGURE 29: NUMBER OF SOIL CLASSES LIMITING HRU DEFINITIONS IN THE SWAT 2000 MODEL FOR SWAT PROJECT WITH 206 HRU'S FOR THE WULKA CATCHMENT	- 84 -
FIGURE 30: WATERSHED DELINEATION FOR THE WULKA CATCHMENT WITHIN THE SWAT 2000 MODEL WITH LOCATION OF PRECIPITATION AND TEMPERATURE STATIONS WITH THE ADEQUATE INTERVAL OF DATA AVAILABILITY	- 85 -
FIGURE 31: COMPARISON OF OBSERVED AND SIMULATED RIVER DISCHARGE FOR THE WULKA CATCHMENT (VERSIONS WITH 106 HRU'S AND 206 HRU'S) USING THE SWAT 2000 MODEL FOR THE SUBCATCHMENTS WALBERSDORF, EISBACH AND THE MAIN WATERSHED OUTLET SCHUETZEN FOR THE CALIBRATION PERIOD 1995-1997.....	- 86 -
FIGURE 32: COMPARISON OF SIMULATED AGAINST OBSERVED DISCHARGES FOR THE WATERSHED OUTLET SCHUETZEN (VERSION WITH 106 HRU'S) WITH CONSIDERATION OF LOW FLOW CONDITIONS ($Q < 0.5 * Q_M$), MODERATE FLOW CONDITIONS ($0.5 * Q_M \leq Q < 1.5 * Q_M$) AND HIGH FLOW CONDITIONS ($Q \geq 1.5 * Q_M$) RELATED TO THE MEAN DISCHARGE Q_M	- 87 -
FIGURE 33: DETAILED SIMULATED WATER CYCLE FOR THE YBBS CATCHMENT WITH AVERAGE ANNUAL VALUES FOR THE WATER BALANCE COMPONENTS CALCULATED FOR THE PERIOD 1992-2000	- 89 -
FIGURE 34: CUMULATIVE FREQUENCY OF THE DAILY CONTRIBUTIONS OF SIMULATED RUNOFF COMPONENTS FOR THE YBBS CATCHMENT USING THE SWAT 2000 MODEL FOR THE PERIOD 1992-2000	- 91 -
FIGURE 35: DETAILED SIMULATED WATER CYCLE FOR THE WULKA CATCHMENT WITH AVERAGE ANNUAL VALUES FOR THE WATER BALANCE COMPONENTS CALCULATED FOR THE PERIOD 1992-1999	- 96 -
FIGURE 36: CUMULATIVE FREQUENCY OF THE DAILY CONTRIBUTIONS OF SIMULATED RUNOFF COMPONENTS FOR THE WULKA CATCHMENT USING THE SWAT 2000 MODEL FOR THE PERIOD 1992-1999	- 98 -
FIGURE 37: LONG-TERM AVERAGE VALUES (1992-2000) OF PRECIPITATION COMPARED TO SIMULATED WATER BALANCE COMPONENTS EVAPOTRANSPIRATION, GROUNDWATER RECHARGE, SOIL PERCOLATION AND SIMULATED RUNOFF COMPONENTS GROUNDWATER RUNOFF, LATERAL RUNOFF AND SURFACE RUNOFF CALCULATED FOR THE YBBS CATCHMENT USING THE SWAT 2000 MODEL	- 102 -
FIGURE 38: SEASONAL CYCLE OF LONG-TERM AVERAGE VALUES (1992-1999) OF PRECIPITATION (P), EVAPOTRANSPIRATION (ET), GROUNDWATER RECHARGE (GWRCHRG) AND BASE FLOW (GWQ) AND OF SURFACE RUNOFF (SURQ), LATERAL RUNOFF (LATQ) AND BASE FLOW (GWQ) AND TILE DRAINAGE (TILE D) CALCULATED FOR THE WULKA CATCHMENT USING THE SWAT 2000 MODEL.....	- 104 -
FIGURE 39: COMPARISON OF LONG-TERM AVERAGE MONTHLY VALUES FOR PRECIPITATION, EVAPOTRANSPIRATION AND GROUNDWATER RECHARGE BETWEEN THE YBBS CATCHMENT AND THE WULKA CATCHMENT CALCULATED BY THE SWAT 2000 MODEL.....	- 105 -
FIGURE 40: LONG-TERM AVERAGE MONTHLY VALUES (1992-2000) FOR SURFACE RUNOFF, LATERAL RUNOFF AND GROUNDWATER RUNOFF AND THE FRACTIONS OF THE RUNOFF COMPONENTS ON TOTAL RIVER DISCHARGE FOR THE YBBS CATCHMENT CALCULATED BY THE SWAT 2000 MODEL.....	- 106 -
FIGURE 41: LONG-TERM AVERAGE MONTHLY VALUES (1992-1999) FOR SURFACE RUNOFF, LATERAL RUNOFF, GROUNDWATER RUNOFF, RUNOFF FROM DRAINED AREAS (TILE DRAINAGE) AND FOR CONTRIBUTIONS FROM WASTE WATER TREATMENT PLANTS (POINT SOURCES) AND THE FRACTIONS OF THE RUNOFF COMPONENTS ON TOTAL RIVER DISCHARGE FOR THE WULKA CATCHMENT CALCULATED BY THE SWAT 2000 MODEL	- 107 -
FIGURE 42: COMPARISON OF CALCULATED AVERAGE ANNUAL GROUNDWATER RECHARGE RATES ON SUBCATCHMENT LEVEL BETWEEN THE YBBS CATCHMENT AND THE WULKA CATCHMENT BASED ON SWAT 2000 MODEL RESULTS	- 107 -
FIGURE 43: OBSERVED AVERAGE NITRATE CONCENTRATIONS IN THE GROUNDWATER OF THE WULKA CATCHMENT (1995-2003).....	- 111 -
FIGURE 44: CUMULATIVE DISTRIBUTION FUNCTION OF THE OBSERVED TOTAL INORGANIC NITROGEN CONCENTRATIONS IN THE GROUNDWATER WITH > 100M DISTANCE, WITH < 100M DISTANCE TO THE SURFACE WATER, IN THE SURFACE WATER (1992-2002) IN RELATION TO THE CALCULATED POTENTIAL NITRATE CONCENTRATIONS IN THE LEAKAGE (PERCOLATION) WATER.....	- 112 -
FIGURE 45: COMPARISON OF OBSERVED NITRATE AND CHLORIDE CONCENTRATIONS IN THE GROUNDWATER OF THE WULKA CATCHMENT WITH <100M AND >100M DISTANCE TO SURFACE WATER AND IN SURFACE WATER.....	- 114 -
FIGURE 46: CUMULATIVE DISTRIBUTION FUNCTION (CDF) OF O ₂ -CONCENTRATIONS AND DOC CONCENTRATIONS IN THE GROUNDWATER WITH < 100M AND > 100M DISTANCE TO SURFACE WATER AND DOC CONCENTRATIONS IN SURFACE WATER (1992-2002)	- 115 -
FIGURE 47: AVERAGE GROUNDWATER TABLE DEPTH AND STANDARD DEVIATION OF GROUNDWATER TABLE DEPTH OF GROUNDWATER OBSERVATION WELLS WITH <100M AND >100M DISTANCE TO SURFACE WATER.....	- 116 -
FIGURE 48: CUMULATIVE DISTRIBUTION FUNCTION (CDF) OF Fe ²⁺ CONCENTRATIONS AND SO ₄ ²⁻ CONCENTRATIONS IN THE GROUNDWATER WITH < 100M AND > 100M DISTANCE TO THE SURFACE WATER (1992-2002).....	- 116 -
FIGURE 49: TERTIARY PLOT OF ANION MOL EQUIVALENTS IN GROUNDWATER OBSERVATIONS OF THE WULKA CATCHMENT WITH FRACTIONS OF SPECIFIC ANIONS ON TOTAL ANION AMOUNT	- 117 -

FIGURE 50: NITRATE CONCENTRATIONS IN THE GROUNDWATER OF THE WULKA CATCHMENT IN RESPECT TO THE LOCATION OF THE GROUNDWATER OBSERVATION WELLS IN DIFFERENT LAND USE CLASSES (LEFT) AND DIFFERENT GEOLOGICAL FORMATIONS (RIGHT)	- 118 -
FIGURE 51: AVERAGE NITRATE CONCENTRATIONS IN THE GROUNDWATER OF THE YBBS CATCHMENT (1985-2003).	- 119 -
FIGURE 52: CUMULATIVE DISTRIBUTION FUNCTION OF THE OBSERVED TOTAL INORGANIC NITROGEN CONCENTRATIONS IN THE GROUNDWATER WITH > 100M DISTANCE, WITH < 100M DISTANCE TO THE SURFACE WATER, IN THE GROUNDWATER IN CATCHMENT PARTS UPSTREAM OF KEMATEN AND IN THE SURFACE WATER (1992-2002) IN RELATION TO THE CALCULATED POTENTIAL NITRATE CONCENTRATIONS IN THE LEAKAGE (PERCOLATION) WATER	- 121 -
FIGURE 53: COMPARISON OF OBSERVED NITRATE AND CHLORIDE CONCENTRATIONS IN THE GROUNDWATER OF THE YBBS CATCHMENT WITH <100M AND >100M DISTANCE TO SURFACE WATER FOR THE PART DOWNSTREAM OF KEMATEN IN COMPARISON TO THE GROUNDWATER IN THE PART UPSTREAM OF KEMATEN AND THE SURFACE WATER.....	- 123 -
FIGURE 54: CUMULATIVE DISTRIBUTION FUNCTION (CDF) OF O ₂ -CONCENTRATIONS AND DOC CONCENTRATIONS IN THE GROUNDWATER WITH < 100M AND > 100M DISTANCE TO SURFACE WATER FOR THE PART DOWNSTREAM OF KEMATEN AND FOR THE GROUNDWATER UPSTREAM OF KEMATEN (1992-2002)	- 123 -
FIGURE 55: AVERAGE GROUNDWATER TABLE DEPTH AND STANDARD DEVIATION OF GROUNDWATER TABLE DEPTH OF GROUNDWATER OBSERVATION WELLS WITH <100M AND >100M DISTANCE TO SURFACE WATER.....	- 125 -
FIGURE 56: CUMULATIVE DISTRIBUTION FUNCTION (CDF) OF Fe ²⁺ CONCENTRATIONS AND SO ₄ ²⁻ CONCENTRATIONS IN THE GROUNDWATER WITH < 100M AND > 100M DISTANCE TO THE SURFACE WATER FOR THE PART DOWNSTREAM OF KEMATEN AND FOR THE GROUNDWATER UPSTREAM OF KEMATEN (1992-2002)	- 125 -
FIGURE 57: COMPARISON OF OBSERVED NITRATE AND SULPHATE CONCENTRATIONS IN THE GROUNDWATER OF THE YBBS CATCHMENT WITH <100M AND >100M DISTANCE TO SURFACE WATER FOR THE PART DOWNSTREAM OF KEMATEN	- 126 -
FIGURE 58: TERTIARY PLOT OF ANION MOL EQUIVALENTS IN GROUNDWATER OBSERVATIONS OF THE YBBS CATCHMENT WITH FRACTIONS OF SPECIFIC ANIONS ON TOTAL ANION AMOUNT	- 127 -
FIGURE 59: NITRATE CONCENTRATIONS IN THE GROUNDWATER IN RESPECT TO THE LOCATION OF THE GROUNDWATER OBSERVATION WELLS IN DIFFERENT LAND USE CLASSES AND DIFFERENT GEOLOGICAL FORMATIONS	- 128 -
FIGURE 60: COMPARISON OF SIMULATED RUNOFF COMPONENTS SURFACE RUNOFF, LATERAL RUNOFF, GROUNDWATER RUNOFF AND PERCOLATION COMPARED TO LONG-TERM AVERAGE NITRATE LOADS VIA SURFACE RUNOFF, LATERAL RUNOFF, GROUNDWATER RUNOFF AND PERCOLATION WITH CONSIDERATION OF N INPUTS BY LONG-TERM AVERAGE FERTILIZER APPLICATIONS AND ATMOSPHERIC DEPOSITION AND N LOSSES BY LONG-TERM AVERAGE DENITRIFICATION IN SOIL CALCULATED FOR PERIOD 1992-2000 FOR THE YBBS CATCHMENT	- 134 -
FIGURE 61: SIMULATED LONG-TERM AVERAGE NITRATE LOADS VIA SURFACE RUNOFF, LATERAL RUNOFF AND GROUNDWATER RUNOFF IN COMPARISON TO LONG-TERM AVERAGE NITRATE LOSSES BY DENITRIFICATION IN THE SOIL AND PERCOLATION TO THE GROUNDWATER CALCULATED FOR PERIOD 1992-2000 FOR THE YBBS CATCHMENT	- 135 -
FIGURE 62: DETAILED SIMULATED NITROGEN CYCLE FOR THE YBBS CATCHMENT WITH AVERAGE ANNUAL VALUES OF THE NITROGEN BALANCE CALCULATED FOR THE PERIOD 1992-2000 USING THE SWAT 2000 MODEL.....	- 136 -
FIGURE 63: COMPARISON OF SIMULATED RUNOFF COMPONENTS SURFACE RUNOFF, LATERAL RUNOFF, GROUNDWATER RUNOFF, PERCOLATION AND RUNOFF FROM TILE DRAINAGES COMPARED TO LONG-TERM AVERAGE NITRATE LOADS VIA SURFACE RUNOFF, LATERAL RUNOFF, GROUNDWATER RUNOFF AND PERCOLATION WITH CONSIDERATION OF N INPUTS BY LONG-TERM AVERAGE FERTILIZER APPLICATIONS AND ATMOSPHERIC DEPOSITION AND N LOSSES BY LONG-TERM AVERAGE DENITRIFICATION IN SOIL CALCULATED FOR PERIOD 1992-1999 FOR THE WULKA CATCHMENT.....	- 137 -
FIGURE 64: SIMULATED LONG-TERM AVERAGE NITRATE LOADS VIA SURFACE RUNOFF, LATERAL RUNOFF AND GROUNDWATER RUNOFF IN COMPARISON TO LONG-TERM AVERAGE NITRATE LOSSES BY DENITRIFICATION IN THE SOIL AND PERCOLATION TO THE GROUNDWATER CALCULATED FOR PERIOD 1992-1999 FOR THE WULKA CATCHMENT	- 138 -
FIGURE 65: DETAILED SIMULATED NITROGEN CYCLE FOR THE WULKA CATCHMENT WITH AVERAGE ANNUAL VALUES OF THE NITROGEN BALANCE CALCULATED FOR THE PERIOD 1992-1999 USING THE SWAT 2000 MODEL.....	- 139 -
FIGURE 66: PATHWAYS AND PROCESSES WITHIN MONERIS (SCHREIBER ET AL. 2003).....	- 141 -
FIGURE 67: NITROGEN EMISSIONS CALCULATED USING THE MONERIS MODEL FOR THE YBBS AND WULKA CATCHMENT WITH SPECIFICATION OF EMISSION PATHWAYS (FROM ZESSNER ET AL. 2004) IN RELATION TO RUNOFF COMPONENTS CONTRIBUTIONS.....	- 145 -
FIGURE 68: SPECIFIC NITROGEN EMISSIONS VIA GROUNDWATER IN THE PERIOD 1998-2002 (FROM SCHREIBER ET AL. 2003).....	- 146 -

FIGURE 69: SPECIFIC NITROGEN EMISSIONS FOR BACKGROUND CONDITIONS IN THE PERIOD 1998-2002 (FROM SCHREIBER ET AL. 2003)	- 147 -
FIGURE 70: TOTAL NITROGEN EMISSIONS WITH RELATION TO THE AREA SPECIFIC SURPLUS ON THE TOTAL AREA OF THE CATCHMENT AND THE RIVER LOADS FOR THE YBBS AND THE WULKA CATCHMENT (FROM ZESSNER ET AL. 2004, MODIFIED)	- 148 -
FIGURE 71: ANNUAL RIVER DISCHARGES IN COMPARISON WITH MEASURED AVERAGE TN CONCENTRATIONS IN THE YBBS RIVERS AND THE WULKA RIVER (FROM ZESSNER ET AL. 2004, MODIFIED)	- 149 -
FIGURE 72: FACTORS INFLUENCING LOCAL ENVIRONMENTAL CONDITIONS, WHICH ARE FAVOURABLE FOR DENITRIFICATION IN GROUNDWATER.....	- 151 -
FIGURE 73: GROUNDWATER RESIDENCE TIME [YEARS] AND STANDARD DEVIATION [YEARS] ESTIMATED BASED ON TRITIUM ANALYSIS IN THE WULKA CATCHMENT	- 154 -
FIGURE 74: RESIDENCE TIME AND STANDARD DEVIATION ESTIMATED BASED ON TRITIUM ANALYSIS IN THE YBBS CATCHMENT	- 155 -
FIGURE 75: SPATIAL EXTENT OF THE INTERPOLATED GROUNDWATER TABLE INFORMATION LIMITED BY THE NUMBER OF GROUNDWATER OBSERVATION WELLS (STATIONS: GREEN POINTS).....	- 161 -
FIGURE 76: COMPARISON OF HISTOGRAMS OF GROUNDWATER RESIDENCE TIME DISTRIBUTIONS USING DIFFERENT GEOLOGICAL INPUT INFORMATION WITH CONSIDERATION OF A CONSTANT (LEFT) AND A VARIABLE (RIGHT) POROSITY	- 165 -
FIGURE 77: AREA-SPECIFIC NITROGEN EMISSIONS VIA GROUNDWATER CALCULATED FROM THE RESIDENCE TIME DISTRIBUTIONS OF THE DIFFERENT CALCULATION VERSIONS WITH CONSIDERATION OF HALF-LIFE-TIMES OF 2 YEARS AND 4 YEARS, RESPECTIVELY (CALCULATION AREA = 100.5 km ²)	- 165 -
FIGURE 78: CONTRIBUTION (RELATIVE AND CUMULATIVE) OF AREAS WITH CERTAIN GROUNDWATER RESIDENCE TIMES TO TOTAL NITROGEN EMISSIONS VIA GROUNDWATER USING A HALF LIFE TIME FOR DENITRIFICATION OF 4 YEARS.....	- 167 -
FIGURE 79: CUMULATIVE DISTRIBUTION FUNCTION OF FRACTIONS OF AREAS WITH A CERTAIN GROUNDWATER RESIDENCE TIME ON THE TOTAL AREA	- 167 -
FIGURE 80: LOCATION OF AREAS RELATED TO SPECIFIC CUMULATIVE CONTRIBUTION TO THE TOTAL NITROGEN EMISSIONS VIA GROUNDWATER TO SURFACE WATERS (HALF-LIFE TIME = 4 YEARS).....	- 168 -
FIGURE 81: SPATIAL EXTENT OF THE INTERPOLATED GROUNDWATER TABLE INFORMATION LIMITED BY THE NUMBER OF GROUNDWATER OBSERVATION WELLS (YELLOW, STATIONS GREEN); ADDITIONAL INFORMATION ON GROUNDWATER SURFACE WAS OBTAINED FROM MEASUREMENTS USING APPOINTED DATES (RED-BROWN)	- 169 -
FIGURE 82: COMPARISON OF HISTOGRAMS OF GROUNDWATER RESIDENCE TIME DISTRIBUTIONS USING DIFFERENT INPUT INFORMATION WITH CONSIDERATION OF A CONSTANT (LEFT) AND A VARIABLE (RIGHT) POROSITY	- 173 -
FIGURE 83: AREA-SPECIFIC NITROGEN EMISSIONS VIA GROUNDWATER CALCULATED FROM THE RESIDENCE TIME DISTRIBUTIONS OF THE DIFFERENT CALCULATION VERSIONS WITH CONSIDERATION OF HALF-LIFE-TIMES OF 2 YEARS AND 4 YEARS, RESPECTIVELY (AREA=176 km ²)	- 174 -
FIGURE 84: CONTRIBUTION (RELATIVE AND CUMULATIVE) OF AREAS WITH CERTAIN GROUNDWATER RESIDENCE TIMES TO TOTAL NITROGEN EMISSIONS VIA GROUNDWATER USING A HALF LIFE TIME FOR DENITRIFICATION OF 4 YEARS.....	- 175 -
FIGURE 85: CUMULATIVE DISTRIBUTION FUNCTION OF FRACTIONS OF AREAS WITH A CERTAIN GROUNDWATER RESIDENCE TIME ON THE TOTAL AREA	- 176 -
FIGURE 86: LOCATION OF AREAS RELATED TO SPECIFIC CUMULATIVE CONTRIBUTION TO THE TOTAL NITROGEN EMISSIONS VIA GROUNDWATER TO SURFACE WATERS (HALF-LIFE TIME = 4 YEARS).....	- 177 -
FIGURE 87: HISTOGRAM AND DENSITY OF CALCULATED GROUNDWATER RESIDENCE TIME DISTRIBUTIONS [YEARS] OF THE WULKA CATCHMENT USING INTERPOLATED GROUNDWATER SURFACE GRID WITH 150M CELL SIZE AND VARYING GEOLOGICAL INFORMATION	- 199 -
FIGURE 88: HISTOGRAM AND DENSITY OF CALCULATED GROUNDWATER RESIDENCE TIME DISTRIBUTIONS [YEARS] OF THE WULKA CATCHMENT USING INTERPOLATED GROUNDWATER SURFACE GRID WITH 25M CELL SIZE AND VARYING GEOLOGICAL INFORMATION	- 200 -
FIGURE 89: COMPARISON OF HISTOGRAM AND DENSITY OF CALCULATED GROUNDWATER RESIDENCE TIME DISTRIBUTIONS [YEARS] OF THE WULKA CATCHMENT USING INTERPOLATED GROUNDWATER SURFACE GRID WITH 25M CELL SIZE AND VARYING GEOLOGICAL INFORMATION WITH A CONSTANT AND VARIABLE POROSITY	- 201 -
FIGURE 90: HISTOGRAM AND DENSITY OF CALCULATED GROUNDWATER RESIDENCE TIME DISTRIBUTIONS [YEARS] OF THE YBBS CATCHMENT USING INTERPOLATED GROUNDWATER SURFACE GRID WITH 100M CELL SIZE, DETAILED GEOLOGICAL INFORMATION AND WITH CONSIDERATION OF DIFFERENT ORDERS OF THE RIVERS AS BARRIER FOR GROUNDWATER FLOW.....	- 203 -

FIGURE 91: HISTOGRAM AND DENSITY OF CALCULATED GROUNDWATER RESIDENCE TIME DISTRIBUTIONS [YEARS] OF THE YBBS CATCHMENT USING INTERPOLATED GROUNDWATER SURFACE GRID WITH 25M CELL SIZE WITH CHANGING GEOLOGICAL INFORMATION AND WITH CONSIDERATION OF DIFFERENT ORDERS OF THE RIVERS AS BARRIER FOR GROUNDWATER FLOW..... - 204 -

FIGURE 92: HISTOGRAM AND DENSITY OF CALCULATED GROUNDWATER RESIDENCE TIME DISTRIBUTIONS [YEARS] OF THE YBBS CATCHMENT USING INTERPOLATED GROUNDWATER SURFACE GRID WITH DIFFERENT CELL SIZES, CHANGING GEOLOGICAL INFORMATION, DIFFERENT SPATIAL EXTENT AND WITH CONSIDERATION OF DIFFERENT ORDERS OF THE RIVERS AS BARRIER FOR GROUNDWATER FLOW..... - 205 -

Table of Tables

TABLE 1: SUMMARY OF THRESHOLD VALUES GIVEN IN LITERATURE, ABOVE WHICH DENITRIFICATION RATES SHARPLY INCREASES WITH SOIL WATER CONTENT (FROM DE KLEIN ET AL. 1996)	- 36 -
TABLE 2: MEAN MICHAELIS-MENTON PARAMETER FOR DENITRIFICATION CORRECTED FOR RESPIRATION (TAKEN FROM STRONG ET AL. 2002, MODIFIED) WITH V_{MAX} AND $K_M \pm$ STANDARD DEVIATION	- 38 -
TABLE 3: OVERVIEW ON MEAN DENITRIFICATION RATES IN UNSATURATED ZONES REPORTED IN THE LITERATURE	- 41 -
TABLE 4: OVERVIEW ON DENITRIFICATION RATES IN SATURATED ZONES REPORTED IN THE LITERATURE	- 48 -
TABLE 5: OXYGEN CONCENTRATIONS BEING REPORTED AS LIMITING FOR DENITRIFICATION IN GROUNDWATER BY LISTED AUTHORS (FROM WENDLAND ET AL. 1999, MODIFIED)	- 50 -
TABLE 6: MAIN CHARACTERISTICS OF CASE STUDY REGIONS, SUBDIVIDED IN INTO SUB-CATCHMENTS (FROM ZESSNER ET AL. 2004)	59
TABLE 7: CALCULATION OF THE NITROGEN SURPLUS IN DIFFERENT SUBCATCHMENTS AT THE YBBS FOR THE YEAR 1999 (FROM ZESSNER ET AL. 2004)	- 62 -
TABLE 8: CALCULATION OF THE NITROGEN SURPLUS IN DIFFERENT SUBCATCHMENTS AT THE WULKA FOR THE YEAR 1999 (FROM ZESSNER ET AL. 2004)	- 67 -
TABLE 9: OVERVIEW ON CLIMATIC DATA WERE USED AS INPUT DATA FOR THE SWAT 2000 MODEL	- 72 -
TABLE 10: DIFFERENCES IN MAIN CHARACTERISATIONS BETWEEN THE YBBS CATCHMENT AND THE WULKA CATCHMENT AFTER WATERSHED DELINEATION IN THE SWAT 2000 MODEL	- 75 -
TABLE 11: CALIBRATION PARAMETER OF THE SWAT 2000 MODEL USING A TRIAL AND ERROR METHOD	- 75 -
TABLE 12: CALIBRATION PARAMETER OF THE SWAT 2000 MODEL USING THE SCE-UA-ALGORITHM	- 76 -
TABLE 13: MODEL PERFORMANCE (NASH-SUTCLIFFE-COEFFICIENT - NSC) OF THE SWAT 2000 MODEL FOR THE YBBS CATCHMENT IN RELATION TO DIFFERENT SOIL INPUT DATA AND THE NUMBER OF HRU'S	- 78 -
TABLE 14: MODEL PERFORMANCE (NASH-SUTCLIFFE-COEFFICIENT - NSC) OF THE SWAT 2000 MODEL FOR THE WULKA CATCHMENT IN RELATION TO DIFFERENT SOIL INPUT DATA AND THE NUMBER OF HRU'S	- 85 -
TABLE 15: MAIN ANNUAL WATER BALANCE COMPONENTS (1992-2000) OF THE YBBS CATCHMENT CALCULATED USING THE SWAT 2000 MODEL (VERSION 205 HRU'S)	- 90 -
TABLE 16: MAIN AVERAGE ANNUAL WATER BALANCE COMPONENTS (1992-2000) OF THE SUBCATCHMENTS OPPONITZ, KRENSTETTEN AND THE WATERSHED OUTLET GREIMPERSDORF OF THE YBBS CATCHMENT CALCULATED USING THE SWAT 2000 MODEL (VERSION 205 HRU'S)	- 92 -
TABLE 17: COMPARISON OF THE CALCULATED WATER BALANCE COMPONENTS USING THE SWAT 2000 MODEL FOR THE WATERSHED OUTLET GREIMPERSDORF WITH THE RESULTS FROM DIFGA 2000 AND THE MONERIS MODEL	- 93 -
TABLE 18: COMPARISON OF LONG-TERM AVERAGE ANNUAL WATER BALANCE COMPONENTS FROM THE HAÖ (HYDROLOGIC ATLAS OF AUSTRIA) WITH WATER BALANCE COMPONENT CALCULATED USING THE SWAT 2000 MODEL FOR THE YBBS CATCHMENT	- 95 -
TABLE 19: ANNUAL WATER BALANCE COMPONENTS (1992-1999) OF THE WULKA CATCHMENT CALCULATED USING THE SWAT 2000 MODEL (VERSION 106 HRU'S)	- 97 -
TABLE 20: MAIN AVERAGE ANNUAL WATER BALANCE COMPONENTS (1992-1999) OF THE SUBCATCHMENTS WALBERSDORF, WULKAPRODERSDORF, EISBACH AND NODBACH IN RELATION TO THE MAIN WATERSHED OUTLET SCHÜTZEN OF THE WULKA CATCHMENT CALCULATED USING THE SWAT 2000 MODEL (VERSION 106 HRU'S, WITHOUT POINT SOURCE CONTRIBUTIONS)	- 99 -
TABLE 21: COMPARISON OF THE WATER BALANCE COMPONENTS CALCULATED USING THE SWAT 2000 MODEL FOR THE WATERSHED OUTLET SCHUETZEN WITH RESULTS FROM DIFGA 2000 AND THE MONERIS MODEL .	- 99 -
TABLE 22: ADVANTAGES AND DISADVANTAGES OF APPLICATION OF THE SWAT 2000 MODEL	- 108 -
TABLE 23: AVERAGE CONCENTRATIONS IN GROUNDWATER OF THE WULKA CATCHMENT (FROM ZESSNER ET AL. 2004, MODIFIED)	- 110 -
TABLE 24: OVERVIEW ON CONCENTRATIONS IN GROUNDWATER OF THE YBBS CATCHMENT (FROM ZESSNER ET AL. 2004, MODIFIED)	- 119 -
TABLE 25: NITROGEN TURNOVER MODELLED BY THE SWAT 2000 MODEL	- 131 -
TABLE 26: MODEL COEFFICIENTS FOR DETERMINATION OF NITROGEN RETENTION IN AREAS WITH VARIOUS HYDROGEOLOGICAL CONDITIONS	- 144 -
TABLE 27: CALCULATED NITROGEN EMISSIONS VIA PATHWAYS USING THE MONERIS MODEL FOR THE YBBS AND THE WULKA CATCHMENT (FROM ZESSNER ET AL. 2004)	- 144 -
TABLE 28: DEFINITIONS FOR CALCULATION VERSIONS IN TERMS OF VARIATIONS OF THE DIFFERENT INPUT INFORMATION	- 162 -
TABLE 29: STATISTICAL VALUES OF THE CALCULATED RESIDENCE TIMES OF SELECTED VERSIONS [IN YEARS]-	163 -

TABLE 30: COMPARISON OF CALCULATED AREA-SPECIFIC NITROGEN EMISSIONS VIA GROUNDWATER USING THE GROUNDWATER RESIDENCE TIME DISTRIBUTION AND CHANGING HALF LIFE TIMES WITH CALCULATED AREA-SPECIFIC NITROGEN EMISSIONS USING THE MONERIS MODEL AND OBSERVED IN-STREAM NITROGEN LOAD ..	- 166 -
TABLE 31: DEFINITIONS FOR CALCULATION VERSIONS IN TERMS OF VARIATIONS OF THE DIFFERENT INPUT INFORMATION.....	- 171 -
TABLE 32: STATISTICAL VALUES OF THE CALCULATED RESIDENCE TIMES OF SELECTED VERSIONS [IN YEARS]-	172 -
TABLE 33: COMPARISON OF CALCULATED AREA-SPECIFIC NITROGEN EMISSIONS VIA GROUNDWATER USING THE GROUNDWATER RESIDENCE TIME DISTRIBUTION AND CHANGING HALF LIFE TIME WITH CALCULATED AREA-SPECIFIC NITROGEN EMISSIONS USING THE MONERIS MODEL AND OBSERVED IN-STREAM NITROGEN LOAD ..	- 175 -

Abstract

Extended industrialisation and agricultural production led to increased availability of nitrogen in terrestrial and aquatic ecosystems during the past decades. Since nitrate is subject of enhanced leaching from soils towards the groundwater due to its high mobility, denitrification in groundwater is an important process, which counteracts to nitrogen transport by groundwater to surface water bodies. Denitrification in groundwater was subject of several scientific studies indicating the importance of denitrification for reducing nitrogen levels in groundwater and therewith of diffuse nitrogen emissions to surface waters.

Up to now *in-situ* assessments of denitrification in groundwater are highly uncertain. Additionally, the consideration of denitrification processes in groundwater in several quantification tools for nitrogen emission estimations differs considerably in regard to model complexity, the approaches that account for nitrogen losses via denitrification and the variability in denitrification potential due to catchment-specific conditions.

In two selected Austrian case study regions denitrification in groundwater could be observed based on nitrogen surplus assessments in relation to groundwater and surface water quality observations. Differences between the selected case study regions in respect to nitrogen fluxes and denitrification activity in subsurface zone could be related to hydrological circumstances, which were characterised by water balance calculations using the conceptual SWAT 2000 model. Using the empirical emission model MONERIS the total nitrogen emissions were calculated for both case study areas with specification of all involved emission pathways. The groundwater could be identified as the major emission pathways for nitrogen emissions to surface waters in both case study areas.

An approach was developed for the calculation of diffuse nitrogen emissions to surface waters with consideration of denitrification processes in groundwater based on calculated groundwater residence times. This approach enabled the identification of catchment areas, which are responsible for most of the diffuse nitrogen emissions to the surface water and which are therefore highly sensitive in terms of controlling diffuse nitrogen emissions to the receiving coastal waters of the Black Sea. These areas could be clearly distinguished from areas, which are important for local groundwater protection and revealed the contrarious effects of measures related to specific protection goals with focus on either the reduction of nitrogen levels in groundwater or the reduction of nitrogen emissions to surface waters.

Keywords: denitrification, groundwater, groundwater residence time, nitrogen emission estimation, water balance calculation

1 Introduction

The second half of the past century was subject of permanent increasing industrialisation and urbanisation because of an ongoing technical progress. Industrial practises in agriculture considerably increased the crop yield and similarly the supply of biologically available nitrogen due to fertilizer applications in terrestrial ecosystems (Jordan et al. 1998). Advancements in agricultural and residential development resulted in serious ecological problems due to massive point discharges of waste water to the rivers and immense nutrient loads from agriculture to groundwater and surface water. Oxygen depletion and excessive algae growth in surface waters and coastal waters of the receiving seas (eutrophication) due to enlarged nutrient loads were the result. Within the 80's and early 90's the critical ecological status of several water bodies raised the awareness for necessity of river protection, which led to several national regulations and guidelines for reglementation of waste water discharges and nutrient emissions from agriculture. The replacement of phosphate containing detergents decreased the phosphate loads to surface waters and coastal waters considerably and contributed to a stabilisation of nutrient levels. In result, phosphorus was mainly the limiting nutrient in coastal waters, but several water bodies turned to be nitrogen limited in primary production, e.g. the Western Black Sea during the 90's (Cociasu et al. 2004). The evaluation of the ecological status of rivers and seas requires the assessment of nitrogen and phosphorus sources and emissions from catchments to the rivers with consideration of the specific emission pathways and retention processes at the catchment scale.

In Austria, the commercial use of nitrogen in fertilizers has increased between 1961-2000 from 52 Mt/a to 117 Mt/a with peak consumptions in 1985 (165 Mt/a) (FAOSTATdata 2004). Compared to natural ecosystems, agroecosystems are leaky systems with greater amounts of nutrients flowing in and out. Intensive nitrogen fertilization and disrupted nitrogen cycles have brought about the emission of considerable amounts of nitrogen compounds (Haag et al. 2001). Once applied, nitrogen fertilizer is subject to soil biogeochemical processes that can redistribute nitrogen through fixation, mineralisation, nitrification and immobilisation (Wilkison et al. 2000). When surface application of nitrogen fertilizers exceeds plant requirements, the soluble and mobile nitrate is leached into the underlying groundwater (Pauwels et al. 1998, Forth 1990). At the local scale, groundwater quality and headwaters are affected by high levels of nitrates (NO_3^-) (Willems et al. 1997), at the regional scale, rivers and lakes receive large nitrogen loads (Haag et al. 2001). With 40%-60% most of the nitrogen is derived from agriculture and more than 50% from diffuse sources (Hefting et al. 1998, Kroiss et al. 1998). Enhanced nitrogen levels in water bodies are directly related to social and economic issues (e.g. drinking water supply, tourism, fishery) (Kroiss et al. 2005). In Austria almost half of drinking water demand is provided by groundwater from porous aquifers. Most of the groundwater is situated in the tertiary or quaternary aquifers of bigger river basins in regions, which are industrialised to a high extent resulting in considerable conflicts in terms of utilisation (Stalzer 1991). In response, there have been numerous international directives that aim to lower nutrient levels in groundwater, rivers and receiving seas (Goodchild 1998).

Denitrification is a process in unsaturated and saturated zone reducing nitrogen loads to surface water considerably (Hefting et al. 1998, Schilling et al. 2005).

Progress in understanding denitrification has been hampered by the technical difficulties of measuring denitrification directly in the field (Jordan et al. 1998). In subsurface zone denitrification is dependent on several environmental conditions regulating this process (Smith et al. 1998, Willems et al. 1997, Ettema et al. 1999), and it appears that the catchment specific hydrological conditions are the most important factor governing nitrate removal by denitrification (Willems et al. 1997). The physical and chemical conditions in soil and groundwater are interactive and result in complex spatial and temporal variability of denitrification activity (Simek et al. 1998).

In recent years various modelling approaches have been developed with a focus on the estimation of nutrient emissions at the catchment scale. Depending on the modelling approach the temporal or spatial resolution of the models vary significantly with consequences on process descriptions in regard to nutrient release and retention in the catchments. Often, different models describe only selected facets of nutrient dispersal in soil, groundwater and surface water (de Wit 2001). However, the number of international transboundary research projects, which focus on identification of sources and sinks, transport and transformation processes of nitrogen and phosphorus on various scales, increased considerably. In parts this development was initiated by efforts for the implementation of EU water framework directive in member states of European Union (Schilling et al. 2006). Similarly, the development of various quantification tools increased. Falling back on readily available modelling approaches the identification of nutrient sources and estimation of nutrient loads to surface waters was a question of selecting the appropriate modelling approach reflecting the chosen scales and required information (de Wit et al. 1999, van Herpe et al. 1998, Reckhow et al. 1999, Viney et al. 2000, Warwick et al. 1999). A number of physically based complex models have been applied for nutrient emission estimation for several catchments in and outside of Europe (Francos et al. 2001, Perkins et al. 1999).

The daNUbs project (EVK1-CT-2000-00051) which operated for the period 2001-2005, significantly contributed to our understanding of the processes controlling nitrogen emissions to surface waters at the catchment scale in the Danube basin and subsequent transport to the receiving Black Sea. The Danube basin is the second largest river basin in Europe, and processes controlling nitrogen emissions are diverse in the temporal and spatial aspect within the Danube basin. One major task of the daNUbs project was to carry out nutrient balance estimations for the Danube basin at the subcatchment level, and for selected case study areas of the Danube basin using different modelling approaches. A previous research project highlighted the heterogeneity of the Danube basin in respect to sources of nutrient loads to surface waters (Kroiss et al. 1998). Therefore, an empirical emission model (Behrendt et al. 1999) was applied for the calculation of nutrient emissions for all subcatchments of the Danube basin. In addition, for selected case study areas the empirical model was applied on a considerably smaller scale to validate the model performance under changing climatic and hydrologic conditions. Similarly, two other modelling approaches, the conceptual SWAT 2000 model (Arnold et al. 1999) and the hydrograph separation technique DIFGA (Heinecke 2004) were applied in terms of comparison of applicability and reliability of modelling approaches in regard to water and nutrient balance calculations at the catchment scale.

This work presents the scientific investigations on the two Austrian case study regions, the Ybbs catchment and the Wulka catchment as part of the daNUbs project. The location of the catchments within climatologically and morphologically diverse parts of Austria enabled the identification of processes at the catchment scale, which significantly influence nitrogen emissions to surface waters and in particular denitrification in the subsurface zone. In both case study regions, groundwater and surface water observations in connection with statistical analyses of nitrogen inputs to the land surface were carried out. For both case study areas, water balance calculations were performed using the conceptual SWAT 2000 model for the identification of hydrological differences between the catchments. Additionally, significant differences in specific contributions of considered runoff components and related nitrogen emissions from the catchments to surface waters were investigated. Using the empirical emission model MONERIS, nitrogen emission calculations were performed on the subcatchment level to indicate differences in total nitrogen emissions to surface waters as well as in nitrogen emission pathways. Additionally, the conceptual SWAT 2000 model was used for nutrient balance calculations. A modelling approach was developed for a fully-distributed quantification of diffuse nitrogen emissions to surface waters with consideration of denitrification processes in groundwater. Using this approach which is based on calculated groundwater residence times, the possibility was established to connect the location of catchment areas directly to their contributions to nitrogen emissions to surface waters by groundwater. This approach provided the opportunity to effectively distinguish catchment areas in terms of their protection requirements. The reduction either in the nitrogen concentrations in local groundwater bodies or in the nitrogen loads to surface water bodies could therefore be associated with the location of areas within the catchment and their specific diffuse nitrogen emissions.

2 Nitrogen in the environment

2.1 Nitrogen cycle

Nitrogen is one of the essential elements of life. Most of the nitrogen exists as molecular nitrogen N_2 in the air. The nitrogen content of the dry air is 78.1%. The only way to recycle the nitrogen naturally into the molecular form is by denitrifying bacteria via nitrate (Rohmann et al. 1985). High nitrogen inputs to soils are from fertilizer application using organic (manure, dung) or mineral fertilizers (mainly as Ammonium). Additionally, considerable amounts of nitrogen input to soils are possible by atmospheric deposition and nitrogen fixation by plants (legumes) or bacteria, where molecular nitrogen from atmosphere is stored in roots as organic nitrogen. Outputs from soils are through volatilisation of ammonia (NH_3), nitrous oxide (N_2O) or N_2 and nitrate (NO_3) leaching.

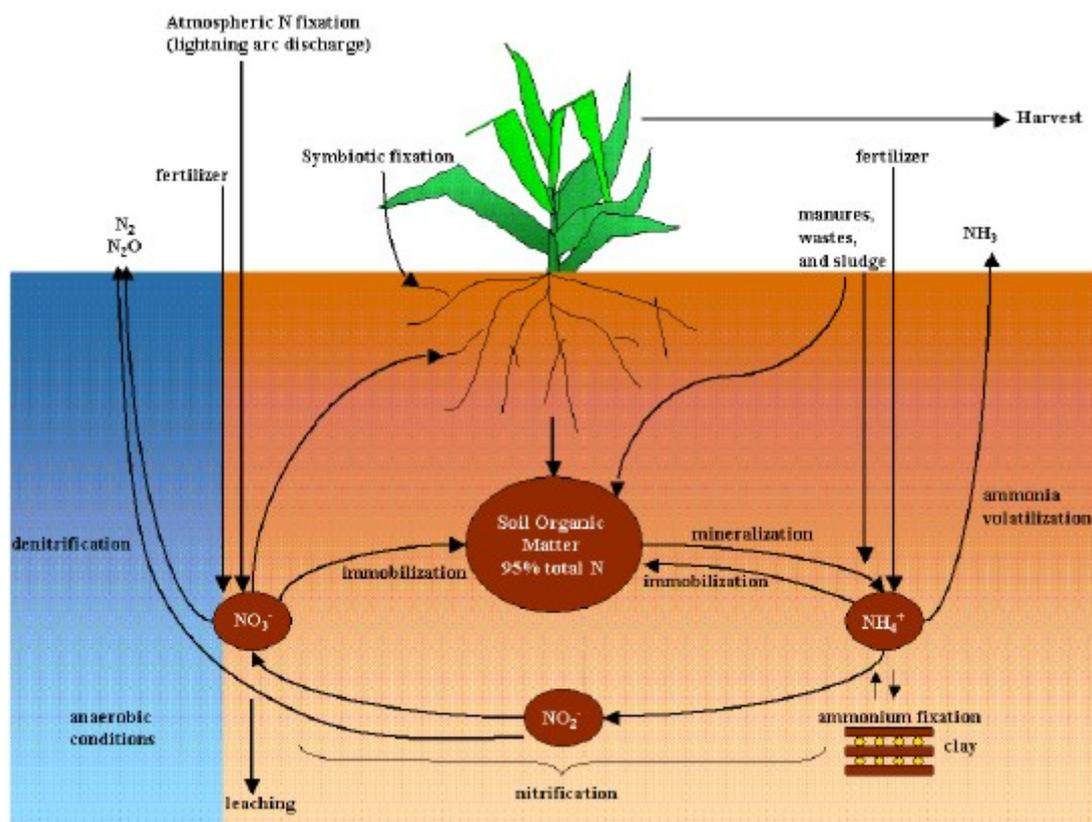


Figure 1: Nitrogen cycle in soils (from Neitsch et al. 2001)

In soils nitrogen is subject to a permanent circular flow (see Figure 1) between organic and inorganic nitrogen compounds (Schachtschabel et al. 1992). Harvested food contains nitrogen mostly in organic forms. Due to human (and animal) nutrition nitrogen is excreted as organic nitrogen (**urea** - $CO(NH_2)_2$). In soils the organic nitrogen consists of humic substances, plant residue, biomass and dead organisms and is strongly related to soil organic carbon content. Bacterial decomposition converts organic nitrogen into inorganic nitrogen (**ammonium** - NH_4). This process is called **ammonification** or **mineralization**, naturally this process occurs in soil profiles (mineralisation of organic nitrogen pool) as well as in channels collecting and discharging the waste water to treatment facilities. The reverse process of mineralization is called **immobilisation**, the conversion of inorganic nitrogen to organic nitrogen. Under aerobic conditions ammonium is converted by micro

organisms to **nitrate** (NO_3) via **nitrite** (NO_2). This process is called **nitrification**. **Denitrification** is the reductive microbial turnover of nitrate to **molecular nitrogen** (N_2) under anoxic conditions. Under strict anaerobic conditions the nitrate may be turned to ammonium (**nitrate ammonification**) again. The nitrogen conversion processes mentioned above are discussed in more detail.

2.1.1 Ammonification (mineralization)

Ammonification or mineralisation is the bacterial decomposition of organic nitrogen to inorganic nitrogen (ammonium). The driving force of this process is the requirement of the micro organisms to maintain their metabolism. More precisely, the nutrients are used by micro organisms for energy generation (metabolism) and to build up cellular substances (anabolism). Thus, this process depends on the activity of micro organisms and is influenced by surrounding conditions which can be characterised as 'living conditions'. Suboptimal living conditions will lead to suboptimal activity and to an inhibition of the mineralisation process. Environmental influences on these conditions in soils are (Rohmann et al. 1985):

- *Temperature:* the optimum temperature for mineralisation is between 25 and 35°C; between 0 and 10°C a small increase in temperature causes a large increase of mineralisation process
- *C/N ratio:* the optimum C/N ratio for mineralisation is between 10 and 30; C/N ratios > 50 cause an oversupply of carbon and have to be compensated by the micro organisms by using additional inorganic nitrogen (mainly ammonium from immobilisation) to gain the optimum C/N ratio for anabolism resulting in a longer decomposition time
- *Water content* to maintain their metabolism micro organisms require water, their activity increases with increasing soil moisture; the alternation between drying and wetting as well as cultivation increase mineralisation; microbial activity may be associated with optimal water content, exceeding this threshold value may again result in a decrease in microbial activity
- *pH-value* outside the range of pH 5-8 the sensitivity of the ammonifying bacteria to changing environmental conditions increases significantly
- *Availability of organic nitrogen*

Ammonification proceeds in two steps. The first step is the turnover of organic nitrogen to ammonia (NH_3), in a second step the ammonia is dissolved in the soil water forming ammonium ions (NH_4^+).

Ammonium is produced continuously by ammonification but there is no enrichment in the soil column because the microbial conversion to nitrate (see chapter 2.1.2) is faster than the ammonification itself. In clayed and silicated soils ammonium is fixed in the soil matrix and little available for leaching (Rohmann et al. 1985, Schachtschabel et al. 1992).

2.1.2 Nitrification

The nitrification is the second step of the mineralisation process and is the bacterial conversion of ammonium to nitrate under aerobic conditions (Rohmann et al. 1985, Schachtschabel et al. 1992). The oxidation process is a two-stage process. First ammonium is converted to nitrite by autotrophic bacteria of genus nitrosomonas. This reaction is called **nitritation**:



The soil water buffering capacity is used for the reaction of H^+ -ions with hydrogen carbonate ions producing carbon dioxide and water (see equation 2). In the case of a sufficient buffering capacity this reaction keeps the pH-value of the soil water stable.

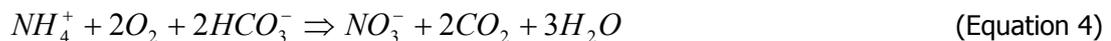


The nitrite is converted by autotrophic bacteria of genus nitrobacter to nitrate, the reaction is called **nitratation**.



This genus of bacteria is very sensitive to changes of pH-value. Equation 1 shows, that the nitritation produces H^+ -ions, what may lead to a decrease of the pH-value in case of low buffering capacity of the water and may result in an inhibition of nitratation. The enrichment of nitrite in water (soil/groundwater) would be the consequence.

The whole nitrification reaction can be described by the following equation:



For nitrification process oxygen supply is needed. For the oxidation of 1g ammonium 4.3g oxygen are required.

Nitrification process is dependent on (Rohmann et al. 1985):

- *Temperature* the optimum temperature for nitrification is between 25 and 35°C; a decrease in temperature results in decreasing activity of bacteria ($\Delta T = -10^\circ\text{C}$ means a bisection of activity), nitrification takes place until temperatures close to 0°C
- *pH-value* the optimum pH-value is between 6.5 and 8, pH-values < 6.5 and > 8 (production of NH_3) may lead to inhibition of nitratation and to enrichment of ammonium or nitrite in soil
- *Water content* the activity of bacteria increases with rising water content of soil (optimum 50 - 80% of field capacity), water contents > 80% may have a negative effect on the oxygen supply of soil matrix and may result in lower nitrification rates
- *O₂-content* the nitrification activity is dependent on oxygen supply in the soil matrix which is highly correlated to water content of the soil, dissolved oxygen concentrations in soil water of < 2 mgO₂/l are significantly correlated with higher NO₂-

concentrations (Kroiss et al. 2002) (possibly as a consequence of incomplete nitrification)

- *Availability of ammonium*

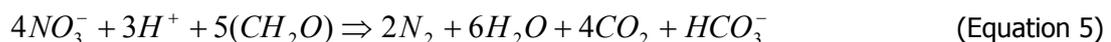
Nitrate is the nitrogen compound with the highest oxidation level. Thus, under aerobic conditions there is always the ambition of complete oxidation of ammonium to nitrate.

The nitrification process is rapid leading to low ammonium and nitrite concentrations in soil water. Nitrate is water soluble and can not be eliminated from the water column by adsorption or precipitation. Particularly in winter seasons when the nitrification activity is higher compared to nitrate reduction and plant uptake is limited due to harvesting, an enrichment of nitrate in the soil may be the result which is highly fragile in terms of leaching to subjacent saturated zone (Rheinheimer et al. 1988, Rohmann et al. 1985, Schachtschabel et al. 1992).

2.1.3 Denitrification

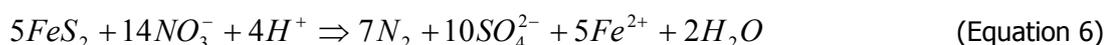
Nitrate is probably the most important source of inorganic nitrogen in aquatic ecosystems in terms of mass flow and is therefore used as a nitrogen source by a large number of micro organisms (Rheinheimer et al. 1988). In terms of natural nitrogen cycle the mineralization process of nitrogen always results in the formation of the nitrogen compound having the highest oxidation level – the nitrate. Due to that fact water bodies normally show a biogenous basic load of nitrate resulting from a balance between composition (mineralisation) and decay (denitrification).

The denitrification process is the microbial turnover of nitrate to molecular nitrogen N_2 . Both autotrophic and heterotrophic bacteria are able to use nitrate as electron acceptor for metabolism instead of dissolved oxygen under anoxic conditions (facultative anaerobe). However, for anabolism of these denitrifying bacteria additional substrate (carbon sources for heterotrophic denitrification or pyrite (sulphide) for autotrophic denitrification) is needed. In equation 5 the heterotrophic denitrification is shown (biomass synthesis is neglected) (Rohmann et al. 1985):

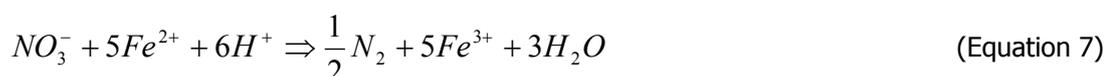


For heterotrophic denitrification, carbon hydrate (organic carbon) is used as substrate for carbon degrading species (i.e. *Pseudomonas stutzeri*). According to equation 5 denitrification of about 1 g nitrate (NO_3^-) or related to nitrogen about 0.22g NO_3^- -N requires about 0.24g organic carbon. The ion composition of the water changes due to denitrification in a way that the concentration of hydrogen carbonate rises adequate to the decomposed nitrate mass (see equation 5).

For autotrophic denitrification, inorganic carbon (CO_2 , HCO_3^-) is used as a carbon source. In presence of Pyrite (FeS_2) the species *Thoibacillus denitrificans* oxidises sulphide to sulphate in the following way:



As reported by Pauwels et al. (2000), denitrification also occurs through ferrous iron oxide:



As a consequence of equation 6 the sulphate concentration in groundwater rises as well as the ion concentration of Fe^{2+} . For the autotrophic denitrification of 1g nitrate (NO_3) 0.69g pyrite is needed, and the sulphate concentration rises equivalent about 1.1g.

In regard to equation 5 the concentration of dissolved ferrous oxide in groundwater decreases. For this reaction about 4.5g ferrous oxide are needed to denitrify about 1g nitrate (NO_3).

Both heterotrophic as well as autotrophic denitrification do consume hydrogen ions what may result in changes of pH values in cases of a low buffering capacity of water. Due to the microbial turnover the denitrification process is dependent on environmental conditions (Rohmann et al. 1985, Rheinheimer et al. 1988, Schachtschabel et al. 1992, Nikolavcic 2002, Hiscock et al. 1991):

- *Temperature* between 10°C and 65°C a increase of about 10°C results in an activity doubling of micro organisms; below 10°C the decomposition rate decreases rapidly and dies down nearly around 5°C
- *pH-value* the influence of pH-value is important due to a possible enrichment of by products (NO_2 , N_2O), an optimum of nitrate decomposition is assumed to be between pH 7 and pH 8, the denitrifying species are viable between pH 6.2 and pH 10.2; low pH conditions enforce the inhibition of turnover from N_2O to N_2 ; especially N_2O generated as a by-product of denitrification in the upper soil is released to the atmosphere and is associated with the well-known depletion of ozone layer
- *redox potential* the redox potential is a criteria for evaluating soil water or aquifer conditions in terms of reducing or oxidizing conditions; between $E_h = 300$ mV and $E_h = 700$ mV the denitrification is favoured (anoxic conditions), below $E_h = 300$ mV the nitrate ammonification is favoured
- *oxygen content* nitrate is used as an oxygen source by denitrifying bacteria only if dissolved oxygen concentrations in the water phase are very low or absent (denitrification yields the most free energy once dissolved oxygen is no longer available (Dahm et al. 1998); of decisive importance are not anoxic conditions in the water phase but the oxygen supply to the active liquid film; denitrification may take place in spite of dissolved oxygen concentration up to 5 mg/l in soil water or groundwater; the diffusion rate of oxygen in water saturated micro-pores favours denitrification, particularly in dense or poorly drained soils
- *Water content* an increasing water content in soil restrains the oxygen diffusion in soil column and benefits the creation of anaerobic micro zones; additionally nitrogen gas from denitrification may displace the oxygen containing air and may increase the extension of anaerobic zones presuming

a water saturation of soil of > 80% for denitrification, the diffusion rate of oxygen in water filled pores is low, consequently anoxic zones are created by microbial activity and nitrate will be used as oxygen source

- *Availability of organic carbon*

In the root zone there is usually no limitation of heterotrophic denitrification by organic substances, after Schachtschabel et al. (1992) forested and agricultural soils comprise of organic carbon contents of 7.5-20g/kg and 1-10g/kg for deep soil horizons; presuming an available fraction of soil organic carbon of 2-7% averagely 500mg/kg soil organic carbon would be available (Polzer 2005); in upper soil zones (unsaturated zone) organic carbon is available from soil organic matter or to a limited extend from leakage water containing dissolved organic carbon; in deep soil zones or in groundwater availability of organic carbon is considerably lower and is available from deposits only, DOC concentration in leakage water are not sufficient to meet the demands of organic carbon for heterotrophic denitrification in groundwater, solid organic carbon (SOC) sources in aquifer are probably potentially oxidizable sources of carbon (Grisczek et al. 1998)

- *Availability of pyrite or ferrous oxide*

Autotrophic denitrification can be important in aquifers containing large quantities of the compounds Mn^{2+} , Fe^{2+} , pyrite and HS^- (Grisczek et al. 1998),

- *Availability of nitrate*

Nitrate availability may limit denitrification activity due to transport (diffusion/dispersion) limitation, nitrate is predominantly transported via leaching to groundwater and via convective transport with groundwater flow

Both autotrophic and heterotrophic denitrification are characterised by requirements for additional substrate as electron donor for the denitrification processes. If these substrate requirements are insufficient or environmental conditions are suboptimal, denitrification activity will be limited.

2.1.4 Nitrate ammonification

In previous chapters nitrate ammonification was mentioned already. Nitrate ammonification stands for the microbial turnover of nitrate to ammonium under strong reducing conditions in soil water or aquifer (redox potential < 300 mV). In comparison to denitrification, nitrate ammonification proceeds very slowly. Nitrate ammonification is limited in large quantity by subsequent production of organic nitrogen (Rheinheimer et al. 1988). As result a significant decrease in nitrate decomposition rate is expected.

2.1.5 Immobilisation

Immobilisation is the conversion of inorganic nitrogen compounds (NH_4^+ , NH_3 , NO_2^- , NO_3^-) to organic nitrogen and is the reverse process of mineralization

(mobilisation). Immobilisation processes are mainly influenced by the C/N-ratio of the soil. In terms of organic carbon it has to be distinguished between easily degradable organic substances and humic substances, which were already matter of long-term turnover processes. The N mineralisation rate increases with lower C/N-ratios.

Immobilisation particularly occurs if the C/N-ratio of degradable organic substances is > 25 due to an oversupply of carbon. The deficiency in organic carbon supply due to slow mineralisation activity is then compensated by enhanced immobilisation of nitrogen (Schachtschabel et al. 1992).

2.2 Nitrogen leaching from soils and its relevance for groundwater quality

2.2.1 Sources of nitrogen for leaching from soils

Nitrogen losses from agriculture are very important sources for nitrogen emissions to groundwater and surface waters (Schipper et al. 2001, Wilkison et al. 2000, Cey et al. 1999, Wendland et al. 1999). For nitrogen, the losses to the atmosphere (mainly gaseous NH_3 losses from animal farming and N_2O losses from denitrification) exceed the direct losses to hydrosphere (mainly percolation), but indirectly they contribute via deposition to emissions to groundwater and surface water too (Zessner et al. 1999, Zessner et al. 2002). Nutrient balances calculated for Austria showed that almost 40% of total nitrogen emissions (1992) to surface waters stem from agriculture (Kroiss et al. 1998). In terms of activities in the subcatchments of the Danube basin, agricultural diffuse sources contributed the majority (45%) of the total nitrogen emissions to the Danube (Schreiber et al. 2003).

The leached nitrogen from the soils stems mainly from organic and mineral fertilizer, or from mineralization of organic nitrogen pool in soil. Mineral fertilizer (NO_3^- as well as NH_4^+) will be taken up immediately or will be immobilized and afterwards released (mobilised) according to requirements of plants. They are used most suitably at times of higher nutrient demand of plants. Organic fertilizers will be stored in organic N pool and mineralized subsequently and will be available for plant uptake or leaching with a certain time delay. Thus, organic nitrogen fertilizers are often used for fertilization building up an inventory stock. However, most of the nitrogen is stored in soil as organic nitrogen in organic N pool. For incorporation into biomass the nitrogen uptake is possible for plants in a mineral form only. Nitrogen is leached out from soils predominantly when the nitrogen content in the soil exceeds the nitrogen demand of the plants or at times when crops are not available to use it. By fertilization, crop yield is enhanced as well as the quantum of organic nitrogen pool in soil and residues, which is easily available for mineralization. An associated increase in nitrogen leaching with fertilization can be suppressed by fertilizer application according to the nitrogen demand of plants (potentially fertilization in several single doses) or by cultivation of intercrops, which incorporate the available mobile nitrogen into plant biomass during periods of potentially higher nitrogen leaching (outside the vegetation period). The amount of fertilizer which exceeds the actual amount to be utilized by plants immediately or stored in organic N-pool, will be washed out from soil. However, the utilisation of mineral or organic fertilizer depends also from regional aspects. If local animal production sites (husbandry) offer

the possibility of utilizing manure and dung for agricultural fertilization, mineral fertilizer application rates will be comparably low (Freudenthaler 1991, Rohmann et al. 1985, Schachtschabel et al. 1992).

Tillage operations stimulate microbial activity in the soil due to its associated aeration of upper parts of soil profile and thus, of mineralization too. In spring, when the plant activity as nitrate consumer is still low, fertilization may lead to a higher nitrate percolation to deeper soil zones. An early harvesting of crops in periods with higher bioactivity (regions with warm and humid climate) and following tillage may enhance the washout of mineral nitrogen from the root zone to subsurface zones. The risk of enhanced nitrate loads to groundwater can be much reduced by cultivation of intercrops and by reducing fallow periods (Freudenthaler 1991).

The crop inventory influences nitrogen leaching by its density and the duration of coverage as well as by the depth of the root zone. Nitrogen leaching from pastures is due to additional supply by urine and faeces from animals higher compared to highly fertilized meadows. In agricultural sandy soils with medium fertilization nitrogen losses by leaching up to 90 kg/ha*a have been observed. Obviously higher nitrate contents during harvesting or mineralization of organic nitrogen from soil or from plant residue are reasonable for higher nitrogen leaching from agricultural soils. Under similar conditions percolation to deeper zones and nitrogen leaching is higher in sandy soils compared to silty – loamy (heavier) soils (Schachtschabel et al. 1992).

Despite fertilization and mineralization, which indeed are the major sources of potentially leachable nitrate, other sources of nitrate are (Klaghofer 1991, Mehlhorn 1991, Rohmann et al. 1985):

- Nitrate from infiltration of treated waste water (underlies strong regulations in terms of treatment performances of wwtp; nowadays most of wwtp are equipped with ongoing nitrogen purification ensuring nitrification and denitrification)
- Nitrate in percolation water from dumping sites (local influence only)
- Nitrate from geochemical composition of underground
- Nitrate from precipitation (atmospheric deposition)
- Nitrate from surface waters

Nitrate availability due to agricultural utilisation (fertilization, mineralization, tillage operation) has by far the highest relevance in terms of nitrate loads to groundwater. Nitrate loads from infiltration of waste water are of minor relevance, nitrate loads from dumping sites are of a local and remedial importance only. Nitrate loads in surface waters are particularly lower than in neighbouring groundwater. Thus, the relevance of this pathway is of minor importance too. Partly, higher nitrate loads in surface waters are the consequence from inlets of waste water treatment plants (Zessner et al. 2004). But in relation to diffuse contributions from groundwater these loads are mostly comparably low. Nitrogen loads from atmospheric deposition may be relevant in regard to spacious nitrogen balances. Diffuse nitrate loads due to geochemical composition of subsurface strata are background loads and of local importance only (Freudenthaler 1991).

2.2.2 Seasonal aspects of nitrogen leaching

Nitrogen inventory of soils consists of organic and mineral nitrogen. More than 95% of the nitrogen is organic nitrogen stored in organic N pool. Between the organic N pool and mineralized nitrogen there is a constant turnover from organic to mineral nitrogen by mineralization and reverse by immobilisation (Rohmann et al. 1985). Nitrogen is leached from the root zone of soils to groundwater predominantly as nitrate due to its high mobility, to some extent in cases of highly permeable sandy soils as ammonium too (Schachtschabel et al. 1992). Anyway, nitrogen can be leached from soil in mineral form only. Nitrogen leaching fluctuates throughout a year as result of seasonally dependent nitrogen uptake by plants as well as mineralization-, immobilisation or denitrification processes, intra-annual fluctuations in groundwater recharge or the kind and intensity of land utilisation.

The amount of nitrogen washed out from the soil is closely connected to groundwater recharge. The higher the rate of evaporation is and the more water can be stored in soil matrix due to soil specific field capacity, the less nitrogen will be leached from soil to subjacent saturated zone. Under central European climate conditions nitrogen leaching rarely occurs in agriculturally used soils during vegetation growth period. Most of the nitrogen is washed out in-between September and April, when the crops are removed. Do to high residence time of nitrogen in saturated zone seasonal variations are mostly not detectable in nitrogen concentrations in groundwater. Exceptions can be observed in shallow aquifers or solid rock aquifers characterised by short travel times in unsaturated and saturated zones. Then, elevated nitrate concentrations in groundwater in the winter months can be detected due to an increase in maximum percolation of water and leaching of nitrogen (Pauwels et al. 2001), but also due to high rates of mineralization (mineralization of plant residue) and an almost negligible uptake of nitrogen by plants in this period (Schachtschabel et al. 1992).

2.2.3 Runoff processes and nitrate transport

The hydrologic processes which are responsible for runoff generation span a wide range of space and time scales. Different types of pattern are encountered at different time and space scales and these are associated with different processes (Grayson et al. 2001), this is shown in Figure 2. Precipitation dominates hydrological response and its pattern is dependent on the types of storms (Grayson et al. 2001).

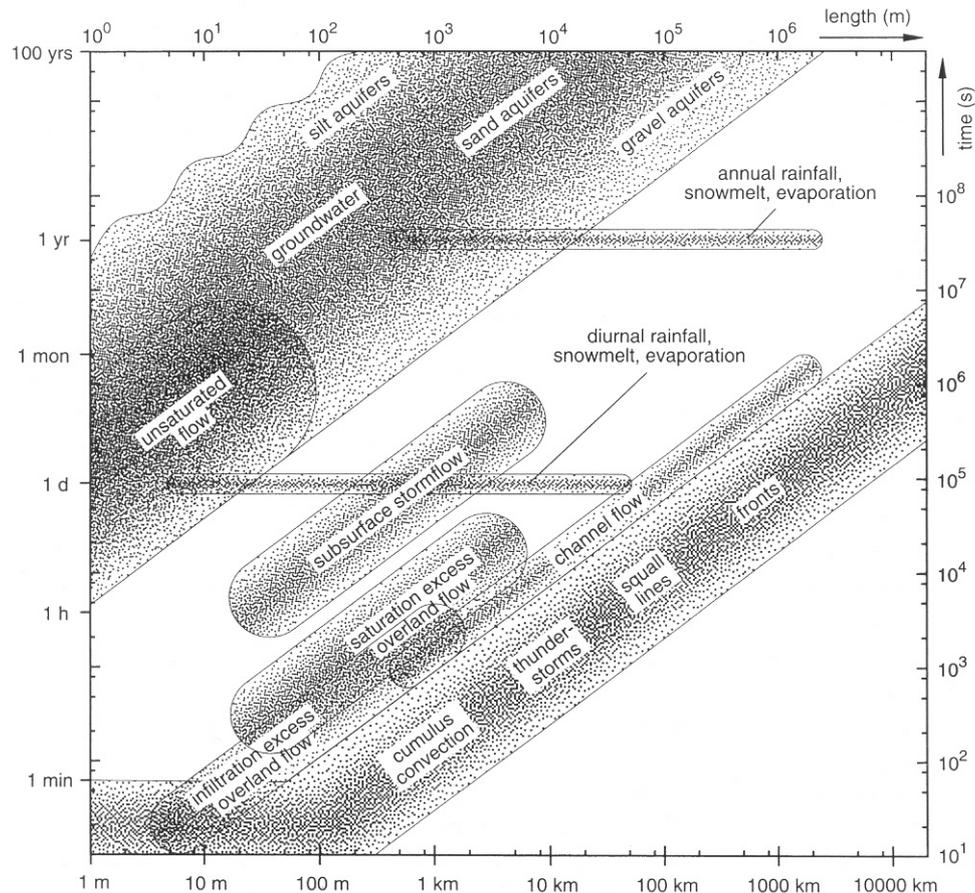


Figure 2: Schematic relationship between spatial and temporal process scales for a number of hydrologic processes (from Grayson et al. 2001, reproduced from Blöschl et al. 1995)

Runoff to surface waters consists of three main runoff components contributing in different intensities temporally as well as spatially to total runoff: the surface runoff, the lateral runoff (interflow) and groundwater runoff (base flow). To which extend each runoff component contributes to total runoff is related to pattern of soil, vegetation, micro topographic features and pattern of rainfall (Grayson et al. 2001). In addition to the three runoff components point discharges to surface waters may become of local importance, if the contribution has a significant share on the total river discharge. Furthermore, discharges from drainages have to be considered with locally different interest. Anyhow, in this chapter the three main runoff components are a matter of interest only.

Each runoff component is characterised by a certain travel time and reaches the surface water with a specific time delay (Dyck et al. 1983). While the surface runoff and interflow have a relatively short time delay in a range of hours to days (and therefore can be summarized to direct runoff), the base flow (groundwater flow) is characterised by a time delay ranging from several months to years and mainly contributes to basic runoff of surface waters (see Figure 2).

Surface runoff is linked to the occurrence of storm events generating partially temporal and spatial soil saturation conditions (precipitation intensity is higher than infiltration capacity of soils (Dyck et al. 1983)) leading to temporarily saturated flow on the soil surface. According to Figure 2 surface runoff generating processes (overland flow) are linked to temporal appearances of minutes to hours covering a spatial expansion of 10m up to 1km. Due to the high flow velocity and the high shear

stress nitrogen is transported via surface runoff as suspended solids via erosion. In regard to temporal variation, this kind of transport process fluctuates throughout the year and naturally requires a precipitation event with minimum precipitation intensity (means it is event-based only).

Interflow (lateral flow) occurs mainly in unsaturated, subsurface zones. This runoff component is likely to occur in soils on boundary layers with an abrupt change (decrease) in vertical hydraulic conductivity or in macro pores promoting preferential flow of infiltrating water. Soils which are characterised by high slopes (mountainous regions) with multiple layers with significant deviations in hydraulic conductivities or high fractions of rock fragments promote interflow generation to a high extent. Transport processes associated with interflow are very much dependent on soil type, and predominantly soluble transport processes are associated with interflow. In macro pores with higher flow velocities, transport of suspended solids is likely to occur. Similar to surface runoff, the temporal variation of interflow is connected to periods with higher precipitation intensities, when precipitation amount exceeds the amount of soil water, which is needed to replenish the soil water content to exceed field capacity and becomes therefore available for downwards flow. According to Figure 2 interflow (subsurface storm flow) is associated with a temporal scale covering hours up to months with spatial expansion of up to 10km.

Groundwater flow or base flow is known as saturated, subsurface flow from confined or unconfined aquifers with different hydraulic conductivities. Bedrocks are characterised by a very low hydraulic conductivity, but can transport considerable amounts of water over large distances due to rifts and disruptions. Groundwater recharge mainly stems from precipitation, which infiltrates into the soil and percolates to the groundwater surface against suction power or soil matrix potential. Only the amount of percolation water which exceeds the field capacity of the soil will become available for flow due to gravity (Burt et al. 2002). Groundwater flow can be characterized by Darcy's law (Dyck et al. 1983):

$$v_f = k_f * \frac{\Delta h}{\Delta x} \quad (\text{Equation 8})$$

with v_f = Darcian (discharge) velocity; k_f = saturated hydraulic conductivity; Δh = difference in groundwater head; Δx = flow distance. When all the pore space is occupied, a distance groundwater velocity v_a can be calculated:

$$v_a = \frac{v_f}{n_e} \quad (\text{Equation 9})$$

with n_e = effective porosity. Groundwater flow is possible in primary or secondary hollows only. These hollows significantly define the hydraulic conductivity and the storage capacity of an aquifer (Busch et al. 1974). Despite the hydraulic gradient, groundwater flow therefore depends on the aquifer type and the associated saturated hydraulic conductivity. Heterogeneities in aquifer materials are responsible for local differences in saturated hydraulic conductivities resulting in ranges of discharge velocities covering some hundred meters per day for highly permeable, coarse gravels down to several decimetres per day for very low permeable, fine sands (Spitz et al. 1996). This explains both the time delay in groundwater flow related to precipitation events, and transport of matter in soluble form only due to the low discharge velocity and the filter effect of the saturated aquifer material.

Groundwater flow is the basic flow component contributing to river discharge and occurs permanently throughout the year with little variations in contribution only. Variability in the amount of groundwater flow due to variations in groundwater recharge rates and seasonality of evapotranspiration are superposed by temporal scales covering months up to hundreds of years with spatial contributions from hundreds of kilometres reasonable for groundwater flow (Figure 2).

Figure 3 gives an overview about differentiation of main runoff components in terms of their time delay and spatial appearance in regard to contributions to the surface water. If precipitation intensity exceeds the soil infiltration capacity, surface runoff is generated and contributes directly to surface waters with a short time delay only. Additionally, lateral flow (interflow) is generated in the soil profile. With short distances to surface water, lateral flow may directly contribute to surface water. If lateral flow is generated in soils far away from the surface water, most of the lateral flow will contribute to the subjacent saturated zone (groundwater).

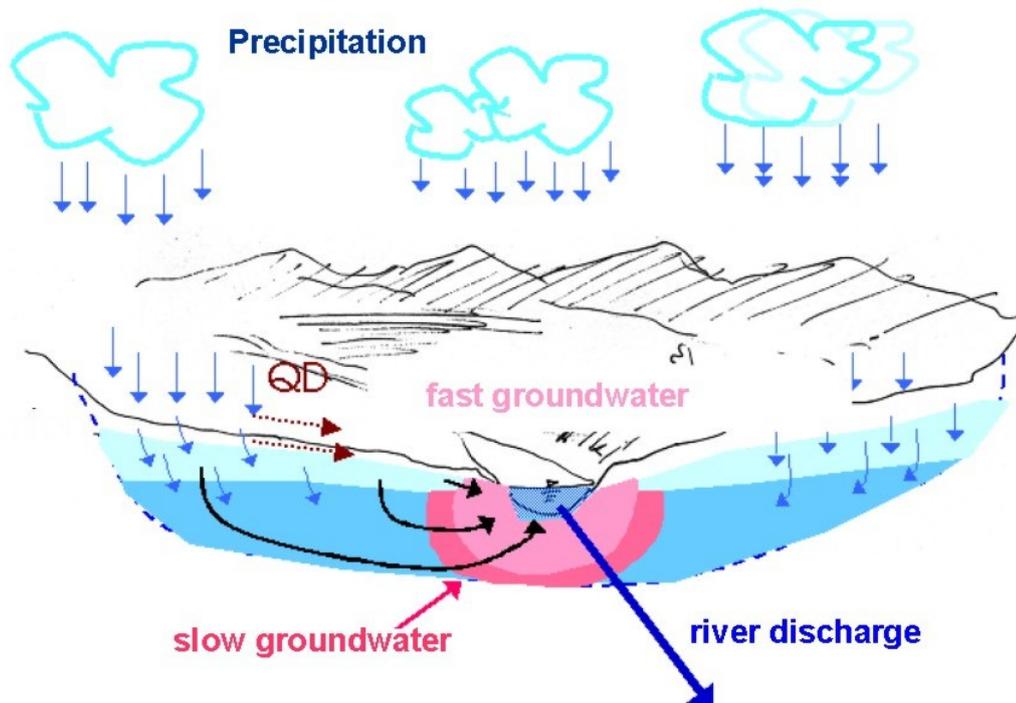


Figure 3: Visualisation of the concept on runoff components and their time delay in terms of contribution to surface waters (from Heinecke 2004, modified)

Groundwater flow (base flow) is generated by percolation from soil, which reaches the saturated zone across the catchment area. Due to the contribution of percolation the groundwater head rises and groundwater flow will be initiated. Percolation water, which infiltrates groundwater at high distances to surface water will contribute to the surface water with a high time delay (according to streamlines – see Figure 3 black lines). This groundwater can be termed slow groundwater. Percolation water, which infiltrates the groundwater near the surface water, will become available for surface water with a shorter time delay. This groundwater can be termed fast groundwater and will be a mixture of 'old' groundwater with a long travel time (groundwater residence time) and 'young' groundwater from percolation and partially from interflow near the surface water (see also Figure 4).

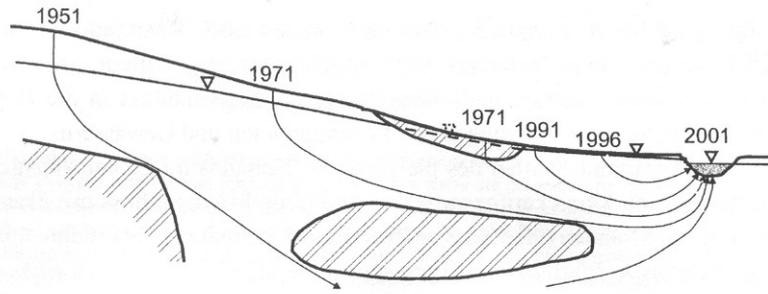


Figure 4: Connection between distances of catchment areas to surface waters and groundwater residence time (from Quast et al. 2001, modified)

In Figure 4 the influence of location of catchment areas in relation to the groundwater residence time is shown. The groundwater from areas with large distances to surface waters is characterised by long travel times until infiltration into the surface water. As closer the groundwater flows towards the surface water, the more the groundwater becomes a mixture of 'old' and 'young' groundwater.

Nitrate is the nitrogen compound with the highest mobility and is transported in a soluble form. It is leached from the unsaturated zone with percolation (groundwater recharge). Thus, nitrate transport occurs via interflow and groundwater flow (Wilkison et al. 2000, Haag et al. 2001). In surface runoff organic nitrogen and ammonium is transported. Thus, nitrogen transport varies between the runoff components in terms of nitrogen compounds, transport mechanisms and seasonal variations.

In regard to Figure 3 and the statements in terms of runoff generation under different time and spatial scales it can be expected, that nitrogen is contributed to surface waters predominantly as nitrate via groundwater. The location of areas within the catchment can affect nitrate emissions by groundwater to a different extent. Denitrification processes in groundwater are a function of groundwater residence times and they affect the nitrate loads considerably, which are contributed to surface waters. Thus, nitrogen contributions to surface waters are influenced by the location of areas within the catchment, by the hydrologic and hydrogeological conditions (which are reflected in specific groundwater residence times) and by nitrate concentrations in percolation water.

2.2.4 Nitrate transport under the aspect of heterogeneous groundwater flow pattern

In groundwater, nitrate is primarily transported convectively by water drift. The convective transport is superposed by diffusion and dispersion effects caused by several stochastic circumstances of aquifer textures, namely aquifer anisotropy or heterogeneity in vertical and horizontal direction.

Molecular movement accounts for diffusion effects leading to a compensation of concentration gradients. The diffusion rate is independent from groundwater flow velocity. Naturally, the fraction of diffusion contributing to mass transport can be neglected in comparison to convective transport. The more the groundwater discharge velocity will converge closer to laminar flow conditions, the higher diffusion effects will become considerable (Ohlenbusch 2000).

The transport vector at every aquifer spot consists of a vertical and a horizontal component (Rohmann et al. 1985). Due to aquifer anisotropy and heterogeneity and hence a heterogeneous distribution of grain and pore sizes, almost all aquifer spots have a unique composition of the vertical and horizontal flow component leading to a gradually transversal widening of the flow pattern by hydro mechanical dispersion. In relation to the considered scale, different reasons are encountered for hydro mechanical dispersion effects as shown in Figure 5.

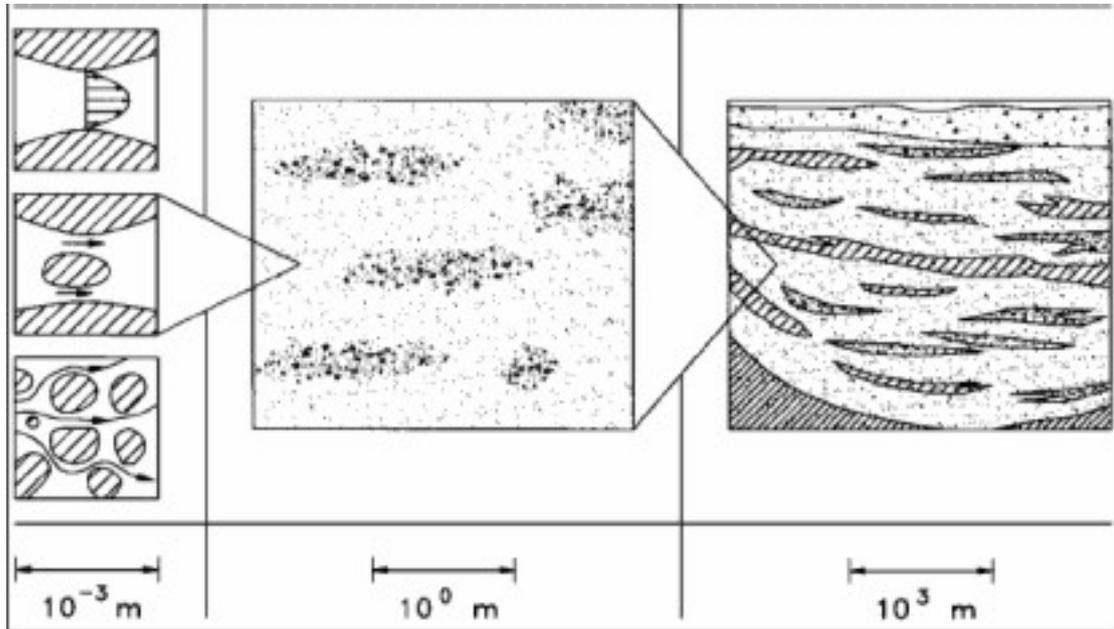


Figure 5: Reasons for scale-related dispersion effects (micro scale dispersion by granular structure – left; small scale macro dispersion – middle; big scale macro dispersion – right) (from Ohlenbusch 2000, modified)

At the micro scale (Figure 5 - left side), dispersion effects are mainly caused by heterogeneities in granular structure and differences in flow distances. Moving to a bigger scale (small scale macro dispersion, Figure 5 – middle), aquifer heterogeneities due to different grain sizes distributions and bulk densities are reasons for dispersion effects. At the local or regional scale the big scale macro dispersion (Figure 5 - right) is caused by aquifer anisotropy (horizontal hydraulic conductivity \neq vertical hydraulic conductivity) and heterogeneities due to different aquifer materials and layers becoming the dominant reason for heterogeneous flow pattern. Dispersion effects are related in amount and direction to groundwater flow pattern. Longitudinal dispersivity (in flow direction) is generally higher as compared to transversal dispersivity (across flow direction). Furthermore, the longitudinal dispersivity is enhanced with an increasing flow distance leading to a protraction of groundwater flow pattern (Ohlenbusch 2000).

Retention elements and corridors are of oppositional significant influence on nitrate transport due to the retention time being a crucial factor for nitrogen removal. Retention elements are defined as locations where the transfer rates change abruptly due to storage, elimination or transfer processes to other compartments. Retention is largely determined by retention time and the area of contact. In contrast, corridors of preferential flow are matter of rapid translocation, so that residence time is shortened, retention zones are bypassed and spatial distances are bridged (Haag et al. 2001). However, the nitrate transport in saturated zones is the consequence of

hydraulic convection due to a certain hydraulic gradient with major influence of dispersion and diffusion on temporal and spatial dissemination of groundwater plume. The lower the convective groundwater velocity then diffusion effects will become considerable for transport processes.

2.2.5 Relevance for groundwater quality

Nitrogen is stored in soil as organic nitrogen compounds. Via mineralisation processes the organic nitrogen will be transformed to ammonium NH_4^+ and nitrate NO_3^- . Nitrate is the mineral nitrogen species having the highest oxidation level. Therefore, mineralisation processes are targeted on oxidation of nitrogen to nitrate. Since the soil matrix is usually well vented, mineral and organic fertilizers will be transformed to nitrate. Nitrate is the most important nitrogen species, that is translocated via percolation to the groundwater body and is therefore of great importance in terms of impacting groundwater quality.

Therefore, impacts of nitrate on groundwater quality are dependent on:

- Nitrogen surplus on top soil (as function of fertilizer application, N-fixation and nitrogen input by atmospheric deposition)
- Precipitation and average groundwater recharge rate
- Fertilizer application (kind of fertilizer, doses of application)
- Specific nitrogen uptake by crops
- Moment of fertilizer application(s) (seasonal aspects, nitrogen demand of plant due to growing stage)
- Soil conditions (available organic carbon) and soil thickness

If the available nitrate in the soil profile exceeds the actual nitrogen demand of plants, the nitrate will be irretrievably leached out from the soil to groundwater.

In the groundwater body the nitrate is subject of microbial decay via denitrification, if the required environmental conditions are sufficiently met. As a function of the groundwater residence time (reaction time), the presence of anoxic conditions and the availability of organic carbon or alternative electron donors, nitrate will be denitrified subsequently leading to a constant decrease of nitrate concentrations in groundwater towards the surface water. Nitrate concentrations in groundwater are therefore balanced between nitrate inputs via leakage water and nitrate reduction via denitrification. Assuming a constant nitrogen surplus and a constant groundwater recharge rate on catchment area, according to explanations in chapter 2.2.3 nitrate concentrations in groundwater will decrease with decreasing distances to surface waters due to the increasing influence of denitrification activity in groundwater.

2.3 Identification of denitrification processes in subsurface natural zone

2.3.1 Kinetics of denitrification

The denitrification rate can be described by law of Michaelis-Menton:

$$\frac{dc(NO_3^-)}{dt} = -k \frac{c(NO_3^-)}{K_S + c(NO_3^-)} \quad (\text{Equation 10})$$

with k as denitrification rate (maximum reaction rate, V_{\max}) and K_S as Michaelis-Menton-constant (substrate specific constant; is equal to substrate concentration, at which reaction rate is half of k) (Rohmann et al. 1985, Kreuzinger 2005, Strong et al. 2002).

If there is no limitation by diffusion or substrate availability the reaction can be characterised as zero order kinetic reaction, the reaction rate is constant and independently from substrate concentration. If there is limitation by substrate (nitrate) availability, the reaction rate is dependent on substrate concentration and can be characterised as first order kinetic reaction. The decay coefficient k (denitrification rate coefficient) is dependent on environmental conditions as temperature, pH, oxygen conditions and availability of electron donors (organic carbon/pyrite) or nitrate (limiting substrate concentrations).

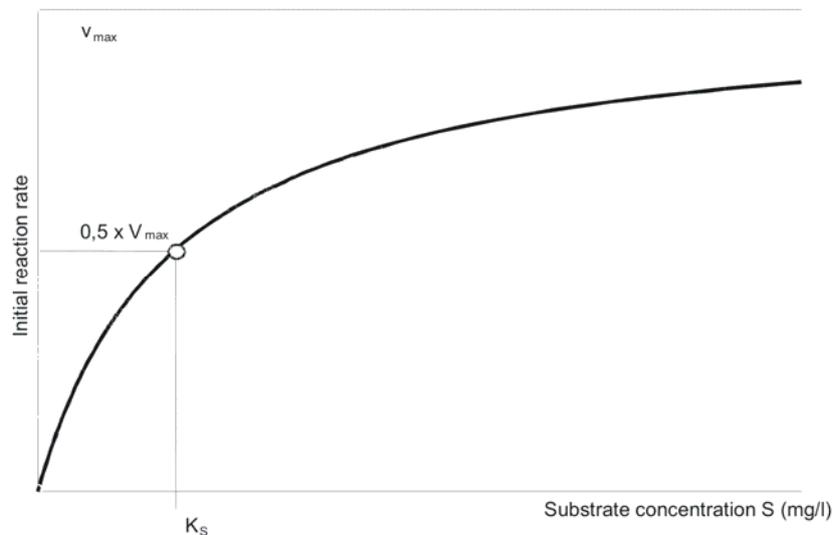


Figure 6: Relation between reaction rate and limiting substrate concentration of an enzyme reaction of a first order kinetic (from Kreuzinger 2005)

For a first order kinetic reaction a half life time τ can be calculated from equation 10:

$$\ln \frac{c(NO_3^-)}{c_0(NO_3^-)} = -k\tau \quad (\text{Equation 11})$$

with k as denitrification rate. The half life time describes the time, after which half of the initial concentration is turned over (Kreuzinger 2005).

Several half life times for denitrification are reported in literature distinguishing strictly between autotrophic and heterotrophic denitrification. Substrate availability

(organic carbon, pyrite) as well as boundary conditions (denitrification in unsaturated or saturated zone, aquifer thickness) are of significant importance and do influence half life times for denitrification considerably. Thus, reported half life times cover a wide range from several days up to several years.

Clay et al. (1996) report half life times for heterotrophic denitrification in a shallow aquifer of approximately 28 days. Pauwels et al. (2000) found for small scale tracer tests undertaken to evaluate denitrifying capacity of lower aquifer compartments of a schist aquifer, where pyrite is present, half life times of 7.9 days for a high-permeability aquifer medium and of 2.1 days for a low-permeability aquifer medium. Pauwels et al. (1998) and Wendland et al. (1999) report nitrate half life times for autotrophic denitrification have been observed in the Fuhrberg field (Germany) in a range of 1 to 2.3 years. Additionally Wendland et al. (1999) report a half life time for heterotrophic denitrification of 4 years, whereby the nitrate transformation using easily degradable carbon sources in undisturbed aquifers is assumed to proceed much faster (factor 2) than nitrate transformation using reduced sulphur species. Polzer (2005) calculated average half life times for heterotrophic denitrification in two Austrian aquifers ranging between 1.2...6 years. In DVWK et al. (1999) a half life time of 10 years was used for nitrogen emission calculations with consideration of denitrification processes in the saturated zone.

Using a half life time for the characterisation of denitrification means that nitrate reduction is first of all limited by nitrate availability. The wide ranges of the reported half life times are matter of individual environmental conditions and reflect e.g. the availability of electron donors. Half life times for denitrification within several days suggest rapid nitrate transformation and high denitrification rates with good substrate availability and optimal environmental conditions (anoxic status, pH), whereas from half life times of several years substrate limitation of nitrate and the specific electron donor (organic carbon / pyrite / iron) or suboptimal environmental conditions can be concluded, what results in comparably low denitrification rates. Assuming a certain half life time for the denitrification process therefore requires information on limiting substrate availability (nitrate, organic carbon or pyrite) and aeration status (unsaturated zone, shallow or deep saturated zone) of the considered compartment.

Reduction of nitrate concentrations in groundwater can not only be attributed to denitrification processes. Likewise decreases in nitrate concentrations in groundwater may be caused by underflow of low-nitrate-concentration-groundwater from changing landuse (Böttcher et al. 1990) or by dissimilatory nitrate reduction to ammonium (Matheson et al. 2002). Thus, methods quantifying denitrification rates were developed aiming at the assessment of biological end- or by-products related to denitrification rates, adequate changes in environmental conditions due to denitrification (e.g. isotope fractionation of groundwater) or of denitrifying enzyme activity. The most common methods will be briefly presented in the following chapters.

2.3.2 Current methods for estimation of *in-situ* denitrification rates

2.3.2.1 Isotope analysis

Several studies reported measurements of denitrification rate in groundwater using isotope analysis of ^{15}N / ^{14}N ratios from groundwater samples (Vidon et al. 2004,

Cey et al. 1999). Generally typical $^{15}\text{N} / ^{14}\text{N}$ ratios can be associated with different nitrogen transformation processes, and therefore isotope analysis of nitrate are often used for identification of *in-situ* denitrification processes. $\delta^{15}\text{N}$ signatures can be calculated using the following equation:

$$\delta^{15}\text{N} = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \right] * 1000 \quad (\text{Equation 12})$$

where R_{sample} and R_{standard} are the $^{15}\text{N} / ^{14}\text{N}$ ratios of the sample and the standard, respectively. The reference standard is atmospheric nitrogen for $^{15}\text{N} / ^{14}\text{N}$ (Cey et al. 1999, Vidon et al. 2004).

Typical $\delta^{15}\text{N}$ signatures are 0 to +4 ‰ for nitrate derived from inorganic (nitrogenous) fertilizers, +9 to +20 ‰ for nitrate derived from sewage waste and +4 to +9 ‰ for nitrified soil organic nitrogen (Griseck et al. 1998, Cey et al. 1999, Feast et al. 1998). Denitrification processes typically deplete nitrate concentrations resulting in isotopically heavier $\delta^{15}\text{N}$ signatures for residual nitrate (Feast et al. 1998, Griseck et al. 1998, Böttcher et al. 1990). Pauwels et al. (2000) could observe a hyperbolic relation between $\delta^{15}\text{N}$ signatures and nitrate concentrations providing $\delta^{15}\text{N}$ signatures of hypothetical partially denitrified groundwater samples of $\delta^{15}\text{N}=25\text{‰}$. Also Böttcher et al. (1990) confirm that $^{15}\text{N}/^{14}\text{N}$ ratios can be valuable for revealing the significance of denitrification. A significant relationship could be observed between the logarithm of the unreacted residual nitrate fraction and the isotope ratio ($\delta^{15}\text{N}$) for ^{15}N with constant enrichment factors (ϵ), which amount to $\epsilon = -15.9\text{‰}$ (see Figure 7).

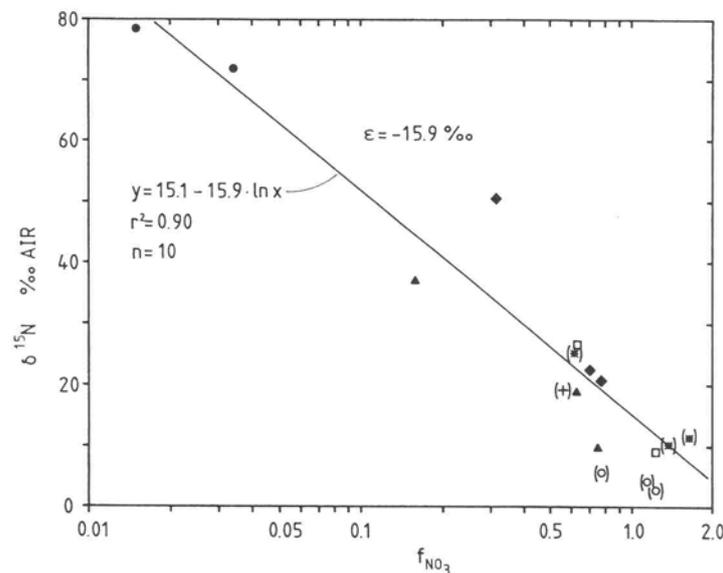


Figure 7: Dependence between nitrogen isotope ratio in the residual nitrate ($\delta^{15}\text{N}$) and the fraction of the unreacted residual nitrate ($\ln(f_{\text{NO}_3})$) in denitrification in the groundwater of the 'Fuhrenberger Feld' (from Böttcher et al. 1990)

The enrichment of $\delta^{15}\text{N}$ values from 8.6‰ in river water (median value) to 14.6‰ in granular aquifer material under anaerobic conditions could be attributed by Griseck et al. (1998) to microbial denitrification in the zone of river-water infiltration. Vidon et al. (2004) found that $\delta^{15}\text{N}$ values in groundwater flowing from upstream cropland to riparian zones generally ranged between +3.8 to +5.5 ‰. Groundwater discharging towards the ground surface near the riparian sites showed enriched $\delta^{15}\text{N}$ values between +10.5 to +34.6 ‰ in conjunction with a large

reduction in nitrate concentrations. In addition a strong inverse relationship between the dissolved oxygen concentration in the groundwater and the $\delta^{15}\text{N-NO}_3\text{-N}$ values was evident.

However, the variability of landuse specific nitrate concentrations in groundwater recharge and the variability of the initial isotope ratios in nitrate may be factors masking the specific isotope fractionation of nitrate-nitrogen because of denitrification processes and thus preventing definite and consistent interpretations (Böttcher et al. 1990). The resultant $\delta^{15}\text{N}$ signature is often the product of multiple sources mixing which further complicates the source identification (Wilkison et al. 2000).

2.3.2.2 Acetylene inhibition method

Denitrification rates vary greatly in time and space and are very sensitive to physical and chemical conditions in soil and groundwater. Direct measurements of denitrification activity cannot be undertaken by quantification of N_2 -production against the background of atmospheric N_2 (Jordan et al. 1998). Denitrification activity in soil and groundwater can be assessed indirectly by quantification of by- or endproducts of denitrification. Using acetylene, the last step of denitrification process (conversion from N_2O to N_2) will be suppressed and denitrification results in formation of nitrous oxide (N_2O) (Smith et al. 1979). The produced nitrous oxide can be analysed using a gas chromatograph. The amount of nitrous oxide which is produced, provides evidence on the occurrence of denitrification and can be fully attributed in quantity to denitrification activity, as reported in several studies (Clay et al. 1996, Vidon et al. 2004, Hefting et al. 1998, Stevens et al. 1997, Pavel et al. 1996, Ettema et al. 1999, de Klein et al. 1996).

Vidon et al. (2004) reported that the use of *in-situ* acetylene injections confirmed the occurrence of considerable denitrification activity in riparian zones, where isotope analyses of the ^{15}N revealed a small enrichment and no clear evidence on denitrification activity. Likewise acetylene inhibition technique was found to be more sensitive for assessing of denitrification activity as compared to experiments measuring nitrate loss rates (Clay et al. 1996). Hefting et al. (1998) revealed that according to other studies measured denitrification rates are frequently too low to account for the total amount of nitrate removed from groundwater. This was explained by high spatial and temporal variability of denitrification. Additionally, using the acetylene inhibition method, the contribution of nitrification to nitrous oxide production should not be neglected (Hefting et al. 1998, Stevens et al. 1997).

Results found by Burt et al. (1999) for field measurements of denitrification using intact soil cores with acetylene indicated denitrification to be the main source of $\text{N}_2\text{O-N}$, but nitrification being a relatively significant component at times of low absolute emissions from predominantly aerobic soils.

Both presented methods for estimation of *in-situ* denitrification give a strong evidence for occurrence of denitrification activity in soil and groundwater. Nevertheless, both methods implicate high uncertainties in reliability in regard to the significance of the observed denitrification activity due to specific environmental conditions.

Due to the fact that denitrification activity cannot be measured directly, the present *in-situ* methods are widely used in practise for quantification of denitrification rates in

soil and groundwater. The following chapters (2.3.3 and 2.3.4) will deal with environmental conditions, which were observed being favourable for denitrification in unsaturated and saturated zone. Most of the studies presented, are based on measurements of *in-situ* denitrification activity using the previously presented methods.

2.3.3 Denitrification in unsaturated zones

In Austria almost half of the drinking water demand is provided by groundwater from porous aquifers. Additionally, the resource groundwater is used for water supply for industry and agriculture. Most of the groundwater is situated in the tertiary or quaternary aquifers of bigger river basins. Especially these areas are intensively used by agriculture, industry or settlements resulting in considerable conflicts in terms of utilisation (Stalzer 1991).

Therefore, the reduction of diffuse nitrate pollution from agriculture is one of the main objectives of the EC Nitrates Directive (1991) to prevent further groundwater pollution. The criterion for identification of affected water bodies is a nitrate concentration above 50mg/l in freshwater (Goodchild 1998). The drinking water ordinance being the statutory framework for utilisation of groundwater for drinking water supply defines the limit value for nitrate concentration to 50 mg/l NO₃ (TWV 2001). Additionally, the regulation for precautionary protection of groundwater (Austrian groundwater threshold regulation (BGBl213 1997)), which aims to prevent contaminations from groundwater by specifying threshold values for groundwater parameter, defines a groundwater threshold value for nitrate of 45 mg/l NO₃. Exceeding this threshold values permanently would mean to recommend actions for restoration of the respective groundwater body in order to avoid a further increase in nitrate concentrations.

As reasons for the systematic increase of nitrate concentrations in groundwater Stalzer (1991) mentions despite the loads from settlements (waste water, husbandry) aberrations in agricultural practise like:

- Artificial increase in soil fertility due to excessive fertilization over long periods of shallow soils
- Failures due to inappropriate fertilizer application of manure
- Over-fertilization by non-observance of manure applications
- Cultivation of monocultures, insufficient use of intercrops
- Grassland conversion
- Relatively high fertilization level with possibly high leaching or shifting capabilities in shallow soils

However, the nitrate concentrations in groundwater often are considerably lower than theoretically expected from long term groundwater recharge rates in connection with nitrate loads from percolation can be expected (Rohmann et al. 1985). There is agreement that the two major processes responsible for the removal of nitrate from groundwater recharge are denitrification and plant uptake (both by vegetation and the soil microbial biomass) but there is no agreement on the relative importance of these two processes in many landscape situations (Gilliam et al. 1997). In agricultural areas plant uptake considerably dominates nitrogen removal from soils in

comparison to denitrification processes. In regard to excessive nitrogen in soils, which exceeds the amount of nitrogen is taken up by plants, investigations by Schilling et al. (2005) and Rohmann et al. (1985) indicated that decreases in nitrogen concentrations in unsaturated zone during unsaturated subsurface flow are mainly caused by denitrification. In the unsaturated zone (as well as in the saturated zone) the denitrification capacity is largely determined by environmental conditions. Prior to nitrate availability, the availability of organic substances and the degree of soil saturation (soil water content) significantly specify denitrification rates in soils. The physical and geochemical soil conditions are site-specifically unique and interactive to a high degree resulting in complex interrelations impeding exact declarations of the controlling factors limiting denitrification activity in particular cases. Numerous studies were conducted focussing on identification of decisive environmental conditions inducing denitrification in soil and subsurface, unsaturated zones.

Burford et al. (1975) reported that denitrification in soils under anoxic conditions is controlled largely by the supply of readily decomposable organic matter, which is required by bacterial community to sustain their metabolism (Burt et al. 1999). To ensure anoxic conditions in soil profile, the soil water content is of decisive importance regulating predominantly oxygen and nitrate diffusion rates. Hydraulic conductivity of unsaturated zone is determined by soil water content (matrix potential) and reaches its maximum value with 100% soil saturation (saturated hydraulic conductivity). The lower the soil water content becomes, the more diffusion processes are limited by insufficient conductivity of soil profile for dissolved transport (nitrate limitation).

According to equation 5 in chapter 2.1.3 1g NO₃-N requires about 1.1g of organic carbon to be denitrified. It is not clear whether soluble carbon in percolation and subsurface runoff is sufficient or if the soil or vegetation provides the dominant supply of carbon. The upper horizons of soils are mostly rich in organic carbon and denitrification appears to operate effectively, but these horizons are unsaturated for most of the time, and if soil water conditions are inappropriate, actual rates of denitrification will fall greatly below their potential maximum (Burt et al. 1999).

Field measurements of denitrification in riparian buffer zones using intact soil cores showed higher denitrification rates for floodplain soils associated with low bulk density, microporous and waterlogged conditions (thus anaerobic), with relatively high nitrate and available carbon content. Lower denitrification rates on hillslope soils were related to higher bulk density, more open-textured coarse sandy loam soil that remained relatively dry (thus aerobic) and had low soil nitrate and available carbon content. Denitrification rates were estimated from intact soil cores via average N₂O soil fluxes to be between 4.9 kgN/ha*a (no acetylene added) and 13.3 kgN/ha*a (with acetylene added) (Burt et al. 1999). Soil nitrate was revealed to be the primary control of denitrification in these riparian soils. The principal function of soil water in floodplain soil was to cause of anaerobiosis, and in the hillslope soil it was in leaching nitrate. This underlines the importance of soil water regulating diffusion limitations both of nitrate as well as of oxygen.

De Klein et al. (1996) confirmed that denitrification rates in grassland soils were primarily affected by soil water conditions. Increased denitrification rates following irrigation on investigated study plots were attributed to increased soil water contents which increased the development of anaerobic zones. They give a summary on

several soil specific threshold values given in literature, above which denitrification rates sharply increased with soil water content (Table 1) in relation to the soil type.

Table 1: Summary of threshold values given in literature, above which denitrification rates sharply increases with soil water content (from de Klein et al. 1996)

Denitrification measured using	Threshold	Soil type	% Clay	References
Soil covers	pF 2.4	Sandy to silty loam	13-28	(Ryden et al. 1980)
	62% WFP ^a	Loam	NG ^b	(Grundman et al. 1987)
Repacked core air dried and sieved	6-90% WFP	Sand loam	11	(Aulakh et al. 1991)
	60-90% WFP	Silt loam	21	
	60-90% WFP	Silty clay	44	
	89% WFP	Loamy sand	NG	(Pilot et al. 1972)
	88% WFP	Fine sandy loam	NG	
	86% WFP	Silty clay loam	NG	
	88-90% WFP	Loess	14	(Prade et al. 1988)
	90% WFP	Silt loam	24	(Weier et al. 1993)
Intact soil core	90% WFP	Silty clay loam	34	
	42-55% WFP ^c	Loam	19	(Klemedtsson et al. 1991)
	57% WFP	Loam	15-20	(Johnsson et al. 1991)
	100% WHC ^d	Loam	19	(Nommik et al. 1989)
	100% WHC	Clay	68	
	60% WFP	Clay loam	34	(Sextone et al. 1988)
	82% WFP	Sand	3	(de Klein et al. 1996)
	83% WFP	Loam	23	
71% WFP	Peat	22		

^aWFP = water-filled porosity.

^bNG = not given.

^coriginally given as 160-210 ng H₂O g⁻¹ dry soil but recalculated assuming a bulk density of 1.2 g cm⁻³ and a total porosity of 45%.

^dWHC = water-holding capacity.

Most soils showed a non-linear relationship between denitrification activity and soil water content. In general, water thresholds for denitrification activity decreased when soil textures became finer (see Table 1). This effect was attributed to oxygen availability. Even at relatively low WFP (water filled porosity) values in a fine-textured soil, anaerobic microsites are present in which denitrification can occur (de Klein et al. 1996). The Investigations showed increased denitrification rates by factor 3...10 when temperatures were increased from 10°C to 20°C. Differences were obtained between irrigated and non-irrigated study plots indicating the larger increase for non-irrigated plots. Beside the enhanced activity of denitrifying bacteria the temperature indirectly affects denitrification activity by increased respiration rates which result in an increase in the volume of the anaerobic zones.

Ettema et al. (1999) found positive correlations of denitrification dynamics to soil moisture in riparian soils as well. The soils near the stream (Zone 1: av. 75% WFP (water filled porosity), 2-5% soil carbon content) showed 10-fold higher denitrification (average denitrification rate 84 ngN g⁻¹soil d⁻¹) rates than 10m upslope situated soils (Zone 2: av. 51% WFP, 1-3% soil carbon content; average denitrification rate 9 ngN g⁻¹soil d⁻¹), the latter being primarily limited by lower soil moisture providing insufficient anaerobicity than by availability of organic carbon. As zone 1 soils were water-saturated at least for 50% of the experimental period, the availability of oxidizable C probably limited denitrification rates in this zone. Hefting et al. (2003c) found clear indications for environmental controls on process rates of denitrification. Spatial pattern in denitrification were observed to coincide with spatial

pattern of pH and of water filled pore space. Low denitrification activity coincided with soil pH below 4.0 and water filled pore space below 70%. Contrary to the expectations the spatial pattern of denitrification rates did not resemble clearly nitrate concentrations in pore water. However, denitrification was significantly influenced by soil variables influencing the moisture and oxygen status as well as pH of soil. The role of soil pH was confirmed by Simek et al. (1998) for fertilized and unlimed soils too. The study revealed a coinciding acidification of the studied soils due to fertilization and an insufficient soil buffer capacity resulting in reduction of soil pH.

Smith et al. (1998) reported dramatically increased denitrification activity when water filled pore space exceeded 80% in the investigated clay loam soil. Adelman et al. (1996) reported that denitrification occurs at moisture levels above 60% of the water holding capacity for sandy soils regardless of the carbon hydrate supply, nitrate concentrations or pH. Above this moisture level the denitrification rate is directly related to moisture content.

In surface soils of a riparian forest Jordan et al. (1998) investigated the influence of water, nitrate and carbon additions on denitrification rates. Water and sucrose additions resulted in a remarkable increase in denitrification activity due to the expansion of anaerobic conditions into formerly aerobic, nitrate-rich zones by filling soil pores with water and restricting oxygen diffusion and by enhanced respiration activity, respectively. These surface soils showed a large potential for rapid increase in denitrification rates, when conditions become favourable and not limited by nitrate and oxygen diffusion or by the presence of organic carbon.

Water table fluctuations of groundwater in riparian zones are of significant importance for denitrification rates in respect to soil water conditions in unsaturated zones too. The key role of groundwater table level in soil N cycling processes in riparian zones was confirmed by Hefting et al. (2004) emphasising oxygen diffusion limitation by filling the soil pore space and triggering anoxic conditions. When the water table is high, reaching into the upper parts of the soil profile where denitrification potential is greatest, denitrification rates will be maximized. Denitrification rates reported by Hefting et al. (2004) were directly related to the water table level. That poses seasonal effects in riparian buffer zone functioning by hydrology, which was reported by Burt et al. (2002), where water tables of riparian zones in summer (dry conditions) fell below the surface organic horizon. Then, denitrification can only occur in fine-textured soils and is probably triggered by short-term events such as rainfall or flash floods that generate partial anaerobiosis in these fine-textured soils (Hefting et al. 2004).

Relating denitrification activity to the depth profile, the highest denitrification activity (60%) was found by Burt et al. (1999) in the top 10cm, whereas little denitrification activity occurred below 40cm as consequence of availability of organic carbon sources. Similar changes in denitrification rates with depth were found by Strong et al. (2002), which attributed the wide range of denitrification rates observed in sandy soils to both the wide range of carbon contents in soils as well as the range of matrix potential (the experimental design applied certain suction powers to the studied soil cores for a certain time, afterwards the volumetric water content and the water-filled pore space was calculated for each soil core). In most of the studied soil cores (26 out of 36) denitrification responses could be described by a Michaelis-

Menton function with parameters given in Table 2. Calculated mean half life times from Michaelis-Menton-parameter in Table 2 reveal the large denitrification potential due large quantity of nitrate and organic carbon in the upper parts of soil layers, if water saturation in soil provides the development of anoxic conditions. In comparison to half life time reported for saturated zone (chapter 2.3.1), values in Table 2 show significantly larger denitrification activity in soils with sufficient soil water content.

Table 2: Mean Michaelis-Menton parameter for denitrification corrected for respiration (taken from Strong et al. 2002, modified) with V_{\max} and $K_m \pm$ standard deviation

Matrix potential (kPa)	Mean volumetric Water content [cm ³ cm ⁻³]	V_{\max}	Michaelis-Menton-constant K_m [mgN l ⁻¹]	Calculated mean half life time ^b (in days) after (Bengtsson et al. 1995)
0-3 cm depth				
-0.5	0.448	549 ± 135	43 ± 17	0.028
-1	0.446	399 ± 117	24 ± 9	0.015
-4	0.350	73 ± 35	29 ± 13	0.10
3-10 cm depth				
-0.5	0.383	259 ± 138	20 ± 16	0.019
-1	0.335	52 ± 11	5 ± 2	0.024
-4	0.284	41 ^a	60	0.37
15-20 cm depth				
-0.5	0.303	2 ± 0.3	20 ± 14	1.98
-1	0.268	16	22	0.34
-4	0.236	0.7	9	3.12

^a only one core sample, ^b calculated related to reported V_{\max} -values given as [g N ha⁻¹ d⁻¹]

The matrix potential characterises the bond strength of soil water to the soil matrix. This dimension indicates the water volume which is stored in the soil against gravity. The matrix potential is equivalent to a negative hydrostatic pressure and is therefore usually identified by a negative algebraic sign (Dietrich et al. 2003). The observed decreasing denitrification rates in Table 2 with increasing depth were attributed to decreasing availability of organic carbon, to increasing presence of O₂ in pore space with decreasing matrix potential and to limited diffusion of nitrate with lower water content in soils. The water content of soil interacts with soil matrix and determines the flux density of a diffusing ion by determining the cross-sectional area available to diffusion and by altering the tortuosity of the diffusion path (Strong et al. 2002). The two aspects are multiplicative in their effects on diffusion, and therefore lower water contents in soil core require stronger concentration gradients of nitrate between the bulk solution and the active enzyme to sustain sufficient NO₃⁻ transport for denitrification. For the investigated soil cores it was found, that at lower water contents diffusion limitation is relevant to denitrification, at higher water contents availability of organic carbon will be relevant to denitrification in terms of limiting denitrification rates.

Willems et al. (1997) investigated nitrate removal in riparian wetland soils distinguishing between surface and subsurface soils. It was reported that denitrification activity was significantly higher in surface soils (0-15cm depth) than in the subsurface soils (25-75cm depth). Differences in denitrification activity were attributed to 20-200 times higher organic C in surface soils than in subsurface soils. The large nitrate removal capacity of surface soils masked the effect of changing

flow rates, especially at higher temperatures. In subsurface soils increased pore flow velocities further reduced microbial activity, and denitrification was remarkable influenced by temperature at all flow rates. The effect of temperature on denitrification was highest at faster flow rates due to a combination of temperature effect on biological activity and of physical effects like dilution limitation. The authors stated that at low flow rates, temperature effects on microbial activity will largely dominate diffusion limitations. Clay et al. (1996) compared surface soils to sediments above and beneath the groundwater table in regard to denitrification activity and organic carbon content. Calculated half life times from denitrification rates were substantially lower for surface soils (in average 24 days) than for sediments above the groundwater table (in average 693 days) and indicated limitation of denitrification by substrate availability (organic carbon).

Strong correlations between soil organic carbon, temperature and denitrification rates were observed by Pavel et al. (1996) too. Pondered (permanently saturated) surface soils (1-15cm depth), terrestrial surface (1-15cm depth) and subsurface soil (24-45cm depth) horizons were compared in terms of their denitrification potential at various temperatures. Generally, denitrification rates were higher for the pondered surface horizon for all temperatures compared to the terrestrial surface horizon, and 6-10 times higher compared to the terrestrial subsurface horizon. Although both surface horizons exhibited similar organic carbon contents and soil textures, a substantial difference in denitrification rates was observed which was attributed to differences in the compositional nature of the organic carbon sources and thus, to carbon availability. Mean denitrification rates were significantly higher for soils incubated at 19.9 °C ($0.65 \mu\text{molN g}^{-1}\text{dry soil d}^{-1}$ for surface soil; $0.06 \mu\text{molN g}^{-1}\text{dry soil d}^{-1}$ for subsurface soil) compared to either 16.4 °C or 13.5 °C ($0.4 \mu\text{molN g}^{-1}\text{dry soil d}^{-1}$ for surface soil; $0.04 \mu\text{molN g}^{-1}\text{dry soil d}^{-1}$ for subsurface soil). However, incubation temperature had much less of an effect on denitrification in the subsurface horizon compared to surface horizons. Accounting for total variability of denitrification rates, greatest variability (about 50%) was found between the different soil horizons while spatial variability in denitrification rates was much less (about 10%).

Leidig (1997) investigated denitrification limitation by availability of different organic carbon in soil due to agricultural management. It was found that denitrification was higher when applying dissolved organic carbon with manure than applying solid organic carbon. The latter manure application did not decrease denitrification in the long-term (contribution to organic C pool of soil) but did not substantially increased denitrification immediately. This reveals that solid organic carbon has to be broken down before becoming bioavailable what may result in lower denitrification rates as compared to availability of labile dissolved organic substances. For evaluating the available organic carbon content of soils for denitrification Rolland (1996) reports several assumptions with diverse extraction methods have been used in various studies and their correlations to nitrate reduction rates. Organic carbon content of surface soil, dissolved organic carbon and hot water soluble organic carbon are reported being highly correlated with denitrification rates in soils. The individual extraction methods detect only a fraction of organic carbon composition of the soil and therefore the author recommends to use total organic carbon of soil to predict denitrification, even the composition of organic carbon fraction becomes more homogeneous with increasing depth. He found that

denitrification rates were correlated exclusively to organic carbon content of soils and were therefore significantly higher (one order of magnitude) in surface horizons (0-30 cm depth, $c_{org} \approx 2\%$) than in subsurface layers (70-240 cm depth, $c_{org} \approx 0.2\%$).

Besides effects of soil water content, available organic carbon, soil pH or temperature on denitrification activity, the permeability of soils regulates percolation and influences denitrification. In soils which are highly permeable, the residence time of soil water is not long enough for anoxic conditions to develop. Additionally, coarse grained soils enhance aeration of soil pores space and are less effective in water storage against gravity compared to finer grained soils. In soils which are less permeable, subsurface flux of nitrate can be too small to be effective for nitrate removal from percolation.

Since the denitrification capacity in wet soils is limited by availability of organic carbon it could be expected, that denitrification might become less efficient with time due to carbon limitation by permanently excessive nitrate loads. However, for two chronically nitrate-loaded riparian buffer zones Hefting (2003) could show, that the annual carbon production rate exceeds the annual carbon consumption rate by denitrification. Nitrogen saturation effects were found indicated by a rapid decline of nitrogen removal efficiency with increasing nitrogen loading rates resulting beside lower nitrate removal rates among others in higher N_2O emissions and nitrate concentrations in pore water. Haag et al. (2001) reports that in wetlands only amounts below 200 kg N/ha*a could be removed satisfactorily (>80%), while the long-term application of higher loads resulted in removal of less than 40% of nitrogen load. On basis of incubation experiments Rolland (1996) found presuming a nitrogen surplus of 100 kgN/ha*a that the electron donors (organic carbon) in subsurface soils (70-100 cm depth) will be exhausted after 15 years, if no additional organic carbon will be supplied.

While heterotrophic denitrification in soils is dependent on soil water conditions and organic carbon content, autotrophic denitrification is assumed unlikely to occur in most of the soils. Available S^{2-} compounds are very labile in presence of oxygen and are rapidly oxidized to sulphate. So in aerated soil profiles sulphides are not available for denitrification. Autotrophic denitrification in unsaturated zone may be of importance only, if the soil is permanently free of oxygen (Rolland 1996). Significant autotrophic denitrification rates were observed by the author for gleyic subsurface horizons only. It is important to note that autotrophic denitrification in deeper soil horizons will lead to elevated sulphate concentrations in groundwater.

Summarising the previously cited studies it becomes apparent that denitrification in unsaturated zone is limited first of all by soil water content. Specifying the unsaturated hydraulic conductivity, the soil water content considerably affects nitrate transport in pore space as well as diffusion of oxygen. Permeable and coarse grained soils enhance soil aeration and restrict water saturation due to high permeability and less effective water storage, so the development of anoxic conditions as a result of sufficient soil saturation varies also with soil texture. In presence of anoxic conditions due to sufficient soil saturation, denitrification activity will be determined by activity of denitrifying bacteria as a result of the bioavailability of soil organic carbon as well as of nitrate. Denitrification rates considerably affect the consumption of nitrate and organic carbon and may lead to deficits in supply in organic carbon or nitrate, what results in remarkable declines in denitrification activity due to substrate limitation and

the change of denitrification kinetics from reaction of zero order (linear decay of nitrate) to reaction of first order (exponential decay of nitrate), the latter can be characterised by a certain half life time. Temperature and soil pH regulate microbial activity to a high extent and are therefore crucial for denitrification. The lower denitrification rates are due to suboptimal supply with nitrate or organic carbon or due to presence of oxygen, the higher individual denitrification rates may be impacted by changing environmental conditions (temperature, pH, pore flow velocity).

Denitrification potential of unsaturated zones is largely determined by the existence of optimal physical and geochemical conditions which favour denitrification activity. The reported studies indicate that the site-specific conditions differ from optimal conditions in many cases resulting in denitrification rates, which lag behind potential rates due to limitation effects. Wide ranges of reported denitrification rates reveal the interactive character of limiting conditions (see Table 3) and enforce the need for the determination of controlling factors of denitrification as the case arise. Principles in denitrification limitation are well researched, but variability of natural conditions frequently necessitates more explicit examinations.

Table 3 summarizes denitrification rates which are reported in literature and shows the wide ranges of possible denitrification rates, which are first of all defined by deviating nitrogen inputs from fertilizer applications and distinctive site-specific environmental conditions.

Table 3: Overview on mean denitrification rates in unsaturated zones reported in the literature

Removal rate [kg N ha ⁻¹ year ⁻¹]	removal as	Soil type	References
26	annual max. denitrification rate	clay/ sandy loam	(Burt et al. 1999)
9 - 200 1.2 - 32	average denitrification rate	riparian forest riparian grassland	(Hefting et al. 1998)
189 248	annual denitrification rate	forested zone herbaceous zone	(Hefting 2003)
292	av. denitrification rate	riparian forest/grassland	(Hefting et al. 2003b)
21.9 321 1328 1314	denitrification rates 20°C incubation temp.	sand (64% WFP) sand (79% WFP) sand (97% WFP) sand (100% WFP)	(de Klein et al. 1996)
18.3 113 591 1088	denitrification rates 20°C incubation temp.	loam (74% WFP) loam (81% WFP) loam (88% WFP) loam (97% WFP)	(de Klein et al. 1996)
11 102 219 1058	denitrification rates 20°C incubation temp.	peat (64% WFP) peat (67% WFP) peat (86% WFP) peat (90% WFP)	(de Klein et al. 1996)

Denitrification rates cited by Hefting were observed for highly fertilized and chronically nitrate loaded riparian soils in the Netherlands. If no limitation of denitrification by soil wetness or organic carbon availability is present, high nitrate levels in percolation water result in large denitrification rates. Denitrification rates

cited by (de Klein et al. 1996) were observed for an experimental setup and temperatures of 20°C, reducing the temperature about 10°C a bisection of denitrifiers activity would be expected with adequate declines in denitrification rates. That high denitrification rates are not observable under natural conditions, significant changes in denitrification rates with decreasing water content (WFP... water filled porosity) indicate the remarkable influence of soil water content on limitation of denitrification in unsaturated zone.

While denitrification is dominant process for nitrogen removal in unsaturated zones with a sufficient soil water content, in sites with low soil moisture content plant uptake is significantly higher (Wilkison et al. 2000), when soils are not under agricultural utilisation. Plant uptake was found to be a considerable removal process for nitrogen in riparian buffer zones in the Netherlands with an annual N retention of 13-99% of total N removal, as described by Ettema et al. (1999) as well. N retention by immobilization in litter was small, but with temporarily significant N retention in winter periods. In agricultural soils, due to incorporation of nitrogen into crop biomass nitrogen uptake exceeds nitrogen removal by denitrification considerably (Zessner et al. 2004). Matheson et al. (2002) reported plant uptake of 11-15% of soil nitrate for removal from riparian wetland soils. Dissimilatory nitrate reduction to ammonium (DNRA) was responsible for substantial removal of 49% of nitrate from unplanted, riparian wetland soil, where level of soil oxidation was probably the principle regulator of partitioning between DNRA and denitrification.

2.3.4 Denitrification in saturated zones

Hydrological pathways are important for denitrification in groundwater with respect to dilution, mixing and flow velocity influencing the nitrate loads to groundwater and the groundwater residence time (Hefting 2003, Hefting et al. 2003a). Pauwels et al. (1998) found a significant influence of aquifer permeability on denitrification rates. Higher denitrification rates (2.1 days half life time) were observed for a lower permeable aquifer medium, lower denitrification rates (7.9 days half life time) for a higher permeable aquifer medium indicating the significant dependency of denitrification rates on reaction time, which can be expressed as groundwater residence time. Although landscape hydrogeology does not limit the occurrence of denitrification in particular sites, it does influence the location of areas of high denitrification within the groundwater environment. Key landscape variables as topography, permeable sediment depth and sediment texture influence the linkage of groundwater flowpaths and the supplies of electron donors and acceptors that affect the location of denitrification 'hot spots'. Coarse textured gravels and sands may permit vertical and lateral transport of nitrate-rich groundwater for a considerable distance before reaching zones being favourable for denitrification, or transport may even bypass zones of high denitrification (Vidon et al. 2004). So landscapes have to be taken into account as 'patchworks', in which processes either of transport or of retention of matter dominate (Haag et al. 2001). In sites with low hydraulic conductivity, high denitrification occurs due to a high residence time, but these sites have little effect on nitrogen removal because of the minor flow. Thus, an effective nitrogen removal by denitrification requires a combination of high biological removal, a considerable volume of groundwater flow and a high nitrogen flux through biologically active layers (Maitre et al. 2003).

The residence time of infiltrating water in the unsaturated zone is important in controlling the amount of organic carbon available for oxidation within the saturated zone of shallow, unconfined aquifers as well as the amount of nitrate.

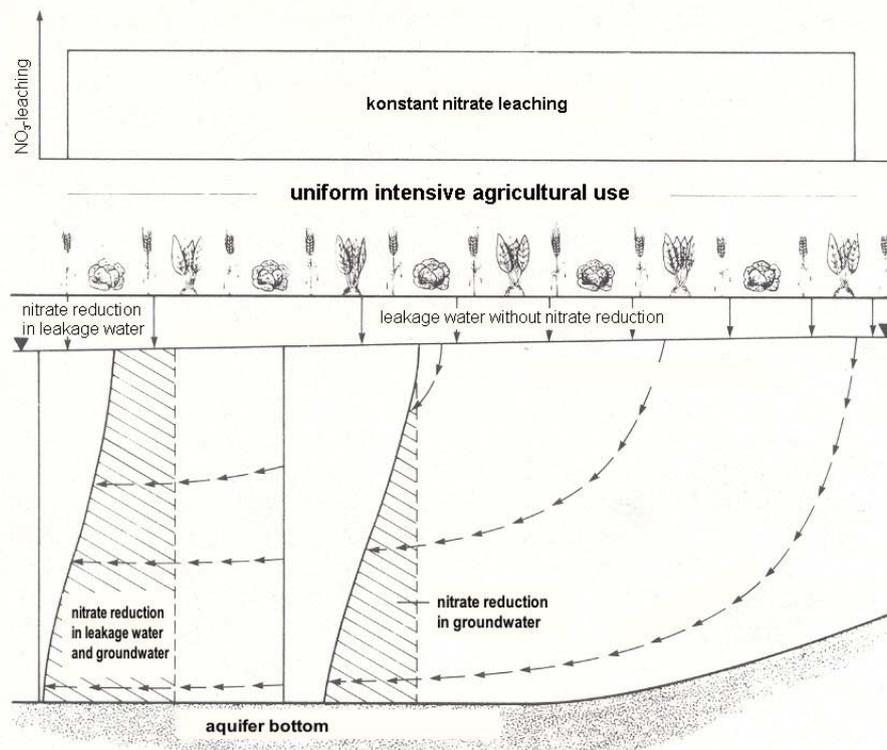


Figure 8: Changes in vertical nitrate profile in groundwater due to denitrification processes in subsurface zone (from Rohmann et al. 1985, modified)

Figure 8 illustrates the concept of residence time in unsaturated zone and in groundwater affecting nitrate reduction via denitrification. Assuming a constant nitrogen surplus over a certain area, a constant nitrate leaching results in uniformly spatially distributed nitrate concentrations in leakage water. According to the streamlines in Figure 8, groundwater with long travel times show extended interactions of nitrate rich groundwater with biologically active aquifer compartments resulting in higher nitrate reductions via denitrification along the flowpath (hatched area on right side with consideration of nitrate reduction in groundwater only). If additionally nitrate reduction in leakage water (unsaturated zone) is considered, reduced nitrate loads to the groundwater result in subsequent nitrate reductions via denitrification in groundwater and further reductions in nitrate levels (hatched area on left side with consideration of nitrate reduction in leakage water and groundwater). Though nitrate availability for denitrification in groundwater may be limited due to previous reduction in unsaturated zone.

Due to nitrate reduction in unsaturated zone and reduced availability of organic substances in groundwater, denitrification capacity in groundwater is limited. In fact that organic carbon limits denitrification capacity, nitrate reduction accords to a zero order kinetic model with a linear decline in nitrate concentrations, where the availability of organic carbon determines the intensity of the reduction and nitrate reduction is independently from nitrate availability. If nitrate limits denitrification capacity, nitrate reduction accords to a first order kinetic model with an exponential decline in nitrate concentrations (nitrate reduction is dependent from nitrate level),

which can be characterised by a certain half life time and where the availability of organic carbon determines the half life time (intensity of nitrate reduction). Thus, characterising denitrification activity in groundwater it has to be distinguished between nitrate limitation due to diffusion or organic carbon limitation.

Natural denitrification in groundwater is slow compared to soil horizons because of a lack of electron donors (Well et al. 2005). Shallow aquifer sediments are normally oligotrophic environments with less than 0.1% of organic carbon and less than 10 mg/l DOC in pore water. Low bacterial population density reflects the oligotrophic conditions of pristine aquifers. Only 1 to 10% of the cells are metabolically active and their activity and growth rates are lower than in bacteria from surface soils and waters (Bengtsson et al. 1995). Shallow groundwater bodies with high seasonal water table fluctuations are likely to interact with surface soil horizons, which are rich in organic carbon and thus, denitrification in shallow aquifers was observed in numerous studies (Vidon et al. 2004).

In deep aquifer systems input of organic carbon from soil reservoir is not important, so the likely source of degradable organic carbon is the geologic material comprising the aquifer matrix (Hiscock et al. 1991). Wassenaar et al. (1991) observed in a shallow unconfined aquifer system in Central Ontario, Canada considerable DOC fluxes recharging the groundwater system which were derived from organic carbon sources in the upper soil zone. In the upper vadose zone DOC flux was estimated to 49 kg/ha*a, in deeper vadose zone a net DOC flux of about 10 kg/ha*a was estimated. In deeper parts of the shallow aquifer sedimentary organic matter contributed more to groundwater DOC. Characterisations of the groundwater DOC suggested a predominance of high molecular weight aquatic fluvic acids and intermediate molecular weight compounds. An earlier study for eight confined and unconfined aquifers suggested already the predominant soil zone origin of groundwater humates, although some groundwater systems were influenced to varying degrees by buried peat or coal (Wassenaar et al. 1990). Siemens et al. (2003) estimated downwards DOC fluxes in permanent vadose zone of 60-90 kg/ha*a at 90cm depth and 9-21 kg/ha*a at > 3m depth for 5 study plots in Germany. Large quantities of organic carbon will be retained in soil profile by sorption along the flowpath downwards. Although significant decreasing nitrate concentrations with increasing depth were observed likely promoted by DOM (dissolved organic matter) from the topsoil, the small amount of DOM degraded in experiments was found being insufficient for a substantial denitrification.

Grischek et al. (1998) investigated the infiltration of river water into a sand and gravel aquifer in Germany and observed denitrification in the upper layer of the aquifer. They found an apparent discrepancy between the total demand for organic carbon for respiration, and denitrification, and the amount of DOC oxidized. This suggested that there must have been additional supply of organic carbon by particles of > 0.45 µm size fraction in river water and the available solid organic carbon (SOC). It is likely that prior to 1990 due to bad water quality the river infiltrate contained a high organic carbon content and probably contributed a pool of organic carbon within the riverbed sediments and the aquifer. Grøn et al. (1996) found significant differences in composition of groundwater humic substances for three Danish aquifers. Since sedimentary humic acids are prevented from solubilisation by high contents of dissolved Ca²⁺, groundwater humic substances constitution depends in deep aquifers mainly upon the substances present in the source rock, but also

upon the hydrochemical conditions in the aquifer. In shallow aquifers groundwater humic substances are a result of mixing of old humic substances released from buried sediments with intruding young humic substances from surficial terrestrial sources, such as soil processes and surface waters. Two aquifers fluvic acids rich in aliphatic, carbohydrate and carboxylic carbon with narrow molecular weight distributions dominated the groundwater DOC. The third aquifer was dominated by humic acids rich in aromatic carbon with a broad molecular weight distribution from exclusion limit down to low molecular weights. Differences in bioavailability or biodegradability were not investigated by the authors, but probably fluvic acids rich in aliphatic carbon with lower molecular weight distributions are more bioavailable for denitrifiers.

Polzer (2005) investigated two Austrian groundwater bodies and observed significant groundwater denitrification in selected cross sections. Starting from the content of available organic carbon in most of the soils varying between 2-7% of total organic carbon pool an available portion of about 500 mg/kg available organic carbon exists in average in soil. The consumption of available organic carbon due to denitrification processes pretends the exhaustibility of organic carbon sources in different manner depending on whether the organic carbon source is reclaimable (organic carbon from root zone, detritus) or of fossil origin (aquifer sediments). In this context, exhaustion of available electron donor substances was investigated by several authors. In dependence of inventory of available electron donors (Mehranfar 2003) and (Böttcher et al.1989) - both cited by Polzer (2005) - estimated approximately 10-200 years and 400 years until electron donor sources in aquifers will be exhausted. Polzer (2005) calculated mean half life times for groundwater denitrification and concluded that the exhaustion of available carbon sources in aquifers was approximately 49-83 years and 103-2700 years, respectively for the two investigated Austrian aquifers. With a long-term perspective Well et al. (2005) argues that because of subsoil pools of possible reductants for denitrification are to a large extent fossil, ongoing denitrification can cause irreversible consumption and thus exhaustion of denitrification potential.

Vidon et al. (2004) investigated eight riparian sites in Canada. Results indicated well organized pattern of electron donors and acceptors, where oxic groundwater containing high concentrations of nitrate entering riparian sites could be clearly distinguished from groundwater with low DO and increased DOC associated with low nitrate concentrations within the riparian zones. Analysis of site lithology suggested that locations with enhanced denitrification activity were associated with organically-enriched substrates. The occurrence of denitrification hot spots near the riparian perimeter could be linked to upward discharge of groundwater, like indicated in other studies (Cey et al. 1999, Maitre et al. 2003). This flow path resulted in the interaction of nitrate-rich groundwater with increased DOC supplies in surface soils creating a narrow zone of enhanced denitrification. Results of Hiscock et al. (1991) confirm the close correlation between denitrification in groundwater and available organic carbon. Well et al. (2005) investigated denitrification capacity near (above and below) the groundwater surface for hydromorphic soils. Significant correlations were observed between the denitrification capacity and total organic carbon and confirmed partial depletion of available reductants above and close below the groundwater surface. Regression analysis revealed further, that samples with largely inert organic C had low denitrification capacity, whereas samples with highly reactive organic C

showed relatively high denitrification capacity. In a previous study Well et al. (2003) found 4-9 fold higher *in-situ* denitrification rates for saturated organic soils (shallow groundwater level) than for saturated mineral soils (deep groundwater level) (see Table 4). Temperature effects were considered additionally resulting in 1.4-3.8 times higher denitrification rates observed for laboratory experiments at 25°C as compared to 9°C.

Analyses by Bengtsson et al. (1995) indicated that differences in groundwater denitrification activity between three specific aquifers in Sweden can be attributed to innate differences in the denitrification populations adapted to specific *in-situ* nitrate concentrations. Denitrification activity was first of all limited by carbon availability because carbon enrichment increased denitrifying enzyme activity between 2 and 2.5 times. Though oligotrophic subsurface environments contain uniformly low bacterial population densities, denitrifying strains from nitrate rich aquifers showed significantly higher ability to reduce nitrate as compared to strains from nitrate low aquifers, indicating adapted growth rates to *in-situ* nitrate concentrations. Maitre et al. (2003) investigated the effectiveness in nitrate removal for two hydrologically isolated shallow aquifers in a riparian zone. Due to geological structure of both aquifers (diminishing aquifer thickness towards the river from 1.4-3.5m to 0.4-0.6m with constant thickness of organic layer) groundwater flow is forced through biologically active layers. Denitrifying enzyme activity were 100 times higher in organic layers than in mineral layers resulted in considerable denitrification rates observed in shallow aquifers of 8-28 kgN/ha*a with seasonal variations (see Table 4). Higher nitrogen removal could be observed in connection with higher groundwater levels, inducing higher flows of groundwater interacting with the microbiologically active layers and emphasised carbon limitation of denitrification in groundwater.

Pfenning et al. (1997) investigated nitrate-rich riverbed sediments for denitrification activity. They found no increases in denitrification rates with increasing nitrate concentrations and that therefore denitrification activity was not limited by nitrate availability. Denitrification activity was generally limited by availability of organic carbon. Potentially the highest denitrification rates occurred in surface sediments containing relatively high organic carbon contents (0.16%) even though nitrate concentrations were low. Lower rates occurred in buried sediments having less organic carbon (0.01-0.04 %), but higher nitrate concentrations. Denitrification rates were related to type of organic carbon present in the sediments. Highest denitrification rates were observed for laboratory experiments using relatively labile form of organic carbon (acetate) following rates using surface-water-derived fluvic acid. Groundwater-derived fluvic acid and sedimentary organic carbon showed the lowest denitrification rates. Again, strong relations of denitrification to incubation temperature were observed. Denitrification rates decreased by 77% for sediments incubated at 4°C compared to sediments incubated at 22°C.

Vidon et al. (2004) observed strong relationships on the occurrence of significant denitrification in groundwater with dissolved oxygen (DO) contents of < 2.1 mg/l only. Cey et al. (1999) found a sharp decline of nitrate concentrations in groundwater of riparian zones when dissolved oxygen fell below concentrations of approximately 2 mg/l, which was attributed to denitrification activity. Similarly, a sharp decrease in nitrate concentrations was associated with a redox potential Eh below ~ 200 mV confirming conditions being favourable for denitrification.

Heterotrophic denitrifying bacteria are more abundant compared to autotrophic denitrifying bacteria and are generally interpreted to be responsible for most observed cases of denitrification in groundwater (Feast et al. 1998). While heterotrophic denitrification is subject of many studies, autotrophic denitrification may become the dominant denitrification process in groundwater with high levels of reduced inorganic species (Mn^{2+} , Fe^{2+} , HS^- , sulphidic minerals). Generally, heterotrophic denitrification using organic carbon results in higher energy yield for bacteria (-28.4 kcal/equiv.) compared to autotrophic denitrification using reduced sulphur S^{2-} as electron donor (-22.3 kcal/equiv.) or reduced iron Fe^{2+} (-19.5 kcal/equiv.). Sources of reduced sulphur are pyrite or melnikovit or secondary amorphous sulphidic formations in aquifers appearing in brown coals or as reactive coatings on gravel and sand grains (Rolland 1996). Grischek et al. (1998) found that autotrophic denitrification is more significant in aquifers with increasing groundwater residence time, when pyrite was present. Pauwels et al. (1998) investigated a pyrite-bearing schist aquifer for denitrification. Biological determinations showed that denitrifying bacteria, both heterotrophic and autotrophic, were present. Considerable reductions in nitrate concentrations in groundwater along the flowpath were observed. Since no organic matter was detected in the rock matrix and the dissolved organic C content in pumping water from aquifer was relatively slow, autotrophic denitrification was concluded being responsible for nitrate reduction in deep aquifer. Analysis of pyrite content of aquifer confirmed, that autotrophic denitrification was not limited by pyrite availability. The isotopic composition of nitrogen confirmed the occurrence of autotrophic denitrification in deeper aquifer compartments in a later study (Pauwels et al. 2000). Additionally it appeared that heterotrophic denitrification takes place in upper aquifer compartments in the absence of pyrite due to dissolved organic carbon intakes from upper soil zones, whereas in the deeper aquifer compartments the autotrophic reaction is the dominant denitrification process.

The predominance of autotrophic processes over heterotrophic processes was already observed at other sites. Several phenomena were found having an influence on autotrophic denitrification kinetics: the solid-phase accumulation of metals (Cu, Pb), which act as catalysts in nitrate reduction through oxidation of iron (II) and the elimination of sulphates through precipitation of amorphous iron sulphates or minerals (jarosite). It was calculated that pyrite amounts are sufficient to preclude electron donor limitation of autotrophic denitrification for the upper 25m of the schist aquifer and would correspond to more than 4000 times the annual NO_3 surplus over the catchment to be denitrified.

Wendland et al. (1999) refer to a couple of consequences that arise from a permanent high nitrate load to groundwater in presence of denitrification with pyrite for water supply, which cannot be assessed as favourable only. In particular, these are:

- groundwater concentrations of iron and manganese ions due to delivery from sulphide, which exceed the level the treatment facilities are designed for,
- delivery of iron ions from pyrite may result in aerobic zones in the formation of iron hydroxide and iron hydroxide depositions in groundwater wells,

- higher sulphate concentrations in groundwater from denitrification may exceed the threshold value is given in drinking water ordinance,
- mobilisation of trace elements from iron sulphide like Ni, Co or As

Table 4 summarizes selected denitrification rates in groundwater from the literature. Beside the influence of the availability of organic carbon on denitrification capacity, temperature effects on denitrification in shallow aquifers can be observed in study of Maitre et al. (2003).

Table 4: Overview on denitrification rates in saturated zones reported in the literature

Removal rate [kg N ha ⁻¹ year ⁻¹]	removal as	site conditions	References
12...27.7	DIN removal ^a	spring	(Maitre et al. 2003)
16.8	DIN removal	autumn	
8.4...9.6	DIN removal	winter	
1180 43	<i>in-situ</i> denitrification rate	organic layer (24-50% C _{org}) mineral layer (0.06-0.1% C _{org})	(Well et al. 2003)

^aDIN removal = biological removal of DIN

In general, denitrification capacity in groundwater is lower in comparison to the unsaturated zone. Groundwater residence times interact with the availability of nitrate due to transport and dilution processes. Denitrification capacity is large if availability of nitrate and organic carbon favours denitrification activity. Fluxes of dissolved organic carbon from soil into upper aquifer compartments are matter of biological decay and may impact heterotrophic denitrification, if groundwater residence time is high enough. On the other hand, high groundwater residence time favours the dissolution of organic carbon from fossil aquifer sediments, dissolved oxygen consumption and enhances diffusive transport of nitrate and organic C to anoxic microsites. Enhanced reaction times in aquifer compartments with moderate biological activity may result in elevated denitrification due to sufficient groundwater residence times. The availability of nitrate as well as electron donors is reflected in denitrification capacity and as well in the reported half life times, which vary considerably from site to site.

2.3.5 Liquid film theory for denitrification processes in subsurface zone

Both in the unsaturated and saturated zone denitrification processes are initiated by bacteria decomposing available nitrate. In contrast to processes in waste water treatment, where bacteria are found suspended to activated sludge in aeration tanks, in subsurface environments bacteria are fixed to soils and sediments being provided with essential substances predominantly by water flows through pore space.

All biological removal processes with a stationary carrier material result in a liquid film growth and furthermore, this liquid film is in equilibrium between a permanent growth of micro organisms and a die off of bacteria as well as a cut off of outward layers by bypassing flow. In saturated zones the aquifer material acts as a carrier material. Nikolavcic (2002) reports that in respect to liquid film 'thickness' substrate availability is not always equally distributed inside the liquid film. Substrate limitation inside the liquid film may occur, when the liquid film is characterized as 'thick'. Furthermore, substrate exchange between liquid film and the surrounding aquatic environment is possible by liquid film diffusion only and is limited by a laminar

boundary layer. With increasing flow velocities, the influence of the laminar boundary layer diminishes.

Since Robertson et al. (1995) reported 'aerobic denitrification' or nitrogen removal from NH_4^+ to N_2 via a simultaneous nitrification/denitrification the assumption would be conceivable, that due to oxygen consumption (in fact by nitrifying bacteria or respiration activity of carbon-depleting bacteria) zones with a depleted oxygen status - anoxic zones – are generated, where heterotrophic denitrification favourably can occur. Hence, denitrification would be possible despite a certain concentration of dissolved oxygen in groundwater.

In case, that the diffusion rate is limited by reaction rate (substrate limitation in liquid film), reaction rates are potentially lower than in surrounding aquatic environment (Nikolavcic 2002), but due to diffusion limitation of oxygen as well denitrification potential might be still high enough for an ongoing denitrification despite present dissolved oxygen in surrounding environment .

Mass transport N via diffusion can be described by first law of Fick (Nikolavcic 2002):

$$N = -D \frac{dS}{dx} \quad (\text{Equation 13})$$

with D as specific diffusion coefficient and dS/dx as substrate concentration gradient between the environment and the liquid film. Usually the biological decay inside the liquid film is limited by one essential substrate, in fact the liquid film can be characterised as "thick" (Nikolavcic 2002). The diffusion rate between the liquid film and surrounding environment is certainly defined by the concentration gradient as well as by diffusion coefficient (see equation 13). Oxygen owns basically a higher diffusion coefficient ($2.42 [10^{-5} \text{ cm}^2 \text{ s}^{-1}]$ at 25°C in solution) compared to nitrate ($1.902 [10^{-5} \text{ cm}^2 \text{ s}^{-1}]$ at 25°C in solution) (Lide 2000). Assuming an equal concentration gradient of both oxygen and nitrate at liquid film boundary layer, due to the discrepancy in diffusion coefficients the oxygen diffusion rate will be 1.27 fold higher of the nitrate diffusion rate. In other words, the concentration of nitrate should be at least theoretically 1.27 times that of the dissolved oxygen concentration to favour sufficient anoxic conditions to ensure denitrification in the liquid film, if denitrification is not limited by the availability of carbon sources. How much the dissolved oxygen concentration has to be lowered in the environment to become limited in the liquid film is actually a function of temperature, the liquid film thickness and of the activity of micro organisms in liquid film (Nikolavcic 2002). Anyway, denitrification in liquid films can occur hence in aquifer hot spots only, where the dissolved oxygen concentration in groundwater is that low to become limited for aerobic respiration activity in liquid film. In literature denitrification activity in groundwater is associated with dissolved oxygen concentrations below 2-3 mg/l. Wendland et al. (1999) give a summary of oxygen concentrations in groundwater limiting denitrification, which explicitly show denitrification in presence of dissolved oxygen concentration in groundwater up to 5 mg/l (Table 5).

Table 5: Oxygen concentrations being reported as limiting for denitrification in groundwater by listed authors (from Wendland et al. 1999, modified)

Author	Oxygen concentration in groundwater
(Hölting 1984)	< 5 mg O ₂ /l
(Rohmann et al. 1985)	< 5 mg O ₂ /l
(Kölle 1990) (in microzones)	< 5 mg O ₂ /l
(Obermann 1982)	< 2 mg O ₂ /l
(Ebeling et al. 1988) (complete denitrification)	< 1 mg O ₂ /l
(DVWK 1988) (organism specific)	< 1 mg O ₂ /l
(Vidon et al. 2004)	< 2.1 mg O ₂ /l

In both cases an aerobic respiration activity or anoxic denitrification activity, CO₂ is produced and has to be transported out of the liquid film by diffusion too. Due to an enrichment of carbon dioxide in the liquid film by denitrification the pH possibly rises with a coinciding change in substantial components of inorganic carbon and alkalinity (Nikolavcic 2002).

From the statements carried out above it arises, that nitrate transport as well as denitrification activity are closely connected and influenced by aquifer texture and saturated flow pattern (see chapter 2.2.3 and 2.2.4). On the basis of liquid film theory denitrification is enhanced when environmental conditions become favourable for diffusion. This includes necessarily at least a modest groundwater velocity and a sufficient groundwater residence time, what is very well in line with findings from chapter 2.3.4, where denitrification rates increase with decreasing flow velocities. A more fine textured and heterotrophic aquifer results in a lower groundwater velocity as well as in more distributed flow pathways with local spots of high respiration activity and long groundwater residence times being a prerequisite for a dissolved oxygen limitation in environment and a sufficient anoxic environment for denitrification and nitrate diffusion to take place.

2.3.6 Alternative nitrate reduction processes

It may be possible for nitrate to be reduced inorganically without the action of bacteria (Feast et al. 1998). Chemical removal of nitrate using nanosized iron was successfully performed by Yang et al. (2005). A synthetically produced zero-valent iron was used to completely remove nitrate under anoxic and acidic (pH = 4) conditions. This process is acid-driven, pH control is of significance and a lower pH enhances the process. But under environmental conditions this process is assessed to be of minor importance.

Aerobic denitrification was investigated i.e. by Robertson et al. (1995) and Cartaxana et al. (1999). Aerobic denitrifying bacteria were found to be present in batch cultures and marsh sediments, and an aerobic reduction of nitrogen oxides by several different bacteria was observed, but with a very low denitrifying activity.

2.4 Consequences from key factors influencing denitrification activity

Denitrification potential depends on certain environmental conditions as reported in many studies resulting in a limitation of denitrification, when these favourable conditions are not met. Spatial and temporal variations in denitrification due to either dominating transport or retention processes are difficult to quantify and partly masked by consideration of different spatial and temporal scales. Furthermore, superposition of actual environmental conditions influencing potentially the amount of denitrification may mask the identification of key limiting factors being the reason for a limited denitrification.

Summarising the previous chapters, the following boundary conditions are of major influence for a potentially high denitrification in soils and aquifers:

Denitrification in the unsaturated zone is determined by:

- *Soil water content*- insufficient soil water content benefits soil aeration and prevent the development of anoxic microzones, nitrate diffusion tends to be suppressed by low unsaturated conductivity and requires larger concentration gradients for mass flow; denitrification activity increases dramatically, when soil saturation exceeds soil-specific thresholds for soil water content; in fine-textured soils development of anoxic zones and denitrification requires lower soil water contents in comparison to coarse-textured soils.
- *Nitrate availability*- nitrate availability from soil surface is dependent from area specific N surplus on soil and amount of leakage water (soil percolation, groundwater recharge rate) as well as by fertilization and crop management, nitrate limitation of denitrification in organic-rich surface soils results in characterisation of denitrification using half life time approaches, reported half life times for denitrification in unsaturated zone range from several hours to days
- *Availability of organic carbon* - availability of soluble organic substances is related to heterotrophic denitrification activity and determines the level of denitrification rates; denitrification capacity is higher in surface, organic-rich soils than in subsurface or mineral soils; in surface soils organic carbon availability is sufficiently met by organic carbon pool (root zone), downwards DOC fluxes considerably supply deeper subsurface zones with organic carbon.
- *Temperature* - increasing temperature results in an increased biological activity of denitrifying bacteria and thus in enhanced denitrification as well as in increased molecular diffusion rates.
- *Residence time* - the residence time in unsaturated zone determines the amount of nitrate (and organic carbon), which is reduced via denitrification and significantly impacts on the downwards nitrate (and organic carbon) fluxes to the groundwater surface.
- *Hydrology* - groundwater recharge rates have a significant influence on the residence time in unsaturated zone, on nitrate fluxes from soil surface to groundwater and on intensity of nitrate reduction via denitrification.

Denitrification in the groundwater is considerably impacted by denitrification in unsaturated zone and is determined by:

- *Nitrate availability*- nitrate fluxes from soil to groundwater are considerably affected by denitrification in the unsaturated zone, though nitrate availability in groundwater is determined to a large degree by denitrification and the residence time in unsaturated zone; vertical and lateral transport of nitrate-rich groundwater in considerable fluxes through biologically active zones stimulates effective denitrification; nitrate limitation of denitrification in groundwater is reflected in reported half life times for denitrification activity within ranges from several days to years.
- *Availability of organic carbon* - organic carbon content in groundwater is smaller compared to surface soils, availability of organic carbon sources for heterotrophic denitrification determines denitrification and half life times for denitrification; considerable vertical DOC fluxes from soil to groundwater as well as enhanced interactions of groundwater table with organic-rich soil layers are reported to provide substantially groundwater humic substances for denitrification in shallow aquifers; in deep parts of aquifers the likely source of organic carbon is the sedimentary organic matter comprising the aquifer matrix.
- *Availability of alternative electron donors* - autotrophic denitrification may become the dominant denitrification processes in groundwater with high levels of reduced inorganic species (e.g. pyrite) and significantly elevated groundwater residence times.
- *Oxygen and redox status* - increasing denitrification activity was correlated with dissolved oxygen concentration below 2-5 mg/l and with redox potential below 200 mV.
- *Hydrology* - groundwater flow and groundwater recharge significantly limit subsurface nitrate (and organic carbon) availability/mobility and determines dilution and mixing of groundwater with different natures; groundwater fluxes directly influence groundwater residence times and the extent of anoxic zones.
- *Groundwater residence time* - denitrification in groundwater is limited by availability of nitrate and electron donors, reduced groundwater flow results in elevated groundwater residence times with enlarged potential for denitrification in zones of microbial activity (enlarged reaction time).
- *Temperature* - influences of temperature on denitrification capacity can be expected to a certain extent in shallow aquifers, decreasing temperatures result in declines in denitrification.

Denitrification during subsurface flow is crucial for nitrogen removal from hydrosphere and is site-specific variable due to changing environmental conditions. It was shown that denitrification activity in unsaturated zone and in groundwater is limited by a number of environmental factors, which are interrelated to a great extent. Hydrology, hydrogeology and land use practises influence nitrate (and organic carbon) availability in the unsaturated and saturated zone and determine the boundary conditions for an effective denitrification.

Hence, the assessment of denitrification capacity in subsurface zone and the calculation of nitrogen balances with consideration of nitrogen losses via denitrification require the identification of hydrological circumstances with linkage to proper nitrogen transport and retention processes. Though, water balance calculations should be the first step towards identifying the main sources for nitrogen emissions and nitrogen losses at the catchment scale.

2.5 Denitrification in nitrogen emission estimation tools

In recent years various models or approaches were developed with a focus on the estimation of nutrient emissions at the catchment scale. In dependency of model type the temporal or spatial resolution of the models vary significantly with consequences on process descriptions in regard to nutrient release and retention in the catchments. Several modelling approaches are reported for assessment of point and non-point source contributions of nutrients, by Macleod et al. (2003) particularly for determination of P loads from selected catchments. In general, these modelling approaches can be grouped into:

- Export coefficient approaches for determination of nutrient loads being transported from a particular source
- Mass balances or flow analysis for determination of nutrient fluxes via input-output-analyses
- Empirical approaches for assessment of nutrient loads based on regression analyses of observed data

Several conceptual models were developed which focus on comprehensive process description. Unfortunately these models are mainly characterised by high model complexity and intense input data requirements for model application.

Often, different models describe only selected facets of nutrient dispersal in soil, groundwater and surface water (de Wit 2001). Furthermore, the modelling approaches differ significantly in applicability in terms of temporal and spatial resolution and thus, in data requirements. Quantification tools range in terms of their spatial resolution from spatially lumped static tools to fully distributed process oriented dynamic tools (Schoumans et al. 2003). A general relation between model complexity in dependency of model type and model output is given in Figure 9.

According to Figure 9 data oriented empirical models require much less input data as compared to process oriented conceptual models. Sometimes, data acquisition can severely limit model application or model complexity. Many empirical modelling approaches were developed and applied for certain regions of Europe and may not be able to handle gradients in climate, hydrology, land use or agricultural practise existing in other parts of Europe or of the world. The data and parameter intense process oriented modelling approaches lack under data availability in many cases requiring assumptions to be made or transfer functions to developed, where empirical and quasi-empirical approaches may be a viable alternative. Many statistical approaches are not able to describe the dynamics in fluxes due to time step limitations. Therefore, the evaluation of quantification tools in terms of limitations should be addressed to the user (Schoumans et al. 2003).

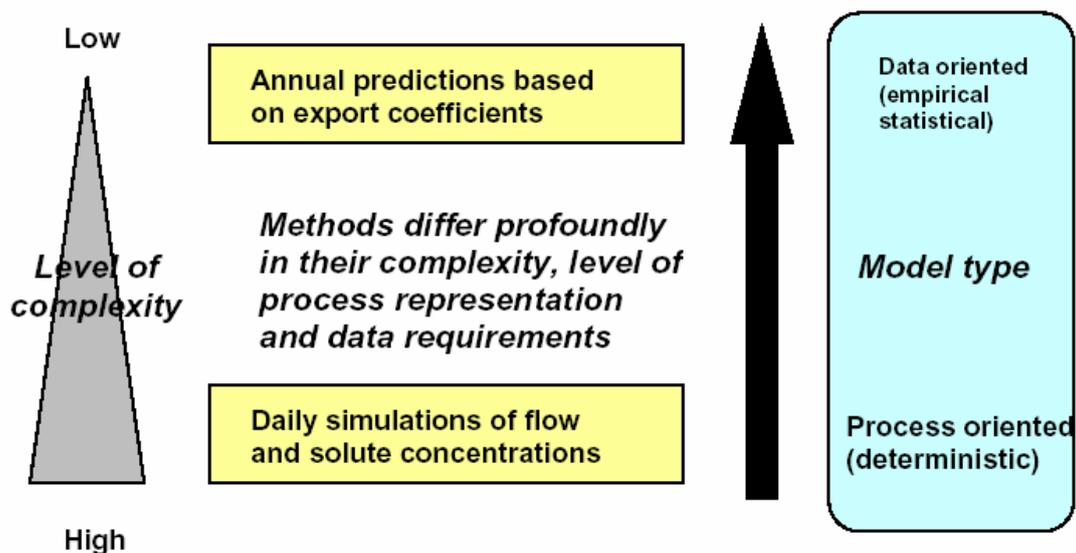


Figure 9: General relation between the complexity of models, model type and the general output (from Schoumans et al. 2003)

Most of the modelling approaches are used for quantification of nutrient emissions and their changes due to different measures for land management. Applications ranging from empirical to conceptual models being successfully used for nutrient emission estimations for selected catchments (Behrendt et al. 1999, de Wit 2001, Grizzetti et al. 2003, Jordan et al. 2005 and Schoumans et al. 2003). But with model complexity also the consideration of N cycle related processes at the catchment scale vary widely with expressiveness of model results in regard to seasonal or perennial dynamics in nitrogen loads as well as in regard to spatial resolution. Due to spatial aggregation within lumped modelling approaches consideration of nitrogen retention processes is desired being incorporated not absolutely as a function of groundwater residence time, approaches reflecting a simple input-output-regression may be more viable. Contrary the consideration of nitrogen retention processes using fully distributed modelling approaches require a certain time or raster dependent relation due to water and nitrogen routing practises. Moreover, as a consequence of spatial and temporal resolution the modelling approaches comprise quite diverse processes for estimation of nutrient emissions.

Taking into account that denitrification in groundwater is a crucial process for nitrogen reduction from diffuse sources at the catchment scale and is mainly a function of hydrological impacts with consequences on groundwater residence times, groundwater recharge rates and nitrate mobility as well as of geochemical, biological and geological conditions, the assessment of diffuse nitrogen emissions for selected catchments depends on correct estimation of catchment hydrology. In addition, the selection of modelling approaches with focus on nitrogen emission estimation at the catchment scale should address the following questions:

- Is denitrification in groundwater of significant importance on total nitrogen emissions for the considered catchment?
- Should therefore the modelling approach include denitrification processes in groundwater for the estimation of total nitrogen emissions?

- To what extent the spatial and temporal resolution of the modelling approach affect the consideration of denitrification in groundwater and to what expressiveness the model results are viable?
- How significant and reliable are the model results in terms of the initiation of measures or management strategies?
- Is seasonality in hydrological processes well considered in terms of modelling nitrogen emissions from point and diffuse sources?

To get to the bottom of these questions is one of the main objectives of this work. The previous chapters were focussed mainly on potential denitrification in the unsaturated and saturated zone. Transport processes in contrast to nitrate reduction processes were discussed since nitrate is the nitrogen compound having the highest mobility, and is due to mineralisation processes of major concern in terms of groundwater interference mainly from areas under intensive use. Denitrification requires anaerobic conditions, sufficient nitrate availability and adequate supply of electron donors. Environmental, site specific conditions do impact favourable conditions for denitrification in a quite different manner. Denitrification processes were shown to be different in unsaturated and saturated zone due to diverging limitation processes on microbial activity. But these compartments can't be considered separately because of mass transfer between the two compartments, which are of significant importance for denitrification too (e.g. vertical DOC fluxes, water table fluctuations).

In frame of the daNUbs project "Nutrient Management in the Danube basin and its impact on the Black Sea" (EVK1-CT-2000-00051) five case study areas were selected within the Danube basin reflecting the diversity of the Danube basin in terms of climatological, hydrological and morphological conditions in interactions with socioeconomic circumstances to investigate catchment specific processes, which induce nitrogen emissions from the catchments and considerably affect processes being beneficial for nitrogen emission reduction, like denitrification. Two of the selected case study areas are located in Austria, the Ybbs catchment and the Wulka catchment.

These two Austrian case study areas will be used in this work to investigate catchment specific differences, which promote nitrogen emissions to surface waters. One of the most important issues is the catchment hydrology. Three different methods were used to investigate hydrological conditions in both catchments. One method, the application of a distributed parameter continuous time model, is presented in this work in detail to emphasis basic hydrological conditions in respect to runoff generation and differentiation between individual contributing runoff components. Individual runoff components are involved in nitrogen mobilisation within the catchments quite dissimilarly, and therefore catchment specific hydrological behaviour results in unique contributions to total nitrogen emissions from individual pathways with relative share. Thus, additionally an empirical emission model was involved for quantification of total nitrogen emissions and for determination of the decisive emission pathways for both catchments. The different natures of the models imply dissimilar requirements on input data and on calibration efforts to run the models. Differences in process descriptions pretend the applicability of these quantification tools for both the extent of catchment areas as well as discretisation in temporal and spatial scale. Restrictions in model discretisation do

influence process description to a high extend. Both models will be presented with focus on the ability of the quantification tools for consideration of nitrate reduction processes in groundwater via denitrification with sufficient resolution in time and space.

Groundwater and surface water observations were performed in both case study areas indicating significant denitrification in both the unsaturated as well as the saturated zone. Indications for catchment-specific significant differences in denitrification were observed, which were attributed to individual hydrogeochemical and geohydraulic conditions. Furthermore, anthropogenic activity in both catchments, particularly in terms of land utilisation and husbandry was evaluated for the constitution of mass balances to affiliate nitrogen inputs to the catchments to output from the catchments via nitrogen emissions in order to identify nitrogen reductions by denitrification in individual compartments. These analyses are presented in this work as well.

Hydrological conditions impact denitrification potential in the unsaturated as well as in the saturated zone. Beside effects on soil wetness and unsaturated as well as saturated transport processes, the groundwater residence time is mainly a result of the predominant hydrological and hydrogeological conditions impacting denitrification by the available reaction time. Due to restrictions of the previously mentioned models in terms of consideration of denitrification processes in groundwater with sufficient spatial resolution, an approach was developed for the calculation of groundwater residence time distributions using observations of groundwater level, geological information and the location of surface water bodies. This approach enables to quantify diffuse nitrogen emissions to surface waters as a function of groundwater residence time distribution and raises the possibility to consider nitrate reduction in groundwater via denitrification with an adequate spatial resolution. Consequently the connection between the diffuse nitrogen emissions to surface waters of specific catchment areas in relation to their location within the catchment was established considering denitrification processes in groundwater as a function of calculated groundwater residence time and a certain half life time. This approach provided the opportunity to effectively distinguish catchment areas in terms of their need of protection, when reduction of nitrogen concentration in local groundwater bodies or nitrogen loads to surface water bodies are matter of interests in assisting to affiliate appropriate management strategies. This approach will be presented finally in this work.

First of all the two Austrian case study areas will be introduced and briefly characterised.

3 Characterisation of the case study regions

3.1 Introduction and general characterisation

The two Austrian case study areas (CSA) of the Danube basin were selected in terms of identification of specific hydrologic circumstances which influence decisively the nutrient emissions from the catchments to surface waters. The selection was addressed forwards representing different conditions in the Danube basin with regard to precipitation, specific surface water runoff, catchment morphology, soil types, land use practises etc. Other important selection criteria were data availability, particularly high-quality, long-term data sets from groundwater and surface water monitoring as well as an easily understandable groundwater situation.

The two case study regions Ybbs and Wulka are located in two different parts and federal states of Austria. The Ybbs catchment is located in the south of the river Danube belonging to the federal state of "Lower Austria" and assimilates 29 municipalities within the catchment area of about 1105 km². The Wulka catchment is located near the border to Hungary in the North-East of the federal state "Burgenland", and with a catchment area of about 383 km², comprising 41 municipalities.

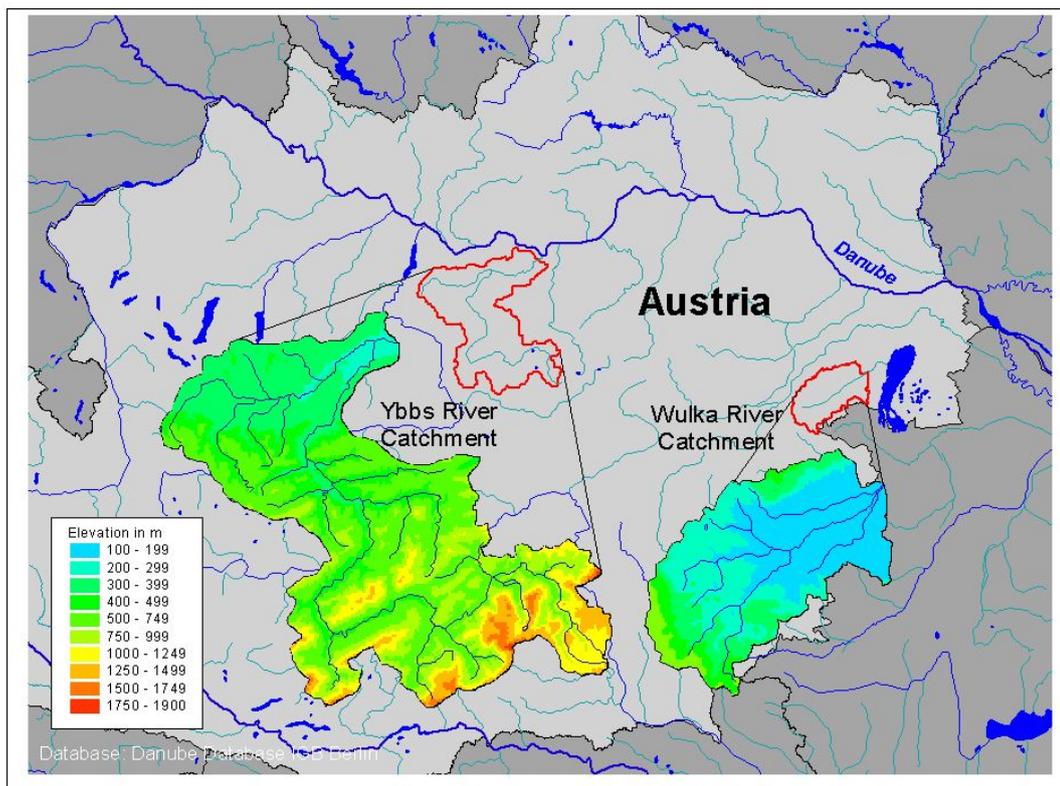


Figure 10: Location of the case study regions in Austria

The Ybbs catchment is situated in the northern pre-alpine region of Austria. It is characterised by humid climatic conditions with an annual precipitation of 1380 mm. The Wulka catchment is situated in the eastern part of Austria upstream of Lake Neusiedl near to the Hungarian border. The climate is classified as a dry pannonian type with an annual precipitation between 670 and 760 mm (Haas et al. 1987c).

The Ybbs catchment was subdivided into three subcatchments: the upstream subcatchment until the Opponitz gauging station at the Ybbs river; the subcatchment of the Url river upstream the Krenstetten gauging station and the remaining subcatchment upstream of the Greimpersdorf gauging station, which is considered a main watershed outlet and represents the whole Ybbs catchment.

The Wulka catchment was subdivided into five subcatchments. The furthest upstream subcatchment is down to the Walbersdorf gauging station on the Wulka river. Wulkaprodersdorf is the next subcatchment at the Wulka river defining the subcatchment between the Walbersdorf gauging station and Wulkaprodersdorf gauging station. The subcatchments Nodbach and Eisbach are tributaries and were named according to gauging stations on Nodbach river and Eisbach river located in St. Margarethen and Oslip, respectively. Schützen subcatchment is the remaining subcatchment upstream the gauging station Schützen, which is also the main watershed outlet of the Wulka catchment. Table 6 shows a summary of the main characterisation of the Wulka and Ybbs catchment with the considered subcatchments.

This chapter will introduce catchment specific conditions in the two selected case study areas with a focus on land use, geology and morphology, which are reflected in different hydrologic circumstances linked to processes controlling nitrogen emissions from the catchments.

Table 6: Main characteristics of case study regions, subdivided in into sub-catchments (from Zessner et al. 2004)

Country		Austria									
		Ybbs				Wulka					
Name of the river											
subcatchment		total	Opponitz	Url/ Krenstetten	Greimpers dorf net	total	Walbersdorf	Wulkaproders dorf net	Nodbach	Eisbach	Schützen net
Total catchment area	km ²	1105	506	151	448	383	76	142	47	64	55
Share of arable land	%	12	0	37	17	54	31	62	64	50	62
Share of agricultural grassland	%	27	12	41	40	12	13	12	14	10	10
Share of forests	%	52	75	20	38	28	50	21	16	29	22
Share of consolidated rock	%	65	79	54	53	56++	26	82	37	68	34
main geological unit		dolomite/ flysch	dolomite/ limestone	sandstone/ flysch	sediments /dolomite	marl/ sediments	-	marl	sediments	marl/ sediments	sediments
main soiltypes		rendzina	rendzina	luvisol	rendzina/ luvisol	chernosem/ luvisol	luvisol	chernosem	chernosem	chernosem	chernosem
N-fertiliser application*	kg/ha _{AA} /a	150	100	178	152	100	110	117	90	81	73
P-fertiliser application*	kg/ha _{AA} /a	43	31	47	44	26	36	32	24	21	20
N-surplus in agriculture	kg/ha _{AA} /a	73	24	88	74	50	43	55	47	55	48
P-surplus in agriculture	kg/ha _{AA} /a	25	15	28	29	17	14	20	14	15	12
N-in agricultural soil	g/kg	3.6	5.9	2.6	3.5	1.5					
P in agricultural soil	g/kg	0.8	0.6	0.8	0.8	0.7	0.7	0.8	0.6	0.6	0.6
N-deposition	kg/ha/a	19	16	24	20	13.5	13.5	13.5	13.5	13.5	13.5
average N-surplus on total area	kg/ha/a	40	17	74	51	38	26	44	40	38	38
average P-surplus on total area	kg/ha/a	10	2	22	17	11	6	15	11	9	9
mean slope	%	30	43	14	32	8	15	10	5	7	8
average precipitation	mm/a	1390	1680	1029	1185	665	711	663	636	653	630
average runoff**	mm/a	868	1170	434	673	49	91	47	54	35	9
share of groundwater flow	%	71	70	67	73	58	78	75	74	25	
share of direct flow	%	28	30	31	25	16	18	21	26	21	
share of point source contribution	%	0.7	0.1	2.4	1.7	26	4	4	0	54	
population density	inh/km ²	68	17	81	122	133	153	101	147	208	89
Share connected to sewerage	%	74	83	63	75	95	87	100	100	94	100
Share connected to wwtp	%	74	83	63	75	95	87	100	100	94	100
predominant waste water treatment		C, N(D), P	C, N, D, P	C, N, P	C, N, (D), (P)	C, N, D, P	C,N, (D), P	no discharge	no discharge	C, N, D, P	C, N, D, P
Industrial activity		medium	no	low	medium	low	low	low	low	low	low
area specific river loads N	kg/ha/a	19	15	23	21	5	5	4	4	6	8
area specific river loads P	kg/ha/a	0.8	0.3	0.6	1.3	0.3	0.3	0.1	0.1	0.3	0.8

* total application of fertilizer (incl. Manure, or sewage sludge) related to agricultural area (ha_{AA})in use (grassland and arable land)

**without contribution from point sources

3.2 The Ybbs catchment

3.2.1 Catchment morphology

Figure 11 shows the distribution of elevations of the Ybbs catchment with the location of the groundwater, surface water level and quality observation stations. Due to the hydro geological conditions most of the groundwater observation wells are located in the north part of the catchment, partly outside the catchment boundaries. This is the part of the catchment where predominantly porous aquifers are located. As you move to the south of the catchment bedrock aquifers and aquicludes become dominant.

The elevation distribution in the Ybbs catchment ranges from 250m to 1900m above sea level (asl) with an average slope of 32%. The Opponitz subcatchment represents the most mountainous part of the watershed with an average slope of 45% (elevation from 390 to 1900masl), whereas the Krenstetten subcatchment has a relatively small elevation range (300-900masl) and an average slope of 14%. In coincidence with the elevation and slope characteristics there is a significant increase in precipitation from the north (Krenstetten, Greimpersdorf) to the south (Opponitz). In Opponitz subcatchment as well as parts of Krenstetten large amounts of snow fall during winter season.

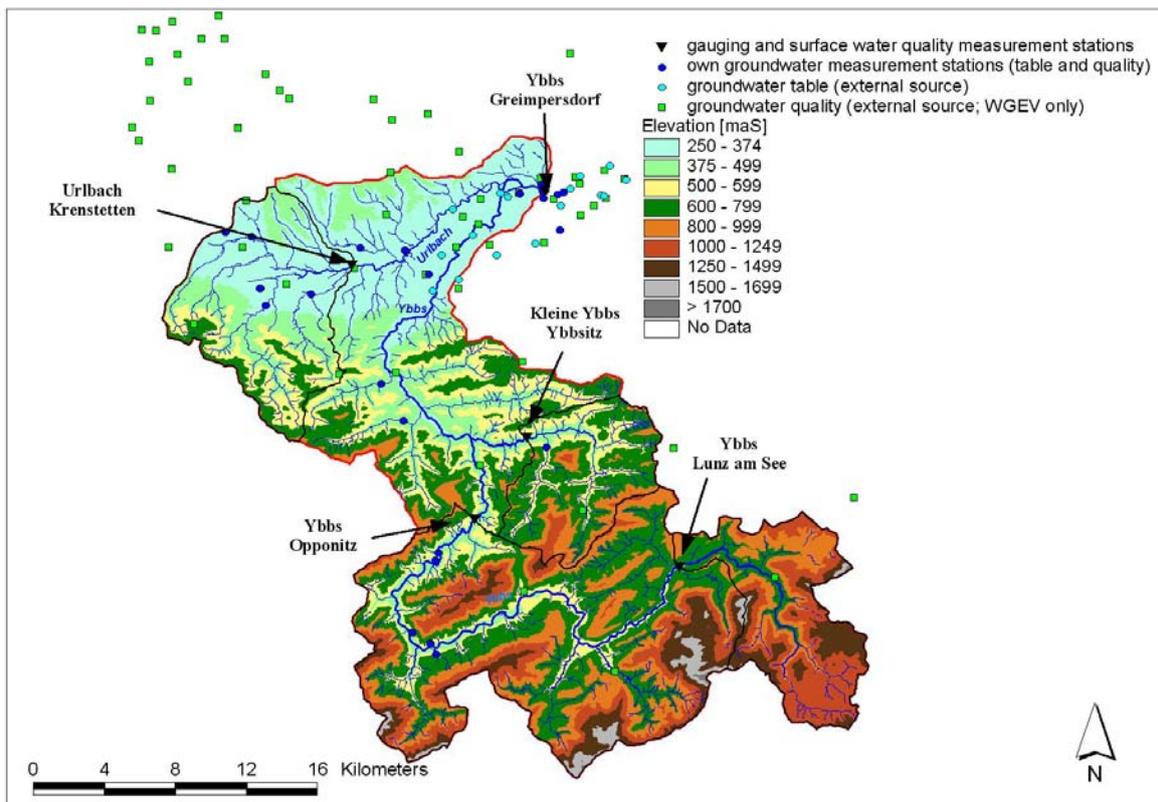


Figure 11: Elevation characteristics and overview on the location of the groundwater and surface water observation stations for the Ybbs catchment

3.2.2 Land use characteristics

In regard to land use the main part of the Ybbs catchment is dominated by forest (52%), then grassland or pasture (32%) and arable land (12%). Settlements and urban areas (3%) are of local importance only. Particularly the southern part of the Ybbs catchment (Opponitz subcatchment) is covered by forest and pasture. Low agricultural activity in these parts of the catchment results in low average nitrogen and phosphorus surpluses in soils (see Table 6). In Krenstetten subcatchment as well as near the main watershed outlet agricultural areas become dominant leading to the highest surpluses of nitrogen and phosphorus calculated for Krenstetten subcatchment.

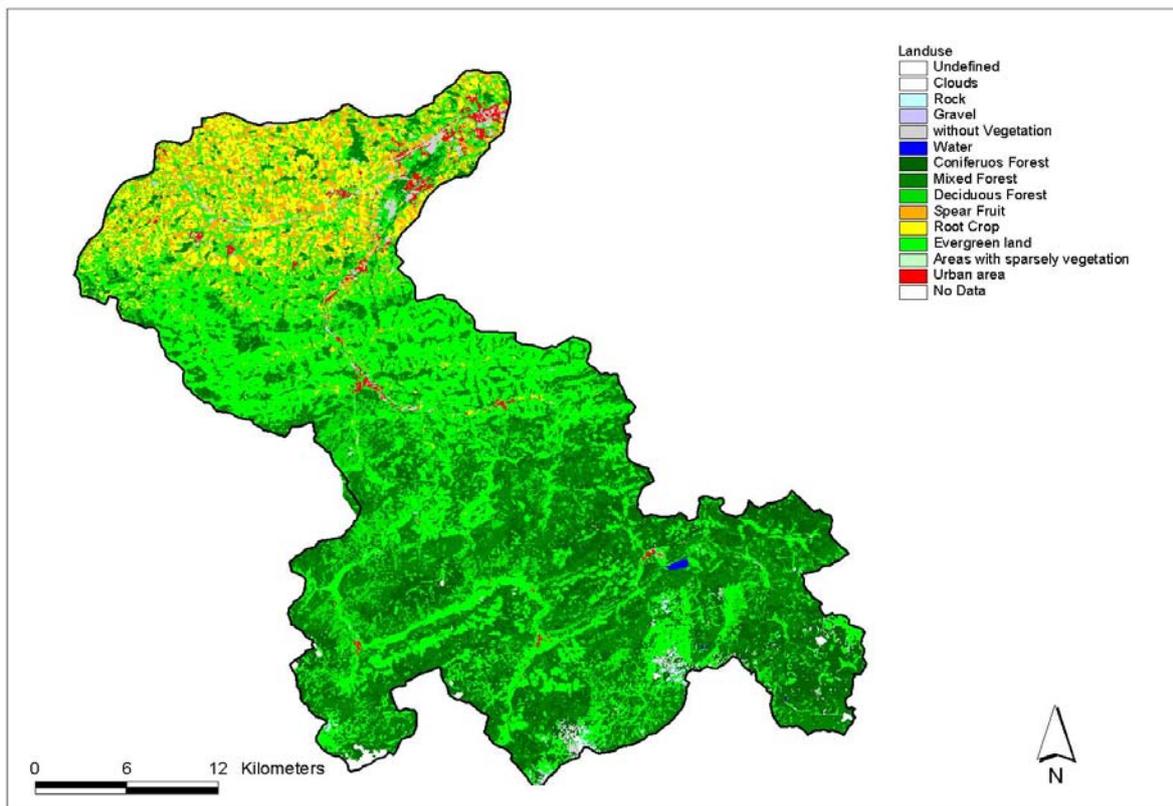


Figure 12: Land use characteristics of Ybbs catchment

Regional differences in land utilisation in the Ybbs catchment result in three main sections with different extent of agricultural practise. The most upstream part (which accords almost to delineation of Opponitz subcatchment) is dominated by forests. A middle section is dominated by pastures and meadows and forms the part downstream of the Opponitz subcatchment towards the watershed outlet. The downstream part (northern part of the Ybbs catchment) is characterised by high intensity of agricultural activity.

The mineral fertilizer utilisation increased significantly since 1965 and reached a maximum in the middle of the 80's with about 50 kgN/ha_{AA}*a related to agricultural area. Since then a slight decrease in mineral fertilizer applications is observable with actual amounts of about 37 kgN/ha_{AA}*a (see Figure 13).

3. Characterisation of the case study regions

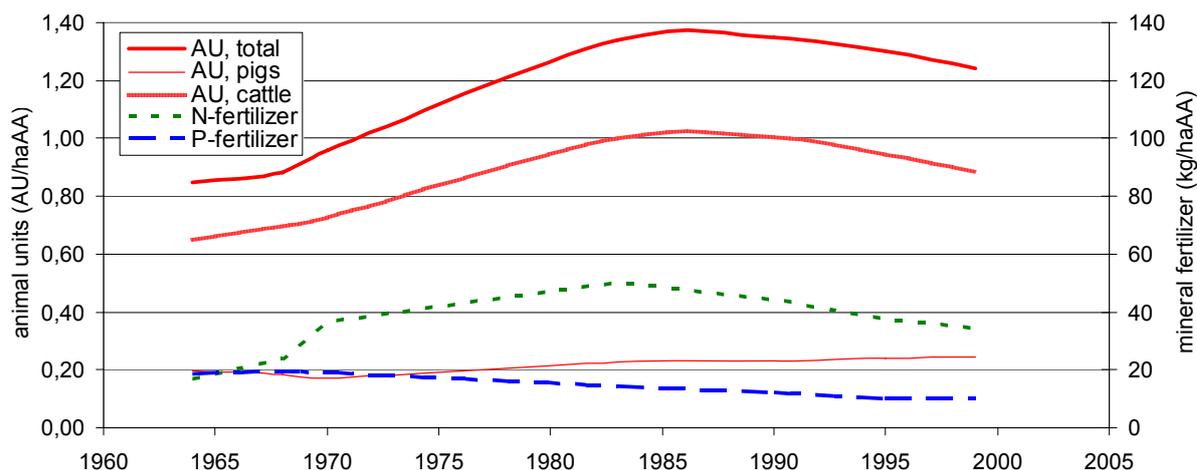


Figure 13: Development of animal units and mineral fertilizer per hectare of agricultural area application in the Ybbs catchment (from Zessner et al. 2004)

Animal husbandry (mainly cattle) is an important sector in the Ybbs catchment. Life stock also reached a maximum in the middle of the 80's and is slowly decreasing since then. Due to the important husbandry sector, the applications of organic additions (manure, sewage sludge) dominate the nitrogen fertilizers which are in use in Ybbs catchment (see Table 7).

Table 7: Calculation of the nitrogen surplus in different subcatchments at the Ybbs for the year 1999 (from Zessner et al. 2004)

N in kg/ha _{AA} ·a	Total	Opponitz	Url/ Krenstetten	Greimperd. net
Input				
Organic fertilizer (manure, sewage sludge)	109-123	57-68	128-144	108-122
Mineral fertilizer	35	36-39	42	37
N-fixation by micro-organisms	7-8	0-1	10-13	7-8
Atmospheric deposition	20-24	14-18	20-28	18-22
Output				
Harvested products	105-119	78-93	98-124	82-102
NH ₃ -N losses	10-16	6-9	13-20	11-16
N-surplus (Input – Output)	72-74	23-24	85-90	71-77
(N-net mineralization)	(-(24-32))			
(Corrected N-surplus)	(48-42)			

Due to intensive agricultural activity in northern parts of the catchment, nitrogen surpluses are highest in these regions. Figure 14 gives an overview on distribution of nitrogen surpluses on agricultural areas on municipality level. Highest nitrogen surpluses were observed with about 75 kgN/ha_{AA}*a in the northern parts of the Ybbs catchment.

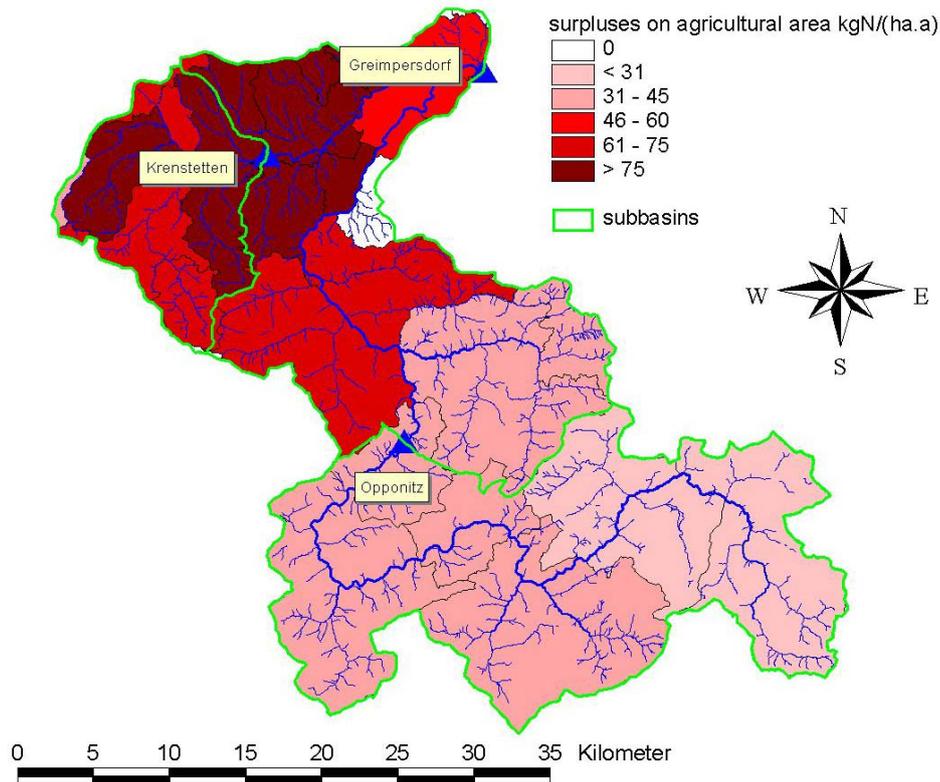


Figure 14: Regional distribution of nitrogen surpluses in the Ybbs catchment for the year 1999 (from Zessner et al. 2004)

Table 6 gives a summary on main characteristics of Ybbs catchment subdivided on subcatchment level. Due to relatively moderate fraction of agricultural areas on the total catchment area, the average nitrogen surpluses related to total catchment area (see Table 6) are significantly lower with about 40 kgN/ha*a.

3.2.3 Geological conditions

The geological formations of the Ybbs watershed can be divided into two main parts consisting of consolidated rocks (covering $\frac{2}{3}$ of the watershed area) and unconsolidated gravels and sediments (covering $\frac{1}{3}$ of the watershed area). The unconsolidated sediments constitute mainly of terrace gravels and alluvial deposits. They can be found in the northern part of the watershed (subbasin Krenstetten and towards the main watershed outlet Greimpersdorf) and define aquifers partly covered by loam. The consolidated rocks mainly consist of limestone, dolomite, flysch and sandstone and can be found mainly in the southern part of the watershed in the subbasin Opponitz. There are only local, river conducted aquifers to be found.

3. Characterisation of the case study regions

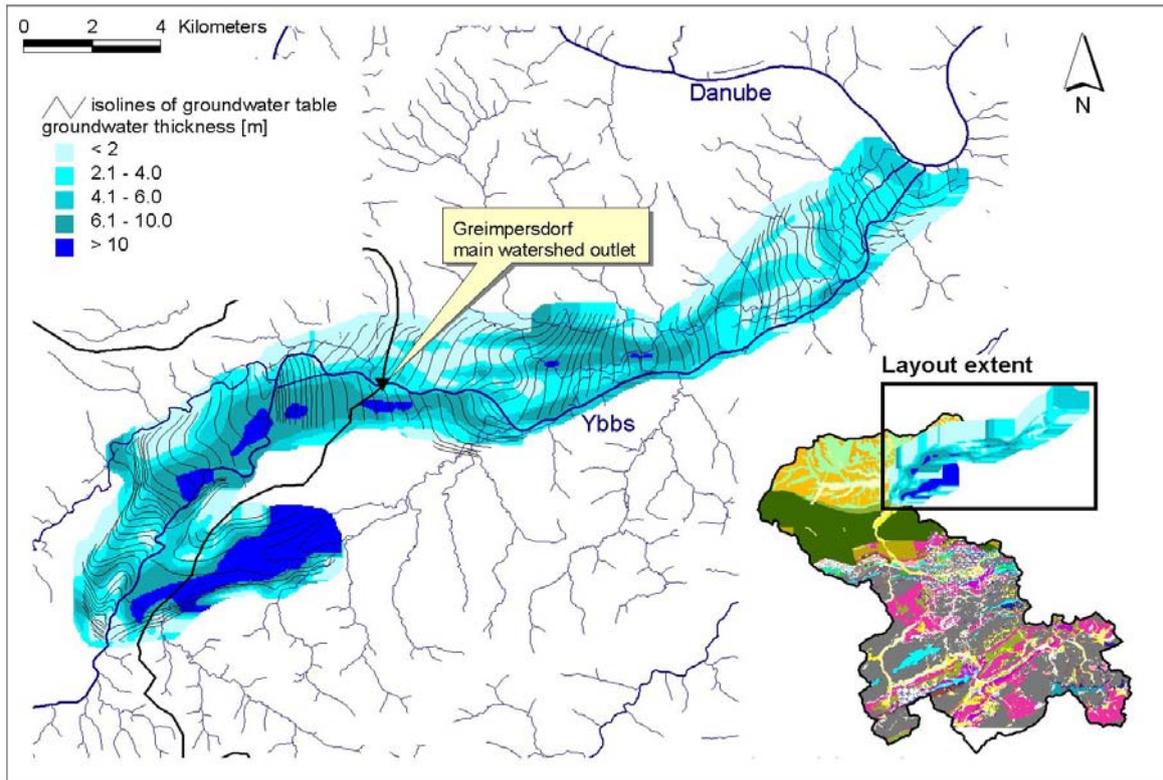


Figure 15: Groundwater thickness and isolines of porous aquifer in Danube river valley in relation to boundaries of the Ybbs catchment

Figure 15 indicates the constitution of geological circumstances in the Ybbs catchment and points up the parts of the catchment dominated by consolidated rocks (grey, magenta and green dominated colours in right side of Figure 15) and the parts mainly consists of porous aquifers (yellow and orange dominated colours). Additionally, boundaries of the aquifer with main aquifer characteristics are shown in Figure 15. Obviously only in the northern part of the Ybbs catchment large continuous aquifers are present.

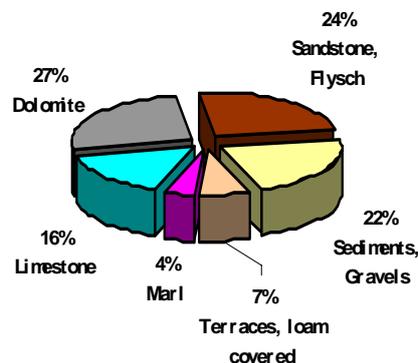


Figure 16: Fraction of the geological formation in the Ybbs catchment

Fractionally, dolomite and sandstone are located under more than half of the catchment area (see Figure 16), particularly in the southern part of catchment. Sediments and gravels constitute nearly one fourth of geological circumstances mainly in the northern part of the catchment. The remaining parts consists of limestone, loam covered terraces (gravels) and marl.

3.3 The Wulka catchment

3.3.1 Catchment morphology

Figure 17 shows the elevation distribution of the Wulka catchment with the location of the groundwater, surface water level and quality observation stations. Due to the hydro geological formations most of the groundwater quality and groundwater level measurement stations are located downstream of the gauging stations Walbersdorf and Wulkaprodersdorf. Nearby the gauging station Schützen the density of groundwater measurement points is higher than in other parts of the catchment. Thus, this region was used for more detailed analyses of the groundwater table, the groundwater flow direction and residence time.

The elevations in the Wulka catchment range from 125 to 750 masl. In comparison to Ybbs catchment it can be characterised as relatively flat with an average slope of about 8%. The most elevated subcatchment is Walbersdorf with an average subbasin slope of 15% due to location of Rosalien Mountains in the south western part defining the watershed boundaries. In the Wulkaprodersdorf subcatchment the average slope is about 10%, the Eisbach subcatchment and the Nodbach subcatchment show the lowest average slopes with 6.5% and 4%, respectively.

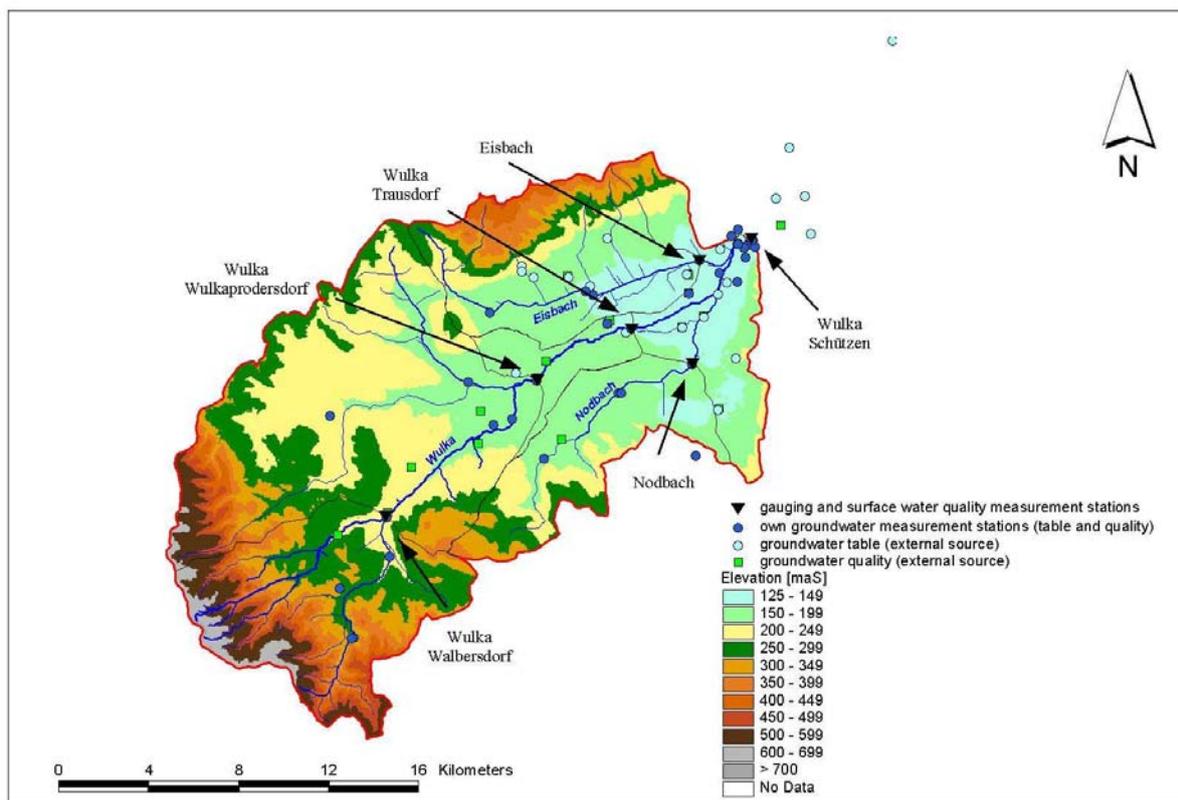


Figure 17: Elevation characteristics and overview on the location of the groundwater and surface water measurement stations for the Wulka catchment

Despite the Rosalien mountains constituting the catchment boundaries in the south west, with elevations > 700 masl, in the northern part the Leitha mountains are situated (north of river Eisbach – see Figure 17) defining the northern catchment boundaries of the Wulka catchment.

3.3.2 Land use characterisation

In terms of land use the main part of the catchment is dominated by agriculturally used areas (54%) followed by forested areas (28%), grassland or pasture (12%). Contrary to the Ybbs catchment main parts of the Wulka catchment are used for agricultural production. Settlements and urban areas (6%) cover a high percentage of areas related to the total catchment area.

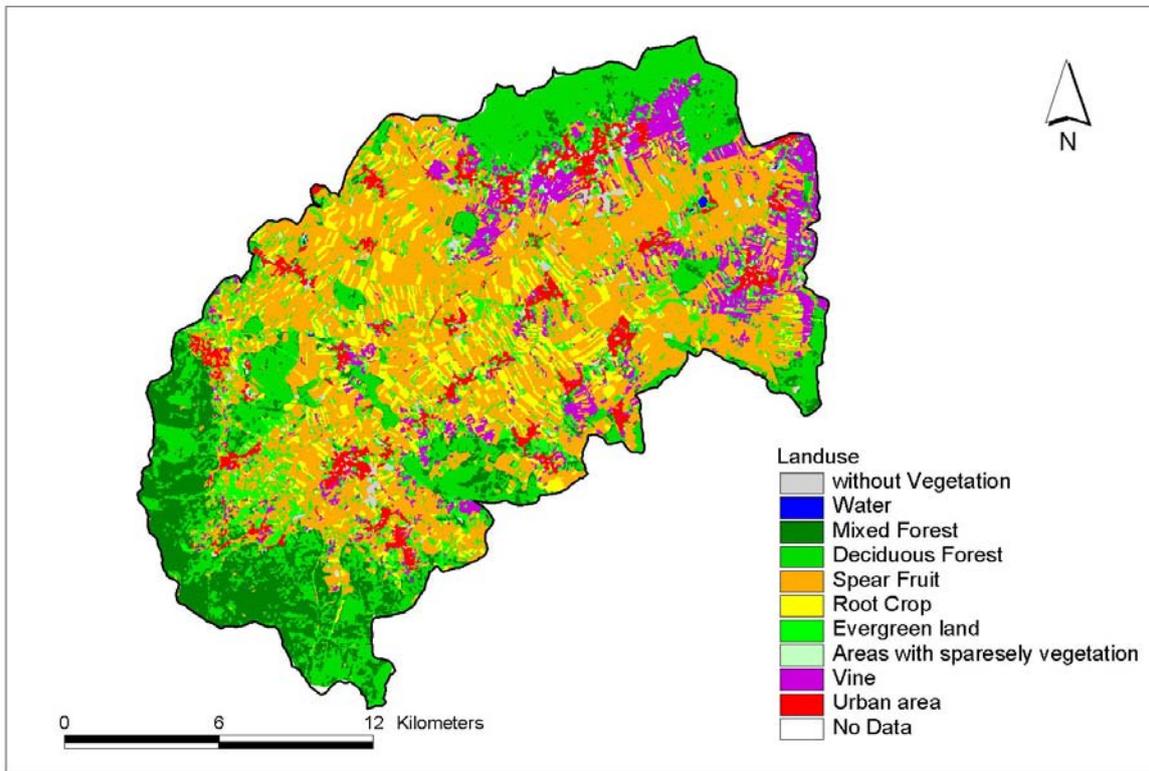


Figure 18: Land use characteristics of the Wulka catchment

More than 50 % of the catchment area in the Wulka catchment is used for agriculture. Together with pastures and meadows 66 % of the area is under agricultural production. The highest share of agricultural area is used for wheat, barley and maize production. Vineyards are of significant importance too. This consequently impacts the average nitrogen and phosphorus surpluses on soil, which are, related to catchment area, comparable to average surpluses calculated for the Ybbs catchment (see Table 6) related to total catchment area.

Similarly to Ybbs catchment, the mineral fertilizer utilisation increased from 1965 and reached its maximum in the middle of the 80's with more than 120 kgN/ha_{AA}*a applied as mineral fertilizers (see Figure 19).

Animal farming is of low importance in the Wulka catchment. The stock of animals (mainly cattle) was significantly reduced since the sixties (see Figure 19).

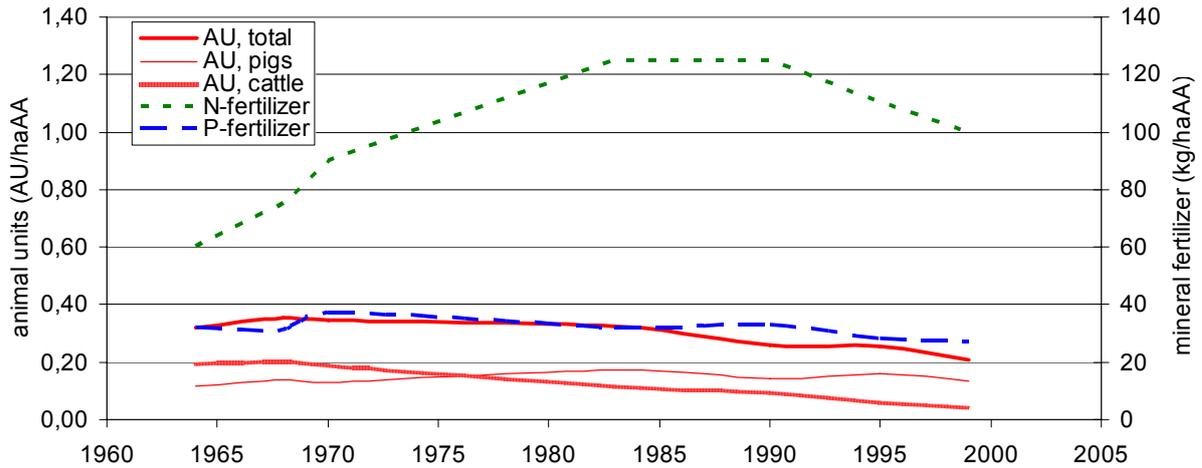


Figure 19: Development of animal units and mineral fertilizer per hectare of agricultural area application in the Wulka catchment (from Zessner et al. 2004)

Due to unimportant husbandry sector in the Wulka catchment mineral nitrogen additions dominate fertilizer applications (see Table 8).

Table 8: Calculation of the nitrogen surplus in different subcatchments at the Wulka for the year 1999 (from Zessner et al. 2004)

N in kg/ha_{AA}-a	Total	Walbersdorf	Wulkaprodendorf	Nodbach	Eisbach	Schützenried
Input						
Organic fertilizer (manure, sewage sludge)	19-21	18-20	34-39	8	5	4
Mineral fertilizer	72-86	80-97	74-87	74-89	69-83	59-72
N-fixation by micro-organisms	3-6	4-8	2-7	3-5	2-3	4-5
Atmospheric deposition	13-17	13-17	13-17	13-17	13-17	13-17
Output						
Harvested products	62-76	76-95	72-89	57-70	43-51	42-49
NH ₃ -N losses	2-3	2	4-5	1	0,2-0,3	0,2
N-surplus (Input – Output)	46-55	39-47	51-58	42-51	49-60	41-52
(N-net mineralization)	(8-10)					
(Corrected N-surplus)	(54-65)					

Except some parts of the Wulka catchment (mainly Walbersdorf subcatchment and parts of Wulkaprodendorf subcatchment), the Wulka catchment is characterised by relatively high and evenly distributed nitrogen surpluses on agricultural areas (see Figure 20). The average nitrogen surplus for the Wulka catchment related to agricultural area is about 50 kgN/ha_{AA}*a.

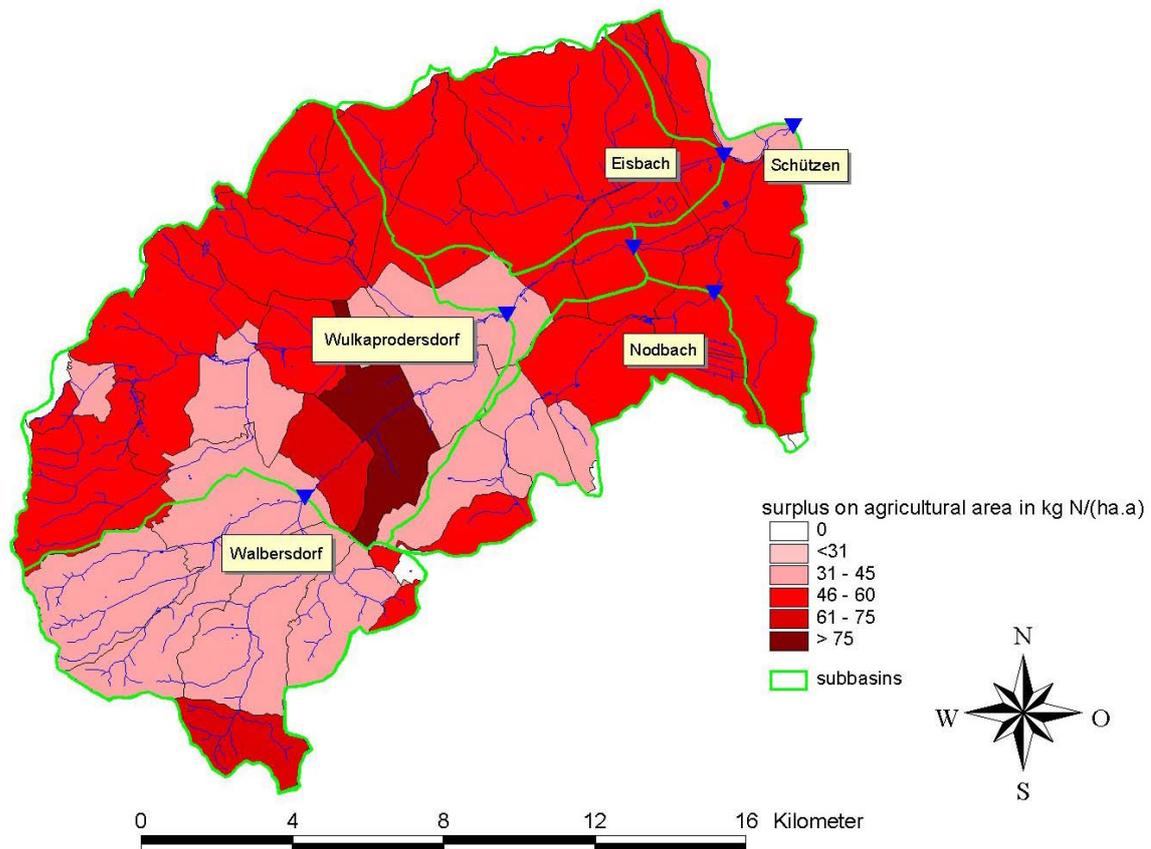


Figure 20: Regional distribution of nitrogen surpluses in the Wulka catchment for the year 1999 (from Zessner et al. 2004)

Due to relatively high fraction of agricultural areas on the total catchment area, the average nitrogen surpluses related to total catchment area (see Table 6) is not significantly lower with about 38 kgN/ha*a.

3.3.3 Geological conditions

The geology of the Wulka catchment consists mainly of fluvial deposits and gravels (48%) and marl (37%) situated along the river Wulka. Also considerable fractions of consolidated rocks (limestone, dolomite, sandstone) are located in the Wulka watershed, mainly in the north (Leitha Mountains) and in the south-west of the watershed (Rosalien Mountains).

Unfortunately no geological map with spatial extent covering the total catchment area of the Wulka catchment was available. From available geological information covering the Wulka catchment with exception of Walbersdorf subcatchment the distribution of geological formations was calculated in relation to catchment area (see Figure 21).

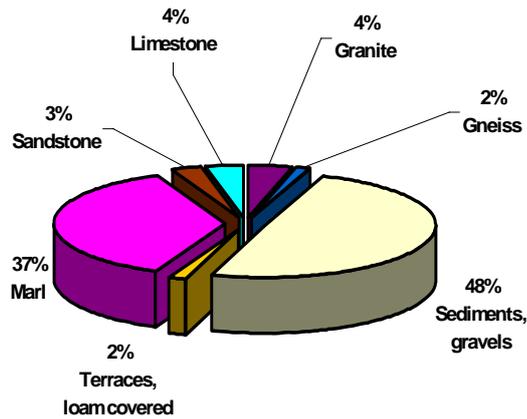


Figure 21: Fraction of the geological formation in the Wulka catchment

Obviously nearly half of catchment areas are dominated by sediments and gravels defining local and regional aquifers. According to Haas et al. (1987c) two main aquifers can be confined: one in upstream part of the Wulka catchment mainly located within the subcatchments Walbersdorf and Wulkaprodersdorf, and the second in downstream section of Wulka catchment around main watershed outlet Schützen. Due to Leitha Mountains the Wulka catchment consists of considerable fractions of marl, limestone and granite too (Figure 21).

4 Water balance calculations using the SWAT 2000 model

4.1 Introduction and motivation

The strong connection between hydrology and water quality is the main scope of this work. Individual species of relevant water quality parameters are characterised by specific abilities of mobility in the environment. Particularly for nitrogen and its species their mobility is dependent on the spatial and temporal occurrence of transport-causing runoff components. In addition, watershed hydrology is not only decisive for transport processes at the catchment scale; retention/reduction processes (denitrification in unsaturated and saturated zones) are influenced by climatic/hydrologic conditions. Thus, focussing on nutrient balance estimations on catchment scale, a well grounded knowledge of the hydrologic cycle is required. The determination of water and water related nutrient dynamics in watersheds is a necessity for the estimation of both the total nutrient emissions and the specific nutrient emission pathways for every catchment.

For the estimation of the water balances and the ratios of the runoff components for the two case study regions of the daNUbs project, three different methods were applied (Blaschke et al. 2003). Firstly, the distributed parameter continuous time model SWAT 2000 was used to calculate the water balance based on observed climatic data. Secondly, the empirical emission model MONERIS was applied for nutrient emission estimations for both catchments. Calculated model specific runoff components have been compared to other methods. The MONERIS model uses observed river discharges to determine groundwater runoff as the difference between the observed discharges and empirically estimated remaining runoff components. Thirdly, a hydrograph separation technique (DIFGA 2000 model) was applied to determine the fraction of the three main runoff components based on frequency analyses of the observed river discharges. Detailed information concerning the application of the DIFGA 2000 model can be found in (Heinecke 2004).

The modelling approaches SWAT and MONERIS differ significantly in their process representation as well as in their temporal and spatial resolution. Whereas the conceptual model SWAT 2000 requires a sound database from observation stations in terms of climate, hydrology, morphology and water quality to ensure an adequate spatial and temporal resolution (input data on daily time step), the empirical MONERIS model, which was initially developed for predictive simulation of large river basins, uses spatially and temporarily aggregated input data. Consequently output information of the modelling approaches differs significantly in terms of reproduction of catchment dynamics and spatial heterogeneities.

The application of the conceptual SWAT 2000 model will be introduced and discussed in terms of the model capability to reproduce observed hydrologic conditions, advantages and disadvantages of the methodology in regard to water and nutrient balance calculations with focus on estimation of nitrogen emissions.

Since three different methods were applied for estimation of catchment specific water balances, the definition of runoff components of the individual modelling approaches differ from each other as a consequence of varying model concepts as well as their resolution in time and space. Both DIFGA 2000 and the MONERIS model

use observed river discharges for selected gauging stations. Therefore, spatial resolution is limited to subcatchment definition according to the location of river gauging stations. In terms of the temporal resolution DIFGA 2000 operates on a daily time step, whereas the MONERIS model uses 5-year average values for temporal discretisation. The SWAT 2000 model operates on a daily time step as well, but with more detailed spatial resolution using confluence sites of the river system for the definition of subbasins. To ensure comparability, subbasins were aggregated to subcatchments according to the location of river gauging stations.

In this chapter results from the SWAT 2000 model application for water balance calculations are presented. To evaluate the calculated runoff components, a comparison to calculated runoff components using DIFGA 2000 and the MONERIS model are presented discussing likewise differences in runoff components definitions.

4.2 Model description

For the calculation of the detailed water balances for the Ybbs and the Wulka catchment the SWAT 2000 model (a distributed parameter, continuous time model) was used (Arnold et al. 2000, Neitsch et al. 2001), which is designed to simulate the hydrologic cycle on the watershed level. Watershed-specific conditions are incorporated into the model via ArcGIS maps joined by attribute lookup tables to the SWAT database.

A Digital Elevation Model (DEM) is used to delineate the watershed boundaries and the river network. The watershed is structured in subbasins arising from confluences of tributaries, river sections or locations of gauging stations, what is particularly beneficial when different areas of the catchment are dominated by land uses or soils being dissimilar enough in properties to impact local hydrology. Furthermore, the land use and soil distribution is used to generate hydrologic response units (HRU's) for every subbasin and thus for a further assembling into lumped areas with similar hydrologic response.

The water balance is calculated on a daily time step for every HRU and printed out for every HRU and every subbasin (as average of all HRU's belonging to a subbasin), summarized as annual values for every HRU and subbasin, and as average annual values for the whole watershed. The simulation of the hydrology is separated into two major parts: a land phase and a water phase. The land phase of the hydrologic cycle defines the amount of water, sediment, nutrient and pesticide loadings to the main channel in each subbasin. The second part is the water or routing phase of the hydrologic cycle, which defines the movement of water, sediments, etc. through the channel network of the catchment to the watershed outlet.

The input information is provided by several input files, where watershed-, river-, subbasin- or HRU-specific data are stored:

- Soil input file (.sol)*
- Subbasin input file (.sub)*
- HRU input file (.hru)*
- River reach input file (.rte)*
- Groundwater input file (.gw)*

- Management input file (.mgt)*
- Pond/Wetland input file (.pnd)
- Weather generator input file (.wgn)
- Water use input file (.wus)
- Stream Chemical input file (.chm)

The *-labelled input files were predominantly used for the calibration of the SWAT 2000 model.

The simulated river discharge (water yield) mainly consists of the contribution of three runoff components:

- Surface Runoff (**SURO**): amount of water, which can not infiltrate into the soil due to saturated conditions in the top soil layer, impervious areas or closed seeded land cover types; it flows directly to the river
- Lateral Runoff (**LATQ**): fast saturated water movement, which is caused in the soil profile by underlying less conductive layers, preferential flow (macro pores) or saturated conditions in soils with a higher slope exposition
- Groundwater Runoff (**GWQ**): saturated water movement in the shallow aquifer caused by differences in the potential head; occurs under the bottom layer of the soil

Besides these components also runoff from tile drained areas is calculated completing the simulated river discharge. Additional inlets from waste water treatment are considered as constant loadings within a defined time step (daily/monthly/annual average loadings).

4.3 Input data

4.3.1 Climatic data

The climatic data are the main input of the SWAT 2000 model. They represent the driving force of the water and energy cycle. The following data were used to define the climatic conditions:

Table 9: Overview on climatic data were used as input data for the SWAT 2000 model

Ybbs catchment (No. stations/time period)	Wulka catchment (No. stations/time period)
Precipitation (15/1971-2001)	Precipitation (15/1971-2001)
Air Temperature (14/1946-2001)	Temperature (7/1989-2001)
Solar Radiation (5/1990-2000)	Solar Radiation (1/1990-2000)
Relative Humidity (5/1990-2000)	Relative Humidity (1/1990-2000)
Wind Speed (5/1990-2000)	Pot. Evapotranspiration (1/1961-2000)
Snow cover (8/1970-2001)	Snow cover (15/1970-2001)

Precipitation

The SWAT 2000 model incorporates daily precipitation values. If data are missing in the period of simulation, the model provides a simple weather generator to estimate the missing daily values based on calculated statistics. For every subbasin, the nearest precipitation station will be used without consideration of any

adjustments. A possibility to enter a precipitation-laps-factor (changes in precipitation due to changes in elevation) is given in the (.sub)-file.

Temperature

The SWAT 2000 model incorporates daily maximum and minimum temperature values. Missing data can be generated based on calculated statistics.

Solar Radiation, Relative Humidity, Wind Speed

The SWAT 2000 model incorporates daily values of these measurements. Missing data can be generated based on calculated statistics. The data will be used to calculate potential Evapotranspiration.

Potential Evapotranspiration

The SWAT 2000 model incorporates daily values of potential evapotranspiration (PET), if these data are available. Otherwise, PET will be calculated using temperature, solar radiation, relative humidity and wind speed data. Several methods are provided to estimate PET: after Penman-Monteith (Monteith 1965), Priestley-Taylor (Priestley et al. 1972) or Hargreaves (Hargreaves et al. 1985). In the Wulka basin, daily values of PET estimated with the Penman-Monteith-Method were provided by local authorities and were used for definition of PET values.

4.3.2 Data about waste water treatment plants (wwtp)

Water inlets from wwtp's will be considered in the SWAT 2000 model, too. The incorporation into the model is possible as measured values or as constant daily, monthly or annual loadings.

In the Ybbs catchment water inlets from wwtp will be considered as a constant monthly load. The 7 WWTP have been implemented with monthly loadings based on measurements between 80 and 2500 m³/d.

In the Wulka catchment water inlet from wwtp will be considered as monthly measured values for 2 wwtp's (1981-2000). In this catchment wwtp outflow contributes significantly to river discharge. About 30% of the total river discharge of the Eisbach river consists of wwtp outflow.

4.4 Model calibration and validation

4.4.1 Main definitions

The calibration of the SWAT 2000 model was dedicated to refine originally pre-set model parameters (see Table 11 and Table 12) to obtain minimal deviations between the observed and simulated **river discharges** in order to get an optimal model performance.

Model calculations were performed for the time period of 1991-2000 for the Ybbs catchment and 1992-1999 for the Wulka catchment. For model **calibration**, the time period **1995-1997** was used. For model **validation**, the time period **1992-1994** and **after 1997** was taken into account.

4.4.2 Estimation of the model performance

The model performance was estimated using the Nash-Sutcliffe-Coefficient (**NSC**) (Nash et al. 1970).

The *Initial variance* F_0^2 of the measured values (River discharge) is given as:

$$F_0^2 = \sum (q - \bar{q})^2 \quad (\text{Equation 14})$$

with q ... observed (measured) discharge

\bar{q} ... mean of the observed (measured) discharge

The *Residual variance* F^2 is given as:

$$F^2 = \sum (q' - q)^2 \quad (\text{Equation 15})$$

with q' ... calculated discharge

q ... observed discharge

The *Efficiency of the model* R^2 is given as:

$$R^2 = \frac{F_0^2 - F^2}{F_0^2} \quad (\text{Equation 16})$$

Additionally, the volumetric error **VE** between the simulated and the observed river discharge was taken into account:

$$VE = \frac{V'}{V} * 100\% \quad (\text{Equation 17})$$

with V' ... Total amount of water of the simulated river discharge in the period

V ... Total amount of water of the observed river discharge in the period

4.4.3 Modifications and catchment specific definitions

Due to the scarce number of the precipitation stations and their uneven distribution in the catchment, problems with precipitation events and the corresponding river discharges occurred. Originally, the model uses the nearest precipitation station for rainfall generation and considers the observed rainfall for these subbasins without any adjustment. Following this method, deviations between rainfall events and observed river discharge responses were observed initially. Daily Kriging interpolation of the precipitation values for a period of 30 years was performed for the whole watershed. A grid was created, and for every subbasin the average area-weighted precipitation amount was estimated. In that way, for every subbasin a virtual rain gage station with daily precipitation values for 30 years in the centroid of the subbasin was built.

Due to the wide range of elevations in the Ybbs catchment problems arose in consideration of snow fall and snow melt events in the watershed. Thus, elevation bands have been introduced for the Ybbs catchment associated with an elevation dependent decrease in temperature (-6.3°C/1000m elevation increase) based on statistical evaluations of the observed temperatures.

After watershed delineation the Ybbs catchment consisted of 73 subbasins with 205 HRU's, the Wulka catchment consisted of 45 subbasins with 106 HRU's (see Table 10).

Table 10: Differences in main characterisations between the Ybbs catchment and the Wulka catchment after watershed delineation in the SWAT 2000 model

Ybbs catchment 1108 km ²	Wulka catchment 390 km ²
73 subbasins	45 subbasins
205 HRU's	106 HRU's
7 landuse classes	7 landuse classes
5 soil classes	5 soil classes
7 point sources (wwtp)	2 point sources (wwtp)
1 reservoir (lake Lunz)	

4.4.4 Model calibration

The calibration was started using a trial and error method. Calibration was carried out for simulated river discharge against the observed river discharge. Due to the large number of model parameters a satisfying model performance could not be obtained. The model parameters used for calibration are listed in Table 11.

Table 11: Calibration parameter of the SWAT 2000 model using a trial and error method

Input-file	Parameter	Description	Variation of parameters on
.sol	SOL_Z	Soil layer depth [mm]	HRU-level
	SOL_K	Saturated hydraulic conductivity [mm/h]	HRU-level
	SOL_AWC	Soil available water capacity [mm]	HRU-level
.sub	TLAPS	Temperature laps rate [°C/km]	Subbasin-level
	ELEVB	Elevation bands [m]	Subbasin-level
	ELEVB_FR	Fraction of the subbasin in the Elevation band	Subbasin-level
.gw	ALPHA_BF	Baseflow alpha factor	Subbasin-level
.bsn	SFTMP	Snow fall temperature [°C]	Watershed-level
	SMFMX	Maximum melt rate during summer [mm/°C*d]	Watershed-level
Input-file	Parameter	Description	Variation of parameters on
	SMFMN	Minimum melt rate during winter [mm/°C*d]	Watershed-level
	TIMP	Snow pack temperature lag factor	Watershed-level
	SNOCVMX	Minimum snow water content, that corresponds to 100% snow cover	Watershed-level
	SNO50COV	Snow water equivalent that corresponds to 50% snow cover	Watershed-level

As a consequence an automatic calibration tool (van Griensven et al. 2002), which was developed for the ESWAT model, was applied for the SWAT 2000 model. This tool uses the Shuffled Complex Evolution Algorithm (SCE-UA) (Duan et al. 1992) for optimisation, where several objective functions are aggregated to a global optimisation criterion which has to be minimised.

The model parameters estimated by using the SCE-UA-algorithm are listed in Table 12.

Table 12: Calibration parameter of the SWAT 2000 model using the SCE-UA-Algorithm

Input-file	Parameter	Description	Variation of parameters on
.sol*	SOL_Z	Soil layer depth for every layer [mm]	HRU-level
	SOL_K	Saturated hydraulic conductivity for every layer [mm/h]	HRU-level
	SOL_AWC	Soil available water capacity for every layer [mm]	HRU-level
.gw	ALPHA_BF	Baseflow alpha factor	Subbasin-level
	GW_DELAY	Groundwater delay [d]	Subbasin-level
	GW_REVAP	Groundwater "re-evaporation" coefficient	Subbasin-level
	RCHRG_DP	Deep aquifer percolation fraction	Subbasin-level
	REVAPMN	Threshold value for 'revap'/percolation to deep aquifer to occur [mm]	Subbasin-level
	GWQMN	Threshold value for return flow (base flow) to occur [mm]	Subbasin-level
.mgt .rte	CN2	Curve number for moisture condition II	HRU-level
	CH_K2	Effective hydraulic conductivity for the main channel [mm/h]	Subbasin-level
	CH_N2	Manning's 'n' value for the main channel	Subbasin-level
.bsn	SMTMP	Snow melt temperature [°C]	Watershed-level
	SFTMP	Snow fall temperature [°C]	Watershed-level
	SMFMX	Maximum melt rate during summer [mm/°C*d]	Watershed-level
	SMFMN	Minimum melt rate during winter [mm/°C*d]	Watershed-level
	TIMP	Snow pack temperature lag factor	Watershed-level
	SNOCOVMX	Minimum snow water content, that corresponds to 100% snow cover	Watershed-level
	SNO50COV	Snow water equivalent that corresponds to 50% snow cover	Watershed-level
SURLAG	Surface runoff lag time [d]	Watershed-level	

Similarly up to 5 parameters have been optimised within each optimisation procedure. The parameters listed in Table 12 represent only a small fraction of parameters, which are used to run the SWAT 2000 model. Consequently, using the SCE-UA-algorithm the progress in model calibration was limited by large number of model parameters. Over-parametrisation in conceptual models is well-known (van Griensven et al. 2006), and the identification of sensitive model parameter is difficult. Using the SCE-UA-algorithm improved the model performances, but did not result in acceptable performances. Therefore further activity for model calibration had to be made.

Based on the calculated fractions of the runoff components using the DIFGA 2000 model, the calibration of the SWAT 2000 model was carried on with the prior optimised parameters. First, the surface runoff was adjusted by changing the Curve Numbers of the land use classes. Afterwards, the hydraulic conductivity was redefined in order to catch nearly the value for the lateral runoff, which was estimated for the fast groundwater flow with DIFGA 2000 model. At least, the groundwater parameters have been redefined in order to align the groundwater runoff of SWAT 2000 with the slow groundwater component of DIFGA 2000 model.

The calibration in regard to the parameters listed in Table 11 and Table 12 was performed for both the Ybbs catchment and the Wulka catchment starting from the most upstream subcatchment and the tributaries. First the model parameters were calibrated for the first subcatchments with subsequent definition for the next downstream subcatchment in case of a sufficient model performance. Last, the whole watershed was calibrated starting with parameter definitions obtained from the individual subcatchment calibrations.

4.4.5 Model performance for the Ybbs catchment

Initially, the calibration was started using the delineated watershed according to specifications listed in Table 10.

An FAO soil map (250m grid resolution) was used to define soil types. A corine land cover map (30m grid resolution) was used to define landuse classes. Via intersection of both maps the definition of the HRU's was executed. For each subbasin, every soil class was superposed by every land use class creating a HRU, what resulted in 205 HRU's (see Figure 22).

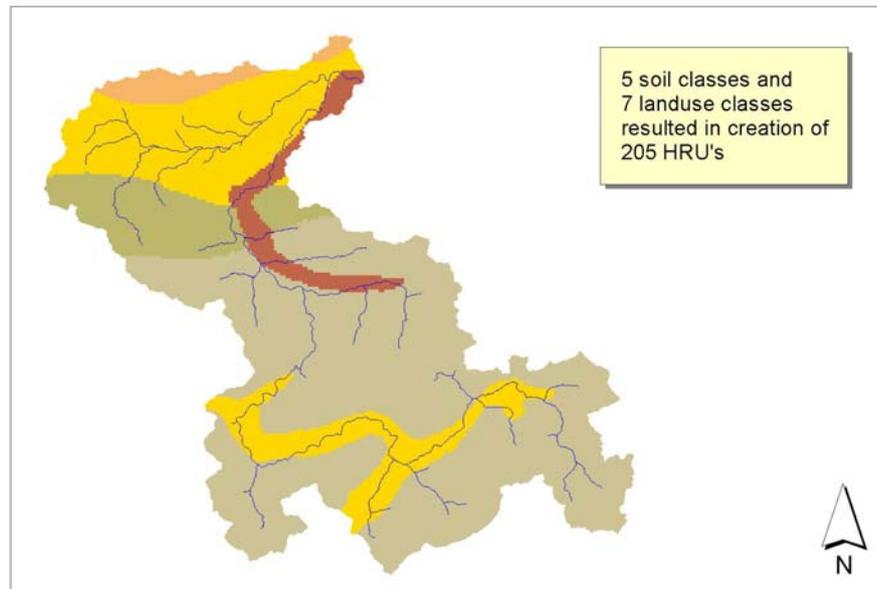


Figure 22: Number of soil classes limiting HRU definitions in the SWAT 2000 model for SWAT project with 205 HRU's for the Ybbs catchment

Later a more detailed soil map (25m grid resolution) was available for the Ybbs catchment based on geological information (use of geological basics with the Authorisation by the Geological Survey of Austria - ©GBA-2002-ZI.29/1/02). A second SWAT project (calculation version) was defined using the more detailed soil map, what resulted in similar watershed delineations but with 428 HRU's (see Figure 23).

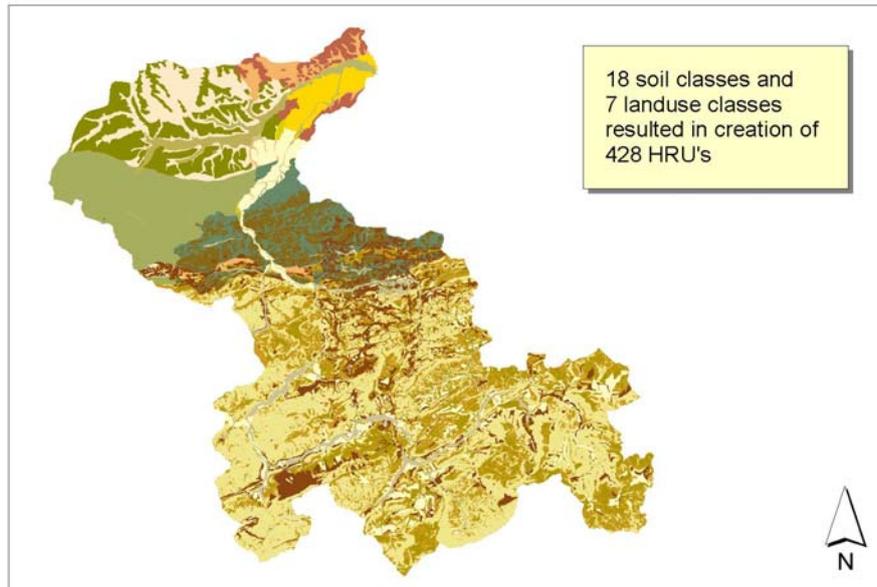


Figure 23: Number of soil classes limiting HRU definitions in the SWAT 2000 model for SWAT project with 428 HRU's for the Ybbs catchment

After the calibration of the different SWAT projects for the Ybbs catchment and an intensive calibration effort the following model performances listed in Table 13 were obtained.

Table 13: Model performance (Nash-Sutcliffe-coefficient - NSC) of the SWAT 2000 model for the Ybbs catchment in relation to different soil input data and the number of HRU's

NSC	205 HRU's			428 HRU's		
	Opponitz	Krenstetten	Greimpers-dorf	Opponitz	Krenstetten	Greimpers-dorf
1992 ^b	0.24	0.30	0.31	0.25	0.45	0.27
1993 ^b	0.30	0.00	0.27	0.23	0.36	0.26
1994 ^b	0.21	0.42	0.38	0.25	0.42	0.37
1995 ^a	0.30	0.25	0.29	0.26	0.41	0.27
1996 ^a	0.68	0.57	0.60	0.56	0.54	0.50
1997 ^a	0.54	0.45	0.44	0.41	0.52	0.32
1998 ^b	-0.07	0.46	0.27	0.06	0.47	0.28
1999 ^b	0.44	0.39	0.52	0.24	0.37	0.50
2000 ^b	0.37	-0.49	0.47	0.27	-0.37	0.47
92-00	0.39	0.32	0.41	0.33	0.37	0.37
VE [%]	100	126	101	95	111	95

^a...calibration period; ^b...validation period

Certainly model performances with NSC > 0.6 are desirable and do enhance the significance and reliability of simulation results, but unfortunately the SWAT 2000 model seems to suffer under the ambition describing almost completely the hydrological processes using physical equations, for what a huge amount of parameter is needed, and additionally needs to be calibrated. Without any model calibration, model performances (NSC) less than -10 - -20 were obtained. In this respect, calibration improved the model performance considerably. The model performances listed in Table 13 are poor, but within an acceptable range.

Model parameters are defined on diverse levels: at watershed, at subbasin or at HRU-level. According to Table 12, the number of calibration parameter can be calculated in dependency of input file:

- *.sol: 3 parameters for each soil layer, 2 soil layer per soil and HRU: 1230 calibration parameters
- *.gw: 6 parameter per subbasin: 438 calibration parameter
- *.rte: 2 parameter per subbasin: 146 calibration parameter
- *.mgt: 1 parameter per HRU: 205 calibration parameter
- *.bsn: 8 parameter per basin: 8 calibration parameter

Using the SWAT project with 205 HRU's, 2027 calibration parameter were the subject of calibration. Using the SWAT project with 428 HRU's, the number of calibration parameters increased to 3588 parameters. It is obvious that the identification of the sensitive model parameters, which significantly affect the model performance, is difficult and similarly the identification of the optimal parameter values to ensure not only a good model performance, but also a correct hydrological behaviour of the model.

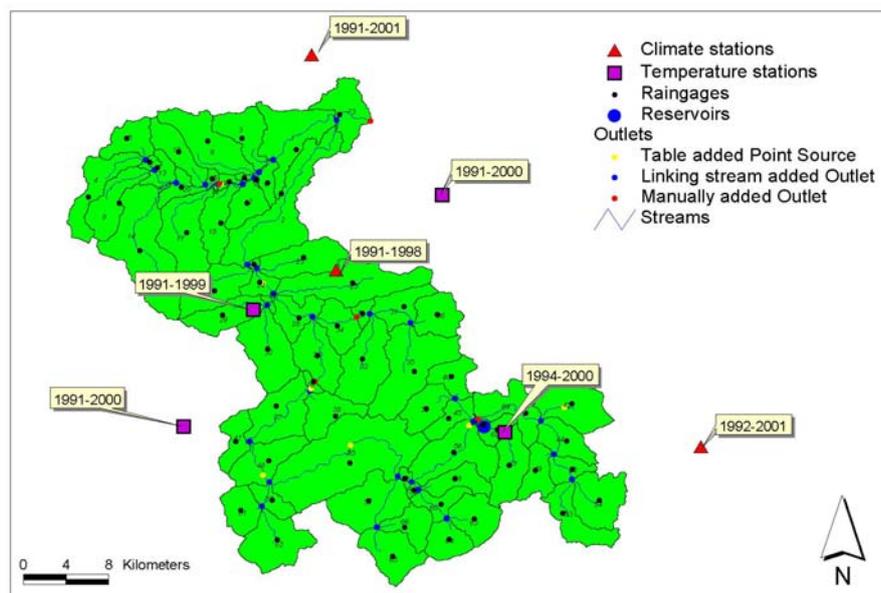


Figure 24: Watershed delineation for the Ybbs catchment within the SWAT 2000 model with location of precipitation, temperature and climate (solar radiation, wind speed, relative humidity) stations with the adequate interval of data availability

Model performances always reflect data availability. If the availability of input data from observations is limited, the model performance will be affected to a large extent. Like indicated by Table 13, the best model performances were obtained for the calibration period. For validation periods, model performances are partly significantly less than those obtained for the calibration period. This decrease can be attributed to limited data availability for climatic data (temperature, solar radiation, wind speed, relative humidity) in respect to both the existence of stations in all parts of the catchment as well as availability of measurements for existing stations. As shown in Figure 24, input data for temperature and climate were provided by 4 and 3 stations, respectively. Two temperature observation stations are located within the

catchment, but provided data only for a limited period of time (1991-1999, 1994-2000). Both stations are used to define temperature values for 63 of 73 subbasins. Only one of the three climate observation stations is located within the catchment and provides data for the period 1991-1998 for 54 of 73 subbasins. Despite the location of the stations and data availability, observed temperature and climate data are used to define the input data for the subbasins without any interpolation in relation to spatial location. For every subbasin, data of the nearest station will be used as they were observed. This results in considerable discrepancies between the data, which have been observed for the limited number of stations and the climatic conditions, which are likely to change with changing positions within the catchment and which could have been observed with more condensed observational networks. However, high uncertainties in the definitions of the input data in terms of temperature and climate are responsible for poor model performances to a great extent, particularly in validation periods.

The SWAT 2000 model simulates snow fall and snow melt processes based on parameter, which are defined at the watershed (catchment) level. Consequently bigger differences of both in time and space between simulated and observed snowmelt, particularly in the most upstream Lunz am See subcatchment (see Figure 25) occur due to the high fraction of precipitation.

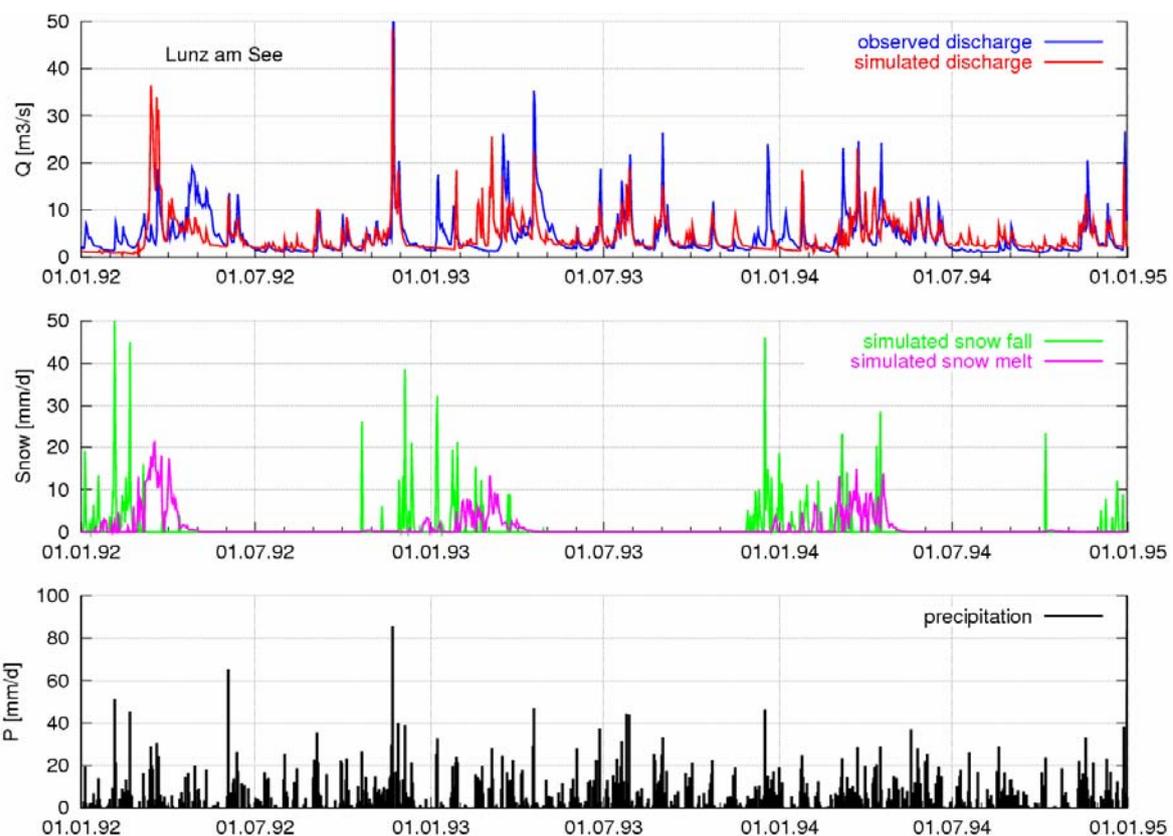


Figure 25: Comparison of observed and simulated river discharge for the Ybbs catchment using the SWAT 2000 model for the most upstream Lunz am See subcatchment in relation to simulated snowfall, snowmelt and to observed precipitation for the period 1992-1994

Simulated snow melt in the 'Lunz am See' subcatchment (Figure 25) caused serious high flow conditions, which are observable in the simulated river discharges, but not in the observed ones. During summer the model is able to capture almost completely the observed river discharges. This reflects the problem of definition of snow related

model parameters on watershed level under conditions as diverse and challenging as in the Ybbs catchment and creates another source of discrepancies between simulated and observed discharges and of poor model performances.

Due to the large variability in model performances the simulated discharges were additionally compared to the observed discharges in respect to changes in model performances for specific discharge conditions. This comparison should also indicate whether the model is able to reproduce low flow or high flow conditions. In Figure 26 this comparison is shown for the watershed outlet 'Greimpersdorf' for the period 1992-2000 (Greimpersdorf all) as well as for selected discharge conditions. The discharge conditions have been defined in relation to mean discharge at gauging station 'Greimpersdorf' ($Q_M=30 \text{ m}^3/\text{s}$). Low flow considered discharges less than 50% of Q_M , and for high flow conditions discharges greater than 150% of Q_M were considered.

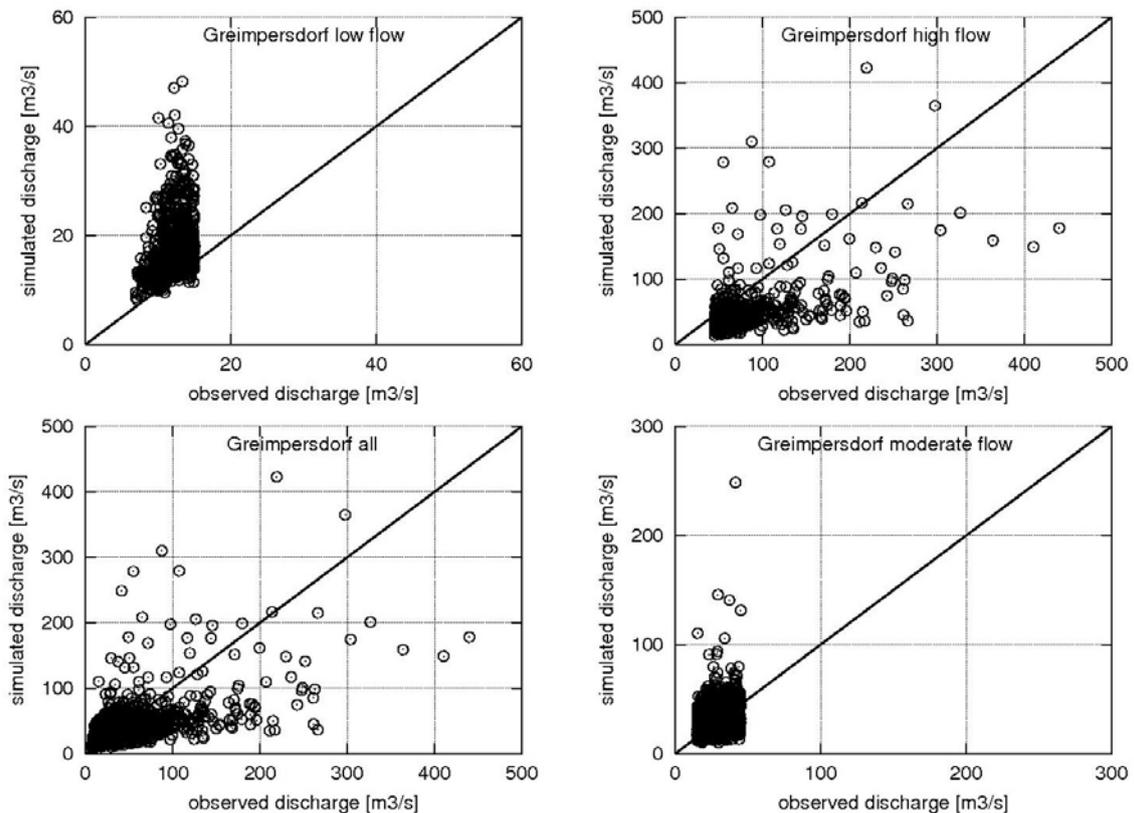


Figure 26: Comparison of simulated against observed discharges for the watershed outlet Greimpersdorf (version with 205 HRU's) with consideration of low flow conditions ($Q < 0.5 \cdot Q_M$), moderate flow conditions ($0.5 \cdot Q_M \leq Q < 1.5 \cdot Q_M$) and high flow conditions ($Q \geq 1.5 \cdot Q_M$) related to the mean discharge Q_M

In general, the comparison between observed and simulated discharges for the period 1992-2000 (Greimpersdorf all) in Figure 26 shows a widespread distribution of under- as well as overestimations of the simulated discharges against observed discharges without a clear trend. Mean deviation of simulated in relation to observed discharges was 119%, what indicates an overestimation of simulated discharges. For low flow conditions, the SWAT 2000 model significantly tends to overestimate simulated discharges (Greimpersdorf low flow in Figure 26). Mean deviation for these discharge conditions was 146%, but NSC indicated a good model performance

(NSC=0.86). This is because NSC takes into account the deviation of observed discharges in relation to the mean discharge (see equation 14). For these low discharge conditions, deviations between the observed and the mean discharges is partly larger than the deviations between the observed and simulated discharges. For moderate flow conditions, deviations between simulated and observed discharges tend to decrease (Greimpersdorf moderate flow in Figure 26), what is indicated by a mean deviation of 121% of simulated discharges in relation to observed ones. NSC of -0.78 was obtained for these flow conditions indicating that the deviations between observed and mean discharges decreased significantly (mean discharges conditions), what results in considerable higher impacts of discrepancies between observed and simulated discharges on NSC in comparison to low flow conditions. High flow conditions show again a widespread distribution of under- and overestimations, mean deviation was 72%, what indicates the tendency of the model to underestimate peak discharges. NSC was 0.46 for high discharge conditions, and again the discrepancies between simulated and observed discharges are masked by large deviations between observed discharges in relation to mean discharge. In fact, using the NSC deviation between simulated and observed discharges during mean flow conditions are of larger influence on the model performance than during low flow or high flow conditions. Evaluating the model performance based on the deviations between simulated and observed discharges related to the observed discharges, model performances of 0.53, 0.64 and 0.61 were obtained for low flow, moderate flow and high flow conditions, respectively. Based on this evaluation criterion, the best model performances were obtained for moderate discharge conditions.

Simulated river discharges are generated in the SWAT 2000 model by contributions of three main runoff components: surface runoff, lateral runoff and groundwater runoff. Contributions by runoff from tile drainages or water discharges from point sources (waste water treatments plants) to total river discharges are optional. Decreasing model performances could be related to particular increases or decreases in fractions of the surface runoff contributions as well as to enhanced fractions of the groundwater runoff contributions, particularly for the Opponitz and Krenstetten subcatchment. For Opponitz subcatchment and Krenstetten subcatchment model performances <0 could be attributed to considerable overestimations of the simulated cumulative river discharges in comparison to the observed discharges within the specific year. Also, general trends could be observed that NSC tends to increase slowly with increasing cumulative discharges for all subcatchments.

Figure 27 shows the comparison between the observed and simulated river discharges in daily time steps for the Opponitz subcatchment, the Krenstetten subcatchment and the main watershed outlet of the Ybbs catchment (Greimpersdorf) using both SWAT model versions (205 HRU's and 428 HRU's) for the calibration period 1995-1997.

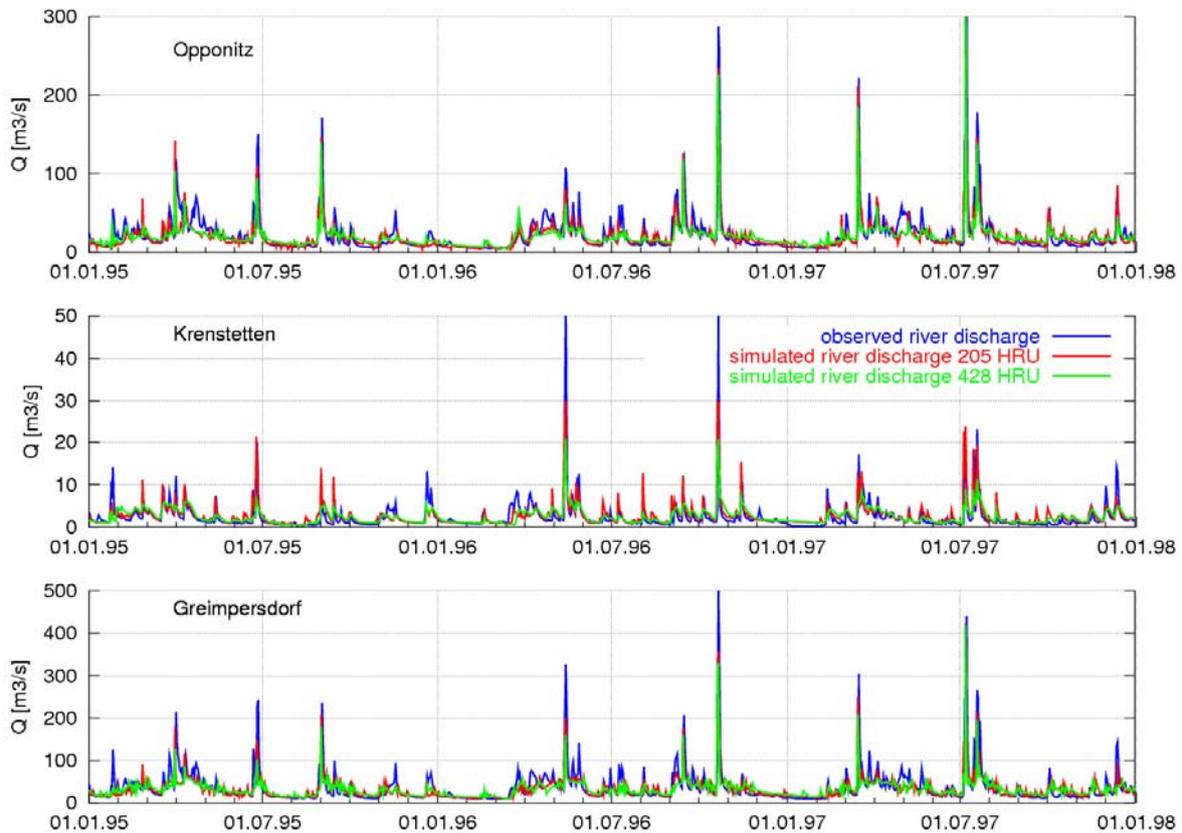


Figure 27: Comparison of observed and simulated river discharge for the Ybbs catchment (versions with 205 HRU's and 428 HRU's) using the SWAT 2000 model for the subcatchments Opponitz, Krenstetten and the main watershed outlet Greimpersdorf for the calibration period 1995-1997

Except for the Krenstetten subcatchment the SWAT model shows systematic displacement of the simulated peak river discharges particularly in spring season. This is most evident for Opponitz subcatchment, which comprises areas with the highest elevations. This effect is not observable in the downstream Krenstetten subcatchment. The problem might be related to general weaknesses of the model to represent snowfall and snowmelt processes for the entire catchment – which is most influential in the high alpine area of the catchment (Carl et al. in prep.). The main watershed outlet Greimpersdorf shows the signature of both alpine and downstream subcatchments just like an enlarged average of both subcatchments.

4.4.6 Model performance for the Wulka catchment

Following the descriptions of the model definitions for the Ybbs catchment, the model calibration for the Wulka catchment also started by using the delineated watershed units according to the specifications listed in Table 10. A FAO soil map (250m grid resolution) was used to define soil types. A corine land cover map (30m grid resolution) was used to define land use classes. Via intersection of both maps the definition of the HRU's was derived. For each subbasin, every soil class was superposed by every land use class creating a HRU resulting in 106 HRU's (see Figure 28).

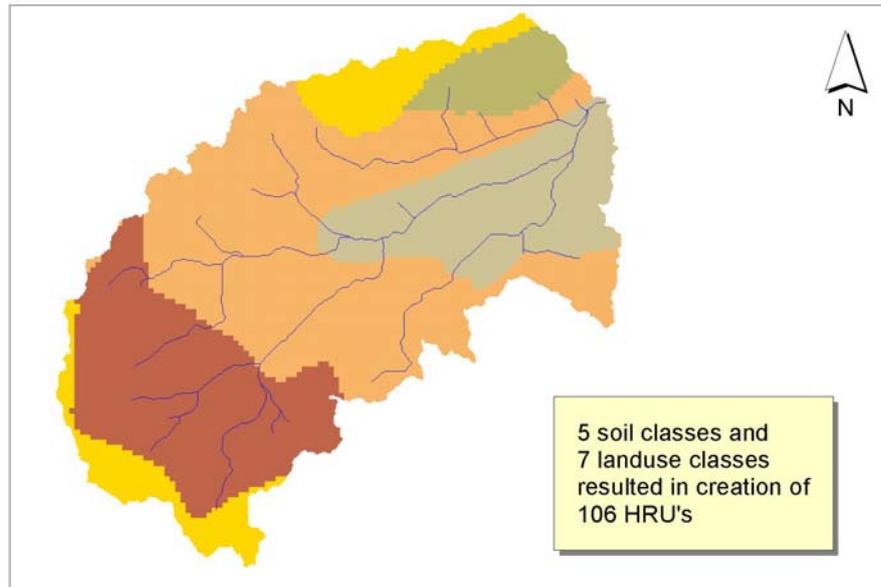


Figure 28: Number of soil classes limiting HRU definitions in the SWAT 2000 model for SWAT project with 106 HRU's for the Wulka catchment

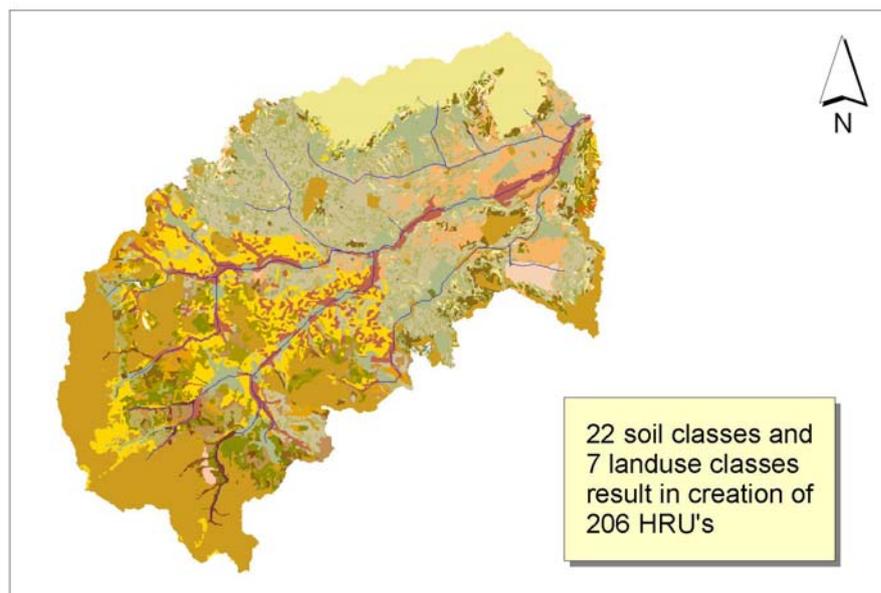


Figure 29: Number of soil classes limiting HRU definitions in the SWAT 2000 model for SWAT project with 206 HRU's for the Wulka catchment

Using a more detailed soil map, when becoming available (25m grid resolution), a second SWAT project was defined similar watershed delineations but with 206 HRU's (see Figure 29).

After the calibration of the different SWAT projects for the Wulka catchment the following model performances were obtained, which are listed in Table 14:

Table 14: Model performance (Nash-Sutcliffe-coefficient - NSC) of the SWAT 2000 model for the Wulka catchment in relation to different soil input data and the number of HRU's

NSC	106 HRU's			206 HRU's		
	Walbersdorf	Eisbach	Schützen	Walbersdorf	Eisbach	Schützen
1992 ^b	0.33	-0.29	-0.62	0.27	-0.54	-0.57
1993 ^b	0.34	-0.20	-0.17	0.03	-0.15	-0.35
1994 ^b	0.32	0.49	0.53	0.19	0.09	-0.14
1995 ^a	0.27	0.33	-0.11	-0.07	-0.17	-1.09
1996 ^a	0.72	0.44	0.48	0.63	0.08	0.09
1997 ^a	0.28	-0.03	0.13	0.22	-0.58	-0.91
1998	-0.52	0.04	-1.37	-0.65	-0.49	-2.86
1999	0.00	0.13	-0.34	-0.32	0.11	-1.55
92-99	0.48	0.28	0.33	0.36	-0.09	-0.14
VE [%]	103	101	108	101	87	111

^a...calibration period; ^b...validation period

In general, the obtained model performances of the SWAT 2000 model for the Wulka catchment were very low and were affected by strong limitations in availability of data about temperature, climate conditions as well as about discharges from wastewater treatment plants and tile drainages.

The best model performances were obtained for most upstream subcatchment Walbersdorf using both SWAT projects. Further downstream the model performances decrease considerably. Particularly for the tributary Nodbach due to extremely low discharges and for the tributary Eisbach due to considerably high fractions of waste water discharges in relation to total river discharge, discrepancies between simulated river discharges and observed discharges results in particularly low model performances. The model performances for the Wulka catchment are moderate and poorer than the model performances obtained for the Ybbs catchment.

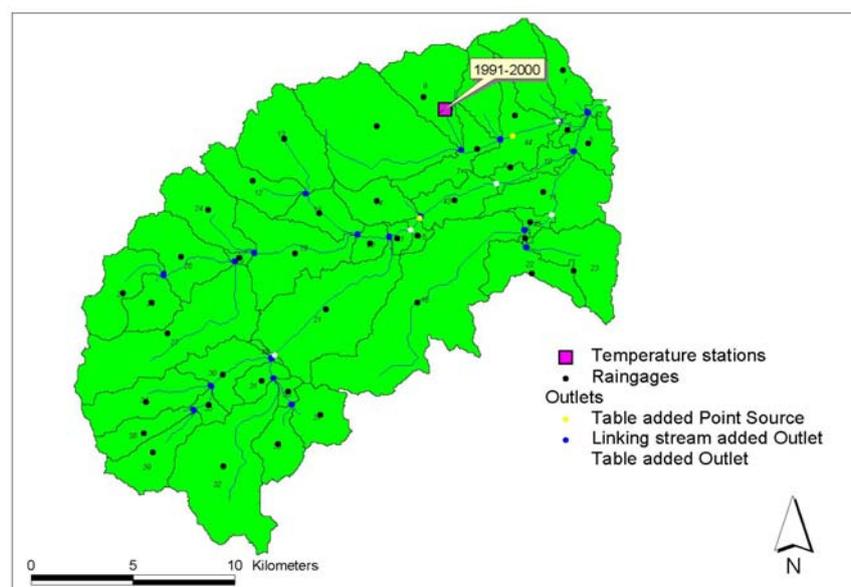


Figure 30: Watershed delineation for the Wulka catchment within the SWAT 2000 model with location of precipitation and temperature stations with the adequate interval of data availability

The reason for the poor model performances may be seen in the insufficient data for the definition of climatic data. Only data of one climatic station were available to

define input data for the whole Wulka catchment (see Figure 30). Furthermore, agricultural soils in the Wulka catchment were extensively drained within the past decades, but sufficient documentations about this is missing. Thus, consideration of tile drainages in certain areas was extremely uncertain. Both the location of tile drainages within the catchment as well as the definition of the model parameters for tile drainages was therefore based on assumptions about agricultural practise. So tile drainages were considered in soils only, which are defined for agricultural utilisation and which have a low hydraulic conductivity. In the tributary Eisbach the contribution of inlets from waste water treatment plants amount to almost 30% of the total river discharge. Observations on treated waste water discharge on daily time step were, however, not available. Therefore, monthly average loadings were implemented into the SWAT 2000 model leading to high uncertainties in simulated river discharges.

Following the descriptions for the Ybbs catchment and with additional definitions for 3 model parameters defining tile drainages on HRU level, 1428 model parameter were subject of calibration using the SWAT model definitions for 106 HRU's for the Wulka catchment. The number of calibration parameters increased to 2428 parameters using the SWAT model definitions for 206 HRU's.

The river discharges of the Wulka catchment are characterised by long periods of low flow conditions with partly strong interruptions by increased river discharges during high flow periods (see Figure 31). In this respect, model performances during low flow and high flow conditions significantly influence the reliability of the modelling results.

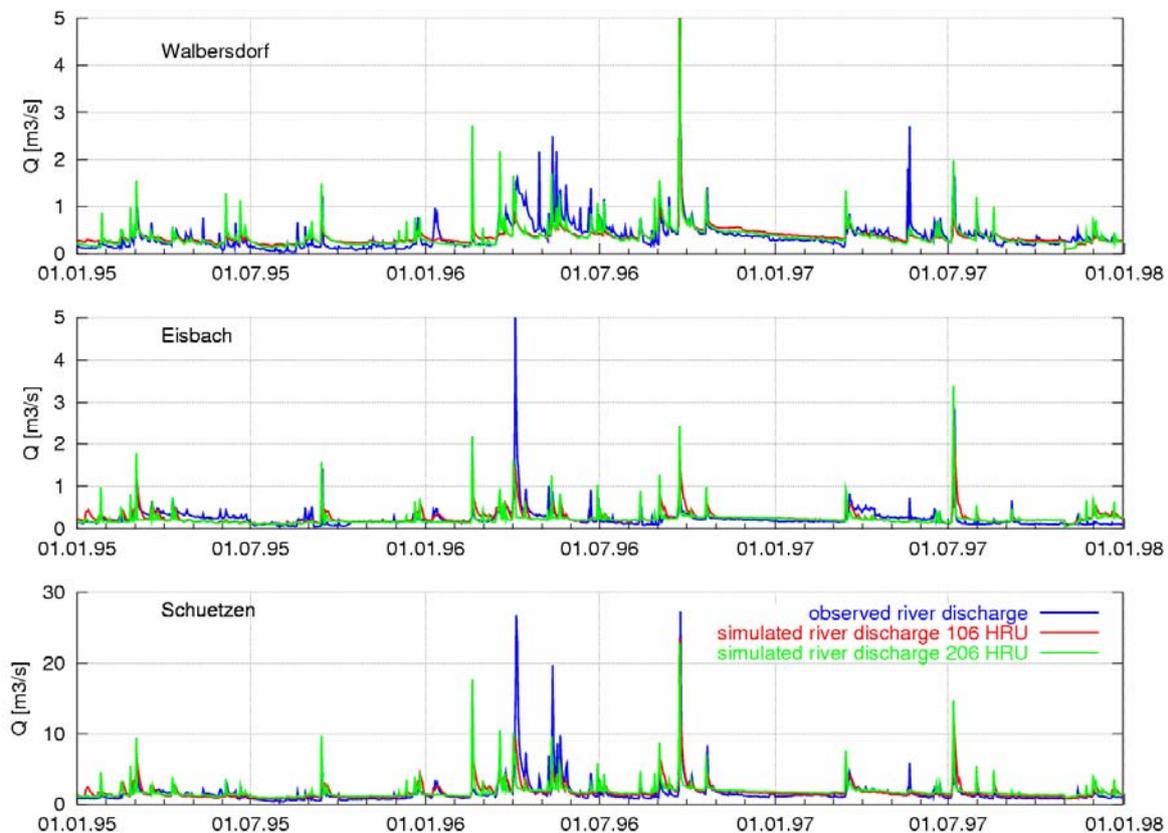


Figure 31: Comparison of observed and simulated river discharge for the Wulka catchment (versions with 106 HRU's and 206 HRU's) using the SWAT 2000 model for the subcatchments Walbersdorf, Eisbach and the main watershed outlet Schuetzen for the calibration period 1995-1997

Figure 31 shows the comparison between the observed and simulated river discharges in daily time step for the gauging stations Walbersdorf and the watershed outlet of the Wulka catchment Schützen using both SWAT model definitions for the calibration period 1995-1997. Obviously similar parameter definitions lead to a basically similar hydrologic response of the different SWAT model definitions. For Walbersdorf subcatchment the SWAT 2000 model tends to fail to correctly simulate peaks in discharges. Particularly for Eisbach subcatchment partly significant discrepancies in peaks between the simulated and the observed discharges due to the limited information on point source contribution were obtained. Additionally enhanced displacements of simulated river discharges are observable particularly in spring seasons for this subcatchment. The Eisbach subcatchment delineates the Wulka catchment to the north including the Leitha Mountains, where enhanced precipitation will fall as snow during winter. There, displacements in simulated river discharges can be attributed to deficiencies in simulated snowmelt parameter definitions, because these snow-affected catchment areas constitute only 15% of the total catchment area, but the snow related parameters will be defined for the whole catchment.

The model performances have been evaluated also in terms of changes in respect to specific discharge conditions. Similar to the Ybbs catchment, low flow, moderate flow and high flow conditions were defined based on mean discharge Q_M ($Q_M=1.3 \text{ m}^3/\text{s}$) at gauging station 'Schuetzen'.

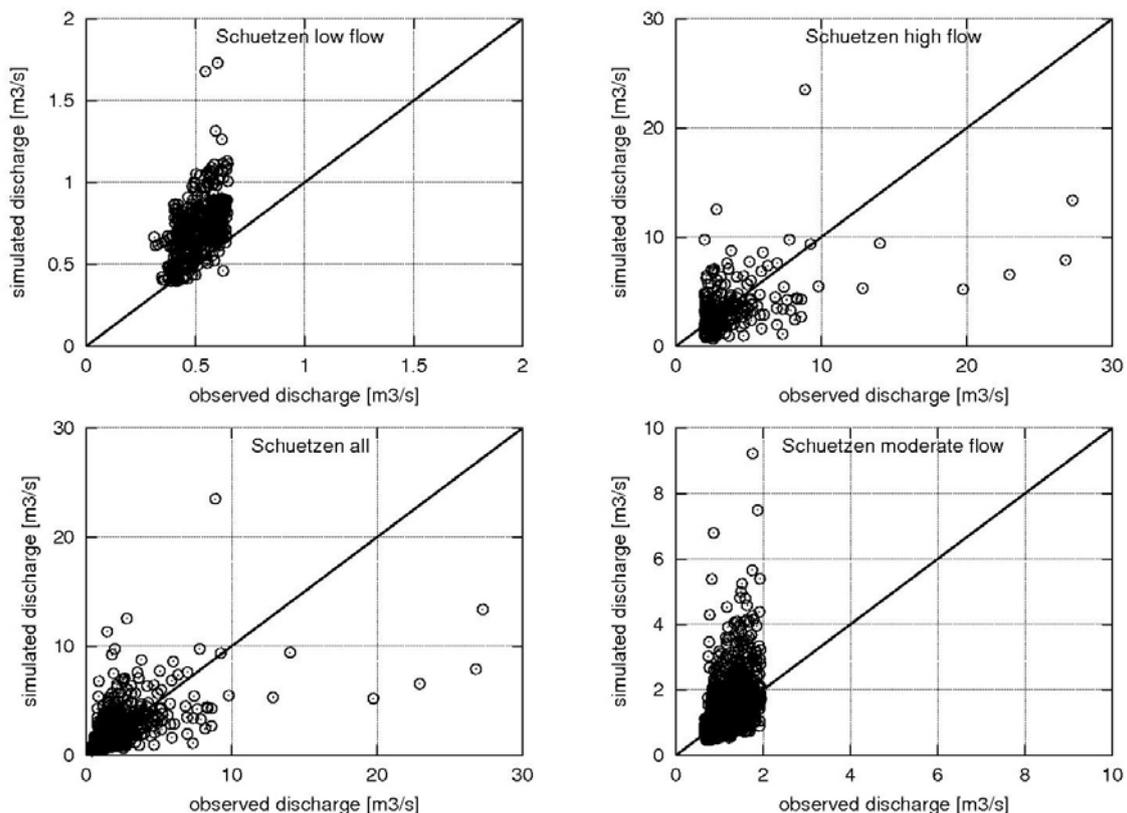


Figure 32: Comparison of simulated against observed discharges for the watershed outlet Schuetzen (version with 106 HRU's) with consideration of low flow conditions ($Q < 0.5 \cdot Q_M$), moderate flow conditions ($0.5 \cdot Q_M \leq Q < 1.5 \cdot Q_M$) and high flow conditions ($Q \geq 1.5 \cdot Q_M$) related to the mean discharge Q_M

The comparison between all observed and simulated river discharges for the period 1992-1999 (Schuetzen all) in Figure 32 revealed a general overestimation of simulated river discharges, what is also confirmed by a mean deviation between simulated and observed discharges of 119%. Regarding low flow conditions (Schuetzen low flow in Figure 32), the SWAT 2000 model tends to overestimate simulated river discharges significantly. The mean deviation for low flow conditions was 146%, but a good model performance (NSC=0.84) was obtained for these discharge conditions. Similar to the Ybbs catchment, the deviations between the simulated and observed discharges are masked by large deviation between observed and mean discharges using the NSC to evaluate the model performance. For moderate flow conditions (Schuetzen moderate flow), the simulated discharges are still overestimated in relation to the observed ones. The mean deviation between simulated and observed discharges decreased to 117% in comparison to low flow conditions, but the model performance using the NSC was very poor (NSC=-3.92). For high flow conditions (Schuetzen high flow), the SWAT 2000 model showed widespread over- and underestimations of the simulated river discharges compared to the observed ones. The mean deviation of 103% indicated in average a good correspondence between the simulated and observed discharges with moderate model performances (NSC=0.46).

Evaluating the model performances for the selected discharge conditions in Figure 32 based on the deviations between simulated and observed discharges in relation to the observed discharges, model performances of 0.58, 0.68 and 0.56 have been obtained for low flow, moderate flow and high flow conditions, respectively. Based on this criterion, the best model performances for the Wulka catchment were calculated for moderate flow conditions. Similarities to model performances for the Ybbs catchment for specific discharge conditions are identifiable: during low flow conditions the largest mean deviations between simulated and observed discharge were obtained, but the best model performances were calculated using the NSC. That reveals that particularly low discharge conditions, predominantly determined by the groundwater runoff of the SWAT 2000 model, is not well defined in the model for both catchments, but is not responsible for the poor model performances. Particularly the definitions for runoff from tile drainages in the Wulka catchment result in immediate responses of the simulated river discharges to precipitation events. In terms of discharge conditions, these responses will be obtained predominantly during moderate flow and partly during high flow conditions. Based on previous analyses, the obtained poor model performances for the Wulka catchment using the NSC can be attributed mainly to inadequate reflection of runoff from tile drained areas due to the uncertainty in the data available for model definitions.

Increasing model performances using the NSC (Table 14) could be related to increasing fractions of the groundwater runoff and the lateral runoff on total simulated discharges, in which increases in the fraction of groundwater runoff were considerably larger for improving the model performance compared to increases in lateral runoff. Increasing fractions of surface runoff did not affect model performances significantly.

4.5 Calculated water balances for the Ybbs and the Wulka catchment

4.5.1 Water balance of the Ybbs catchment

Average values of precipitation, evapotranspiration and groundwater recharge can be calculated also from observed data without using a water balance model. The benefit of the SWAT 2000 model application is in the provision of information about the specific contributions of individual runoff components to the total river discharge. The calculated water balance components for the Ybbs catchment are shown in Figure 33 as long-term average values for the calculation period 1992-2000.

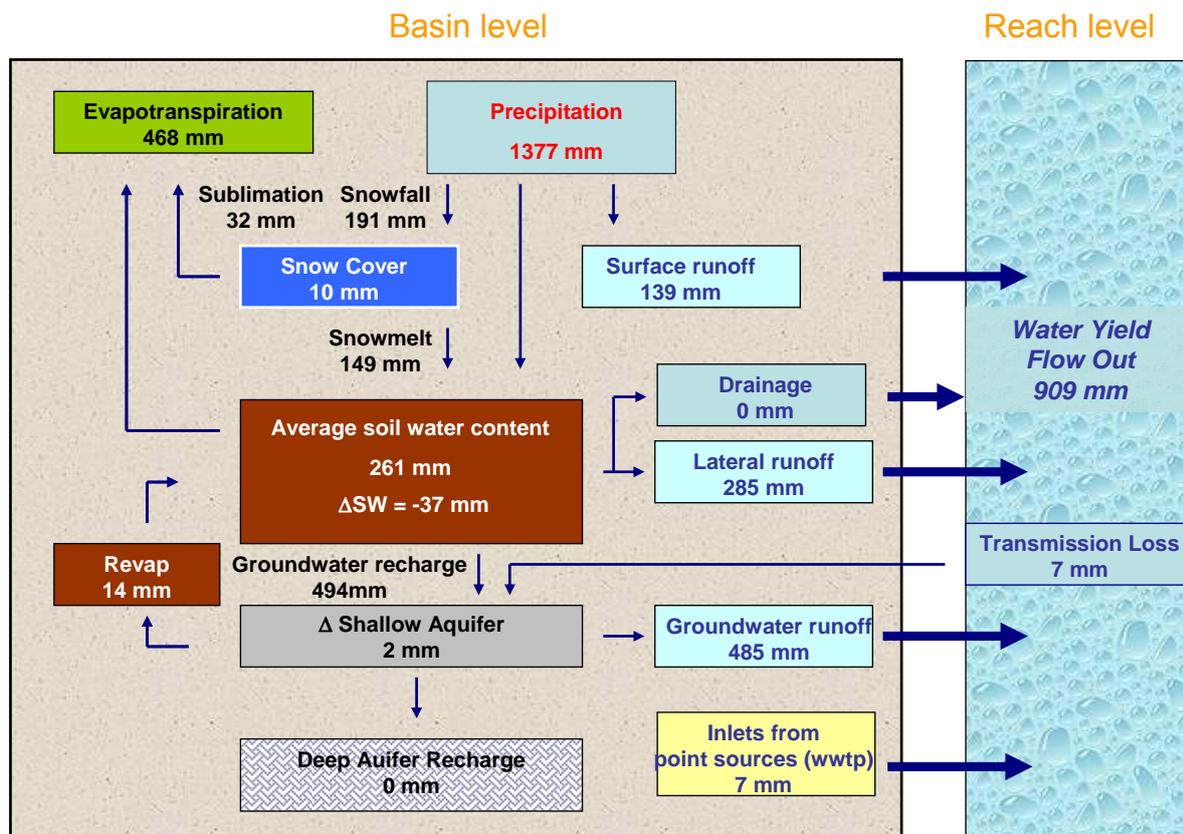


Figure 33: Detailed simulated water cycle for the Ybbs catchment with average annual values for the water balance components calculated for the period 1992-2000

A mean annual precipitation of 1377 mm/a was obtained for the Ybbs catchment for the calculation period. For groundwater recharge in average 36% of the precipitation is used. In average, 34% of the precipitation is subject of evapotranspiration and about 66% of the precipitation contributes to river discharge. Annual average groundwater runoff is not equal to annual average groundwater recharge because water movement within the capillary fringe is simulated from shallow aquifer into the overlying unsaturated zone (groundwater revap).

The calculated water balance consists of changes in snow cover, in soil water content and in shallow aquifer storages (see Figure 33) due to the short period, which was used for water balance calculations. That indicates that the model is not able to close the long-term water balance (no storages) for this short calculation period. In result the calculation period should be extended, but due to limitations in

data availability to determine the input data for the model this was not possible for water balance calculations for the Ybbs catchment.

Annual changes in the main water balance components for the calculation period are shown in Table 15.

Table 15: Main annual water balance components (1992-2000) of the Ybbs catchment calculated using the SWAT 2000 model (version 205 HRU's)

Year	Precipitation [mm/a]	ET [mm/a]	Groundwater Recharge [mm/a]	Surface runoff [mm/a]	Lateral runoff [mm/a]	Groundwater runoff [mm/a]	River* discharge [mm/a]
1992	1302	452	433	143	284	423	850
1993	1316	489	481	109	252	475	836
1994	1274	454	471	118	262	462	842
1995	1400	443	511	109	287	505	901
1996	1434	472	505	143	329	499	971
1997	1509	479	535	153	334	528	1015
1998	1492	477	513	161	312	505	978
1999	1365	455	536	139	259	530	928
2000	1300	497	455	179	248	446	873
Average	1377	468	494	139	285	485	909

*...Simulated river discharge (water yield) does not contain point source contributions; they were added to simulated river discharge as constant daily loadings (see Figure 33)

Runoff will be generated within the SWAT 2000 model basically using the three main runoff components surface runoff, lateral runoff and groundwater runoff. These runoff components are fed independently by individual compartments: surface runoff is generated, when precipitation exceeds soil infiltration and is therefore generated above the soil column. Lateral runoff is fed by the soil column and is generated when soil water content is sufficient for preferential flow and horizontal flow at soil layers with changing conductivity to occur. Groundwater runoff is fed by aquifer compartment and is generated by groundwater recharge from soil to aquifer.

Total runoff of the Ybbs catchment consists based on model results in average of 15% surface runoff, 31% lateral runoff and 54% groundwater runoff. Deviating surface and subsurface runoff, the river discharge of the Ybbs catchment is fed by 85% subsurface runoff and 15% surface runoff. Simulated runoff components change within the calculation period (Table 15) similar to the simulated river discharge, but with only little changes in their fractions. The fraction of surface runoff, which is contributed to simulated river discharge, varies within the calculation period between 12-20% of the simulated river discharge. Similarly, the fractions of lateral runoff and groundwater runoff vary between 28-34% and 50-57%, respectively. Changes in the fractions of the runoff components can't be attributed in general to changes in simulated river discharges. Reasons for increasing simulated river discharges may be diverse, and so the response of the simulated runoff components on various precipitation or snow melt events is likely to be different and can't be evaluated from annual average contributions of the simulated runoff components to total river discharge.

For evaluating changes in runoff components contributions with increasing river discharges, the cumulative frequency of the total daily contributions by the simulated runoff components to the simulated river discharge was used (see Figure 34). Changes in the contribution of the groundwater runoff to the simulated river discharges are very small, the groundwater runoff contributes permanently between

1-2mm/day to river discharge. For 60% of the simulated discharges, river discharges are mainly fed by groundwater runoff. Increases in river discharges in relation to the groundwater runoff are mainly the result of increasing contributions from lateral runoff up to >90% of the river discharges. Only for <10% of the river discharges the contributions from groundwater runoff were exceeded by the contributions from lateral runoff and surface runoff.

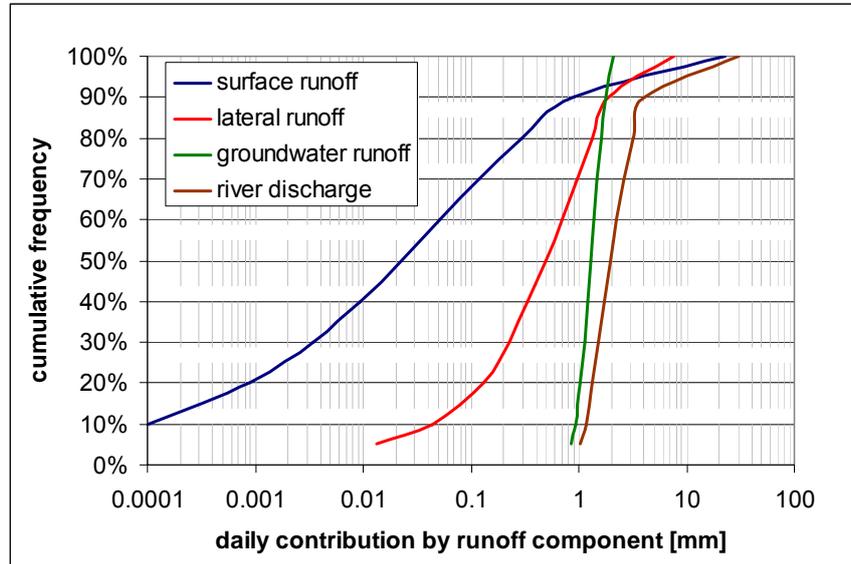


Figure 34: Cumulative frequency of the daily contributions of simulated runoff components for the Ybbs catchment using the SWAT 2000 model for the period 1992-2000

Increases in the contributions of the individual runoff components can be related to the number of days, which the runoff components significantly contribute to the river discharge. For 60% of the simulated river discharges, the groundwater runoff was the dominating runoff component. For the remaining 40% of the simulated discharges, the groundwater runoff was basically contributing to the river discharges, but the contribution from the other runoff components exceeded the groundwater runoff contributions significantly. From the remaining 40% of the simulated discharges, >30% were dominated by contributions from lateral flow (60-92% of cumulative frequency) and 8% were dominated by contributions from surface runoff (92-100% of cumulative frequency). In this way, the calculated fractions of the contributing runoff components can be attributed to certain discharge conditions and adequate to a total number of days within the calculation period, in which these discharge conditions have been observed.

Figure 34 shows the cumulative frequency of the runoff components without any interrelation or a context in time of the components. Deviations between the annual average fractions of the runoff components and the cumulative frequency are due to the variability of the runoff component in terms of their contributions to total river discharges at a specific time. For about 8% of all river discharges, the contributions from surface runoff dominated the contributions of the other two runoff components significantly. Due to the large daily contributions from surface runoff during these discharge conditions, the fraction of the cumulative annual contribution from surface runoff in relation to total simulated river discharges is considerably higher with 15% of the total discharge.

The main calculated water balance components for the subcatchments are shown in Table 16.

Table 16: Main average annual water balance components (1992-2000) of the subcatchments Opponitz, Krenstetten and the watershed outlet Greimpersdorf of the Ybbs catchment calculated using the SWAT 2000 model (version 205 HRU's)

	Precipitation [mm/a]	ET [mm/a]	Groundwater Recharge [mm/a]	Surface runoff [mm/a]	Lateral runoff [mm/a]	Groundwater runoff [mm/a]	River discharge [mm/a]
Opponitz	1685	491	639	180	392	631	1203
Krenstetten	980	430	251	106	196	245	547
Greimp.	1377	468	494	139	285	485	909

Elevated river discharges in the Opponitz subcatchment are caused by higher annual average surface runoff, lateral runoff and groundwater runoff rates. The annual average groundwater recharge rate decreases significantly from Opponitz to Greimpersdorf. The Krenstetten subcatchment shows the lowest annual average precipitation amount in coincidence with the lowest annual average groundwater recharge rates (less than half of the groundwater recharge rate of the Opponitz subcatchment). Contributions of the lateral runoff and groundwater runoff to total river discharges in Krenstetten subcatchment are significantly less than those of the Opponitz subcatchment and the whole Ybbs catchment. Small changes in the fractions, which are contributed by surface runoff, lateral runoff and groundwater runoff to simulated river discharge, are observable for Krenstetten subcatchment in relation to the Ybbs catchment only. There, in average the contributions of the surface runoff (19%) and of the lateral runoff (36%) are larger, contributions of the groundwater runoff (45%) are lower in comparison to the Ybbs catchment at station Greimpersdorf.

4.5.2 Evaluation of the calculated water balance for the Ybbs catchment

Model performances of the SWAT 2000 have already been discussed in chapter 4.4.5. Since results from other model applications are available for the Ybbs catchment, they are used to evaluate the results of the water balance calculations using the SWAT 2000 model too. In frame of the DaNUbs project two additional modelling approaches were used for water balance calculations to identify the main runoff components contributing to river discharge: the DIFGA 2000 model and the MONERIS model. All modelling approaches differ in terms of model complexity and in simulated runoff components, so the calculations were used to evaluate model applicability on the regarded scale as well as to point out the 'weaknesses' and 'advantages' of each modelling approach. Details are reported in (Blaschke et al. 2003).

The DIFGA 2000 model is a hydrograph separation technique, which uses observed time series of river discharges to separate high-frequent (surface runoff) and low-frequent (groundwater runoff) runoff components based on a lithofazies concept. The calculated runoff components are considered as linear storages contributing to river discharge with different (increasing) time delay: direct runoff, fast groundwater runoff and slow groundwater runoff.

The MONERIS model is an empirical emission model. Surface runoff, runoff from urban areas and tile drainages is calculated based on empirical equations, which have been derived from investigations in large German river basins. Point source

contributions are defined based on observations. The amount of base flow is then calculated from the difference between the observed river discharge and the empirically estimated runoff components. The MONERIS model operates with 5-year average values, whereas DIFGA 2000 and SWAT 2000 operate on a daily time step.

In Table 17 the comparison between the results of the water balance calculations using the SWAT 2000 model, DIFGA 2000 and the MONERIS model is presented.

Table 17: Comparison of the calculated water balance components using the SWAT 2000 model for the watershed outlet Greimpersdorf with the results from DIFGA 2000 and the MONERIS model

	SWAT 2000 1992-2000		DIFGA 2000 ¹ 1971-1997		MONERIS ² 1998-2002	
	[mm/a]	[%]	[mm/a]	[%]	[mm/a]	[%]
Precipitation	1377		1377		1395	
Evapotranspiration	468		527		550	
River discharge	909		850		851	
Surface runoff	139	15	243	29	51	6
Lateral runoff	285	31	607	71	-	-
Groundwater runoff	485	53			781	93
Tile Drainage	-		-	-	1	0
Point sources	7	1	-	-	7	1

¹... from (Heinecke 2004), ²... from (Zessner et al. 2004)

Deviations in annual average precipitation and observed river discharges are the result of deviations in the calculation period, which is shown in Table 17. Model complexity largely determines the amount of data, which are needed to run the model. In this respect, the calculation period will be specified by the data availability for each modelling tool. Consequently, the calculation period for the conceptual SWAT 2000 model is significantly shorter compared to the DIFGA 2000 model. The calculation period of the MONERIS model is limited to 5 years due to model definitions. As a consequence of wet or dry years, the annual average precipitation will change noticeably with the considered calculation period.

Evapotranspiration was estimated using the SWAT 2000 model by the Hargreaves-method (Hargreaves et al. 1985), using the MONERIS model the evapotranspiration is defined as constant value and resulted in the highest evapotranspiration. Using the DIFGA 2000 model, the evapotranspiration is estimated from the long-term water balance (precipitation – river discharge). Observations are used to define the total river discharge for the DIFGA 2000 model and the MONERIS model. The calculated river discharge using the SWAT 2000 model is 7% higher in comparison to the DIFGA model and the MONERIS model.

Table 17 shows, that the three runoff components - surface runoff, lateral runoff and groundwater runoff - are calculated by the SWAT 2000 model only. Surface runoff was significantly underestimated by the MONERIS model, what was found to be a weakness of the model also for other applications in the Danube basin (Zessner et al. 2004). Since the model equations have been derived for German river basins, particularly in regions with annual precipitation less than 500 mm/a, due to the empirical nature of the equations the calculated specific surface runoff will become negative (see Behrendt et al. 1999). In the meantime, efforts have been undertaken to use alternative approaches for the calculation of the surface runoff within the MONERIS model. The DIFGA 2000 model calculated the highest fraction of surface runoff (termed as direct runoff in the DIFGA model). The fraction of surface runoff

calculated by the DIFGA model is twice of that calculated by the SWAT model. According to the model definitions, direct runoff in the DIFGA model consists not only of surface runoff, also quick soil response and preferential flow is considered within this runoff component. In contrast, these processes are considered in the SWAT model in contributions by the lateral runoff, what explains the higher fraction of surface runoff calculated by the DIFGA model.

Groundwater runoff by the DIFGA model consists of contributions from fast groundwater and slow groundwater storages. So, two linear storages are used to determine groundwater runoff. In the SWAT model for the definition of groundwater runoff one linear storage is used. Additionally, from the soil column contributions by lateral runoff are considered by the SWAT model. In order to compare the subsurface runoff between the DIFGA model and the SWAT model, the cumulative contribution of the slow and fast groundwater runoff of the DIFGA model was compared to cumulative contribution of the lateral runoff and the groundwater runoff of the SWAT model. So, subsurface runoff calculated by the SWAT model (lateral runoff + groundwater runoff) was significantly higher compared to subsurface runoff calculated by the DIFGA model (fast and slow groundwater runoff), but was well in line with the calculated groundwater runoff by the MONERIS model.

Using different models for water balance calculations may results in considerable differences in calculated water balance components. The evaluation of the calculated water balance components and particularly of the runoff components is difficult due to different model definitions for runoff components. The comparison of the model results provided certain evidence about calculated fractions of runoff components in the Ybbs catchment. Using completely different approaches of conceptual, empirical and structural nature for water balance calculations yielded in comparable results in regard to the fractions of runoff components, if deviations in model definitions for the runoff components are considered. Considerable differences in terms of calculated surface runoff contributions were obtained (-64%...+74% deviation in relation to calculated surface runoff by the SWAT model), deviations in regard to the calculated subsurface runoff contributions were significantly lower (-22%...+1% deviation in relation to calculated subsurface runoff by the SWAT model).

Comparison with hydrological reference book

A comparison of the calculated water balance with a hydrological reference book was done using the digital hydrological atlas of Austria (Bundesministerium für Land- und Forstwirtschaft 2005) (HAÖ), which is available in digital form since 2005 and provides climatic and hydrological information at the catchment level.

Table 18 shows the comparison between the calculated long-term annual average precipitation, potential evapotranspiration (PET) and the actual evapotranspiration (ET) and the values given in the hydrologic atlas of Austria (HAÖ).

Table 18: Comparison of long-term average annual water balance components from the HAÖ (Hydrologic Atlas of Austria) with water balance component calculated using the SWAT 2000 model for the Ybbs catchment

	Long-term av. precipitation SWAT [mm/a]	Long-term av. precipitation HAÖ [mm/a]	Long-term av. PET / ET SWAT [mm/a]	Long-term av. PET / ET HAÖ [mm/a]	Long-term av. discharge SWAT [mm/a]	Long-term av. discharge HAÖ [mm/a]
Opponitz	1685	1764	608 / 491	601 / 588	1203	1177
Krenstetten	980	966	633 / 430	640 / 595	547	371
Greimp.	1377	1439	606 / 468	620 / 596	909	843

The deviations between the calculated water balance components using the SWAT 2000 model and the water balance components from HAÖ are likely to be caused by utilisation of time series covering a different time span (SWAT 2000 model: 1992-2000; HAÖ: 1961-1990). The SWAT 2000 model underestimates evapotranspiration for all subcatchments significantly in comparison to the HAÖ, this was already indicated by the comparison with the other modelling approaches. Deviations in evapotranspiration range between 97mm/a for Opponitz subcatchment and 165mm/a for Krenstetten subcatchment. The estimation of evapotranspiration depends on the method, which is used for the calculation of potential evapotranspiration. Deviations up to 300 mm/a have been obtained during SWAT 2000 model calibration for the Ybbs catchment using different methods for the estimation of the potential evapotranspiration in the SWAT 2000 model.

Calculated values for long-term average precipitation and long-term average potential evapotranspiration for the Ybbs catchment and its subcatchments are within a range of -5%...+11% and -7%...+1% deviation respectively, in relation to values from HAÖ.

Significant overestimations of simulated river discharges in long-term perspective were obtained using the SWAT 2000 model for all subcatchments, particularly for Krenstetten subcatchment. This was already indicated in Table 13 by VE (volumetric error in river discharge). Deviations between the river discharges simulated by SWAT 2000 model and the river discharge from HAÖ range between +2% for Opponitz subcatchment and +47% for Krenstetten subcatchment. Due to lower evapotranspiration rates, calculated average river discharges by the SWAT 2000 model are higher in comparison to the HAÖ.

4.5.3 Water balance of the Wulka catchment

The water balance for the Wulka catchment was calculated for the time period 1992-1999 and is shown with all components in Figure 35. The SWAT 2000 model needs a certain time (approximately 1 year of calculation) in advance to reach a steady state (replenishment of storages). Due to data availability the calculation was started in June 1991. Thus, the calculated water balance components may be affected by a still unsteady state of the model in 1992 till 1993, what appears in low simulated river discharges for this year. In 2000, data availability was limited, so that calculation period was chosen to close with 1999.

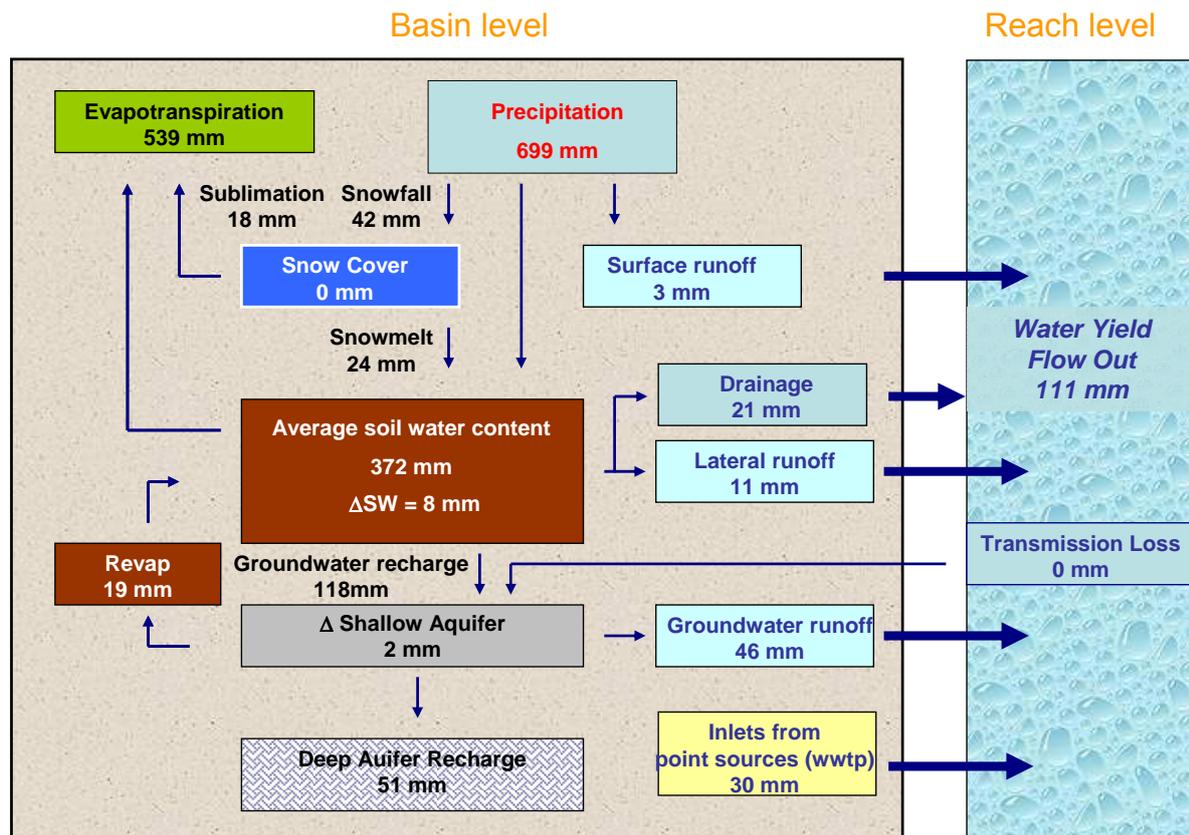


Figure 35: Detailed simulated water cycle for the Wulka catchment with average annual values for the water balance components calculated for the period 1992-1999

For the Wulka catchment, a mean annual precipitation of 699mm/a was calculated, what is half of the annual average precipitation in the Ybbs catchment. For evapotranspiration 77% of the precipitation is used, 12% of the precipitation contributes to river discharge (point source contributions to river discharge are not considered in this fraction). Point source contributions from waste water treatment plants contribute considerably high fractions to total river discharges at the main watershed outlet Schuetzen, these fractions amount in average 26%. These discharges stem from water supplies which are provided partly from water resources outside the Wulka catchment and therefore have to be regarded in terms of a closed water balance as water imports. To compensate these water transfers to a certain extent, donations to a deep aquifer, which do not contribute to river discharges, have been introduced to the water balance calculations for the Wulka catchment. However, similar to the calculations for the Ybbs catchment, the SWAT 2000 model is not able to close the long-term water balance for the Wulka catchment too, since the calculated water balance still consists of storages in soil and aquifer.

For groundwater recharge, in average 17% of the precipitation is used and exceeds the fraction of groundwater runoff considerably due to donations to the deep aquifer. Total simulated river discharge (without point source contributions) consists in average of 4% surface runoff, 13% lateral runoff, 56% groundwater runoff and 27% runoff from tile drainages. Due to insufficient information about tile drainages in the Wulka catchment, runoff from tile drainages was considered in the SWAT 2000 model for areas in agricultural utilisation with low hydraulic conductivity of the soil only. Tile drainage depth was defined as 1m depth below soil surface, and time to

drain the soil to field capacity was defined with 48 hours. Due to missing documentations these assumptions are very uncertain.

Point source contributions from waste water treatment plants have been introduced into the SWAT 2000 model as constant monthly-average daily loadings, which will be added to the simulated daily river discharge. In relation to the total observed river discharge, the largest fractions will be contributed by the groundwater runoff (42%) followed by discharges from waste water treatment plants (point sources, 26%) and tile drainages (20%). Lateral runoff and surface runoff contribute each <10% of the total river discharge.

Annual changes in the main calculated water balance components within the calculation period are shown in Table 19 for the Wulka catchment. River discharge in Table 19 does not contain discharges from point sources, only contributions from runoff components generated within the catchment are considered.

Table 19: Annual water balance components (1992-1999) of the Wulka catchment calculated using the SWAT 2000 model (version 106 HRU's)

Year	Precipitation [mm/a]	ET [mm/a]	Gw Rchg [mm/a]	Surface runoff [mm/a]	Lateral runoff [mm/a]	GW runoff [mm/a]	Tile drainage [mm/a]	River* discharge [mm/a]
1992	650	484	78	3	11	19	25	58
1993	661	508	94	0	9	32	17	58
1994	654	539	118	2	10	44	19	75
1995	698	516	118	1	11	50	21	83
1996	854	570	177	9	17	75	47	148
1997	684	572	143	3	9	67	14	93
1998	675	536	104	3	10	42	16	71
1999	713	586	110	3	10	43	14	70
Average	699	539	118	3	11	46	21	81

*... simulated river discharge (water yield) does not contain point source contributions; they were added to simulated river discharge as monthly-average daily loadings

Changes in simulated runoff components have been observed according to changes in simulated river discharge. Changes in the fractions of the surface runoff within the calculation period were small. The fractions varied between 3...6%, partly the contributions of the surface runoff were <1%. Highest contributions of the surface runoff were obtained for highest river discharge. Contributions of the lateral runoff varied between 10...15%, with increasing river discharges the fraction of lateral runoff contributions tended to decrease. Groundwater runoff contributed except the first year the highest fractions to the simulated river discharge, contributions changes considerably between 32...70%. No significant increases in the fractions of contributions of the groundwater runoff could be obtained with increasing river discharges. The fractions of contributions from runoff from tile drainages were within the range of 16...31% (with exception of the first year). Highest fractions of runoff from tile drainages have been observed with highest river discharges.

According to the analyses in the Ybbs catchment, the simulated daily values of the runoff components were used to derive cumulative frequencies to identify, how the fractions of the simulated runoff components change with increasing river discharges (see Figure 36). Groundwater runoff is the major runoff component also for the Wulka catchment. It constitutes the basic runoff fraction of the river discharge. About 60% of the simulated river discharges are determined predominantly by the groundwater runoff, and within these discharge conditions increases in the river

discharge are associated with similar increases in groundwater runoff. This explains that no significant increases in the fraction of the groundwater runoff could be observed with increasing discharges. Exceeding 60% of the observed cumulative river discharges, a significant increase in river discharges can be observed due to increasing fractions of the lateral runoff and of the runoff from tile drainages. In general, runoff from tile drainages was simulated only for 20% of the river discharges and significantly exceeded the fractions, which have been contributed to river discharge by the lateral runoff. Significant fractions of surface runoff contributions were obtained for <5% of the simulated (increased) river discharges.

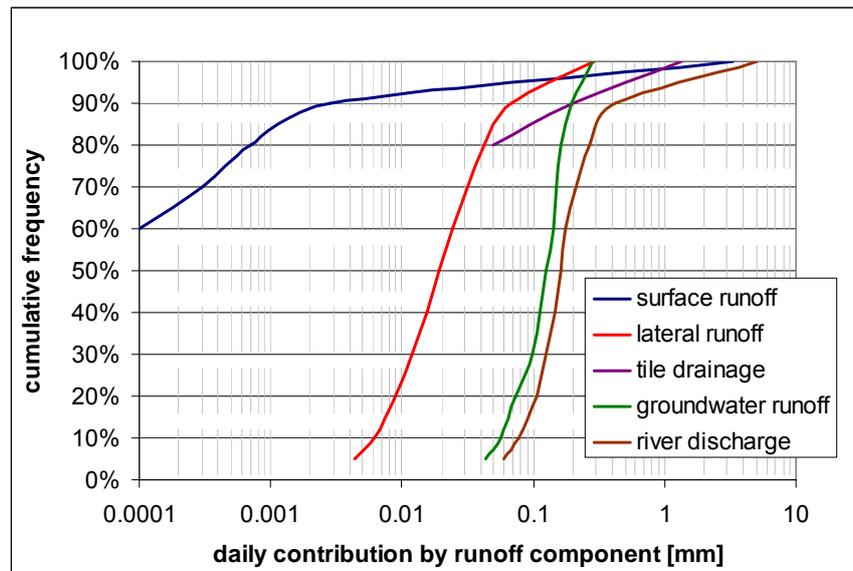


Figure 36: Cumulative frequency of the daily contributions of simulated runoff components for the Wulka catchment using the SWAT 2000 model for the period 1992-1999

Based in these analyses, clear influences of the simulated runoff components on the river discharge can be identified. Simulated river discharges ≤ 0.2 mm/day are clearly determined and dominated by the contributions of the groundwater runoff, this is equivalent to 60% of the cumulative river discharge. With increasing discharge conditions, lateral runoff and runoff from tile drains contribute remarkable fractions to the river discharge and determine 30% of the simulated discharges (between 60...90% of the cumulative river discharges). For 10% of the river discharges, the contribution of runoff from tile drainages exceeded the contributions of the groundwater runoff. Contributions from surface runoff dominated the river discharges only in <2% of the river discharges and exceeded the contributions from groundwater runoff in about 5% of the simulated river discharges. This is in line with the average fractions of runoff components contributions, which are presented in Table 19: surface runoff 4%, lateral runoff 13%, runoff from tile drainages 26% and groundwater runoff 57% in relation to total simulated river discharge.

Changes in the main calculated water balance components between the subcatchments are shown in Table 20 and reveal partly significant differences in the fractions of the simulated runoff components. Highest fractions of groundwater runoff contributions to river discharge were obtained for Walbersdorf subcatchment and Oslip subcatchment. Highest fractions of the runoff from tile drainages were obtained for the Nodbach subcatchment.

Table 20: Main average annual water balance components (1992-1999) of the subcatchments Walbersdorf, Wulkaprodersdorf, Eisbach and Nodbach in relation to the main watershed outlet Schützen of the Wulka catchment calculated using the SWAT 2000 model (version 106 HRU's, without point source contributions)

	Precipitation [mm/a]	ET [mm/a]	GW Rechg [mm/a]	Surface runoff [mm/a]	Lateral runoff [mm/a]	GW runoff [mm/a]	Tile drainage [mm/a]	River discharge [mm/a]
Walbersd.	793	571	176	4	30	87	-	121
Wulkaprod.	733	561	125	4	13	53	25	95
Eisbach	670	500	123	2	12	74	17	105
Nodbach	650	528	80	2	3	21	32	58
Schuetzen	699	539	118	3	11	46	21	81

The highest precipitation was calculated for the Walbersdorf subcatchment, which is a result of subcatchment morphology with highest elevations within the Wulka catchment. In coincidence with the highest precipitation rates the annual average groundwater recharge rates, the evaporation rates and the simulated river discharges are the highest too. No runoff from tile drainages was considered due to the predominance of forest in this subcatchment. The lowest precipitation amount was calculated for the Nodbach subcatchment coinciding with the lowest annual river discharge and the lowest groundwater recharge rate.

Considerable contributions from point sources are observable in the Eisbach subcatchment, which amount to 30% of the total observed river discharges. This results in considerably high fractions of point source discharges on total river discharges also at main watershed outlet Schuetzen.

4.5.4 Evaluation of the calculated water balance for the Wulka catchment

Results from the applications of the DIFGA 2000 model and the MONERIS model were available also for the Wulka catchment. The comparison between the results of the water balance calculations with the SWAT 2000 model for the main watershed outlet Schuetzen with results from the DIFGA 2000 and the MONERIS model is shown in Table 21.

Table 21: Comparison of the water balance components calculated using the SWAT 2000 model for the watershed outlet Schuetzen with results from DIFGA 2000 and the MONERIS model

	SWAT 2000 1992-1999		DIFGA 2000 ¹ 1971-1997		MONERIS ² 1998-2002	
	[mm/a]	[%]	[mm/a]	[%]	[mm/a]	[%]
Precipitation	699		709		648	
Evapotranspiration	535		571		550	
River discharge	115		87		99	
Surface runoff	3	3	10	12	4	4
Lateral runoff	11	10	54	62	-	-
Groundwater runoff	48	41			59	60
Tile Drainage	23	20	-	-	8	8
Point sources	30	26	23	26	29	29

¹...from (Heinecke 2004); ²...from (Zessner et al. 2004)

The lowest evapotranspiration rates were calculated, according to results for the Ybbs catchment, using the SWAT 2000 model. The DIFGA 2000 model showed the highest evapotranspiration rates what was the consequence mainly from the lowest river discharges because of the different observation interval in comparison to the other models. The highest annual river discharges were estimated by the SWAT 2000

model, which exceeded the annual river discharges of the other models considerably (+32% in relation to the DIFGA 2000 model).

Fractions of the surface runoff were quite similar using the MONERIS model in relation to the SWAT 2000 model. The fraction of surface runoff which was obtained using DIFGA 2000 significantly exceeded the fractions, which was calculated by the other models. This was already observed for the Ybbs catchment because of consideration of quick soil responses and preferential flow within this runoff component in the DIFGA 2000 model.

A good coincidence was obtained for subsurface runoff (groundwater runoff + lateral runoff) calculated by the SWAT 2000 model with the groundwater runoff by the MONERIS model as well as with fast and slow groundwater runoff of the DIFGA model. The fractions of the runoff from tile drained areas were considered in the calculated water balances only by the SWAT 2000 model and the MONERIS model. Whereas the MONERIS model calculated a small fraction (due to empirical relations to the soil type), in the SWAT 2000 model definitions of tile drainages resulted in significantly higher contributions to total river discharge. Therefore, soil definitions in both models differ considerably from each other. Because the fraction of point source contributions to total observed river discharge was calculated based on observations, this fraction seemed to be little underestimated by the DIFGA 2000 model.

Compared to analyses for the Ybbs catchment, variations in the fractions of the calculated subsurface runoff were smaller within the range of 0...-9%. Deviations in calculated fractions of surface runoff and runoff from tile drainages were considerably higher due to different model definitions with +30...+300% and -75%, respectively. However, river discharges of the Wulka catchment are most significantly determined by groundwater runoff. Since all models tend to estimate groundwater runoff and lateral runoff (subsurface runoff) with very small deviations, despite poor model performances evidence was provided about good agreements in calculated fractions of the runoff components between the different models.

Comparison with hydrological reference book and other scientific studies

For the Wulka catchment only limited information from HAÖ could be used for a comparison of the calculated water balance components. Information from HAÖ is available for the Wulka catchment on the watershed scale without differentiation of information in respect to subcatchments. Long-term average river discharges could not be obtained from HAÖ.

Average annual precipitation was +14% higher using the SWAT 2000 model (699 mm/a) in relation to average annual precipitation from HAÖ (613 mm/a) due to different calculation periods for the water balances (see chapter 4.5.2). Calculated annual average evapotranspiration by the SWAT 2000 model (539 mm/a) was well in line with annual average evapotranspiration from HAÖ (514 mm/a).

The Lake Neusiedl was object of scientific investigations during the late 80's. The focus was on the identification of geohydrology and the local water balance characteristics of the Wulka catchment. Unfortunately only sparse information could be obtained from these reports in terms of the validation of the calculated water balance using the SWAT 2000 model. The average annual precipitation amount is reported to range between 670mm in the eastern parts and 760mm in the western parts of the Wulka catchment (Haas et al. 1987b). The long-term annual

evapotranspiration is given with averagely 570mm (1961-1980), 450mm in dry years (1978) and 630mm in wet years (1965) (Haas et al. 1987a). These results are very well in line with the results obtained from the water balance calculations using the SWAT 2000 model, the latter correspond to values given in HAÖ.

Information on average groundwater recharge rates could not be obtained. The groundwater flow was estimated during extreme low flow conditions separately for the upper part of the catchment upstream Wulkaprodersdorf, and for the valley located between Wulkaprodersdorf and the main watershed outlet Schützen. The estimated annual load by base flow was estimated to about 50mm/a (Haas et al. 1987a). Compared to calculated groundwater runoff by the SWAT 2000 model for Wulkaprodersdorf subcatchment (55mm/a), this indicates a good agreement with the previous estimations.

4.5.5 Seasonality of water balance and runoff components

The semi-distributed and continuous time model SWAT 2000 provides information about the calculated water balance components and its spatial and seasonal variations within the catchment. This information can be obtained in detail by model application only. A big advantage arises from this possibility. Information, which can be obtained by observations as point information only (climatic stations) is transferable via model application to the whole catchment area. But in return, the reliability of such information decreases significantly from point observations to distributed information produced by model applications. This is in the model purpose to reflect catchment responses using catchment-specific input-output coherences. In consequence, the model is able to describe the catchment response on certain climatic conditions, but not to cover specific processes. The SWAT 2000 model describes these processes based on physical principles, but due to the huge quantity of interrelated processes and of parameters needed to describe the individual processes and the result is that adequate model response will be obtained via calibration and the model accuracy is highly superposed by uncertainties from the model parameter definitions due to model complexity.

However, the information about the simulated water balance components is available for the selected time step and for every subbasin. The simulation results provided time series on the daily time step for the period 1992-2000 for the Ybbs catchment. Figure 37 shows long-term average daily values for selected water balance components of the Ybbs catchment. The long-term average precipitation amount is shown in comparison to the long-term average evapotranspiration rate, the groundwater recharge rate, the soil percolation and the groundwater runoff. In terms of nitrate leaching and transport, the groundwater recharge rate and groundwater runoff are matter of particular interest. Seasonality of these water balance components significantly affects nitrate transport in respect to both, loads which are transported due to daily water fluxes as well as the occurrence due to time-dependent event-based occurrence of the water balance components.

A large seasonal variation was observable in long-term average evapotranspiration. With lowest values in winter, evapotranspiration increases in later spring and reaches its maximum values in summer due to elevated air temperatures and enhanced plant growth. Afterwards, a constant decrease is observable during autumn until winter season with extremely low evapotranspiration rates. The seasonal variations in evapotranspiration rates are of significant influence on soil water movement

processes. Like indicated already in chapters 2.2.4 and 2.3.3, transport processes (diffusion, convective transport, etc.) in unsaturated zone are highly regulated by soil water content. Unsaturated hydraulic conductivity is by definition lower than saturated conductivity. During periods with elevated evapotranspiration rates in summer, soil water is the subject for evapotranspiration and decreases the fraction of soil water, which will be available for downwards transport via percolation. Particularly upper soil layers are exposed to enhanced evapotranspiration, whereas with increasing depth the availability of the soil water for evapotranspiration decreases. Thus, also percolation shows a high seasonal variation. In winter and in summer the lowest percolation rates are observable, but with different reasons. In winter, predominantly snow coverage and temperature in uppermost soil profile below 0°C limit infiltration of water into the soil profile. Additionally, precipitation is likely to fall as snow during winter season and is therefore not immediately available for infiltration into the soil. In summer, enhanced evapotranspiration rates are responsible for increased water losses from the soil to the air, which results in less water which will be available for percolation. The highest percolation rates were observed in spring, where predominantly snowmelt processes and large precipitation rates in connection with moderate evapotranspiration rates are observable.

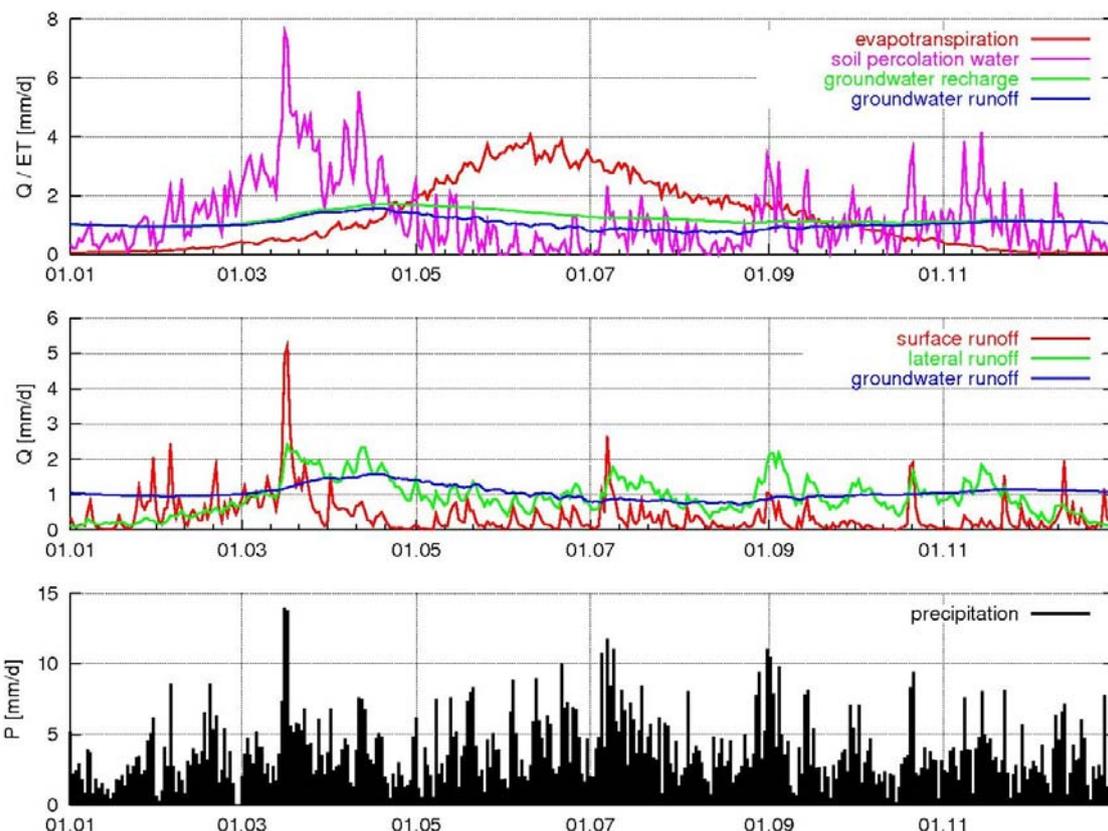


Figure 37: Long-term average values (1992-2000) of precipitation compared to simulated water balance components evapotranspiration, groundwater recharge, soil percolation and simulated runoff components groundwater runoff, lateral runoff and surface runoff calculated for the Ybbs catchment using the SWAT 2000 model

Groundwater recharge rates show a relative constant behaviour throughout the year with minimum values during late winter probably due to snow cover for large parts of the catchment area. A slow increase in groundwater recharge shows the

response to period of snow melt. The time delay between the increase in percolation and the response in groundwater recharge is caused by internal model definitions, where the groundwater recharge is defined as fraction of percolation exiting the bottom of the soil profile, which exponentially decreases in dependence of a drainage time. This definition is for the consideration of diverse geological formations or of specific water table depths. This results in a relatively constant rate of groundwater recharge. The groundwater runoff shows a similar behaviour compared to the groundwater recharge rate during the winter time. The groundwater runoff is simulated based on a storage concept, and it is defined as water which exceeds a threshold in the aquifer. Thus, groundwater recharge induces similarly the same amount of water to be flown out by groundwater runoff for most of the year. Because of an enhanced evapotranspiration rate during the summer, the amount of percolation is limited by water demands in soil profile.

The individual responses of the simulated runoff components surface runoff, lateral runoff and groundwater runoff are related to seasonal pattern as well as to precipitation amount in a quite different manner (see Figure 37). The groundwater runoff contributes constantly with slightly enhanced rates during late spring and autumn due to flood events, and with little reduced rates in summer. This was indicated already by the cumulative frequencies of runoff contributions in Figure 34. The lateral runoff shows significantly higher seasonal variations. After low contributions during the winter months, the daily flow rates increase significantly with the beginning of the snow melt in spring and are significantly influenced during summer and autumn by rainfall events with larger precipitation intensity, which will lead to saturated soil profiles and surface-near subsurface flow. A high interrelation of the percolation to the lateral runoff is noticeable. Enhanced percolation rates result in increased rates of lateral runoff due to increased soil saturation. The surface flow represents the runoff component with the lowest average contribution to total river discharge. The occurrence of surface runoff is essentially related to the storm events during summer and autumn (local and time dependent saturation of surface soil layer), and to a permafrost soil layer or a rain-on-snow-event in winter and spring, what is shown in Figure 37.

Particularly in spring with dramatically increased percolation rates as well as enhanced rates of lateral runoff and surface runoff, soils are highly vulnerable in terms of nitrate leaching, because the spring season is commonly used for first fertilizer applications due to the beginning plant growth. In summer, percolation rates decrease and will be, just as lateral runoff, dependent on precipitation events leading to soil saturation. Due to elevated percolation rates in autumn, nitrate leaching may be relevant particularly in soils, which still contain excessive nitrate due to overfertilization and insufficient plant uptake.

Similarly to the Ybbs catchment, the behaviour of the Wulka catchment in terms of seasonality of simulated water balance components was investigated. Long-term average precipitation is shown in relation to long-term average evapotranspiration, soil percolation, groundwater recharge and groundwater runoff in Figure 38.

Seasonal trends in evapotranspiration, groundwater recharge and groundwater runoff can be observed similarly in calculated water balance components of the Wulka catchment. In contrast to the Ybbs catchment, the average groundwater recharge rate is much lower. The response of groundwater recharge to percolation is

extremely slow (by definition of a long drainage time as function of geology). The groundwater runoff is throughout the year significantly lower than the groundwater recharge rate, what is caused by a constant water flux from shallow aquifer to the deeper aquifer.

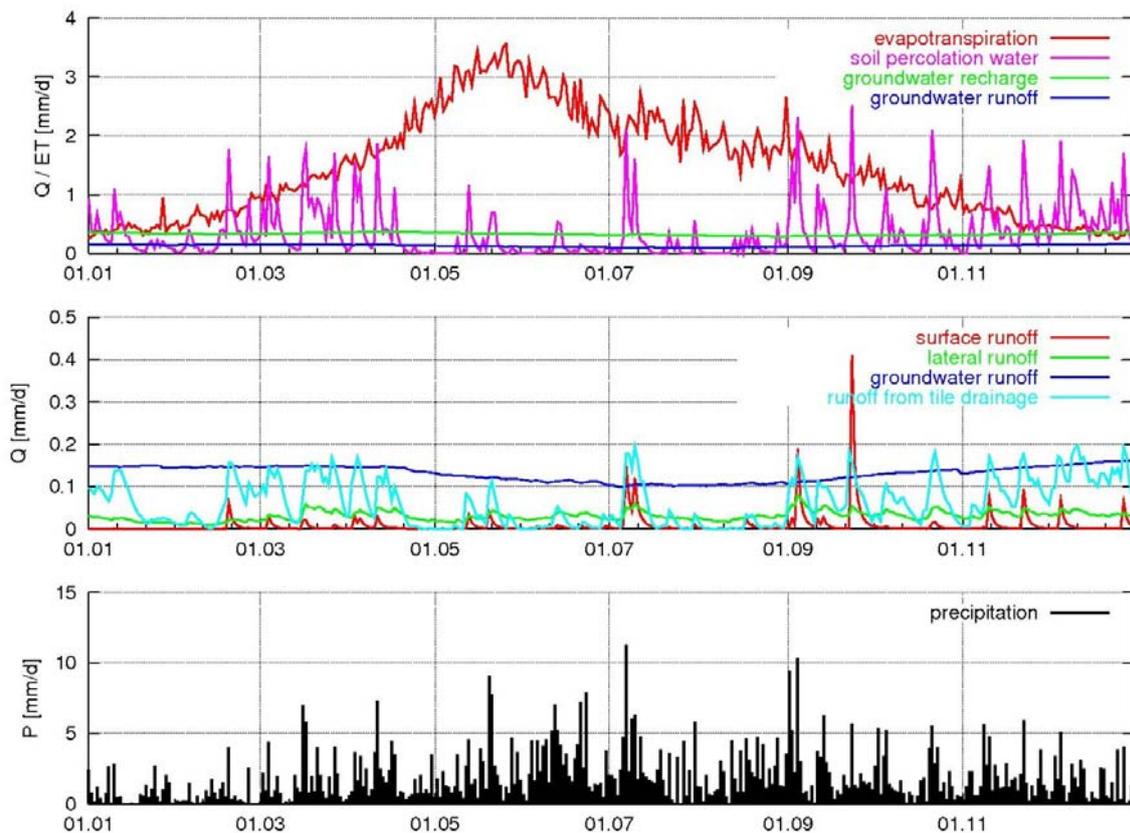


Figure 38: Seasonal cycle of long-term average values (1992-1999) of precipitation (P), evapotranspiration (ET), groundwater recharge (GWRCHRG) and base flow (GWQ) and of surface runoff (SURQ), lateral runoff (LATQ) and base flow (GWQ) and tile drainage (TILE D) calculated for the Wulka catchment using the SWAT 2000 model

Water fluxes in the soil profile by percolation are significantly influenced by elevated evapotranspiration rates, what results in a significantly lower percolation compared to the Ybbs catchment. Seasonality of percolation shows smaller seasonal changes, but a connection to the occurrence of precipitation. A reason therefore is the dominance of the runoff from tile drainages in the Wulka catchment, which is beside the permanent nearly constant contribution of groundwater runoff the second largest runoff component with intensive contributions particularly in spring, autumn and winter season. In these seasons, due to a diminished evapotranspiration more soil water is available for tile drainage, what results in increased runoff rates from tile drained areas. Lateral flow shows nearly no seasonal variations. Significant increases in precipitation intensities results in an immediate and short-term contribution from tile drainages. After short and strong responses of tile drainages, the soil will be drained down to the point of field capacity. The surface runoff shows high seasonal variation with large peaks sometimes, which are correlated partly to increases in runoff from tile drainages, what reveals the quick response on storm events with local importance and small contributions in regard to the annual contribution to total river discharge.

Percolation is decisive particularly in spring and in autumn as well as in early winter. Lateral runoff and runoff from tile drainages is connected to soil water content and therefore, to percolation too. Primarily in spring and from late autumn until winter, vulnerability of the soil in terms of nitrate leaching is essentially high. Surface runoff is not linked to nitrate transport, but due to appearance during soil saturation, peaks in surface runoff indicate enhanced percolation rates in soils resulting in elevated rates of primarily runoff from tile drainages.

Seasonal variations in long-term average precipitation intensity for the Ybbs catchment are shown in Figure 39 (left) in relation to annual average evapotranspiration and groundwater recharge. Precipitation is particularly elevated between March and September. As already indicated, also the evapotranspiration rate increases significantly during the summer months resulting in relatively constant groundwater recharge rates in the Ybbs catchment throughout the year. In average the precipitation amount is exceeded by water demands of evapotranspiration and groundwater recharge in May and June. These demands will be compensated by storages in soil water. Additionally, groundwater recharge rates are defined with a certain time delay in relation to soil percolation water, so groundwater recharge rates in May and June may result from soil percolation rates of previous months.

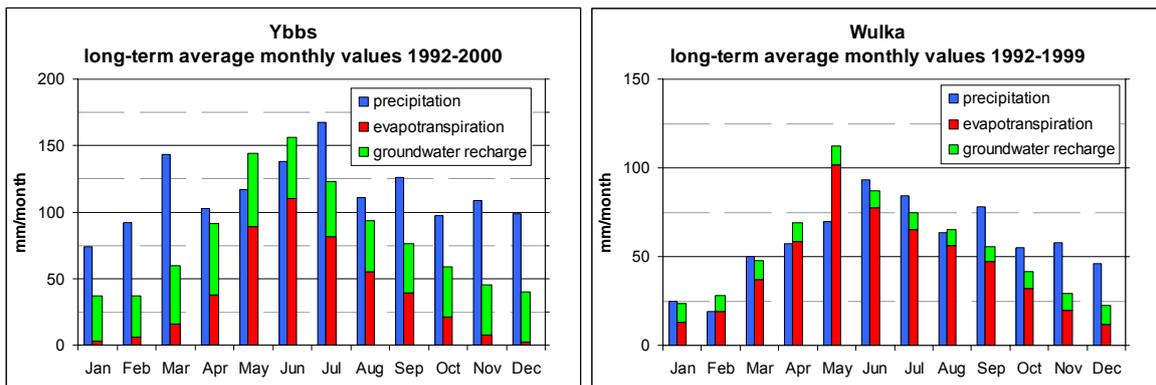


Figure 39: Comparison of long-term average monthly values for precipitation, evapotranspiration and groundwater recharge between the Ybbs catchment and the Wulka catchment calculated by the SWAT 2000 model

Stronger seasonal changes in long-term average precipitation could be observed for the Wulka catchment with significantly smaller intensities in comparison to the Ybbs catchment (see Figure 39 right). The smallest average precipitation was observed in January and February, whereas the largest precipitation was observed from June till September. Significant increases in evapotranspiration rates during the summer months were already discussed, but evapotranspiration with considerable intensity could be observed in winter too. The long-term average groundwater recharge is significantly smaller in comparison to the Ybbs catchment. In February, April and May the long-term average precipitation at the Wulka catchment is smaller than the demands of evapotranspiration and groundwater recharge. This discrepancy was already addressed. Again, water demands during these months due to elevated evapotranspiration are covered by soil water storages. The definitions in groundwater recharge for the Wulka catchment imply significantly larger time delays between soil percolation rates and groundwater recharge, what results in almost constant contributions of groundwater recharge from soil percolation of previous months.

The long-term average contribution of the simulated runoff components surface runoff, lateral runoff and groundwater runoff for the Ybbs catchment is shown in Figure 40 in total amount and as fractions related to the total river discharge. During snow melt (March/April), the river discharge increases dramatically caused by predominantly a significant increase in lateral and surface runoff. The contribution of surface runoff is except during the spring mostly less than 20%. The fraction of lateral flow decreases noticeably during winter months. The groundwater runoff contributes, except in March, between 40-60% permanently throughout the year to the total river discharge and constitutes the major flow component in the Ybbs catchment.

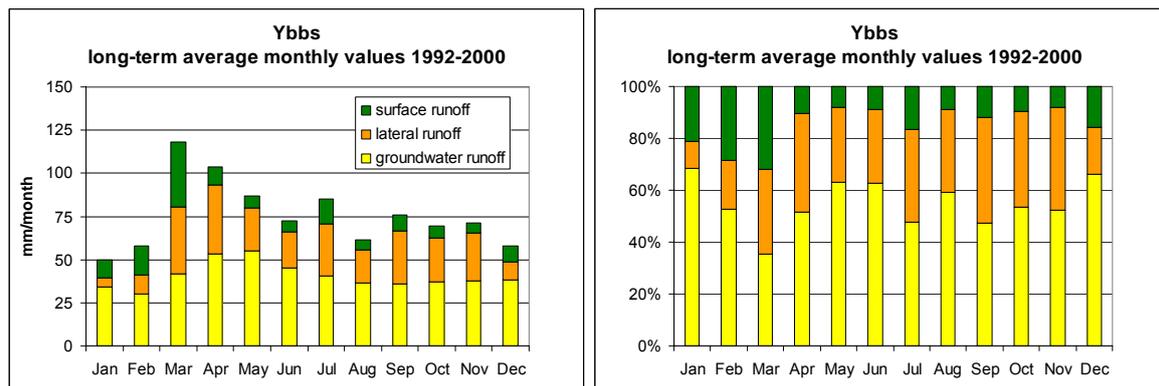


Figure 40: Long-term average monthly values (1992-2000) for surface runoff, lateral runoff and groundwater runoff and the fractions of the runoff components on total river discharge for the Ybbs catchment calculated by the SWAT 2000 model

The long-term average contribution of the simulated runoff components of the Wulka catchment is shown in Figure 41. In contrast to the Ybbs catchment, also point sources (waste water treatment plants) as well as runoff from tile drained areas considerably contribute to the river discharge. The contribution from point sources is relatively constant and constitutes a basic load, they contribute on average 20-26% to the total river discharge. Runoff from tile drained areas shows significant seasonal variations with contributions of <10% to >30% to the total river discharge. The contributions from lateral runoff and surface runoff to total river discharge are smaller compared to the other runoff components, and more inhomogeneous. The lateral runoff contributes averagely 10-20% to the total river discharge, the contributions of the surface runoff are <10% of the total river discharge. The largest fraction to the total average river discharge is contributed by groundwater flow permanently throughout the year with averagely 40-50%.

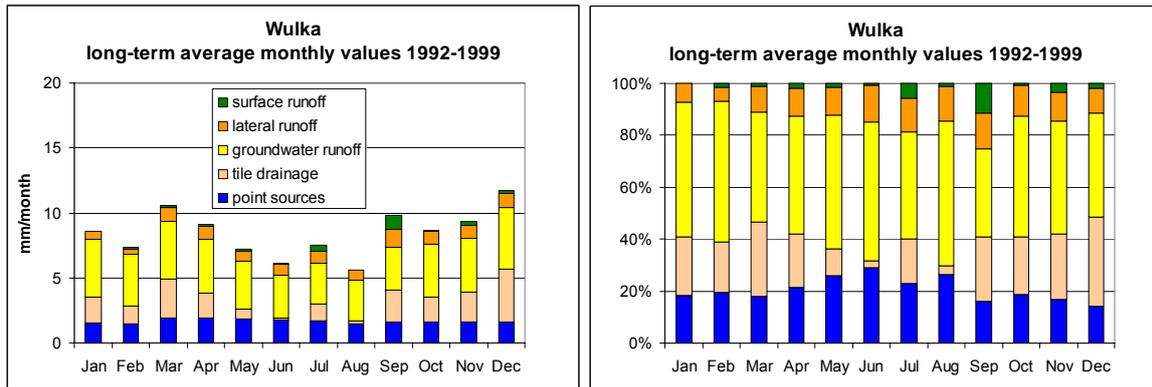


Figure 41: Long-term average monthly values (1992-1999) for surface runoff, lateral runoff, groundwater runoff, runoff from drained areas (tile drainage) and for contributions from waste water treatment plants (point sources) and the fractions of the runoff components on total river discharge for the Wulka catchment calculated by the SWAT 2000 model

Both the Wulka catchment and the Ybbs catchment are dominated by groundwater runoff contributing permanently to the majority to the total river discharge. As a consequence the average groundwater recharge rate is of significant importance in terms of runoff generation. The SWAT 2000 model offers the opportunity to estimate the average groundwater recharge rate at the catchment scale with spatial distribution. The variations in average groundwater recharge rates between and within the Ybbs and the Wulka catchment as a result of catchment morphology and hydrological conditions, is shown in Figure 42. Both catchments show similarities in regard to the changes in groundwater recharge within the watershed. Due to increasing elevations average precipitation as well as the average groundwater recharge increases considerably.

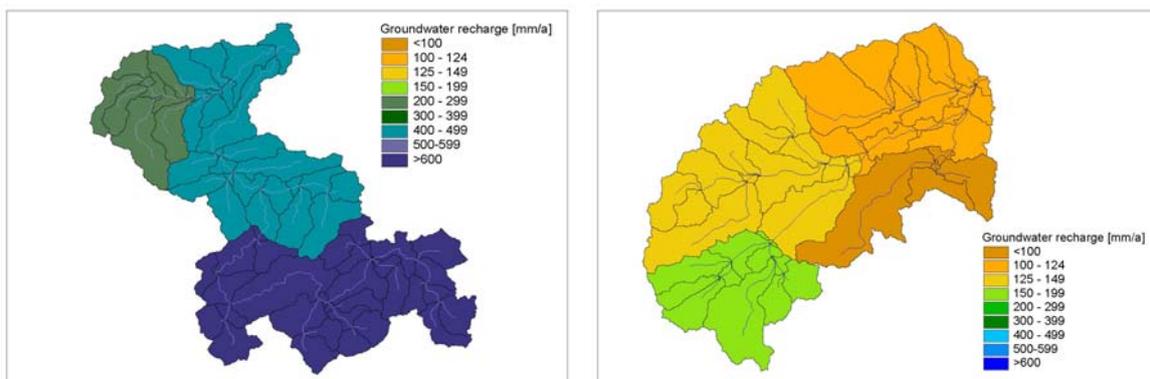


Figure 42: Comparison of calculated average annual groundwater recharge rates on subcatchment level between the Ybbs catchment and the Wulka catchment based on SWAT 2000 model results

The average annual groundwater recharge rate varies within the Wulka catchment between <100...200 mm/a, in the Ybbs catchment between 200...>600mm/a. That means that the Ybbs catchment regionally differentiated, 2 to 3fold higher average annual groundwater recharge rates were calculated compared to the Wulka catchment. Regarding nitrate leaching to groundwater, these differences between both catchments admit contrasting conclusions in terms of groundwater vulnerability.

4.6 Conclusions in terms of water balance calculations

The advantages and disadvantages of the application of the SWAT 2000 model can be contrasted from own experiences in the following way:

Table 22: Advantages and disadvantages of application of the SWAT 2000 model

In terms of:	Advantages	Disadvantages
Definitions of calibration parameters on subbasin and HRU level	- semi-spatial resolution assured, information about hydrological processes on subbasin level	- information as average on subbasin area, no clear spatial reference of HRU's - huge amount of calibration parameter lead to uncertainties in parameter definitions and model results
Input data	- weather generator useful to overcome gaps in observation data (if database is sufficient for calculation of statistical values)	- Very extensive input data requirements (particularly climatic data) - No interpolation of precipitation data
Calculation with daily time step	- inner-annual and perennial information on hydrological components	- required storage capacity and calculation time
GIS interface	- easily incorporation of geo-referenced maps	- mapping of calculated output as average values on subbasin level only
Watershed configuration	- flexibility due to utilization of grids, shapes and manual subbasin definitions	- degree of flexibility is connected with increase of calibration parameter

The SWAT 2000 model was used for the estimation of catchment specific water balances and particularly for the assessment of relative contribution of runoff components to the total river discharge. Spatial variations in water balance and runoff components as well as seasonal changes could be identified. Main differences in the calculated water balances were obtained between the Ybbs and the Wulka catchment. Whereas the fraction of surface runoff and lateral runoff is large in the Ybbs catchment, the Wulka catchment is dominated by subsurface runoff with considerable point source discharges to surface water. Average annual groundwater recharge is significantly higher in the Ybbs catchment, what supposes consequences for nitrate leaching to the groundwater and afterwards, for the intensity of nitrate transport by groundwater runoff.

Data availability for providing input information limited the SWAT 2000 model application to a time period of 8 and 9 years, respectively. For both catchments the SWAT model failed to close to the long-term water balance for the calculation period.

The SWAT 2000 model provides comprehensive possibilities to link catchment hydrology with water quality related transport, transformation and retention processes. Once calibrated, the SWAT 2000 model was used also for nitrogen balance calculations, which are presented in chapter 6.2.

5 Groundwater and surface water characteristics

5.1 Motivation and background

The previous chapter presented water balance calculations at the catchment scale which have been carried out for the two Austrian case study regions. Emphasis of these investigations was on pointing out differences in catchment hydrology due to varying climatic and morphologic conditions. Catchment hydrology is also of decisive importance for groundwater quality and surface water quality. Nutrient fluxes are impacted by catchment-specific hydrologic responses to a different extent, even if area-specific surpluses between catchments are equal, and result in considerably different nitrogen loads to the groundwater and the surface water. Precipitation as the major driving force of material transport, affects runoff generation in terms of amount and distribution between surface and subsurface runoff components as well as retention processes limiting chemical reactions or biological decay because of necessary wetness conditions.

The groundwater quality reflects leakage (soil percolation and groundwater recharge) processes with possibly significant spatial variations. Emissions of nitrogen to the groundwater in general are derived from the area-specific surplus, which is dependent predominantly on land use practises and atmospheric deposition and transported downwards to groundwater by groundwater recharge. Hence, specific land use management strategies impact the regional groundwater quality considerably.

The motivation of the analyses in this chapter was to point out

- Differences between the Ybbs catchment and the Wulka catchment in groundwater and surface water quality as a consequence of the different catchment hydrology and land use practises
- Indicators in groundwater and surface water quality measurements for identification of nitrogen losses by denitrification in the soil and the groundwater
- Differences in denitrification in the groundwater due to different hydrogeological conditions between the Ybbs catchment and the Wulka catchment and consequences on nitrogen emissions from the groundwater to the surface water

In this chapter groundwater quality and surface water quality observations are presented, which were investigated in the Ybbs catchment and the Wulka catchment. Parameters which are indicative of enhanced denitrification in the groundwater were incorporated into the investigations. Significant changes in parameters are presented, which can be attributed to denitrification in the groundwater as well as to different hydrological conditions between the catchments and therefore affect denitrification in the groundwater.

These analyses are based on observations of 89 external and 18 internal groundwater observation wells (most of the observation wells provided data for the period 1990-2002) as well as 3 external and 3 internal surface water observation stations (data availability 1990-2003) in the Ybbs catchment.

In the Wulka catchment, 17 external and 13 internal groundwater observation wells (data availability for most of the observation wells 1991-2003) have been used for data analyses as well as 4 external and 5 internal surface water observation stations.

5.2 Indications for nitrogen loss via denitrification in the groundwater of the Wulka catchment

In Table 23 the main characterisation in terms of groundwater concentrations in the subcatchments of the Wulka catchment is presented. For this characterisation the Wulka catchment was divided in two parts: the upstream part of the catchment which corresponds mainly to delineation of the Wulkaprodersdorf subcatchment, and the remaining downstream part of the catchment towards the main watershed outlet Schuetzen (without the Wulkaprodersdorf subcatchment).

Table 23: Average concentrations in groundwater of the Wulka catchment (from Zessner et al. 2004, modified)

	O ₂	DOC	NH ₄ -N	NO ₃ -N	NO ₂ -N	Fe
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Schuetzen (without Wulkaprodersdorf subcatchment)	4,8	2,8	0,09	16,4	0,03	0,14
Wulkaprodersdorf subcatchment	5,6	2,4	0,04	26,1	0,04	0,13

The observed nitrate concentrations in the groundwater of the two parts of the Wulka catchment in Table 23 indicate groundwater nitrate concentrations in the Wulkaprodersdorf subcatchment, that are nearly 2-fold higher compared to the nitrate concentrations observed in the groundwater of the downstream part of the Wulka catchment. Other parameters in Table 23 do not show large deviations in relation to their location within the two parts of the Wulka catchment. Observed NO₂-N, NH₄-N, DOC or Fe²⁺ concentrations as well as O₂-concentrations in Table 23 do not indicate the presence of reducing conditions in the groundwater of the Wulka catchment.

In Figure 43 average nitrate concentrations in the groundwater are shown for individual groundwater observation wells. The small number of stations and the spatial heterogeneity hamper the observance of a spatial trend in average nitrate concentrations and also our ability to relate individual parts of the catchment to a certain range of groundwater nitrate concentrations. The number of observation wells is substantially higher in the downstream part near the watershed outlet. Figure 43 gives a snapshot about the spatial distribution of the mean groundwater nitrate concentrations, but the identification of denitrification hot spots in groundwater within the Wulka catchment requires the assessment of changes in nitrate concentrations along the flowpath.

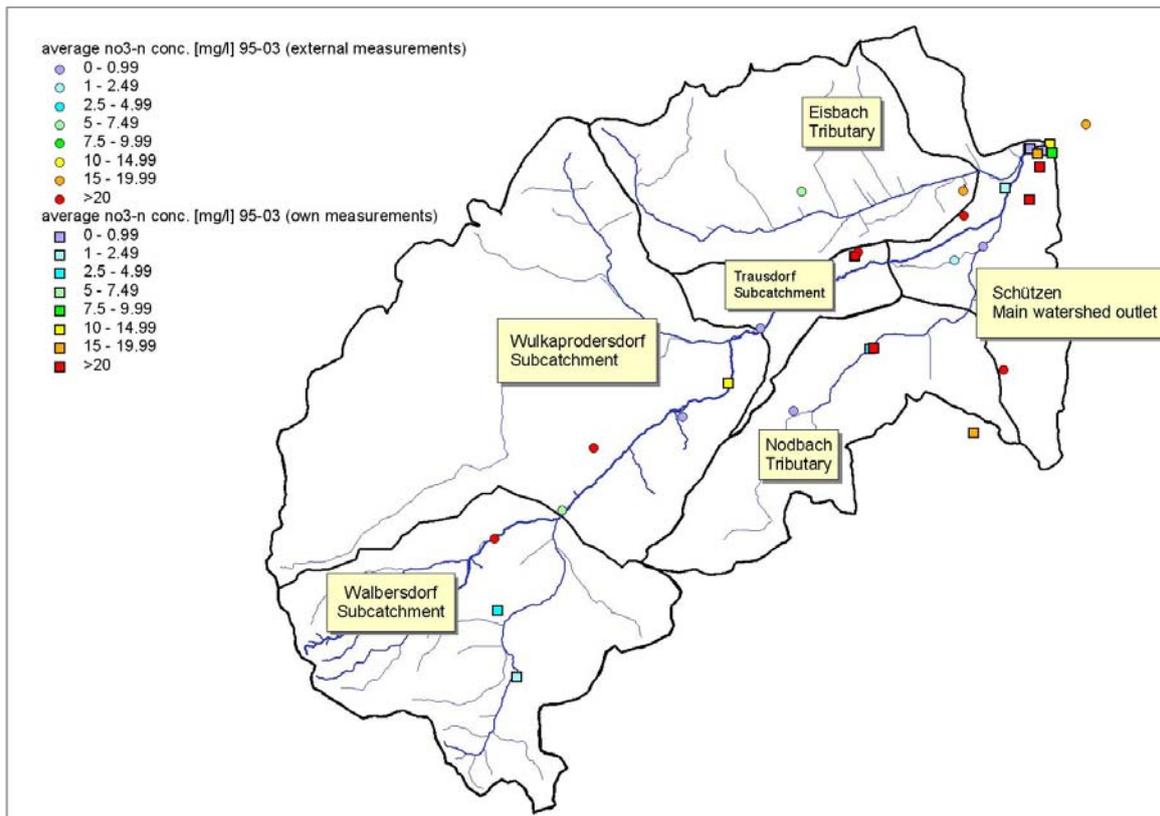


Figure 43: Observed average nitrate concentrations in the groundwater of the Wulka catchment (1995-2003)

In chapter 2.2.3 (Figure 3) the concept was already introduced which related the runoff components to a certain time delay in terms of their contribution to the surface water. According to this concept, groundwater was subdivided and classified as 'young' or 'old' groundwater in relation to their distance from the receiving surface water body. Therein the infiltration by percolation into the groundwater initiates the groundwater flow and leads to exfiltration of river-near groundwater to the surface water. With regard to the travel time, river-near groundwater will therefore contribute to the surface water with a relatively short time delay, whereas groundwater with large distances to the surface water is characterised by a relatively long travel time. As a function of the travel time (groundwater residence time) groundwater nitrate concentrations are likely to be reduced via denitrification in the groundwater. The longer the groundwater residence time the more nitrate concentrations are assumed to be reduced by enhanced access of denitrifying bacteria on available groundwater nitrate. Thus, nitrate concentrations in groundwater should decrease along the flowpath towards the surface water due to increased levels of denitrification in groundwater.

Following this concept, the groundwater observation wells have been grouped according to their distances to surface water bodies. One group of groundwater observation wells is characterised by a distance of > 100m to surface water, the second group by a distance of < 100m to surface water. This selection was made because riparian zones are known to act as buffer zones and show enhanced denitrification activity. The width of the riparian zones was selected to be 100m. The concentrations of selected quality parameter of these two groups have been compared with measurements of concentrations in the surface water.

That denitrification takes place in the unsaturated and saturated zone of the Wulka catchment could be shown clearly by the observations of the groundwater and surface water nitrogen concentrations, and is presented in Figure 44. It shows the cumulative distribution functions of the observed total inorganic nitrogen (TIN) concentrations in the groundwater for observation wells with >100m distance to the surface water and for wells with <100m distance to the surface water compared to the TIN concentrations in the surface water of the Wulka catchment. Additionally to the observations, the cumulative distribution function of the calculated potential nitrogen concentration in the leakage water is shown, which was calculated from the area-specific nitrogen surplus distribution at the municipality level in connection to the distribution of the average groundwater recharge rates.

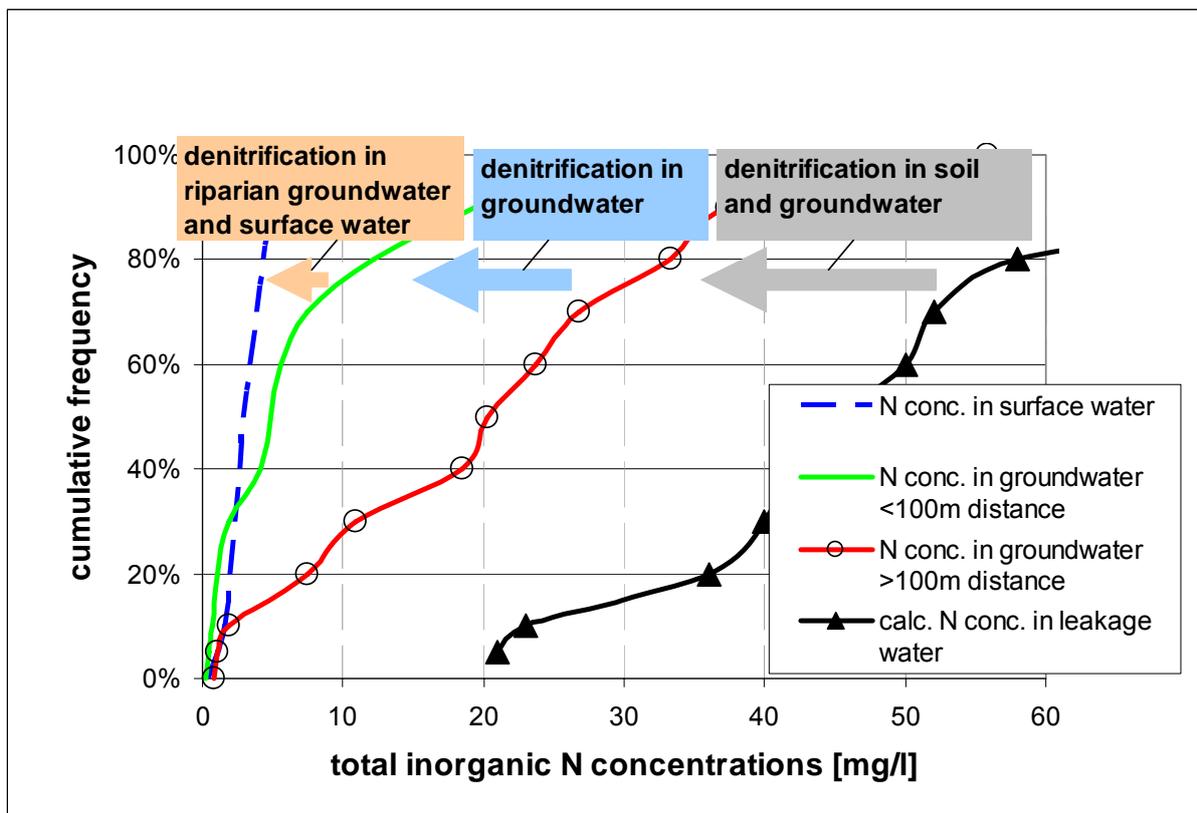


Figure 44: Cumulative distribution function of the observed total inorganic nitrogen concentrations in the groundwater with > 100m distance, with < 100m distance to the surface water, in the surface water (1992-2002) in relation to the calculated potential nitrate concentrations in the leakage (percolation) water

According to the concept of water fluxes at the catchment scale starting from the soil surface through the unsaturated zone to the groundwater and from the groundwater to the surface water, a considerable decrease in the nitrogen concentrations in these compartments can be observed in Figure 44. From the distributions of the area-specific nitrogen surpluses and the groundwater recharge rates the potential nitrogen concentration in the leakage water was calculated, which is shown as cumulative frequency (black line) in Figure 44. On average, 50% of the calculated cumulative nitrogen concentrations in the leakage water exceeded 45 mgNO₃-N/l. In relation to the cumulative frequency distribution of the nitrogen concentrations in groundwater, which was observed in observation wells with >100m distances to surface water (red line), a large decrease in nitrogen concentrations is observable (grey arrow in Figure 44). On average, 50% of the observed nitrogen

concentrations in groundwater wells with >100m to surface water exceeded 20 mgN/l and are considerably lower than the potential nitrogen concentrations in leakage water. This decrease is caused by denitrification processes in the soil and in the groundwater, since total inorganic nitrogen consists predominantly of nitrate (in average 90% of TIN). Denitrification is very effective in the unsaturated zone due to sufficient organic carbon content in the soil layers (in comparison to the groundwater). Since observations in the groundwater presume a certain travel time from the point of infiltration from the unsaturated zone to the groundwater observation well, this decrease in nitrogen concentrations is caused similarly by denitrification in the groundwater too. From our observations it is not possible to distinguish between denitrification in the soil and denitrification in the groundwater. Denitrification rates are likely to be higher in the unsaturated zone than in the groundwater due to the comparably higher organic carbon contents (Well et al. 2005, Bengtsson et al. 1995), but residence time in unsaturated zone is considerably shorter in comparison to the residence time in groundwater.

A further decrease in the nitrogen concentrations in the groundwater is observable along the groundwater flowpath towards the surface water (see Figure 44). The nitrogen concentrations which were observed in groundwater wells with <100m distance to surface water (green line) show substantially lower nitrate concentrations compared to groundwater observation wells with >100m distance to surface water. This decrease can be attributed to denitrification in the groundwater (blue arrow in Figure 44). On average, 50% of the observed nitrogen concentrations in groundwater wells with <100m distance to surface water exceeded only 5 mgN/l. Based on these observations, denitrification in the groundwater could be definitely observed resulting in a further decrease of the groundwater nitrate concentrations on the groundwater flowpath towards the surface water.

The nitrogen concentrations in the surface water had the lowest nitrate levels (blue line in Figure 44) in comparison to the nitrogen concentrations of the river-near (riparian) observation wells. This decrease (orange arrow in Figure 44) is associated with denitrification in the riparian groundwater and the surface water. On average, 50% of the observed nitrogen concentrations in the surface water exceeded 3mgN/l, but nitrogen concentrations in the surface water of the Wulka catchment are also considerably affected by discharges from point sources (inlets from waste water treatment plants). Discharges from point sources enlarge nitrogen loads in the surface water so that observed nitrogen levels in surface water are not solely the result of nitrate-reduced groundwater discharges, and point source discharges enhance denitrification in surface water. Without point source discharges, nitrogen levels in surface waters are likely to be lower.

The measurements in groundwater nitrogen concentrations indicated a considerable decrease in nitrogen levels in the groundwater towards the surface water, which could be attributed to denitrification in the groundwater. Since groundwater chloride concentrations are affected mainly by groundwater inflows from adjacent aquifers and reductions in chloride concentrations are caused by dilution with groundwater of a different qualitative composition, the observed chloride concentrations in the groundwater can be used to verify the results described above about nitrate reduction in the groundwater by denitrification. Chloride is a conservative substance, which is not subject of biological decay in groundwater. If denitrification in groundwater is responsible for the reduction of

nitrate levels in groundwater, chloride concentrations should remain more or less constant within the observed groundwater wells. If dilution is responsible for nitrate reduction in groundwater, this should be observable also by significant changes chloride concentrations in groundwater according to the changes in nitrate concentrations.

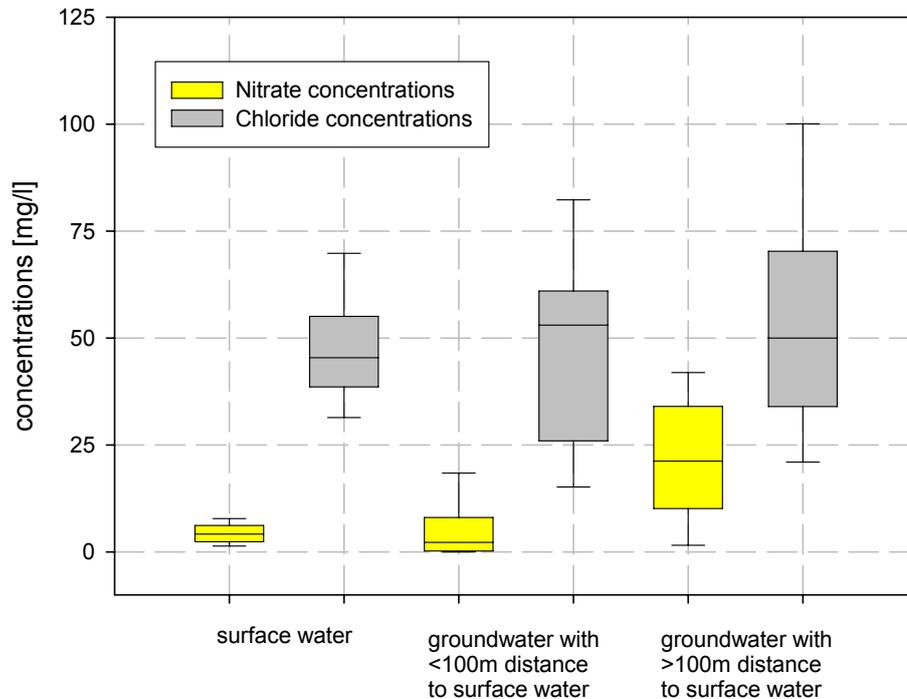


Figure 45: Comparison of observed nitrate and chloride concentrations in the groundwater of the Wulka catchment with <100m and >100m distance to surface water and in surface water

Figure 45 shows a comparison of the observed nitrate and chloride concentrations from observation wells with <100m and >100m distances to the surface water and for the surface water. Whereas the nitrate concentrations decrease towards the surface water, the chloride concentrations show only little variations from the surface water concentrations. So, dilution processes are unlikely to be responsible for the observed decrease in nitrogen concentrations in the groundwater towards the surface water.

Measurements of dissolved oxygen concentrations (O_2) in the groundwater confirm conditions, which are favourable for denitrification in terms of the anoxic status of the groundwater (see Figure 46).

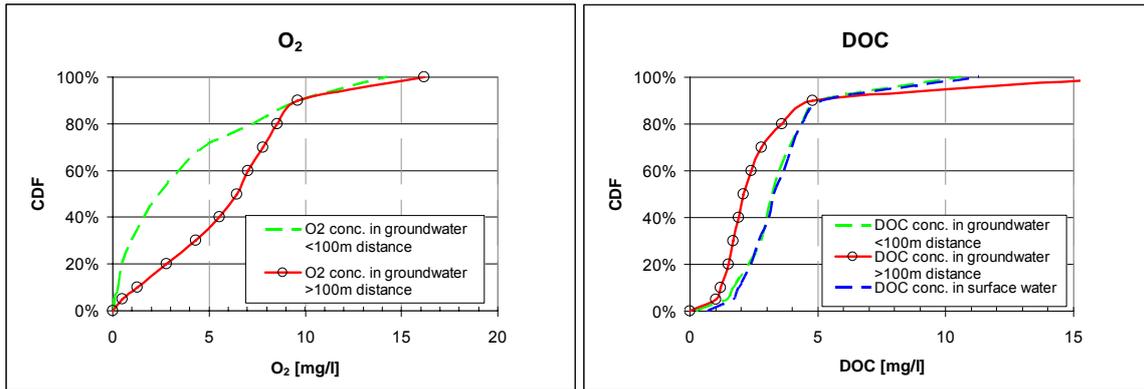


Figure 46: Cumulative distribution function (CDF) of O₂-concentrations and DOC concentrations in the groundwater with < 100m and > 100m distance to surface water and DOC concentrations in surface water (1992-2002)

Whereas 65% of the observed O₂-concentrations in the observation wells with >100m distance to the surface water exceeded 5 mgO₂/l, the riparian groundwater with <100m distance to the surface water showed significantly lower oxygen levels in groundwater (on average, only 30% of observed O₂-concentrations in the groundwater exceeded 5 mgO₂/l). Several threshold values for O₂-concentrations are reported to limit denitrification activity (see Table 5), and denitrification activity in the groundwater was reported when oxygen levels in the groundwater were <5 mgO₂/l. However, towards the surface water decreasing O₂-concentrations in the groundwater could be observed in parallel to decreasing nitrogen concentrations in the groundwater.

Dissolved organic carbon concentrations (DOC) in the groundwater (see Figure 46) tend to increase slowly with decreasing distances to the surface water. On average, 50% of the DOC concentrations in the groundwater exceeded 2mgDOC/l and 3mgDOC/l for the observation wells with >100m distance and <100m distance to surface water, respectively. According to chapter 2.1.3, on average 1.83-2.75 mgNO₃-N/l can be denitrified using 2-3 mgDOC/l from the groundwater. The observed DOC concentrations in the groundwater are much too low to supply sufficient organic carbon for denitrification in the groundwater. Thus, fossil organic carbon sources are likely to be used for denitrification in the groundwater of the Wulka catchment (Hiscock et al. 1991, Wassenaar et al. 1991) what was confirmed by investigations of Polzer (2005).

DOC fluxes from the soil to the groundwater are reported in the literature and have been associated with denitrification activity in deeper soil layers and in shallow aquifers. The groundwater with <100m distance to the surface water shows DOC concentrations which are close to the DOC concentrations of the surface water (see Figure 46). Particularly riparian zones are reported to substantially provide a source of organic carbon for groundwater flow (Spruill 2000) due to highly dynamic interactions between rivers and adjacent aquifers sometimes extending on the order of hundreds of meters into the aquifer (Hinkle et al. 2001). Due to seasonal flooding of riparian soils, organic carbon content of these soils tends to be higher compared to hillslope soils. Since groundwater table depths decreases inline with increasing fluctuations in the groundwater tables (standard deviation) towards the surface water, what is indicated for the Wulka catchment in Figure 47, DOC leaching from soil to shallow groundwater is likely to increase the DOC concentrations in

groundwater towards the surface water due to enhanced interactions of groundwater table with upper organic-rich soil layers in riparian zones. This is also supported by DOC concentrations which have been observed in surface water, which show similar DOC concentrations in comparison to the river-near groundwater. Thus, enhanced DOC leaching from soils near the river by groundwater seems to determine both the DOC concentrations in riparian groundwater as well as DOC concentrations in surface water.

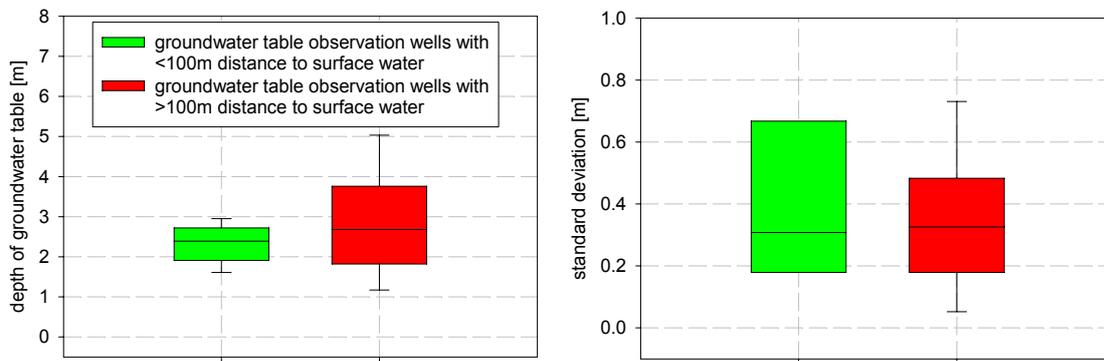


Figure 47: Average groundwater table depth and standard deviation of groundwater table depth of groundwater observation wells with <100m and >100m distance to surface water

Observed Fe^{2+} -concentrations as well as observed SO_4^{2-} -concentrations did not show big deviations in relation to the distance of the observation wells to the surface water (see Figure 48), this implies that alternative electron donors are not used noticeably for denitrification in the groundwater of the Wulka catchment.

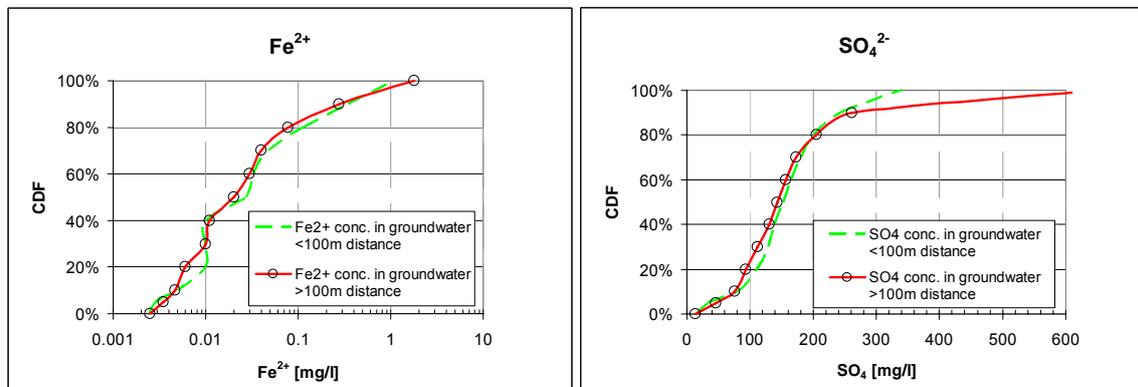


Figure 48: Cumulative distribution function (CDF) of Fe^{2+} concentrations and SO_4^{2-} concentrations in the groundwater with < 100m and > 100m distance to the surface water (1992-2002)

Since no large discrepancies in ferrous oxide and sulphate concentrations within the groundwater of the Wulka catchment could be observed, heterotrophic denitrification is likely to be the main process for nitrate reduction in the groundwater. According to equation 3 the decrease in nitrate concentrations by heterotrophic denitrification is associated with an increase in hydrogen carbonate concentrations in groundwater.

In Figure 49 the anion composition (anion mol equivalents) is shown for the groundwater observation wells with >100m and <100m distance to the surface water. In the groundwater near the surface water (<100m) significantly higher hydrogen carbonate equivalents could be observed than in observation wells with

large distances to surface water (>100m). This reveals heterotrophic denitrification in the groundwater. Changes in SO_4 ion equivalents are marginal in relation to changes in HCO_3 ion equivalents, what indicates that heterotrophic denitrification is likely to be the predominant process for nitrate reduction in the groundwater.

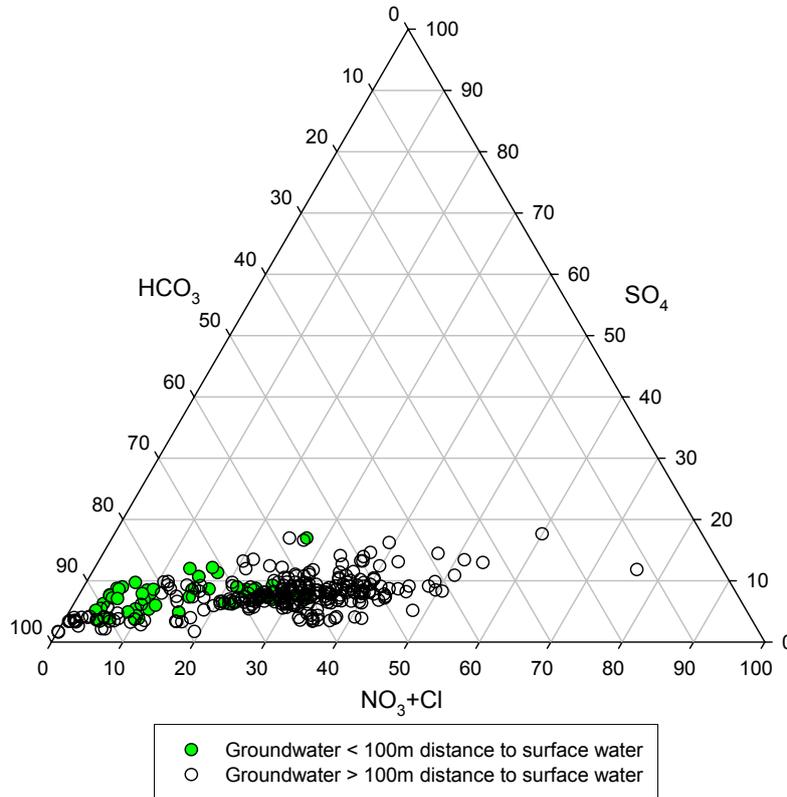


Figure 49: Tertiary plot of anion mol equivalents in groundwater observations of the Wulka catchment with fractions of specific anions on total anion amount

Geology and land use were related to the observed nitrogen concentrations in the groundwater in Figure 50. Whereas land use classes can influence groundwater nitrate concentrations because of specific nitrogen emissions of the individual land use practises, hydrogeological classes affect groundwater nitrate concentrations due to their determination of groundwater flow paths and their specific groundwater residence times. Hence, considerable sources of groundwater nitrate (major emitters) can be indicated using the land use categorisation in respect to nitrate concentrations. Categorisation of hydrogeology in respect to nitrate concentrations indicates predominant groundwater flow paths for nitrate and its reduction potential by denitrification due to specific groundwater residence times.

The largest nitrate concentrations in respect to land use categorisation have been observed in groundwater wells situated on arable land and settlements. Large nitrogen applications due to fertilization in agricultural areas result in higher nitrogen surpluses and in elevated nitrogen concentrations in the groundwater. Elevated nitrogen levels in settlements are indicative for waste water intrusions due to leaching pits or septic tanks. In areas without vegetation, evergreen land or vine yards significantly lower nitrate concentration have been observed with partly large variability in nitrate concentrations. In forested areas the lowest nitrate

concentrations were observed in the groundwater. That indicates that especially agricultural and residential areas are responsible for large quantities of nitrogen disposal to the groundwater.

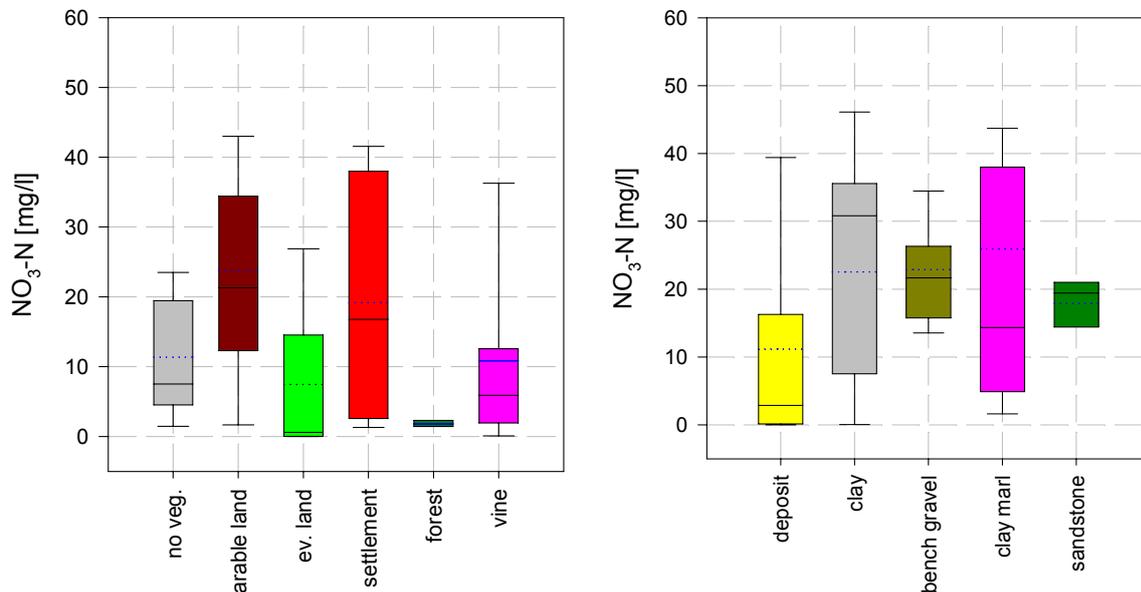


Figure 50: Nitrate concentrations in the groundwater of the Wulka catchment in respect to the location of the groundwater observation wells in different land use classes (left) and different geological formations (right)

In respect to hydrogeological classification, the largest nitrate concentrations have been observed in clay and clay marl. These formations are characterised by a very low conductivity, so groundwater flow is very slow. These formations are situated uphill far-off the surface waters predominantly under areas with agricultural activity. Hence, on the one hand large quantities of nitrogen are leached from soil surface in these formations. Sandstone and bench gravels show lower average nitrate concentrations with considerably lower variations. Bench gravels are usually conductive for groundwater flow and promote nitrate transport via groundwater over considerable distances. Denitrification is likely to be responsible for reduced nitrogen levels in bench gravels since these formations are situated on the groundwater flow path from uphill situated clays to downhill deposits.

Most of the deposits are located nearby the river, where most of the groundwater flows towards the river. So the large reductions in nitrogen concentrations are likely to be the result of long groundwater residence times with enhanced denitrification along the flowpath towards the surface water.

However, observed nitrogen concentrations in the groundwater are point information only and reflect a mixture of groundwater inflow from upstream areas with a specific nitrogen concentration and groundwater recharge with leached nitrogen from soil zone. Hence, relations of nitrogen concentrations to both land use classes and hydrogeological formations does not imply the whole flowpath of groundwater nitrate and does not allow to identify denitrification in the groundwater at these specific locations.

5.3 Indications for nitrogen loss via denitrification in the groundwater of the Ybbs catchment

In Table 24 a main characterisation in terms of groundwater concentrations in the subcatchments of the Ybbs catchment is presented.

Table 24: Overview on concentrations in groundwater of the Ybbs catchment (from Zessner et al. 2004, modified)

	O ₂	DOC	NH ₄ -N	NO ₃ -N	NO ₂ -N	Fe
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Opponitz	10,8	0,88	0,005	1,3	0,001	0,02
Krenstetten	7,6	0,95	0,028	7,4	0,003	0,03
Greimpersdorf, upstream of Kematen	8,5	0,81	0,006	3,3	0,000	0,01
Greimpersdorf, downstream of Kematen	7,83	1,12	0,019	7,7	0,002	0,04

The Ybbs catchment is more heterogeneous in terms of groundwater quality than the Wulka catchment. The upstream located Opponitz subcatchment and the part upstream the gauging station Kematen of the Greimpersdorf subcatchment (see Figure 51) show significantly lower concentrations of nitrate, nitrite, ammonium, DOC and Fe²⁺ in groundwater than the remaining parts of the watershed, which are located in the northern part of the Ybbs catchment towards the watershed outlet. The dissolved oxygen concentration in the groundwater is likewise higher in the upstream parts of the catchment. A spatial distribution of average nitrate concentrations is shown in Figure 51.

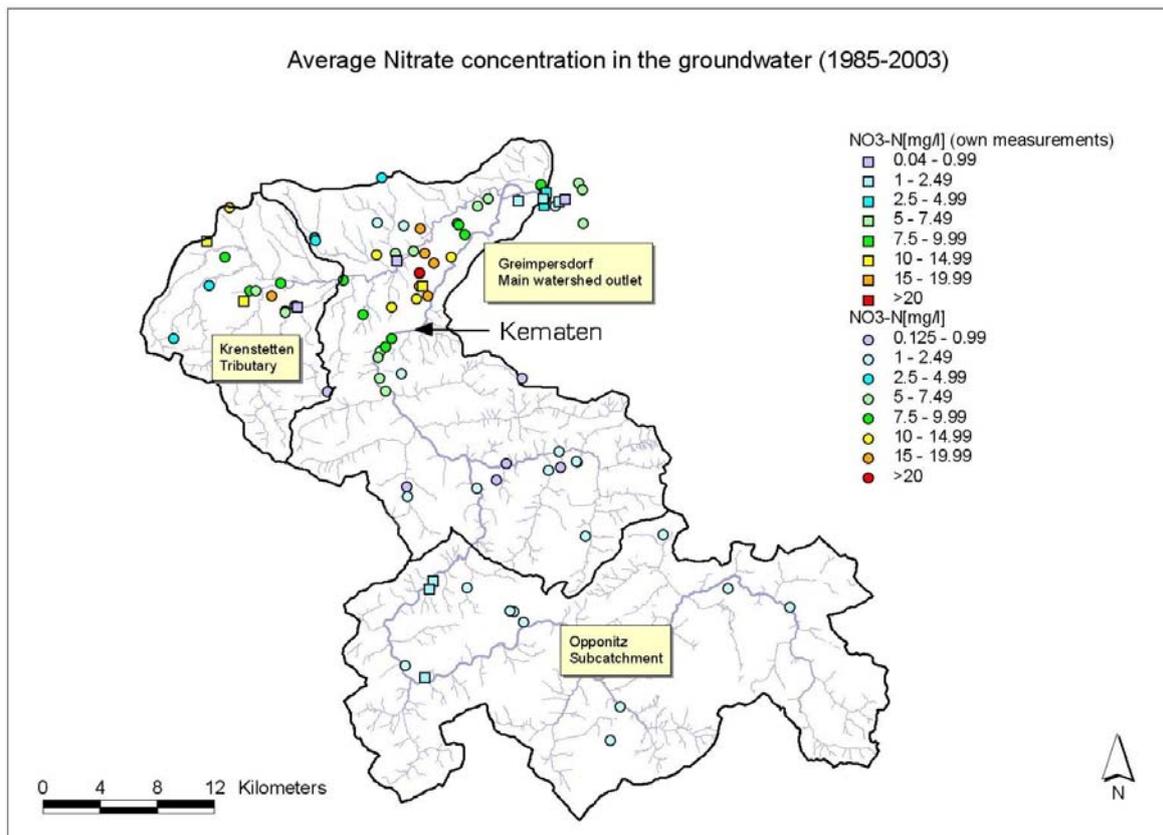


Figure 51: Average nitrate concentrations in the groundwater of the Ybbs catchment (1985-2003)

Due to geological conditions most of the groundwater observation wells are located in the northern parts of the catchment towards the watershed outlet. There, higher fractions of large-area porous aquifers are located. Moving towards the upstream catchment parts (in the south of the catchment) bedrocks and small valleys with only small local aquifers formed by river deposits become dominant. In this part of the catchment a considerable number of karst springs are located. Particularly in the Opponitz subcatchment and the Greimpersdorf subcatchment upstream of Kematen nitrate levels in groundwater are very low. In Krenstetten subcatchment and Greimpersdorf subcatchment downstream of Kematen, average nitrate levels in groundwater are considerably higher, since this part of the Ybbs catchment is dominated by agricultural activity. There, geohydraulic conditions in the porous aquifers are characterised by an almost parallel flow direction of the groundwater flow to the major rivers, what was confirmed by small-scale analyses in terms of groundwater-surface water interactions using multi-level wells in the riparian zone of the Ybbs river at the watershed outlet Greimpersdorf (Zessner et al. 2004).

Similar to the analyses of observations in the Wulka catchment, the groundwater observation wells were grouped in regard to the distances from surface water: one group with > 100m distance to surface water and the second group with < 100m distance to surface water. This diversion was applied only for the observation wells, which are located in the downstream part of the Ybbs catchment, where porous aquifers are present. The observation wells in remaining parts of the Ybbs catchment upstream of Kematen have been introduced into the analyses as a separate, third group.

That denitrification also takes place in the unsaturated and saturated zone of the Ybbs catchment could be shown clearly by the observations of the groundwater and surface water nitrogen concentrations, and is presented in Figure 52. The cumulative distribution functions of the observed TIN concentrations in groundwater for observation wells in the Krenstetten subcatchment and the Greimpersdorf subcatchment downstream of Kematen with >100m distance to the surface water and with <100m distance to the surface water as well as TIN concentrations of the groundwater in the part of the catchment upstream of Kematen are shown in comparison to the TIN concentrations in the surface water of the Ybbs catchment. In addition to the observations, the cumulative distribution function of the calculated potential nitrogen concentration in the leakage water is shown, which was calculated from the area-specific nitrogen surplus distribution at the municipality level in connection to the distribution of the average groundwater recharge rates.

Again, from the distributions of the area-specific nitrogen surpluses and the groundwater recharge rates the potential nitrogen concentration in the leakage water was calculated, which is shown as a cumulative frequency (black line) in Figure 52. On average, 50% of the calculated cumulative nitrogen concentrations in the leakage water exceeded 15 mgN/l, what is considerably lower in comparison to calculated potential leakage water concentrations of the Wulka catchment. Due to the larger average groundwater recharge rates in the Ybbs catchment (see chapter 4.5) nitrogen concentrations are significantly lower, since the area-specific nitrogen surplus on the catchment area is in the same order of magnitude.

The cumulative frequency distribution of the nitrogen concentrations in the groundwater with >100m distances to surface water (red line) show largely

decreased nitrogen concentrations in comparison to calculated potential nitrogen concentrations in leakage water (grey arrow in Figure 52). In average, 50% of the observed nitrogen concentrations in the groundwater with >100m distance to surface water exceeded 6 mgN/l. This decrease is caused by denitrification in the soil and in the groundwater, since also in the Ybbs catchment total inorganic nitrogen consists predominantly of nitrate (in average 97% of TIN).

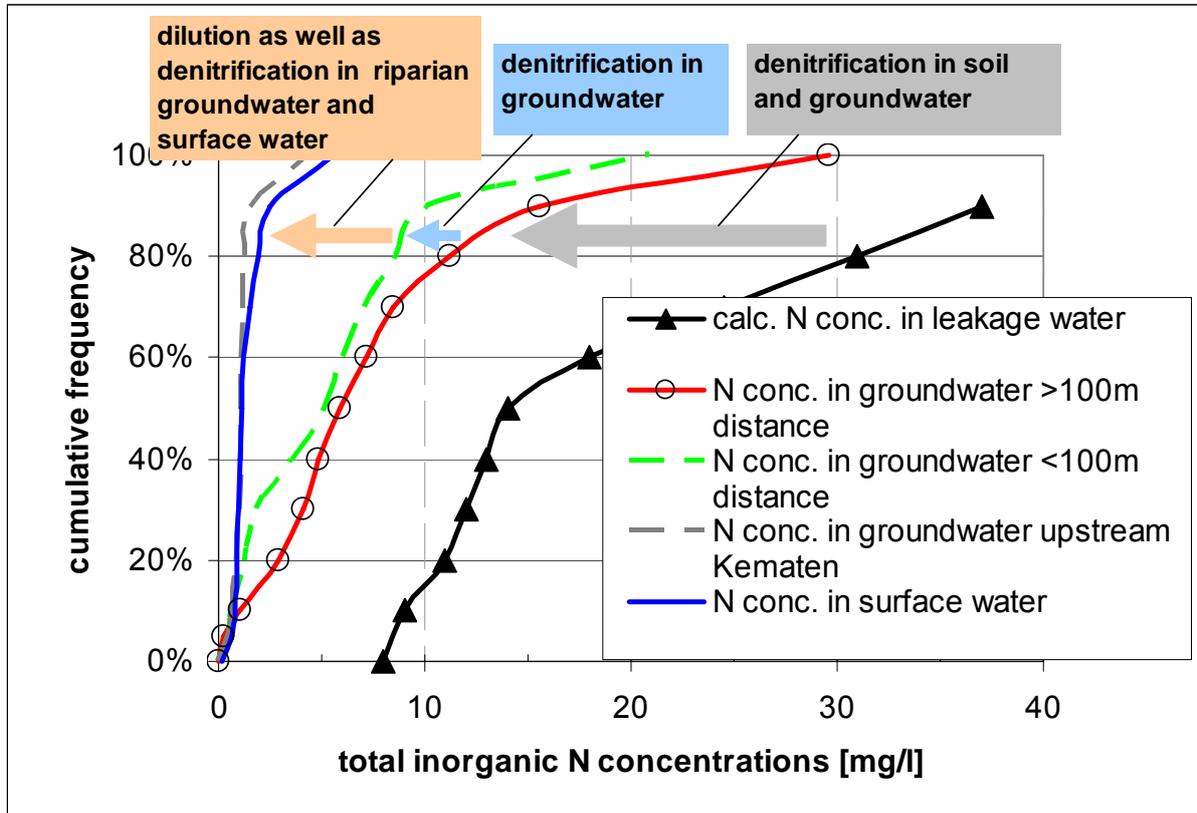


Figure 52: Cumulative distribution function of the observed total inorganic nitrogen concentrations in the groundwater with > 100m distance, with < 100m distance to the surface water, in the groundwater in catchment parts upstream of Kematen and in the surface water (1992-2002) in relation to the calculated potential nitrate concentrations in the leakage (percolation) water

A further decrease in the nitrogen concentrations in the groundwater is observable towards the surface water (blue arrow in Figure 52), but with much lower significance in comparison to the Wulka catchment. The nitrogen concentrations which were observed in groundwater of the Ybbs catchment with <100m distance to surface water (green line) show only slightly lower nitrate concentrations compared to groundwater observation wells with >100m distance to surface water. This decrease can be attributed to denitrification in the groundwater and reveals a lower denitrification intensity compared to the Wulka catchment. In average, 50% of the observed nitrogen concentrations in groundwater wells with <100m distance to surface water exceeded 5 mgN/l. Due to predominant groundwater flow conditions in Krenstetten subcatchment and Greimpersdorf subcatchment downstream of Kematen parallel to the surface water, via differentiation of groundwater observation wells in terms of distances to surface water not necessarily the length of groundwater flowpath is considered. Groundwater/surface water interactions in river-near groundwater observation wells may influence the observed nitrogen concentrations and result in a deficient assessment of denitrification in the groundwater in this part of the Ybbs catchment.

The nitrogen concentrations in the groundwater, which were observed in the part of the catchment upstream of Kematen (grey line in Figure 52) show considerably lower nitrogen levels compared to the groundwater concentrations in the part downstream of Kematen. Due to the predominance of forested areas in this part of the catchment, nitrogen inputs to the groundwater are determined by much lower fertilizer applications and atmospheric deposition (see Table 7), what results in comparably low groundwater nitrogen levels.

The observed nitrogen concentrations in the surface water follow the low nitrate concentrations observed in the groundwater in the part of the catchment upstream of Kematen (blue line in Figure 52). The nitrogen concentrations in the surface water are largely determined by groundwater discharges to the rivers in the upstream part of the Ybbs catchment (predominantly in Opponitz subcatchment). Even at the gauging station Opponitz 70-75% of the total river discharges at the main watershed outlet Greimpersdorf were observed, and that results in a significant dilution of the nitrogen contributions by groundwater flow, which are discharged to the rivers in the part of the catchment downstream of Kematen. Thus, the decrease (orange arrow in Figure 52) in nitrogen concentrations from riparian groundwater to surface water in this part of the catchment is caused by denitrification in the riparian groundwater and in the surface water, but to a considerable extent by dilution too.

To clearly attribute the decrease in groundwater nitrogen concentrations to denitrification, the observed nitrogen concentrations in groundwater were compared to the observed chloride concentrations, what is shown in Figure 53. Whereas the nitrate concentrations decrease slightly towards the surface water, no significant decreases in the chloride concentrations towards the surface water is observable, if the groundwater observations downstream of Kematen are considered. So, for this part of the catchment dilution processes are unlikely to be responsible for the observed drastic decrease in nitrogen concentrations in the groundwater. In comparison to the observed nitrate concentrations in the surface water, dilution effects due to the dominant discharges from upstream parts of the Ybbs catchment (Opponitz subcatchment) were observed, which can be confirmed also by the comparison in Figure 53. It can clearly be seen that in the part of the catchment upstream of Kematen the extremely low nitrate concentrations in the groundwater coincide with distinctively low chloride concentrations in the groundwater. These low levels are caused by high groundwater recharge rates (see Table 16), which cause extreme dilution effects in the groundwater quality parameters. Surface water concentrations of nitrate and chloride reflect a mixture of groundwater concentrations from the part upstream of Kematen and the river-near groundwater from the part downstream of Kematen, what confirms the significant influence of dilution of groundwater exfiltrations in the part downstream of Kematen with surface water from catchment parts upstream of Kematen.

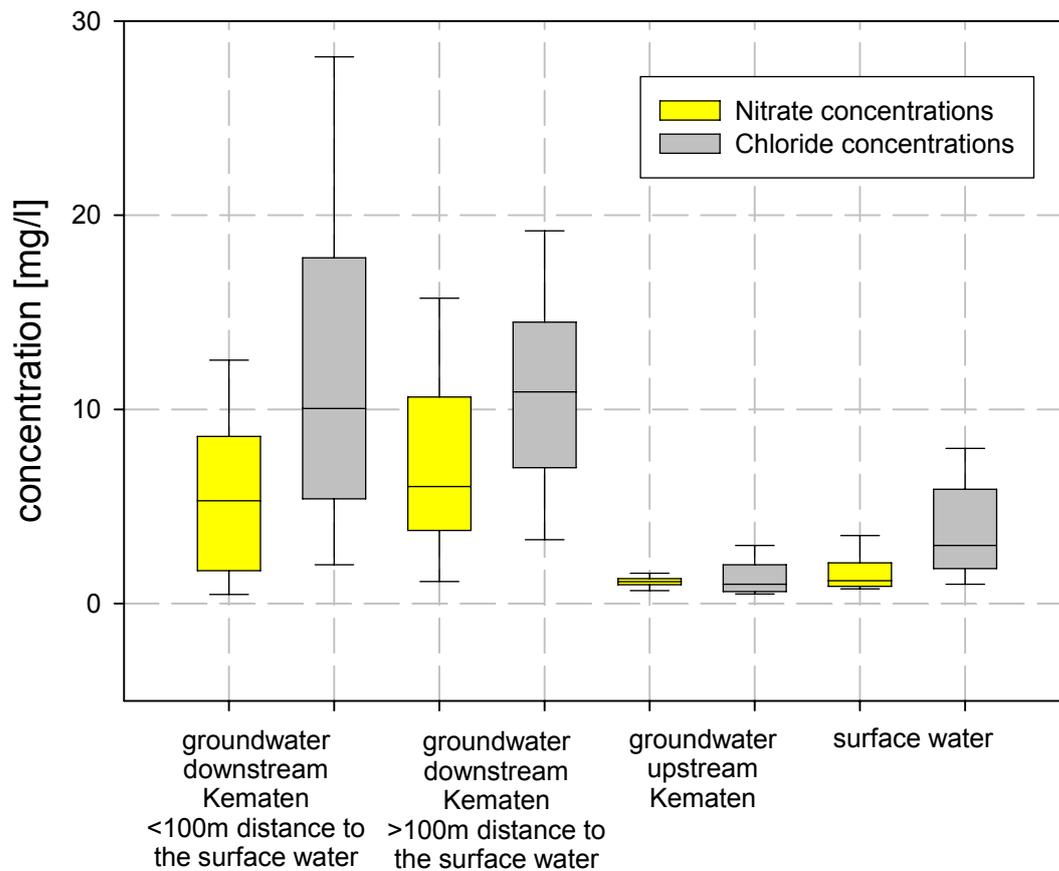


Figure 53: Comparison of observed nitrate and chloride concentrations in the groundwater of the Ybbs catchment with <100m and >100m distance to surface water for the part downstream of Kematen in comparison to the groundwater in the part upstream of Kematen and the surface water

To assess denitrification in the groundwater of the Ybbs catchment, also the oxygen level in the groundwater has to be considered. Generally, the oxygen status of the groundwater is higher compared to the groundwater of the Wulka catchment (see Figure 54). Oxygen levels in the groundwater of the Ybbs catchment tend to decrease towards the surface water. This was already observed for the Wulka catchment.

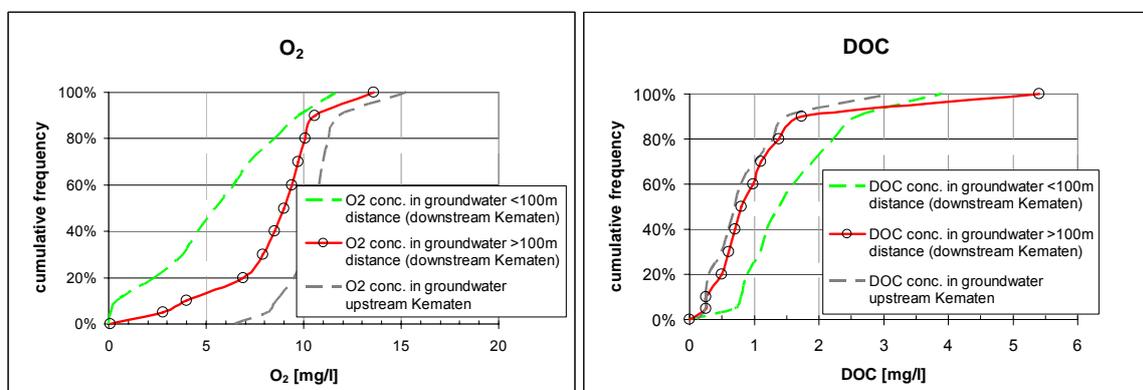


Figure 54: Cumulative distribution function (CDF) of O₂-concentrations and DOC concentrations in the groundwater with < 100m and > 100m distance to surface water for the part downstream of Kematen and for the groundwater upstream of Kematen (1992-2002)

Oxygen levels in the groundwater of the part upstream of Kematen indicated the strong influence of the catchment hydrology on oxygen supply of the groundwater. Due to large groundwater recharge rates in connection with low nutrient and carbon inputs from atmospheric deposition and anthropogenic activities in this part of the catchment, oxygen concentrations in the groundwater are very high in the groundwater. Denitrification in the groundwater of the part upstream of Kematen is unlikely to occur, since nitrate concentrations are very low and 70% of measured oxygen concentrations exceeded 10 mgO₂/l. Additionally, DOC concentrations are the lowest in this part of the catchment as indicated by Figure 54.

For the part of the catchment downstream of Kematen 90% of the observed O₂-concentrations in the observation wells with >100m distance to the surface water exceeded 5 mgO₂/l, the river-near groundwater with <100m distance to the surface water showed significant lower oxygen levels in groundwater (in average, 40% of observed O₂-concentrations in the groundwater exceeded 5 mgO₂/l). Towards the surface water decreasing O₂-concentrations in the groundwater could be observed similarly to decreasing nitrogen concentrations in the groundwater, and reduced O₂-concentrations confirm favourable conditions for denitrification in the groundwater, particularly in the riparian groundwater. Generally, reduced denitrification in the groundwater of the Ybbs catchment in comparison to the Wulka catchment highly corresponds to the observed elevated oxygen concentrations in the groundwater.

Dissolved organic carbon concentrations (DOC) in the groundwater (see Figure 54) tend to increase with decreasing distance to the surface water downstream of Kematen. On average, 50% of the DOC concentrations in the groundwater exceeded 0.8 mgDOC/l and 1.4 mgDOC/l for the observation wells with >100m distance and <100m distance to surface water, respectively. According to chapter 2.1.3, on average 0.73-1.28 mgNO₃-N/l can be denitrified using these average DOC concentrations in the groundwater. The observed DOC concentrations in the groundwater are too low to supply sufficient organic carbon for denitrification in the groundwater. Thus, fossil organic carbon sources or alternative electron donors are likely to be used for denitrification in the groundwater of the Ybbs catchment too (Hiscock et al. 1991, Wassenaar et al. 1991, Polzer 2005).

Riparian soils tend to have higher organic carbon contents because of enhanced interactions with surface water (seasonal flooding) compared to hillslope soils. Enhanced dynamics in groundwater tables in the riparian groundwater are likely to result in elevated DOC concentrations in riparian groundwater because of enhanced DOC leaching by groundwater in riparian areas. Figure 55 indicates similarly to the Wulka catchment, decreasing groundwater table depth towards the surface water with increasing fluctuations in groundwater table, which are characterised by increased standard deviation of the observed groundwater table.

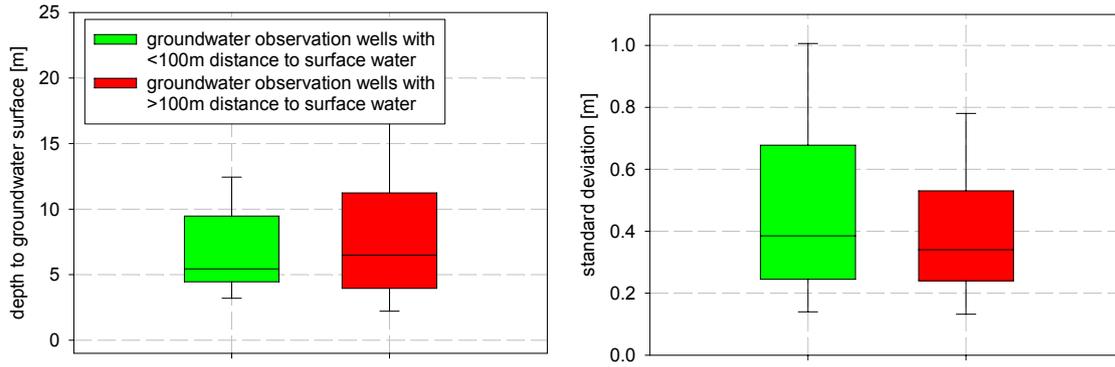


Figure 55: Average groundwater table depth and standard deviation of groundwater table depth of groundwater observation wells with <100m and >100m distance to surface water

Observed Fe^{2+} -concentrations did not show large discrepancies related to the distance of the observation wells to the surface water (see Figure 56). Generally, Fe^{2+} -concentrations in the groundwater of the Ybbs catchment are very low and exceed 0.2 mgFe/l in only 5% of all measurements. Thus, Fe^{2+} -concentrations do not reveal reducing conditions in the groundwater of the Ybbs catchment, what coincides with elevated oxygen levels in groundwater.

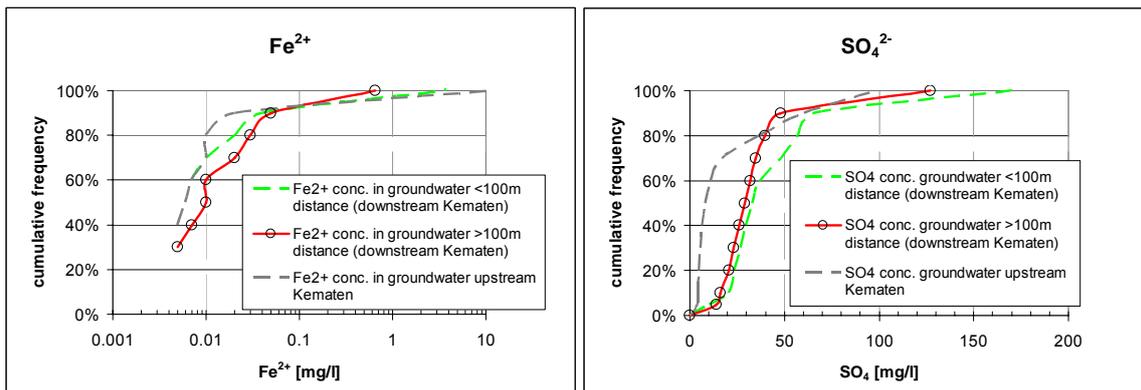


Figure 56: Cumulative distribution function (CDF) of Fe^{2+} concentrations and SO_4^{2-} concentrations in the groundwater with < 100m and > 100m distance to the surface water for the part downstream of Kematen and for the groundwater upstream of Kematen (1992-2002)

In regard to the observed sulphate concentrations an increase with decreasing nitrate concentrations towards the surface water in the groundwater of the Ybbs catchment could be observed (see Figure 56 and Figure 57). Since DOC concentrations in the groundwater are comparatively low, this increase could be an indication for autotrophic denitrification in the groundwater of the Ybbs catchment.

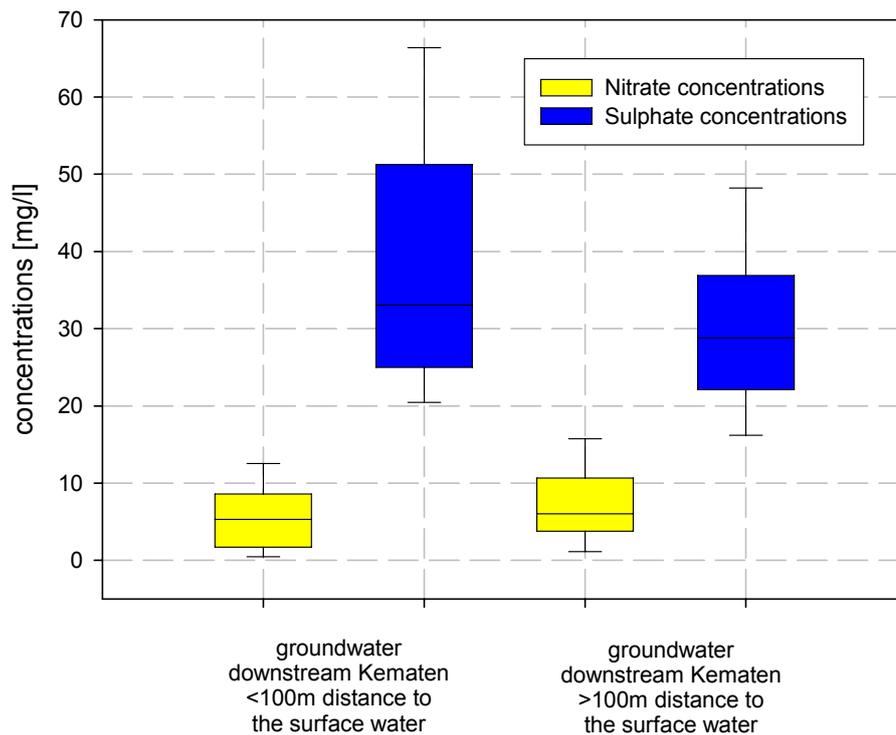


Figure 57: Comparison of observed nitrate and sulphate concentrations in the groundwater of the Ybbs catchment with <100m and >100m distance to surface water for the part downstream of Kematen

Figure 58 illustrates the groundwater conditions of the Ybbs catchment in terms of the anion composition. In comparison to the groundwater of the Wulka catchment the anion composition of the groundwater of the Ybbs catchment is significantly dominated by lower nitrate and chloride equivalents due to generally lower concentrations. Similarly the hydrogen carbonate equivalents dominating the anion composition of the groundwater in general. An increase in the hydrogen carbonate equivalents due to heterotrophic denitrification with decreasing nitrate equivalents in the groundwater was not observable, what confirms the assumption of nitrate reduction in the groundwater predominantly by autotrophic denitrification.

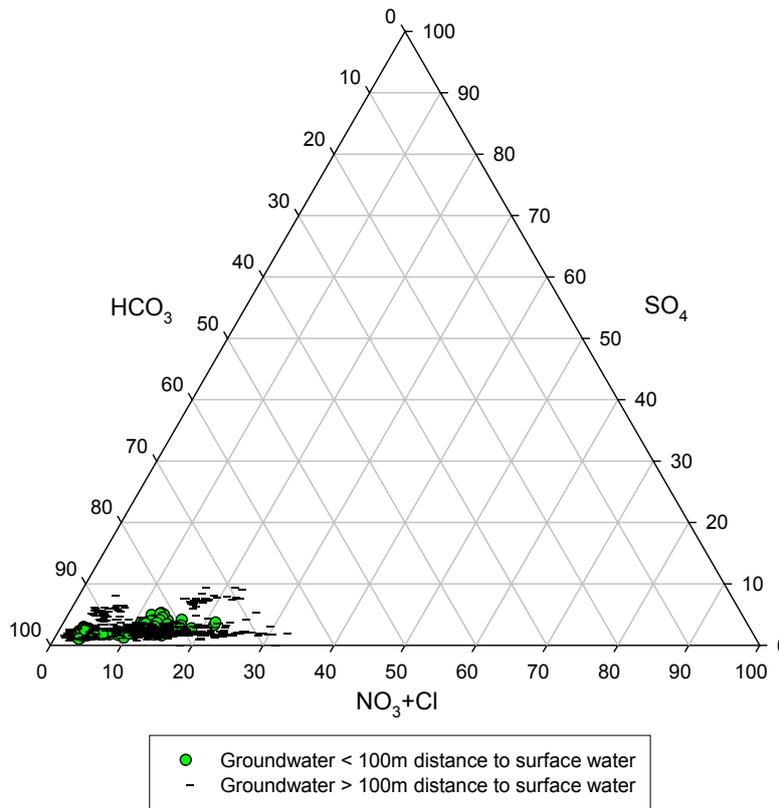


Figure 58: Tertiary plot of anion mol equivalents in groundwater observations of the Ybbs catchment with fractions of specific anions on total anion amount

The relation of the nitrate concentrations in groundwater to different land use classes is shown in Figure 59. The highest average nitrate concentrations were observed in groundwater wells located in regions with arable land due to fertilizer applications and the elevated nitrogen surplus on agricultural areas. The average nitrate concentrations in forested areas or regions with evergreen land are nearly equal and comparable to those in settlements. Areas with no vegetation show elevated nitrogen concentrations in comparison to forest or evergreen land. Due to nitrogen mineralisation processes of organic N pool or of residue, nitrogen leaching from non-vegetated soils can be elevated due to missing plant cover, which is able to take up the available nitrogen. In general, the variance of the nitrate concentrations measured in the groundwater of the Ybbs catchment is high in all land use classes and except the arable land, no large discrepancies between nitrogen concentrations in groundwater attributed to land use classes could be observed.

The impact of different geological formations on nitrate concentrations in the groundwater is also shown in Figure 59. Generally higher concentrations of nitrate were observed in groundwater observation wells located in lower and higher terraces, bench gravels and sand streaks. They are located predominantly in the part of the catchment downstream of Kematen, which is mainly in agricultural use. The mean nitrate concentration is nearly equal in these formations, differences were observed in variances of the concentrations. The average nitrate concentrations in regions dominated by deposits are very low due to the location near the river and interaction with the surface water. In the consolidated formations almost low nitrate

concentrations were observed due to their location in the part of the Ybbs catchment upstream of Kematen with high annual precipitation and low nitrogen surpluses.

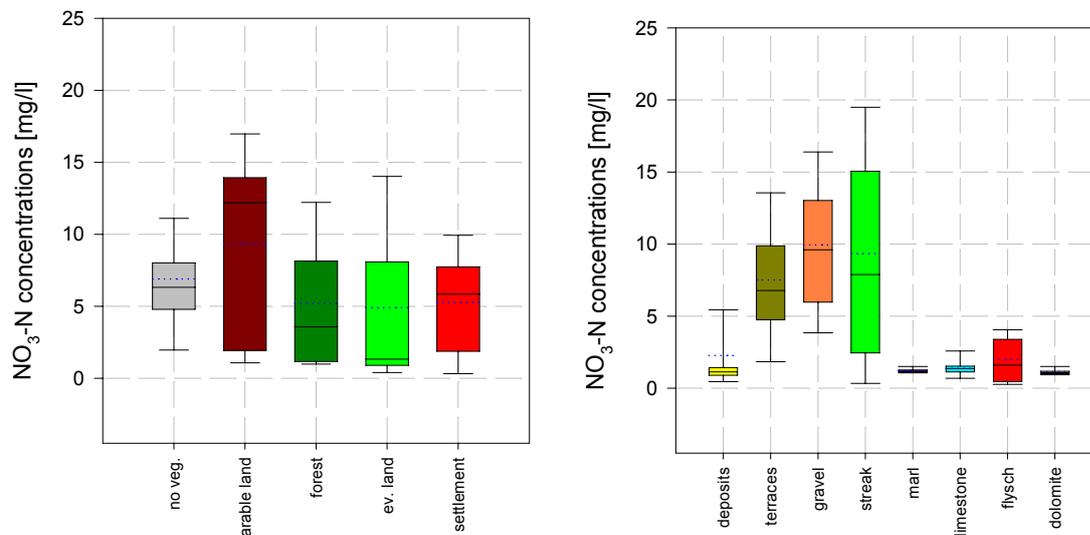


Figure 59: Nitrate concentrations in the groundwater in respect to the location of the groundwater observation wells in different land use classes and different geological formations

Generally, nitrate concentrations in groundwater in areas under agricultural use are significantly higher than in areas without agricultural activity (forests). Nitrate concentrations observed in the groundwater of the Ybbs catchment are lower in relation to the concentrations observed in the groundwater of the Wulka catchment.

In comparison to the Wulka catchment, denitrification in the groundwater of the Ybbs catchment was found to be less extensive in terms of reduction of nitrate levels, since the reduction of nitrate levels from the riparian groundwater to the surface water is significantly influenced by dilution. The observations indicated a lower average groundwater residence time, since elevated groundwater recharge rates cause higher water fluxes through the aquifers. Groundwater quality observations in the Ybbs catchment suggested nitrate reduction is likely to be dominated by autotrophic denitrification.

5.4 Summary and conclusions

It could be shown, that the catchment hydrology of the Ybbs catchment and the Wulka catchment significantly influences groundwater quality and surface water quality. Due to the high precipitation intensity in the Ybbs catchment and associated elevated groundwater recharge rates, concentrations of almost all parameters in the groundwater and surface water were generally lower compared to the Wulka catchment. As a result, nitrogen loss in groundwater by denitrification is assumed to be mainly affected by the different, catchment specific groundwater residence times.

Based on the observations of groundwater and surface water quality the following can be concluded:

- The reduction of inorganic nitrogen concentrations (mainly nitrate) from the topsoil and groundwater towards the surface water bodies can be definitely attributed to denitrification in soil and groundwater

- The lower groundwater recharge rates in the Wulka catchments and as a consequence, the higher groundwater residence times seem to favour anoxic groundwater conditions with zones of high denitrification with partially denitrification limitation by substrate availability (nitrate availability from nitrogen surpluses and groundwater recharge, DOC availability by percolation and availability of fossil organic carbon or alternative electron donors in deep aquifer layers)
- The higher groundwater recharge rates in the Ybbs catchment and therewith the lower groundwater residence times lead to generally lower concentrations in the groundwater, which reduces denitrification potential and results in comparably lower denitrification in the groundwater
- Correlations between nitrate and hydrogen carbonate equivalents underlined the expected heterotrophic denitrification in groundwater in the Wulka catchment (Figure 49), in the Ybbs catchment increases in sulphate concentrations suggested enhanced autotrophic denitrification activity in the groundwater
- In general, denitrification in the groundwater was lower in the Ybbs catchment compared to the Wulka catchment highlighting the significant influence of groundwater residence times on denitrification in the groundwater
- Changes in DOC concentrations in groundwater are not solely the result of denitrification and can be attributed predominantly to enlarged groundwater table fluctuations in areas near the river system and interactions with organic-rich soil zone
- Fe^{2+} concentrations in groundwater are not suitable for the determination of denitrification; they may be used as indicators for reducing aquifer conditions
- The location of observation wells in specific land use classes or geological formations does not provide information about the denitrification capacity in the groundwater at its specific location
- Denitrification in groundwater can be observed along the groundwater flowpath; exact determinations of groundwater flow directions creates the precondition for determination of denitrification capacity in specific groundwater bodies more precisely

Nevertheless, significant indications were found in both catchments that nitrate reduction in groundwater by denitrification despite a high oxygen level is the major process for the reduction of nitrate concentrations in groundwater and as a consequence, the major process for a reduction of nitrogen emission from the groundwater to the surface waters.

6 Nitrogen emission estimations at the catchment scale

6.1 *Introduction and motivation*

Observations of groundwater and surface water quality at the Ybbs and the Wulka catchment indicated significant deviations between the catchments as a result of differences in dominant land utilisation practises and influences from catchment hydrology. Denitrification in the groundwater could be observed in both catchments to a different extent, which could be attributed to differences in water and nitrogen fluxes from soil to groundwater and from groundwater to surface water. Significant reductions in nitrogen levels in groundwater along the flowpath towards the surface water were the result. So assessing total nitrogen emissions to surface waters at the catchment scale requires the consideration of denitrification in groundwater to exactly determine diffuse nitrogen emissions quantitatively.

Nitrogen emission calculations were performed for the Ybbs and the Wulka catchment to identify the main nitrogen emission pathways and to quantify the total nitrogen emissions to the surface water as well as the relative contribution of individual emission pathways.

The SWAT 2000 model was already used for the estimation of spatial distributions and time dependent variations of the water balances and the runoff components. Once calibrated, the SWAT 2000 model was also used for nitrogen emission estimations. The main focus was on nitrate mobilisation by the individual simulated runoff components.

Additionally, the empirical emission model MONERIS (Behrendt et al. 1999), which was used in the daNUbs project for the calculation of nutrient balances for the 273 subcatchments of the Danube basin, was applied at the mesoscale for both Austrian case study regions.

Advantages and weaknesses of both models in regard to nitrogen emission calculations at the catchment scale are compared in this chapter. Based on the results of the water balance calculations, the results of the nitrogen balance calculations point out the processes of nitrate mobilisation and retention at the catchment scale connected to the simulated hydrological processes. Differences in temporal and spatial resolution of the modelling approaches are of importance in terms of fluctuations in nitrogen emissions from the catchments. To emphasise the linkage between hydrology and nitrogen emissions, basically the modelling concept with the high temporal resolution is preferable. Unfortunately, not all emission pathways are considered in the high resolution SWAT 2000 model. Thus, a complementary model application is useful to identify the long-term average nitrogen emissions with consideration of all emission pathways. To point out seasonal variations in hydrological components, which significantly restrict or support the nitrogen emissions at the catchment scale, is the major goal of the nitrogen balance calculations.

6.2 Nitrogen emission estimations using the SWAT 2000 model

6.2.1 Definitions in SWAT 2000 model

Based on the model definitions for the water balance calculations, the SWAT 2000 model was used for nitrogen balance calculations for the Wulka and the Ybbs catchment. The SWAT 2000 model is able to simulate nutrient turnover in soil profiles as well as nutrient emissions to surface water at the catchment scale. Effects of fertiliser application, soil characteristics, and nitrogen surplus distributions on soils as well as enrichment concentrations of nitrogen in the groundwater and influences of inlets from waste water treatment plants to the river are considered.

The SWAT 2000 model is able to consider nitrate, ammonia and organic nitrogen (fresh organic nitrogen, active organic nitrogen and stable organic nitrogen) and the turnover between these nitrogen species in the soil. Table 25 shows the processes which are considered by the SWAT 2000 model.

Table 25: Nitrogen turnover modelled by the SWAT 2000 model

Process	Description	Model restrictions
Decomposition	Breakdown of fresh org. N	in first soil layer only, T > 0°C
Mineralization (net)	Turnover from org. N to inorg. N	in first soil layer only, C : N < 20 : 1 T > 0°C
Immobilisation	Turnover from inorg. N to org. N	C : N > 30 : 1
Nitrification	Turnover from NH ₄ to NO ₃	T > 5°C
Volatilisation	Gaseous loss of NH ₃	T > 5°C
Denitrification	Turnover from NO ₃ -N to N ₂	soil water content >0.95, in soil profile only
N in rainfall	Nitrate added to the soil by rainfall	in the top 10mm only
Fixation	Nitrogen fixation by legumes	
Leaching	Leaching from soil	by surface runoff and lateral runoff only; contribution directly to surface water; leaching by percolation water to groundwater is not tracked through aquifer

The movement of nitrogen is simulated in the following way:

Nitrate: by surface runoff (top 10mm only), lateral runoff and percolation (to underlying layer)

Org. N: by surface runoff (attached to soil particles)

Fertilizer application

Based on fertilizer statistics on the community level for both catchments the fertilizer use was defined in the SWAT 2000 model. A differentiation between the use of mineral fertilizer and manure was made for the subcatchments of both catchments. The fertilizer application was defined in relation to the potential heat

units of the crops (plant growth is defined in the SWAT 2000 model relative to consumed heat units, they are used to define several stages of the plant growth in dependency of air temperature). Three times per year the fertilizer application was defined. For the Wulka catchment, the fertilizer application consisted of two mineral and one organic fertilizer applications per year. For the Ybbs catchment, the fertilizer application consisted of two organic and one mineral fertilizer applications per year. First fertilizer application was defined according to the initiation of plant growth. Second and third fertilizer applications were defined in middle of plant development and a certain time before plant harvest, respectively.

Groundwater (background) nitrate concentration

The nitrate concentration in the groundwater that enters the stream will be specified by the user. For both catchments the nitrogen concentrations in groundwater were defined based on surface water quality observations during low flow conditions for every subcatchment. For Krenstetten subcatchment surface water quality data were not available for the calculation period.

Initial nitrogen concentrations in the soil

Due to insufficient soil observation data initial nitrogen concentrations in the soil were not defined.

Soil enrichment ratio

Based on literature values (Strauss et al. 2004) the enrichment ratios for organic nitrogen (ratio of concentrations transported with the sediment via erosion in relation to the concentration in the soil surface layer) were defined at the catchment scale.

Nitrogen concentration in Rainfall

Based on observed deposition rates the concentration of nitrogen in the rainfall was defined at the catchment scale.

Contributions of the wwtp's

Based on the observations of effluent loads of waste water treatment plants the nitrogen loads to surface water were considered for both catchments.

Other important model parameter

In regard to the nitrogen turnover, further important model parameters have to be taken into account, which influence the simulation of nutrient cycle by the SWAT 2000 model:

- temperature
- water content in the soil layer
- bulk density of the soil layer
- content of organic carbon in the soil layer
- fraction of porosity from which anions are excluded (nitrate transport)
- Humus mineralization factor for active organic nitrogen
- Plant uptake distribution factors for nitrogen
- Percolation coefficients for nitrogen

Schoumans et al. (2003) and Grizzetti et al. (2003) reported the application of the SWAT 2000 model for nutrient emission and retention estimations. The complete description of N cycle by the SWAT 2000 model is reported by both authors. Denitrification is considered in the SWAT 2000 model in the soil layer only. Nitrate, which is not denitrified in the soil, is leached from the soil via percolation to the groundwater or is transported via lateral flow to surface water. After entering the groundwater surface, the nitrate is not tracked through the aquifer afterwards (Neitsch et al. 2001). Simulated groundwater nitrate concentrations which are contributed by the groundwater runoff to the surface water, are defined by the user based on observed nitrate concentrations in surface water during low flow periods. Thus, nitrate loads transported by the groundwater are not the result of modelling nitrate transport through the groundwater as a function of nitrate inputs via percolation and nitrate reduction via denitrification. In fact, denitrification in the groundwater can be obtained from the model results via determination of the differences between the simulated nitrate input to the groundwater surface by groundwater recharge and the user-defined nitrate outputs via groundwater to surface waters. However, denitrification in groundwater is not simulated explicitly. Processes of nitrogen turnover in the groundwater via denitrification and influences of hydrological conditions on denitrification in groundwater (different groundwater residence times) can not be described using the SWAT 2000 model.

To overcome this problem, a linked application of watershed models and groundwater models is desirable and reported in literature (Sophocleous et al. 2000, Sophocleous et al. 1999, Perkins et al. 1999). The linkage requires a well calibrated watershed model first, and secondly a previously calibrated groundwater model operating both on similar time steps and compatible spatial resolutions.

Thus, other methods have to be taken into account in addition for the estimation of nitrogen losses in groundwater by denitrification. Nitrogen emission calculations were performed for both catchments using the SWAT 2000 model to account for differences between the catchments in terms of nitrogen transport by simulated runoff components with variability in catchment hydrology (differences in contributions of individual runoff components). Additionally, information can be obtained using the model about dominating pathways of nitrogen mobility and their seasonal relevance.

6.2.2 Results from nitrogen emission calculations

In Figure 60 the long-term average nitrate loads are shown, which were calculated for the Ybbs catchment using the SWAT 2000 model for the surface runoff, the lateral runoff and the groundwater runoff (by user definitions) in relation to the nitrate transport by percolation from soil to the groundwater and in comparison to the simulated long-term average runoff components.

Nitrogen emissions to the surface water are simulated by the SWAT 2000 model via surface runoff and lateral runoff. The lateral runoff contributes by far the highest fraction of nitrate directly to the surface water. Based on the concept of groundwater flow stimulation, which was discussed in chapter 2.2.3, only a small fraction of the lateral runoff infiltrates directly into the surface water bodies. Most of the catchment areas are located far away from the stream, and due to the distance most of the lateral runoff infiltrates into the groundwater and stimulates the exfiltration of river-near groundwater into the surface water. Nitrogen which is transported via lateral

runoff, is transported according to concept of groundwater flow stimulation predominantly to the groundwater first and then by groundwater runoff to the surface water with an adequate nitrate reduction by denitrification in the groundwater. By model definitions the contributions by lateral runoff differ from this concept. Calculated nitrogen emissions by the lateral runoff to the surface water are therefore not subject of denitrification and may impact calculated total nitrogen loads of the surface water.

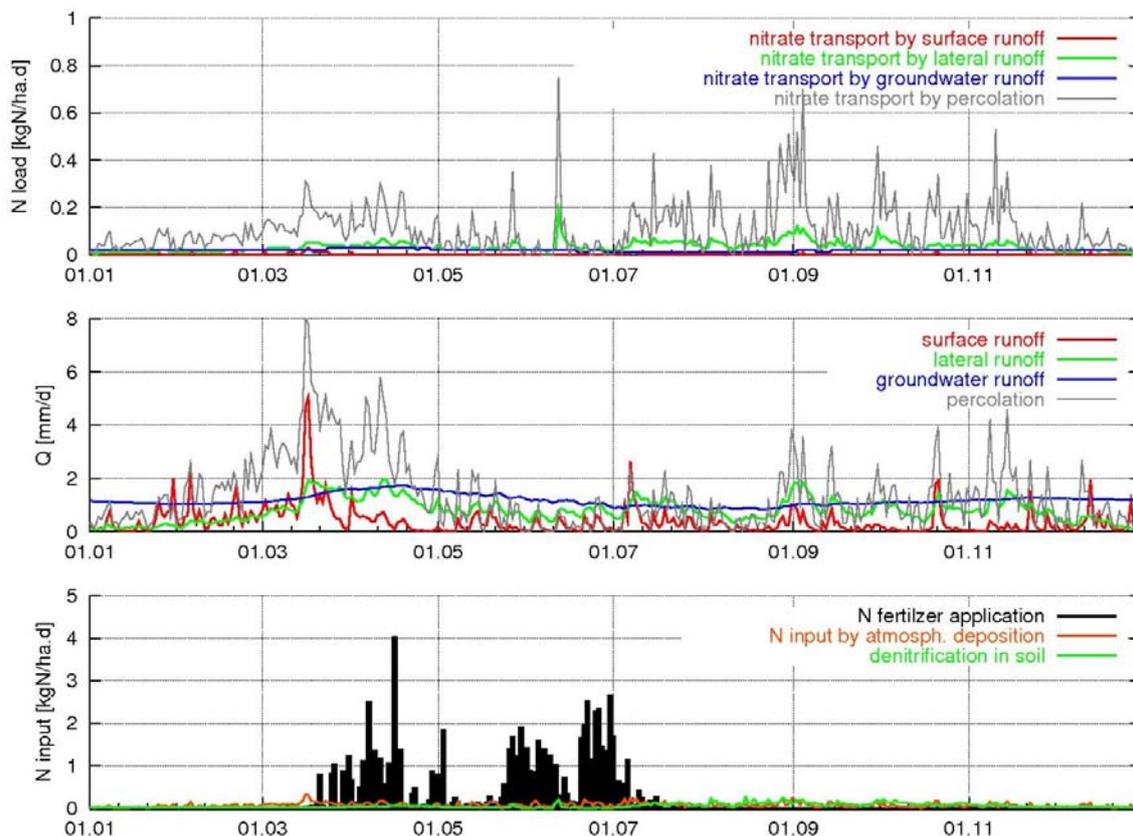


Figure 60: Comparison of simulated runoff components surface runoff, lateral runoff, groundwater runoff and percolation compared to long-term average nitrate loads via surface runoff, lateral runoff, groundwater runoff and percolation with consideration of N inputs by long-term average fertilizer applications and atmospheric deposition and N losses by long-term average denitrification in soil calculated for period 1992-2000 for the Ybbs catchment

Figure 60 indicates that the surface runoff contributes as expected the lowest fractions of nitrate to the surface water. Nitrate loads by the groundwater runoff, which are defined by the user based on observed surface water nitrate concentrations, indicate significant nitrate reductions by denitrification in the groundwater.

By far the highest fraction of nitrate is leached out of the soil by percolation towards the groundwater surface. Compared to the nitrate loads which are transported by groundwater runoff to the surface water, a large discrepancy is observable. This fraction of nitrate is assumed to be removed from groundwater via denitrification, but this process is not simulated by the model. Because of the lack of consideration of the linkage between nitrate loads by percolation (nitrate loads from soil towards the groundwater surface) and the nitrate loads transported by the groundwater runoff, the SWAT 2000 model is not able to establish the relationship between nitrogen emissions due to land use management and adequate nitrogen

emissions by groundwater runoff to the surface water. Figure 60 indicates also that the highest nitrogen inputs to the Ybbs catchment are caused by fertilizer applications.

Due to the predominance of the nitrate leaching by percolation in Figure 60, the nitrate loads to the surface water by the three main runoff components are shown in Figure 61 separately in comparison to the nitrogen losses from the soil by percolation and denitrification. Figure 61 indicates that the nitrate loads to surface water by the lateral runoff show the largest fluctuations with strong connections to the soil water content, and therefore to the percolation. The groundwater runoff contributes more or less a constant nitrate load to the surface water. Nitrate loads to the surface water by the surface runoff can be observed only very sporadically.

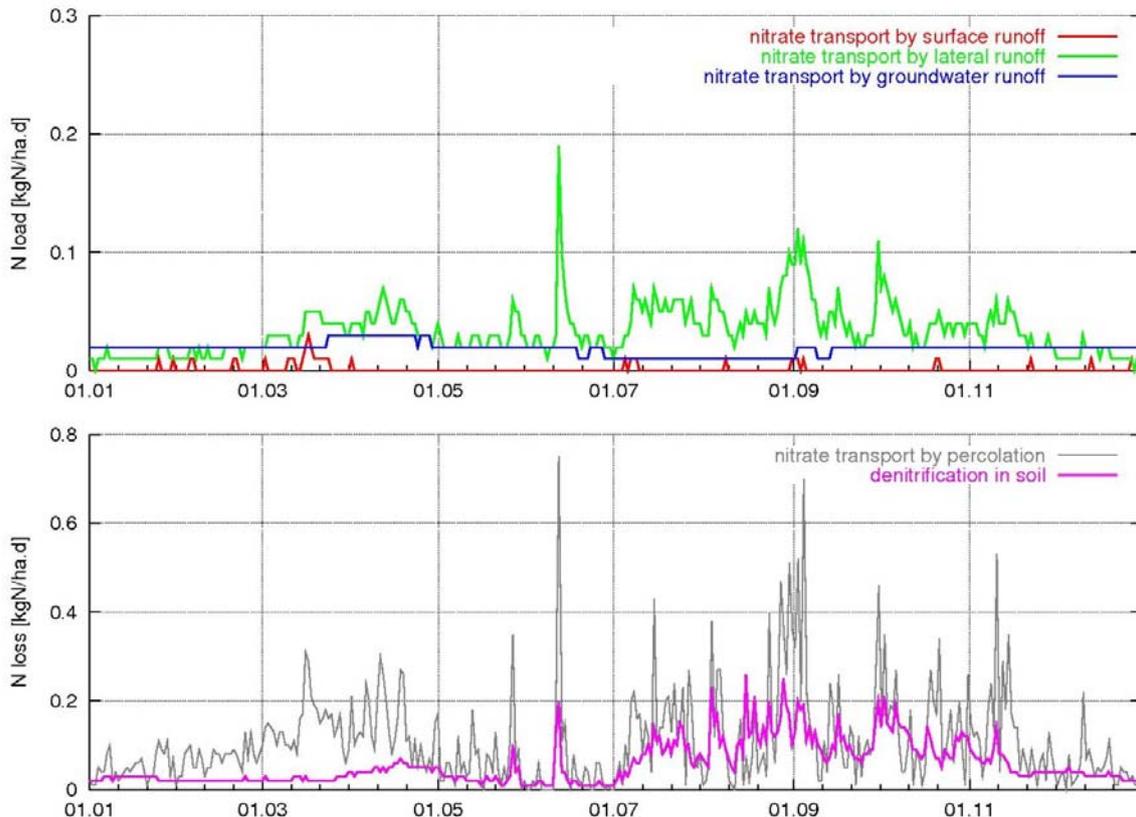


Figure 61: Simulated long-term average nitrate loads via surface runoff, lateral runoff and groundwater runoff in comparison to long-term average nitrate losses by denitrification in the soil and percolation to the groundwater calculated for period 1992-2000 for the Ybbs catchment

Denitrification in the soil mainly depends on three factors: soil organic carbon content, temperature and soil water content. The soil organic carbon content is constant within a soil type and defines the denitrification potential of the soil. Seasonal variations are caused by the two latter factors controlling denitrification. As shown in Figure 61, denitrification is strongly connected to percolation (soil water content) and thus to groundwater recharge. Additionally, during winter and spring, nearly no denitrification activity can be observed due to low temperatures.

The detailed simulated nitrogen cycle by the SWAT 2000 model is shown in Figure 62. Related to the total nitrogen loads to surface water the surface runoff, the lateral runoff and the groundwater runoff contribute about 4%, 60% and 33%, respectively. The remaining 3% of nitrate loads to surface water are contributed by point sources.

According to Figure 62, the difference between nitrogen inputs to surface water and nitrogen outputs by surface water indicates a loss of organic nitrogen as well as of nitrate by mineralisation and denitrification in the surface water of the Ybbs catchment. The average denitrification in the river was estimated to be about 1.3 kgN/ha per annum. The calculated average nitrogen river load of 19.9 kgN/ha per annum coincides well with the observations (see Table 6), where the average area specific nitrogen river load for the total Ybbs catchment was estimated to about 19 kgN/ha per annum.

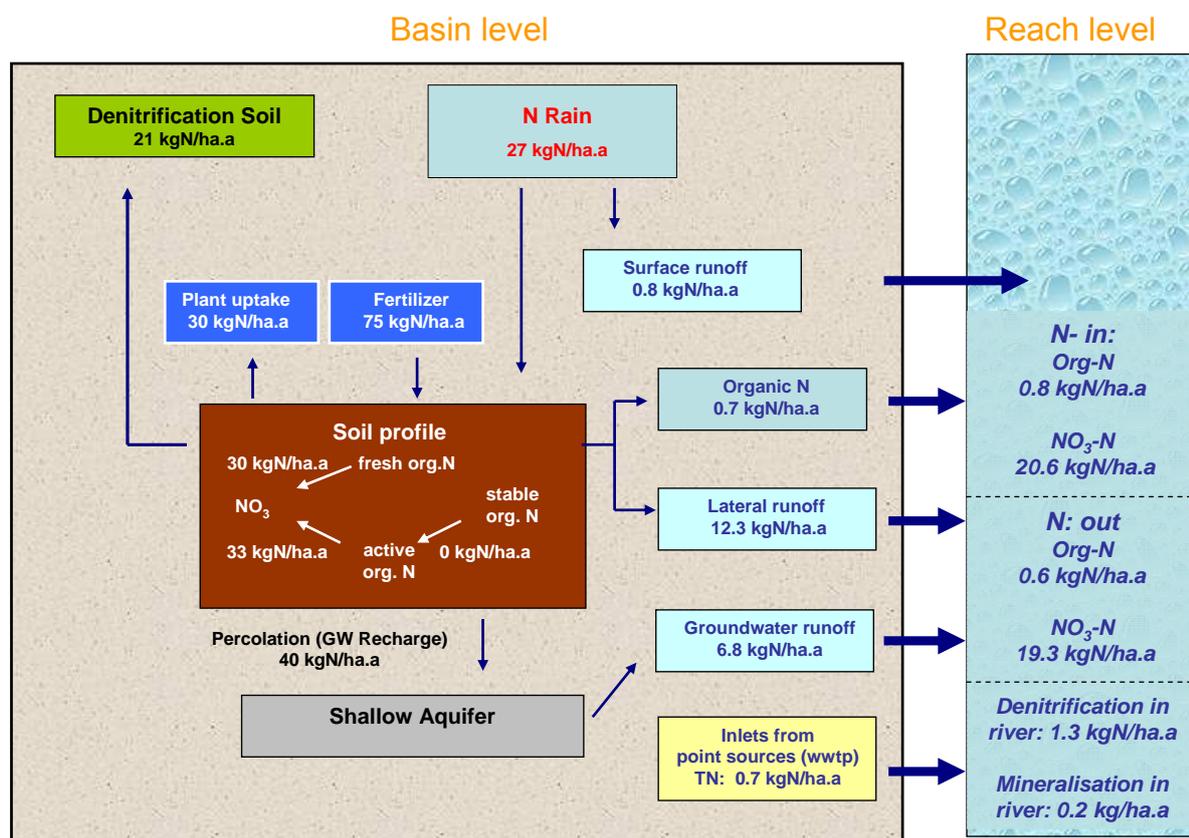


Figure 62: Detailed simulated nitrogen cycle for the Ybbs catchment with average annual values of the nitrogen balance calculated for the period 1992-2000 using the SWAT 2000 model

The average simulated denitrification in the soil of the Ybbs catchment was 21 kgN/ha*a for the Ybbs catchment for the main watershed outlet. This is in line with our own experiences from former investigations in the Ybbs catchment (Kroiss et al. 1998). In comparison to Table 7 nitrogen uptake by plants seemed to be underestimated by the model. From Figure 62 it appears that the calculated nitrogen balance for the Ybbs catchment is well in line with observed nitrogen in-stream loads (see Table 6).

Nitrogen emission calculations were also performed for the Wulka catchment. Comparing the simulated long-term average runoff components to the transported long-term average nitrate loads (Figure 63), similar tendencies in the Wulka catchment could be observed in terms of nitrate transport by the individual runoff components which were already identified for the Ybbs catchment. In the Wulka catchment no contribution of the surface runoff to nitrate transport to the surface water was calculated. Transported nitrate loads by the groundwater runoff are very small. Similar to the Ybbs catchment, the highest nitrate loads are transported directly to the surface water by the lateral runoff temporarily during periods with

enhanced percolation. The highest fraction of nitrate is leached out of the soil by percolation to the groundwater surface. Unfortunately, the SWAT 2000 model does not provide information about nitrate loads which are transported from the soil to the surface water by the runoff from tile drained areas.

For both catchments an increased nitrate transport during the second half of the year is observable. Regardless of the timing of fertilizer applications, the amount of the applied fertilizers seem to exceed the nitrogen uptake by plants and is therefore, particularly after harvesting, easily available for leaching from the soil to the groundwater.

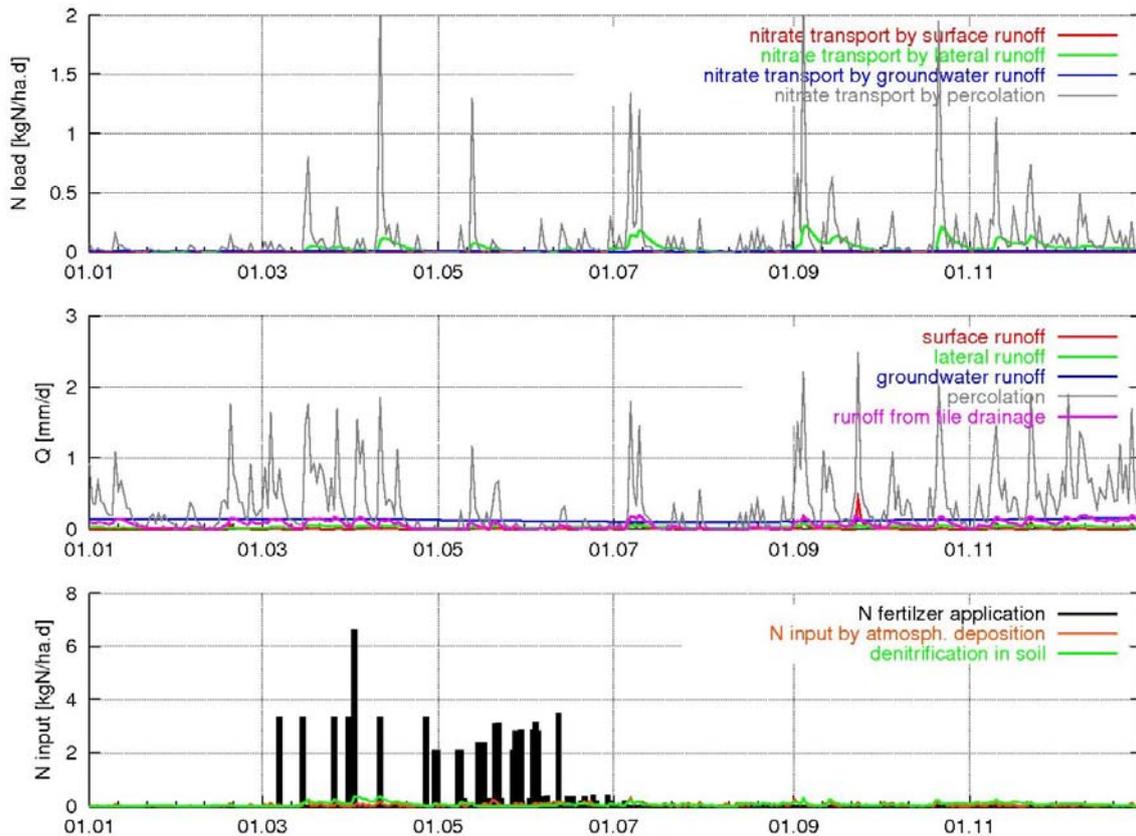


Figure 63: Comparison of simulated runoff components surface runoff, lateral runoff, groundwater runoff, percolation and runoff from tile drainages compared to long-term average nitrate loads via surface runoff, lateral runoff, groundwater runoff and percolation with consideration of N inputs by long-term average fertilizer applications and atmospheric deposition and N losses by long-term average denitrification in soil calculated for period 1992-1999 for the Wulka catchment

The three main runoff components are shown in Figure 64 separately in comparison to the nitrogen leached from the soil by percolation and to denitrification. Surface runoff does not contribute any nitrate to the surface water. The groundwater runoff contributes again a small constant load of nitrate to the surface water. The largest nitrate loads to the surface water are contributed by the lateral runoff, which is strongly connected to the percolation from the soil. Nitrate reduction by denitrification in soil shows again a strong relation to elevated temperatures and high soil water contents. Denitrification in the soil of the Wulka catchment can be observed in contrast to the Ybbs catchment in spring too, what is the result of higher temperatures and a shorter period of snow melt in the Wulka catchment.

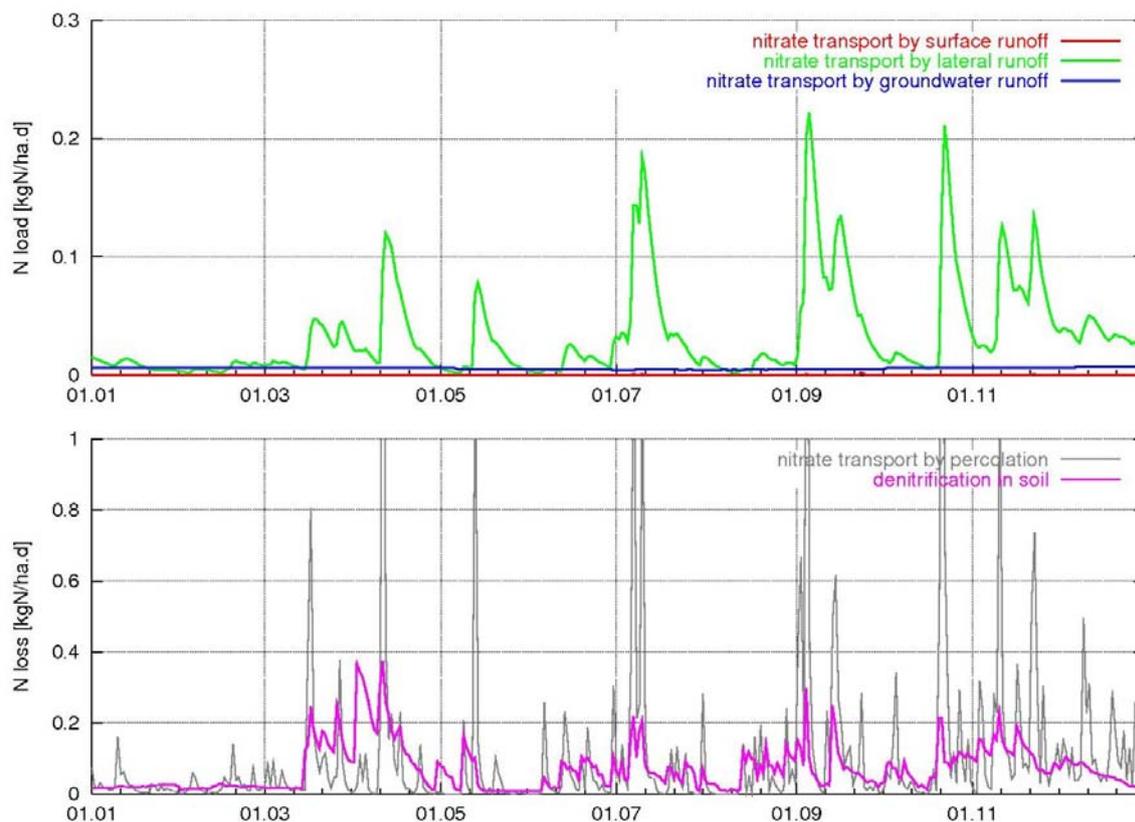


Figure 64: Simulated long-term average nitrate loads via surface runoff, lateral runoff and groundwater runoff in comparison to long-term average nitrate losses by denitrification in the soil and percolation to the groundwater calculated for period 1992-1999 for the Wulka catchment

The detailed simulated nitrogen cycle by the SWAT 2000 model is shown for the Wulka catchment in Figure 65. Related to the total nitrogen loads to the surface water the surface runoff, the lateral runoff and the groundwater runoff contribute about 0%, 79% and 14%, respectively. The remaining 7% of nitrate loads to surface water are contributed by point sources. Mineralisation and denitrification processes were not estimated in the surface water of the Wulka catchment by the model. A main deficiency of the SWAT model is that for the Wulka catchment the runoff from tile drained areas was considered for water fluxes, but no adequate nitrate transport by the runoff from tile drainages was simulated.

The calculated average nitrogen river load was estimated to 15.5 kgN/ha*a and exceeded the observed average nitrogen river load 3-fold (5 kg/ha*a) (see Table 6). Average denitrification in the soil of the Wulka catchment was calculated according to own experiences to about 26 kgN/ha*a for the Wulka catchment at main watershed outlet. In comparison to Table 8, nitrogen uptake by plants was considerably underestimated by the model, what is likely to be one reason for considerable overestimations of the nitrogen river load. Particularly the large contributions of nitrogen by the lateral runoff to the surface runoff are the major reason for the significant overestimations in calculated nitrogen river loads. If these fractions of nitrogen emissions would be subject to denitrification in groundwater (if model definitions would admit the infiltration of lateral flow to groundwater first and then by groundwater runoff to surface water), calculated nitrogen emissions to surface water would decrease considerably.

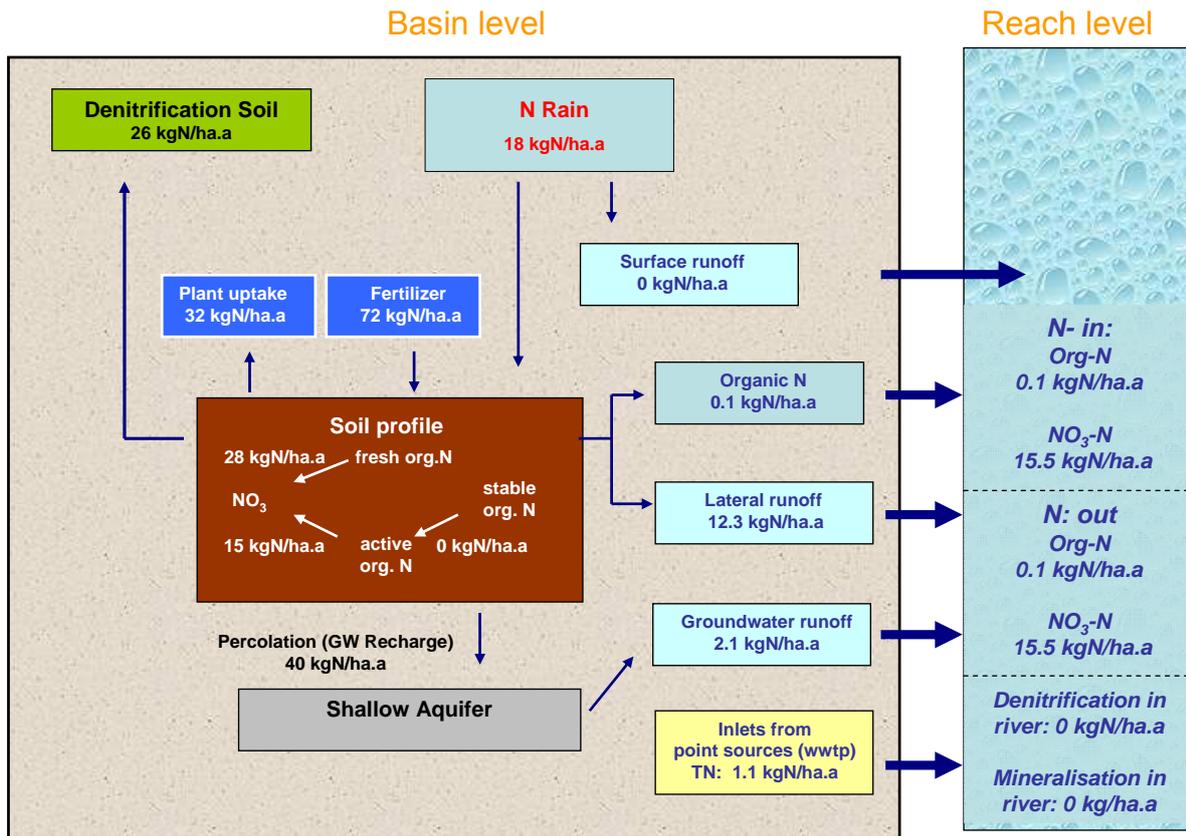


Figure 65: Detailed simulated nitrogen cycle for the Wulka catchment with average annual values of the nitrogen balance calculated for the period 1992-1999 using the SWAT 2000 model

In terms of hydrology the Wulka catchment is more dominated by the groundwater runoff compared to the Ybbs catchment, and denitrification in the groundwater of the Wulka catchment is considerably higher compared to the Ybbs catchment (see chapter 5). The lateral flow contributes nitrogen based on the concept of groundwater flow stimulation to the groundwater, even more in the Wulka catchment (due to higher share of groundwater runoff) than in the Ybbs catchment. So denitrification in the groundwater reducing the nitrate along the groundwater flowpath towards the surface water is of a much higher importance in the Wulka catchment than in the Ybbs catchment, what is obvious in significantly larger calculated nitrogen emissions to surface water of the Wulka catchment in comparison to calculated nitrogen emissions to surface water of the Ybbs catchment.

6.2.3 Conclusions

Denitrification in groundwater is a major process reducing nitrate concentrations in groundwater along the flowpath. Effects of hydrologic circumstances on potential denitrification in soils and groundwater are of manifold characteristics. Assessing denitrification activity for specific sites requires therefore first of all a correct determination of the site specific hydrological conditions. Second, transport and retention processes are affected by hydrology. Therefore, water balance calculations were conducive to identify temporal and spatial variability in water balance components in regard to nitrate transport and denitrification in soil and groundwater.

The application of the SWAT 2000 model in terms of nitrogen emission calculations resulted in significant overestimations of calculated nitrogen in-stream loads for the Wulka catchment. Calculated nitrogen in-stream loads for the Ybbs catchment showed a good correspondence to the observed nitrogen river loads.

The SWAT 2000 model indicated that in both catchments the highest fractions of nitrate were transported to surface water by lateral runoff. This resulted particularly in the Wulka catchment in considerable overestimations of nitrogen loads to surface waters, since the total river discharges of the Wulka catchment consists beside point source contributions mainly of groundwater runoff.

The highest fractions of nitrogen were leached from the soil by percolation towards the groundwater. The high discrepancy between nitrogen loads leached by percolation towards the groundwater surface and nitrogen loads transported by groundwater runoff to surface water indicated denitrification processes in the groundwater and their importance for the reduction of nitrate levels along the flowpath towards the surface water.

For exact estimations of total nitrogen emissions at the catchment scale, the consideration of denitrification in the groundwater is of significant importance. Changes in nitrogen surpluses on catchment area and therefore scenario calculations can't be related to adequate nitrogen emissions to surface waters, unless denitrification in groundwater is not considered for the fraction of nitrogen, which is transported with lateral runoff and with groundwater runoff. This is not possible using the SWAT 2000 model, and consequently this model was found not to be an appropriate tool for the estimation of nitrogen emissions at the catchment scale.

6.3 Nitrogen emission calculations using the MONERIS model

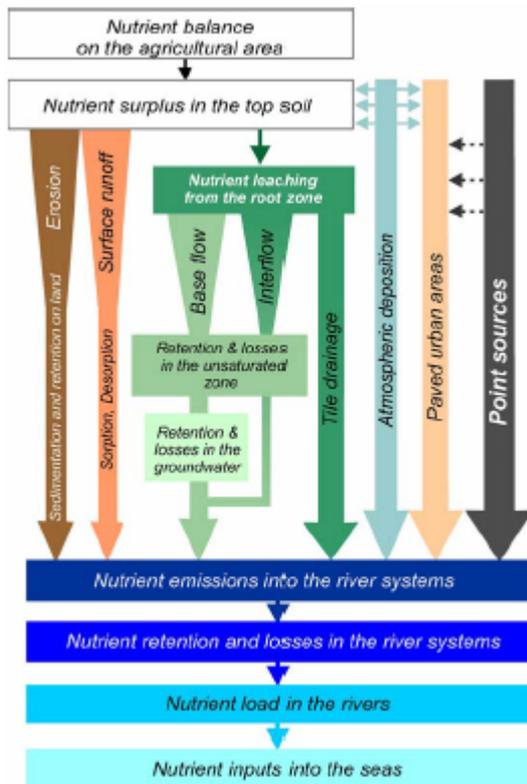
6.3.1 Model description

The **MONERIS** (**MO**delling **N**utrient **E**missions in **R**iver **S**ystems) model was developed and applied to estimate the nutrient inputs into river basins of Germany by point sources and various diffuse pathways. The model is based on data of river flow and water quality as well as a geographical information system (GIS), which includes digital maps and extensive statistical information. The MONERIS model is designed for the analysis of nutrient inputs in catchment areas of more than 500 km² (Behrendt et al. 1999).

The spatial and temporal resolution when compared to the SWAT 2000 model is lower. Calculations are performed on the subbasin level using 5 year average values. The MONERIS model is based on empirical equations and was developed for the modelling of medium and large spatial scale only.

The MONERIS model takes into account point sources as well as contributions from diffuse sources. Point emissions from waste water treatment plants and industrial sources are directly discharged into the rivers, diffuse emissions into surface waters are caused by the sum of different pathways, which are considered as separate flow components.

Figure 66 illustrates the different emission pathways, which are used for calculation of nutrient emissions at the catchment scale. The MONERIS model carries out mass



balances for each input pathway (with exception of atmospheric deposition and direct industrial discharges) resulting in the consideration of specific retentions and losses on the way from the sources to inputs to water bodies for each emission pathway. The total nutrient emissions leaving the catchment are calculated as sum from all individual emission pathways including internal retention and losses of the water body.

The calculated runoff components will be introduced more in detail in chapter 6.3.2.

Figure 66: Pathways and processes within MONERIS (Schreiber et al. 2003)

The emission pathways considered by the MONERIS model are:

- Point sources
- Atmospheric deposition
- Erosion
- Surface runoff
- Groundwater
- Tile drainage
- Paved urban areas

For the emission calculations for the Ybbs and the Wulka catchment the time of 1998 – 2002 was used (Zessner et al. 2004).

6.3.2 Model definitions for runoff components

The MONERIS model considers the following runoff components:

- Groundwater flow (Q_{GW}): Difference between the total measured river discharge at a specific river gauging station and the empirically estimated runoff components
- Overland flow (Q_{RO}): Surface runoff occurs on agricultural or open areas (no forested areas)
- Direct precipitation (Q_{AD}): Balance between the precipitation which falls on water bodies and the evaporation from these water bodies
- Tile Drainage (Q_{DR}): Runoff from tile drained areas as a function of the soil type
- Point sources (Q_{PS}): Amount of water discharges from waste water treatment plant's (WWTP)

- Urban Areas (Q_{URB}): Runoff from sealed areas, which are connected to sewer systems, but not connected to WWTP's; runoff from areas are not connected to a sewer system; runoff from combined sewer overflows and separate sewer systems

The water balance in the MONERIS model is calculated:

$$Q = Q_{GW} + Q_{DR} + Q_{RO} + Q_{URB} + Q_{AD} + Q_{PS} \quad (\text{Equation 18})$$

- with
- $Q_{...}$ average observed river discharge [m^3/s],
 - $Q_{GW...}$ base flow and natural interflow [m^3/s],
 - $Q_{DR...}$ tile drainage flow [m^3/s],
 - $Q_{RO...}$ surface runoff from non-paved areas [m^3/s],
 - $Q_{URB...}$ runoff from urban areas [m^3/s] and
 - $Q_{AD...}$ direct flow, i.e. result of the balance between direct precipitation on the freshwater surfaces and the evaporation from these surfaces [m^3/s]
 - $Q_{PS...}$ discharge from points sources [m^3/s].

The average observed river discharge will be estimated as difference between two observation stations (two subcatchments). The amount of runoff from tile drained areas, from surface runoff, from runoff from urban areas, from direct flow and from point sources are calculated using empirical equations. The baseflow Q_{GW} will be calculated subtracting the calculated runoff components from the total observed river discharge Q .

6.3.3 Consideration of nitrogen losses via denitrification in groundwater

In the MONERIS model denitrification in groundwater will be considered in relation to the nitrogen surpluses on the soil.

First, a leakage water quantity (amount of percolation water) SW is calculated based on the average precipitation and evapotranspiration. Since the model equations were derived for conditions of large river basins in Germany, a minimum flow of at least 5 % of the annual precipitation is taken into account in connection with a highest possible evapotranspiration of 600 mm/a. Basis for the calculations is to derive relationships between the nitrogen concentrations in the leakage water concentrations and the nitrogen concentrations in the groundwater.

The total nitrogen surplus is calculated:

$$N_{UGES} = \frac{N_{\dot{U}LN} * A_{LN} * LKF + N_{DEP} * (A_{EZG} - A_{LN} - A_W - A_{URBV} - A_{GEB})}{A_{EZG} - A_W - A_{URBV} - A_{GEB}} \quad (\text{Equation 19})$$

- with
- $N_{UGES...}$ total nitrogen surplus [kg/ha]
 - $N_{\dot{U}LN...}$ nitrogen surplus on agricultural areas [kg/ha]
 - $LKF...$ correction factor for long-term changes in surpluses
 - $N_{DEP...}$ atmospheric nitrogen deposition [kg/ha]
 - $A_{EZG...}$ catchment area [ha]

$A_{LN...}$	agricultural area [ha]
$A_W...$	total water surface area [ha]
$A_{URBV...}$	impervious urban area [ha]
$A_{GEB...}$	mountain area [ha]

The nitrogen surplus is used to calculate a potential nitrogen concentration in the leakage water for the areas contributing to the groundwater runoff:

$$C_{SWPOT_{NO3-N}} = \frac{N_{UGES} * AF * 100}{SW} \quad (\text{Equation 20})$$

with $C_{SWPOT_{NO3-N}}$ potential nitrogen concentration in leakage water for the total area of groundwater runoff [$g\ N/m^3$] and

$AF...$ exchange factor ($AF = 1$ if $AH \geq 100$); if $AH \leq 100$ then

$$AF = \frac{AH}{100} \quad (\text{Equation 21})$$

$$AH = \frac{SW}{FK_{WE}} * 100 \quad (\text{Equation 22})$$

with $FK_{WE}...$ field capacity in the root zone of soil [Vol.-%]

$$SW = N_J - V - q_{RO} \quad (\text{Equation 23})$$

with $SW...$ leakage water quantity [l/m^2*a]

$N_J...$ annual precipitation [l/m^2]

$V...$ Evapotranspiration [l/m^2]

$q_{RO}...$ specific surface runoff [$mm/(m^2*a)$] and

$$q_{RO} = q_G * 2 * 10^{-6} * (N_J - 500)^{1.65} \quad (\text{Equation 24})$$

with $q_G...$ average yearly specific runoff [$mm/(m^2*a)$] and

$$q_G = 0.86 * N_J - 111.6 * \frac{N_{SO}}{N_{WI}} - 241.4 \quad (\text{Equation 25})$$

with $N_{SO}...$ av. annual precipitation in the summer half year [l/m^2]

$N_{WI}...$ av. annual precipitation in the winter half year [l/m^2]

A relationship between the nitrogen concentrations in the leakage water and in the groundwater was derived. It was assumed that the nitrogen retention in the soil and the groundwater by denitrification is a function of the leakage water level and the hydrological conditions. Hydrogeological conditions were considered by the formation of two particular groups for unconsolidated and consolidated rocks. For both types of rock region, one group with high permeability and one group with low permeability are defined. The nitrogen concentrations in groundwater can then be calculated:

$$C_{GW_{NO3-N}} = \left(\sum_{i=1}^4 \frac{1}{1 + k_{1i}} * SW^{k_{2i}} * \frac{A_{HG_i}}{A_{EZG}} \right) * C_{SWPOT_{NO3-n}}^a \quad (\text{Equation 26})$$

with $A_{HG}...$ area of different hydro geologically rock types [km^2]

$A_{EZG...}$ catchment area [km^2]

a, k_1 and $k_2...$ model coefficients

The empirically derived model coefficients k_1 and k_2 for all types of hydrogeological formations are shown in Table 26.

Table 26: Model coefficients for determination of nitrogen retention in areas with various hydrogeological conditions

Hydrogeological condition	k_1	k_2
Non-consolidated rock with good porosity	2.752	-1.54
Non-consolidated rock with poor porosity	68.560	-1.96
Consolidated rock with good porosity	6.02	-0.90
Consolidated rock with poor porosity	0.0127	0.66

The model definitions for determination of nitrogen retention in the groundwater are decisively dependent on the definition of hydrogeological classes and their fractions on the total area.

6.3.4 Estimation of nitrogen emissions for the Ybbs and the Wulka catchment

Using the MONERIS model for the Ybbs and the Wulka catchment the total nitrogen emissions were calculated with consideration of the individual emission pathways (Table 27).

Table 27: Calculated nitrogen emissions via pathways using the MONERIS model for the Ybbs and the Wulka catchment (from Zessner et al. 2004)

catchment area name	deposition	overland flow	tile drainge	erosion	ground-water	wwtp	urban systems	total N	river load 1998-2002	
	[t/a]	[t/a]	[t/a]	[t/a]	[t/a]	[t/a]	[t/a]	[t/a]	TN [t/a]	DIN [t/a]
Wulka										
Walbersdorf	0.4	0.1	5.0	2.1	25.2	2.9	1.7	37	23	18
Wulkaprod.	1.2	0.2	21.0	11.2	79.6	5.5	3.2	122	77	59
Eisbach	0.6	0.0	8.6	2.5	12.5	18.8	1.6	45	47	41
Nodbach	0.3	0.0	8.4	1.3	6.2	0.0	0.7	17	12	8
Schützen	2.4	0.2	49.3	16.2	99.3	42.6	6.1	216	142	128
Ybbs										
Opponitz	4.1	30.5	24.2	5.8	722.8	6.7	4.8	799	770	495
Krenstetten	1.1	7.7	25.0	6.0	272.6	38.0	6.4	357	352	293
Greimpersd.	12.5	67.0	158.4	38.4	1869.0	75.5	36.0	2257	2065	1895

The total nitrogen emissions were about 216 tN/a for the Wulka catchment and 2257 tN/a for the Ybbs catchment. The Ybbs catchment releases 10 times higher nitrogen emissions to surface waters compared to the Wulka catchment. Compared to the calculated total nitrogen emissions, the observed total nitrogen loads in the river are significantly lower. This decrease is caused by in stream nitrogen reduction by denitrification in the river itself. Comparisons with approaches focusing on estimation of nitrogen retention in the river showed a good coincidence of the results with observed in stream nitrogen retention (Zessner et al. 2004).

The major emission pathway for nitrogen emissions is the groundwater for both the Wulka catchment and the Ybbs catchment (see Figure 67). At the Wulka catchment remarkable emissions from point sources were obtained for the 'Eisbach' subcatchment as well as for the watershed outlet 'Schützen', which significantly contribute to river discharges in these subcatchments (see Figure 67, right). Additionally, emissions from tile drained areas are of significant importance particularly in the 'Nodbach' subcatchment and for the watershed outlet 'Schützen'.

In comparison to the Wulka catchment noticeable contributions from point sources in the Ybbs catchment were calculated for the 'Krensetten' subcatchment only. In terms of nitrogen loads these contributions are of higher importance as in terms of the contributed runoff to total river discharge. In the Ybbs catchment the groundwater has by far the highest importance in terms of contributions to the total nitrogen emissions as well as to total river discharges.

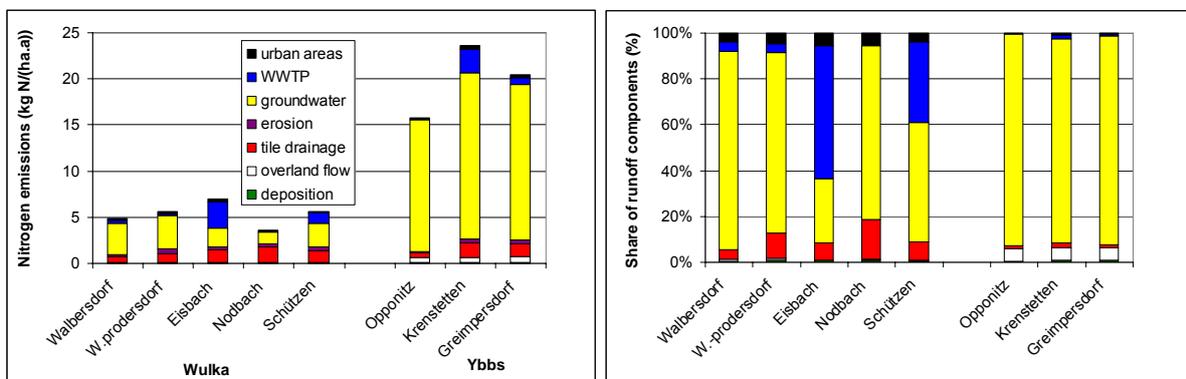


Figure 67: Nitrogen emissions calculated using the MONERIS model for the Ybbs and Wulka catchment with specification of emission pathways (from Zessner et al. 2004) in relation to runoff components contributions

Calculated area-specific nitrogen emissions to surface waters of the Ybbs catchment were about 20 kgN/ha*a and were 4 times larger than the average area-specific nitrogen emissions to the surface waters of the Wulka catchment with about 5 kgN/ha*a (see Figure 67). The comparison of the total amount of the nitrogen emission pathways indicated that except nitrogen emissions from groundwater the individual nitrogen emissions by the remaining pathways are quite similar between both catchments. The large difference between the total nitrogen emissions is therefore predominantly caused by higher amounts of nitrogen emissions, which are contributed to the surface water by the groundwater of the Ybbs catchment.

The significant differences between both catchments in terms of area-specific nitrogen emissions via groundwater, which are presented in Figure 67, point out a spatial variability which is further observable across the whole Danube basin. Nutrient emission calculations for all subcatchments of the Danube basin indicated, that particularly the subcatchments located in the western part of the Danube basin contribute the highest nitrogen emissions via groundwater due to highest annual average precipitation rates in connection with moderate evapotranspiration rates (see Figure 68), this was already indicated by the water balance calculation using the SWAT 2000 model. The locations of the Ybbs catchment and the Wulka catchment are identified by the arrows.

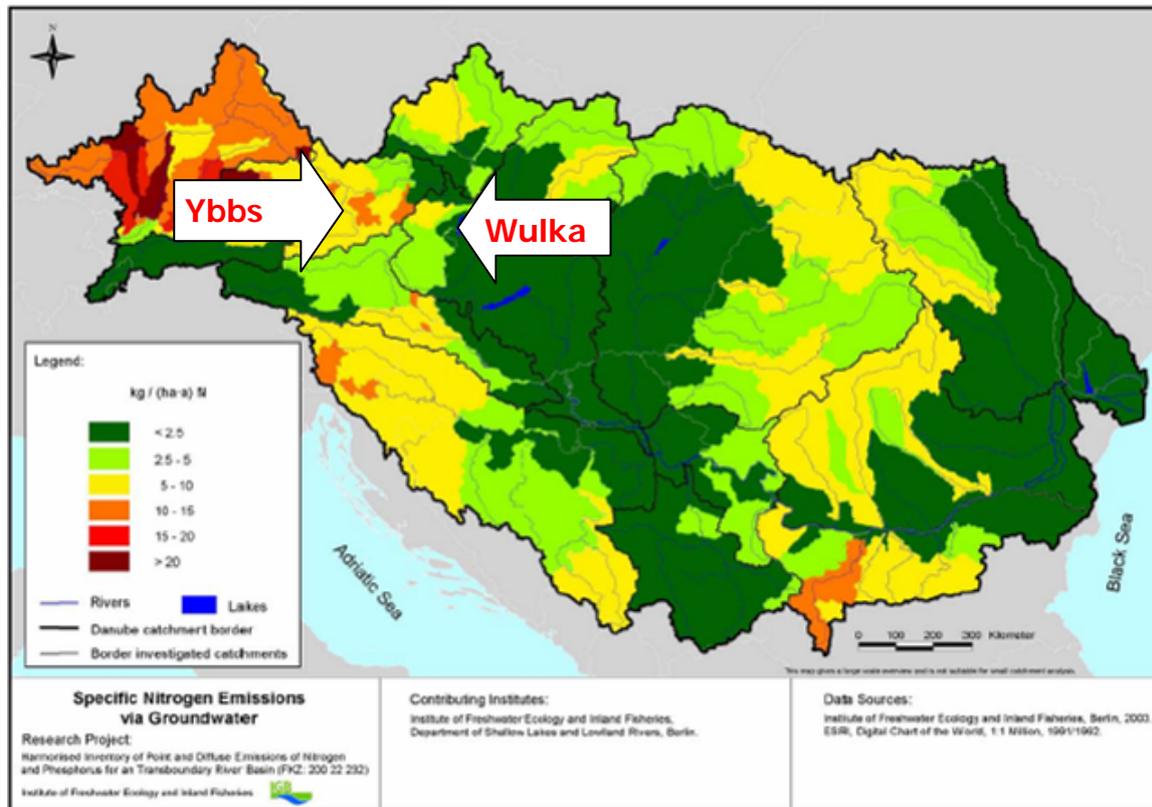


Figure 68: Specific nitrogen emissions via groundwater in the period 1998-2002 (from Schreiber et al. 2003)

In terms of the calculated nitrogen emissions via background loads for the subcatchments of the Danube catchment similar spatial variations are observable (see Figure 69). Again it is noticeable that the subcatchments located in the southwestern part of the Danube basin, contribute significantly higher nitrogen emissions via background loads to surface waters compared to the subcatchments in the eastern part of the Danube basin. In comparison to Figure 68, the nitrogen contributions of the individual subcatchments via background loads are more heterogeneous. The nitrogen background emissions are contributed from the catchments to the surface waters due to local natural conditions and are not influenced by anthropogenic activity. In case of the Ybbs catchment it is observable from Figure 69, that nitrogen emissions for background conditions are in the order of magnitude (about 4-5 kgN/ha*a) of the calculated total area-specific nitrogen emissions calculated for the Wulka catchment.

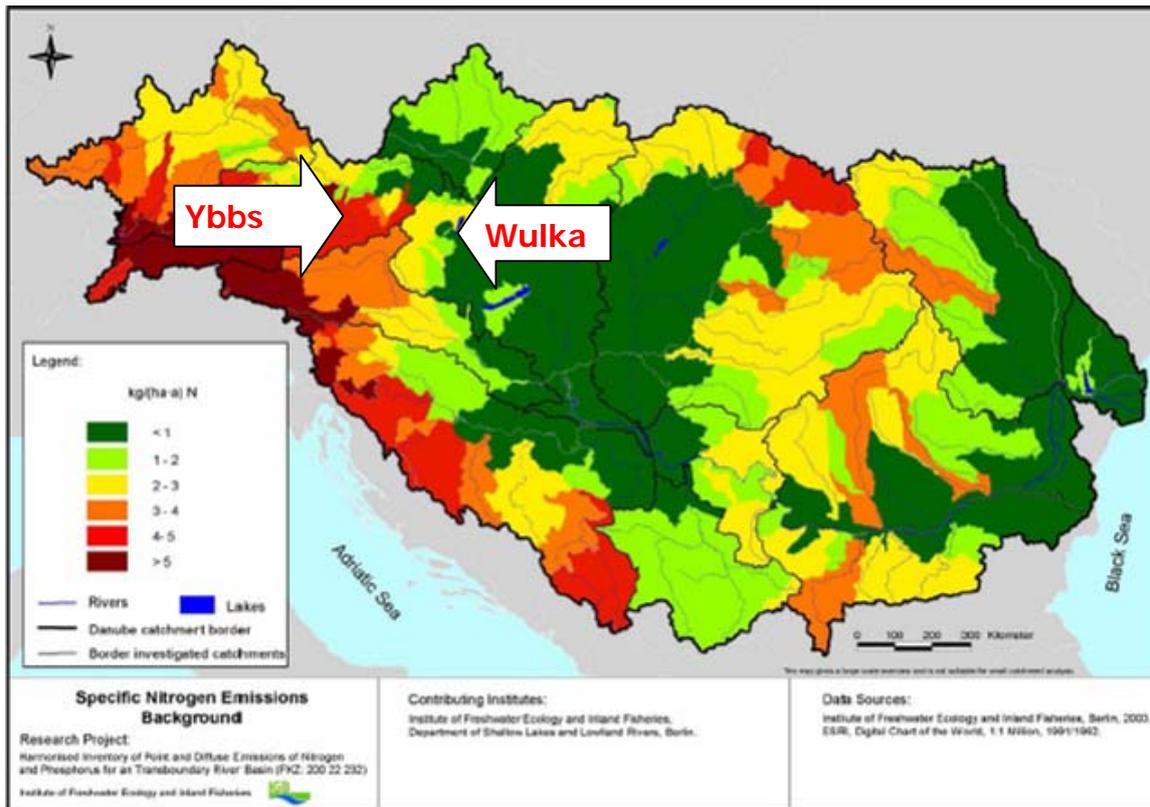


Figure 69: Specific nitrogen emissions for background conditions in the period 1998-2002 (from Schreiber et al. 2003)

Nitrogen emissions to surface waters are decisively dependent on the local climatic conditions (ratio precipitation/evapotranspiration). High precipitation leads to elevated groundwater recharge rates and enhances subsurface water fluxes, which are associated with nitrogen transport. Thus, nitrogen emissions via groundwater (the major emission pathway for nitrogen) increase considerably with increasing precipitation.

Using the MONERIS model the groundwater could be identified as the major source of nitrogen emissions to the surface waters in both the Ybbs catchment and the Wulka catchment. Significant differences were calculated in total and area-specific nitrogen emissions between the Ybbs and the Wulka catchment, which can be attributed first of all to differences in catchment hydrology.

Comparing the calculated area-specific total nitrogen emissions to the area specific nitrogen surpluses on catchment area, nitrogen reduction by denitrification in the subsurface zone can be observed (see Figure 70). The nitrogen surplus on the catchment area was calculated at the municipality level with consideration of nitrogen inputs by fertilizer application, atmospheric deposition and nitrogen fixation. As nitrogen output plant uptake and gaseous losses to the atmosphere (NH_3) were considered (for details in terms of nitrogen surplus calculation see chapter 3.2.2 and 3.3.2). The average area specific nitrogen surplus was estimated about $40 \text{ kgN/ha} \cdot \text{a}$ and $38 \text{ kgN/ha} \cdot \text{a}$ for the Ybbs and the Wulka catchment, respectively (see Table 6). Since the groundwater is the major emission pathway for nitrogen and the travel time for groundwater is in a range of years up to several decades, nitrogen emissions into surface waters are associated to long-term nitrogen inputs from the last 20 to 30 years. Therefore, the long-term average nitrogen surplus was calculated and is shown in Figure 70.

Related to the long-term average nitrogen surplus (Figure 70 – grey dotted line), 55% of the nitrogen surplus from the topsoil is leached to the surface water in the Ybbs catchment (Figure 70). In the Wulka catchment only 13% of the long-term average nitrogen surplus on the topsoil reaches the surface water indicating a larger amount of nitrogen being denitrified in the soil and the groundwater. Regarding the groundwater being the major emission source for nitrogen to total nitrogen emissions of the surface waters, the process of denitrification in the soil and the groundwater is of significant importance in terms of the amount of nitrogen, which reaches the surface water. According to Figure 70, nitrogen emissions are reduced in the soil and the groundwater by denitrification in average between 17 kgN/ha*a and 39 kgN/ha*a for the Ybbs and the Wulka catchment, respectively.

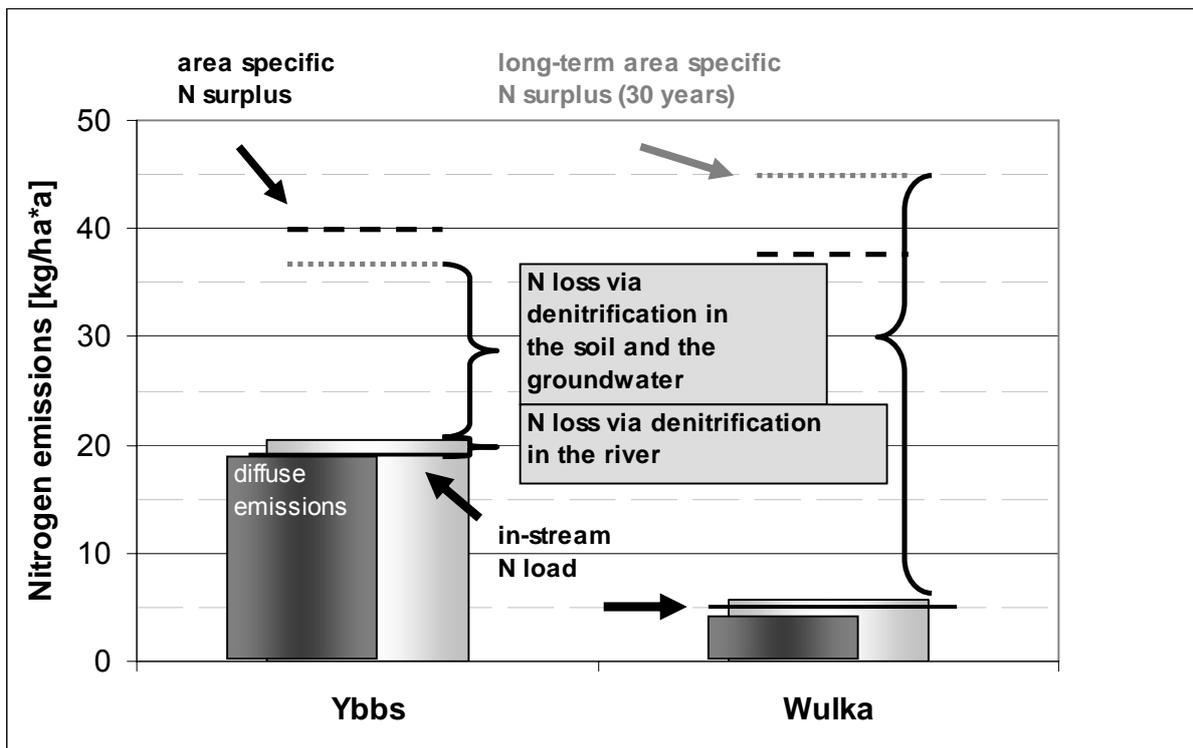


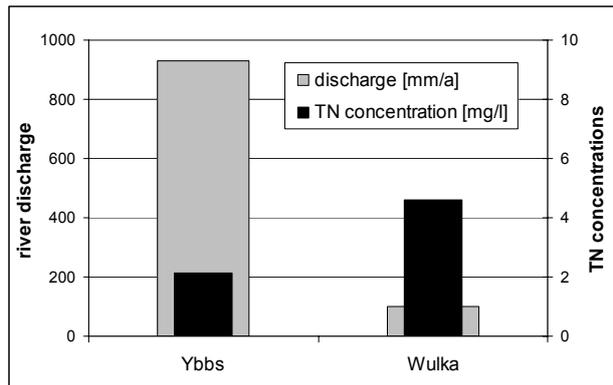
Figure 70: Total nitrogen emissions with relation to the area specific surplus on the total area of the catchment and the river loads for the Ybbs and the Wulka catchment (from Zessner et al. 2004, modified)

Additionally Figure 70 indicates that the calculated average total nitrogen emissions consist mainly of diffuse nitrogen emissions (dark-grey bars) in both catchments.

In regard to the observed nitrogen in-stream loads in the surface waters of the Ybbs and the Wulka catchment (Figure 70 – black line) a further decrease related to the average total nitrogen emissions (light-grey bars) is observable. This decrease in nitrogen emissions is caused by an ongoing denitrification in the river. For total nitrogen emission reduction, the denitrification in the river is of less importance compared to the significant importance of denitrification in soil and groundwater for total nitrogen emissions to surface waters.

Relating the calculated total nitrogen emissions of both catchments to hydrological conditions, the significantly larger average nitrogen emissions to surface waters of the Ybbs catchment are predominantly the result of larger average water fluxes in the catchment due to the significantly higher precipitation. Although in both

catchments the average nitrogen surplus on the catchment area is nearly similar, the Ybbs catchment contributes 4 times larger nitrogen emissions to the surface water. Because of the elevated water fluxes in the Ybbs catchment, consequences for nitrogen turnover at the catchment scale are quite different in comparison to the Wulka catchment. Groundwater residence times in the Ybbs catchment are expected to be comparably lower due to the larger water fluxes, what would result in shorter reaction times and less denitrification potential in the groundwater compared to the Wulka catchment. In contrast, larger water fluxes induce larger fluxes of nitrogen and DOC through the aquifer, but also the supply of dissolved oxygen. And, as already shown in chapter 5, enhanced water fluxes resulted in significantly lower nitrogen concentrations in both the groundwater and the surface water of the Ybbs



catchment compared to the Wulka catchment. Observed nitrogen concentrations in the Ybbs river were half of the nitrogen concentrations that could be observed in the Wulka river, but the decisively larger river discharges result in decisively larger average in-stream nitrogen loads from the Ybbs river compared to the Wulka river (see Figure 71).

Figure 71: Annual river discharges in comparison with measured average TN concentrations in the Ybbs rivers and the Wulka river (from Zessner et al. 2004, modified)

It is obvious that the river discharge is of higher importance for the determination of the transported in-stream nitrogen loads in surface waters than in-stream nitrogen concentrations. Nevertheless, transported nitrogen loads in surface waters are highly dependent on nitrogen emissions from the catchment and from anthropogenic activity in the catchment.

Increasing water fluxes reduce nitrogen concentrations, but enhance considerably the nitrogen fluxes at the catchment scale and similarly restrain nitrogen reduction due to limited access of denitrification, when reaction times are shortened.

6.4 Discussion and conclusions for estimating nitrogen emissions

Nitrogen emission calculations for the Ybbs catchment and the Wulka catchment were performed using the SWAT 2000 model and the MONERIS model. Differences in the results reflected the different modelling concepts with consideration of nitrogen emission pathways in different ways. First of all differences in the temporal resolution resulted in a distinctively varying expressiveness of the calculated nitrogen balance for each model. Whereas the SWAT 2000 model is able to identify seasonal changes and spatial heterogeneity in nitrogen emissions due to seasonality and fluctuations in simulated runoff components, the MONERIS model is more favourable at pointing out long-term average nitrogen emissions with identification of the relative importance of the individual emission pathways.

The SWAT 2000 model application was beneficial in terms of simulating a long-term seasonal cycle of water balance components and to link them to nitrogen transport

at the catchment scale. It was found that surface runoff is of negligible importance in terms of contributing nitrogen emissions to surface waters. Nitrogen was emitted directly to the surface water predominantly by the lateral runoff following the groundwater runoff in the SWAT 2000 model. The model definitions in respect to direct contributions of the lateral runoff to the surface water were the reason for considerable overestimations of simulated nitrogen in-stream loads in surface waters particularly in catchments with dominant contributions of the groundwater runoff to the total river discharge. It could be shown that most of the nitrogen was leached from the soil to the groundwater by percolation. The large discrepancy between the nitrogen loads leached out from the soil to the groundwater by percolation and the nitrogen loads transported by the groundwater runoff to the surface water indicated the significant importance of denitrification in the groundwater, which is responsible for a considerable reduction in the nitrogen levels during groundwater passage.

Using the SWAT 2000 model nitrogen balances were calculated for both catchments. Whereas the calculated nitrogen emissions to the surface water for the Ybbs catchment corresponded to the observed nitrogen in-stream loads in the Ybbs river, the calculated nitrogen emissions to surface water of the Wulka catchment exceeded more than 3-fold the observed nitrogen in-stream loads in the Wulka river. For both catchments similar fertilizer loads to soil surface were calculated as well as similar loads of nitrogen, which is leached out from the soil to the groundwater by percolation. Nitrogen reductions in the groundwater by denitrification are of much higher magnitude in the Wulka catchment, what could be shown using the observed in-stream nitrogen loads in relation to calculated nitrogen surplus. Simulated nitrogen emissions to the surface water by direct contributions of the lateral flow are of much larger impact in the Wulka catchment, since the fraction of lateral runoff contributing to total river discharge is much smaller for the Wulka catchment. Since most of the catchment areas own large distances to the surface water, simulated lateral runoff is likely to infiltrate into the groundwater and to stimulate groundwater exfiltration to the river. Therefore, this runoff component is likely to be subject of denitrification processes in the groundwater to a high extent. In the Ybbs catchment larger contributions of lateral runoff and surface runoff to total river discharge were obtained. Thus, the simulated direct contribution of the lateral flow to the surface water has less significant effects on nitrogen in-stream loads due to the less significant influence of denitrification processes on the fraction of nitrogen, which is contributed by the lateral runoff to the groundwater even under natural conditions.

The empirical emission model MONERIS was found to be an appropriate tool for nitrogen emission estimations at the catchment scale. Individual emission pathways are considered as well as a spatial resolution by operating at the subcatchment level. Calculated emissions have been successfully validated against observations, this is not presented in this work. More detailed information can be found in (Zessner et al. 2004).

Significant differences in calculated total nitrogen emissions from both catchments were indicated using the MONERIS model. The calculated total nitrogen emissions from the Ybbs catchment exceeded 4-fold the calculated total nitrogen emissions from the Wulka catchment. The groundwater was identified as the major emission pathway of nitrogen loads to the surface water in the Ybbs catchment as well as in the Wulka catchment. Therefore, the consideration of nitrogen losses by denitrification in the groundwater is of essential importance for the quantification of

nitrogen emissions at the catchment scale exactly. The MONERIS model considers nitrogen concentrations in the groundwater as a function of nitrogen concentrations in leakage water. The retention approach for denitrification in the groundwater is realised allocating the catchment hydrogeology into particular groups with different nitrogen retention potential.

Several factors have a significant influence on local environmental conditions, which determine denitrification in the groundwater. A visualisation of interrelations between these factors and in which way they affect local groundwater conditions is given in Figure 72. These factors facilitate the reflection of denitrification in the groundwater with varying temporal and spatial resolution and should therefore be used as far as possible to determine denitrification in groundwater in modelling approaches.

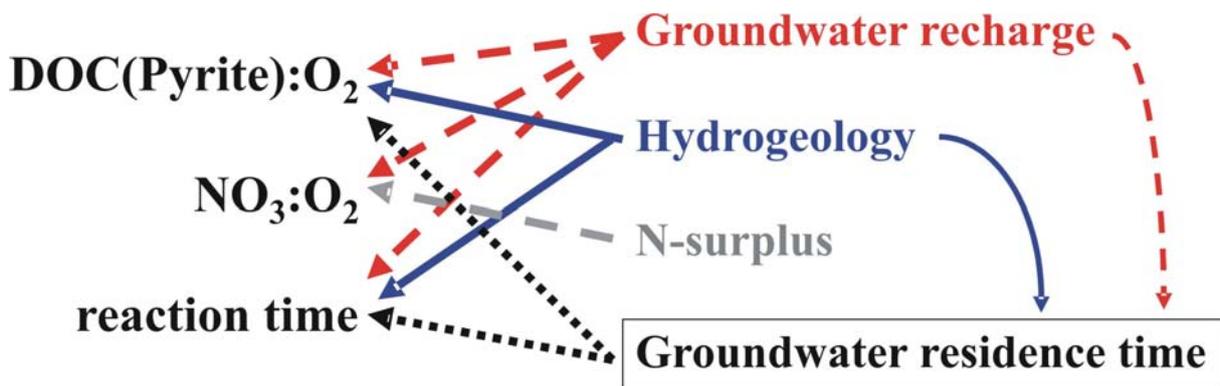


Figure 72: Factors influencing local environmental conditions, which are favourable for denitrification in groundwater

Denitrification in the groundwater is almost limited by the availability of nitrate, and electron donors and the presence of dissolved oxygen. Denitrification rates reflect the local environmental conditions and potential limitations in one of these essential elements. What is additionally needed is a sufficient reaction time to ensure the development of anoxic conditions and a sufficient contact time between nitrate rich groundwater flow and biologically active layers (liquid films) in the aquifer matrix. In this respect catchment hydrology (groundwater recharge), hydrogeology and nitrogen inputs by land use are of decisive importance affecting substrate availability for denitrification, the oxic status and groundwater flow velocity to a large extent and a different manner, like indicated in Figure 72. The availability of electron donors is determined first of all by groundwater recharge (downwards DOC-fluxes) and hydrogeology (fossil carbon sources, alternative electron donors), the availability of nitrate by nitrogen surplus on the soil surface and the leaching from soil towards the groundwater by groundwater recharge. Groundwater recharge and hydrogeological circumstances in turn define geohydraulic conditions with specific groundwater residence times, which largely determine reaction time for denitrification and substrate availability. With increasing groundwater residence times bioavailability of heavier organic carbon sources increases, and similarly oxic conditions are likely to become anoxic due to microbial respiration activity.

Since the denitrification reaction time is one of the most critical conditions determining the total amount of nitrate, which is reduced to atmospheric nitrogen via denitrification, the groundwater residence time seems to be well suited to reflect denitrification processes in modelling approaches. Additionally, local groundwater

residence times comprise specific geological conditions with certain hydrological characteristics (see Figure 72) and consequently permit the definition of an individual, catchment specific denitrification for selected parts of the catchment using only one parameter. Information about denitrification kinetics (nitrate availability) can't be provided by groundwater residence time, but they can be complemented using a half life time approach for the characterisation of the denitrification (see chapter 2.3.1).

The nitrogen retention approach used in the MONERIS model for the consideration of denitrification in groundwater is based on the concept of different groundwater residence times for diverse hydrogeological formations. Thus, a certain spatial resolution can be provided by the MONERIS model classifying the catchment areas under hydrogeological aspects and ensures a spatial heterogeneity in nitrogen reductions via denitrification in the groundwater to a limited extent. Unfortunately, the specific nitrogen losses in groundwater of individual hydrogeological formations can't be linked to a specific landscape position within the catchment. So information about nitrogen reductions via denitrification in the groundwater of the catchment can't be related to groundwater flow paths or distances to surface water bodies.

Half life time approaches for the determination of denitrification in groundwater were already reported. In literature approaches can be found about the estimation of nitrogen retention potential in groundwater as a function of hydrogeology (Wendland et al. 1999). Additional considerations of groundwater residence times in connected to nitrogen emissions from groundwater are reported by Quast et al. (2001). Quantifications of nitrogen emissions via groundwater using a mean estimated travel time of nitrate to the groundwater surface, and a groundwater residence time combined with a half life time approach for denitrification is reported by DVWK et al. (1999).

Implementation of the groundwater residence times in models would enhance and simultaneously simplify the possibility of consideration denitrification in groundwater by using half life time approaches. This would give the opportunity to estimate nitrogen emissions at the catchment scale more process-oriented with a spatial differentiation between catchment areas, which are largely affected by enhanced denitrification in the groundwater due to long travel times and catchment areas with marginal influences of denitrification in the groundwater in respect to the reduction of nitrogen loads, which are contributed to the surface water by the groundwater flow.

Regarding both the consideration of groundwater residence time for denitrification in groundwater as well as the linkage of the location of catchment areas to their contribution of diffuse nitrogen emissions to surface water is desirable not only in terms of indication of catchment areas, which are highly sensitive for implications on total nitrogen emissions to surface waters changing nitrogen surpluses. In order to consider this linkage using readily available data and an easily applicable approach, a new methodology was introduced and will be discussed in the next chapter.

7 Quantification of groundwater residence times and the influence on nitrogen emissions from groundwater to surface waters

7.1 Motivation

Retention processes in the groundwater are important for the reduction of nitrogen loads to surface waters and significantly affect nitrogen emissions into the river system. The analyses of the observed groundwater quality data indicated denitrification in the groundwater in both the Ybbs catchment and the Wulka catchment, but with varying intensity. Hydrology was identified to strongly influence total concentrations in the groundwater and the surface water, and additionally to determine groundwater flow and groundwater residence times.

Of major importance for the retention potential of nitrogen in the groundwater is the groundwater residence time (Haag et al. 2001). The removal of nitrate from groundwater in field may be linked in part to low hydraulic gradients and long groundwater residence times (Vidon et al. 2004). Groundwater residence time is defined as time the groundwater needs from the point of groundwater recharge (of percolation from the soil to the groundwater) in the catchment to the point of infiltration of the groundwater into the surface water.

Approaches for the estimation of the denitrification potential in the groundwater are reported in the literature via analyses of groundwater quality data (e.g. by Wendland et al. (1999)). Quantifications of diffuse nitrogen emissions to surface waters using mean estimated travel times for nitrate in the unsaturated zone and using estimated groundwater residence times for the saturated zone is reported by DVWK et al. (1999) and Quast et al. (2001) with utilisation of half life time approaches for the consideration of denitrification in the groundwater.

A common method for estimating the age and residence times of groundwater is based on tritium analyses. Due to the enhanced anthropogenic release of tritium to the atmosphere in frame of nuclear weapon tests during the 50ies, groundwater ages can be detected using stable tritium concentrations due to specific temporal decreases in tritium concentrations in the atmosphere which had been registered during the past decades. Analysing tritium concentrations in the groundwater and surface water should reveal average groundwater residence times in the catchments.

7.2 Estimation of groundwater residence times using tritium analyses

7.2.1 Wulka catchment

Most parts of the Wulka catchment are dominated by unconsolidated fluvial sediments defining the porous aquifer conditions. Only in the north (Leitha Mountains) and in the south-west (Rosalien Mountains) of the catchment consolidated rocks (limestone, crystalline) are located.

In order to get information on the groundwater residence times, tritium analysis has been carried out. In groundwater as well as in surface water tritium samples

were taken at low flow conditions (no rainfall for several days, temperature < 10°C). Due to the high fluctuations of the tritium levels in the atmosphere during the last decades and the extremely low detection values, estimated tritium values resulted in widespread ranges estimated groundwater residence times of up to 10-12 years. The mean value and the standard deviation was calculated for each sample (for each sample two minimum and maximum residence time's using different reference concentrations were estimated), what is shown in Figure 73.

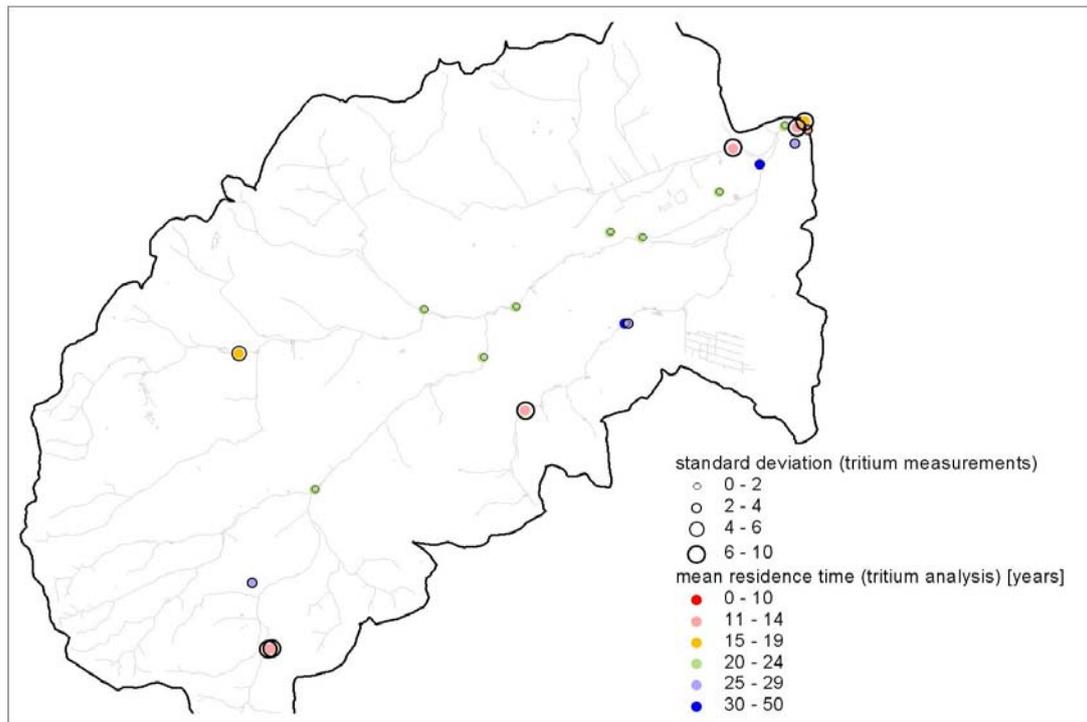


Figure 73: Groundwater residence time [years] and standard deviation [years] estimated based on tritium analysis in the Wulka catchment

Along the Wulka river, consistent groundwater residence times of 20-24 years were observed. Particularly in the tributaries and at the main watershed outlet, the observed groundwater residence times decreased considerably with increasing standard deviations. Isolated analyses showed groundwater residence times >30 years. In connection with interpolated groundwater table information, groundwater flow seems to be directed from catchment boundaries (tributaries) towards the major rivers (Wulka river). Surface water samples of the Wulka river at low flow conditions consisted predominantly of groundwater with considerable groundwater residence times (>20 years). The number of samples was too small to calculate statistically significant residence time distributions.

7.2.2 Ybbs catchment

The estimated groundwater residence times for the Ybbs catchment on basis of tritium analyses is shown in Figure 74 in connection with calculated standard deviations of the groundwater residence times.

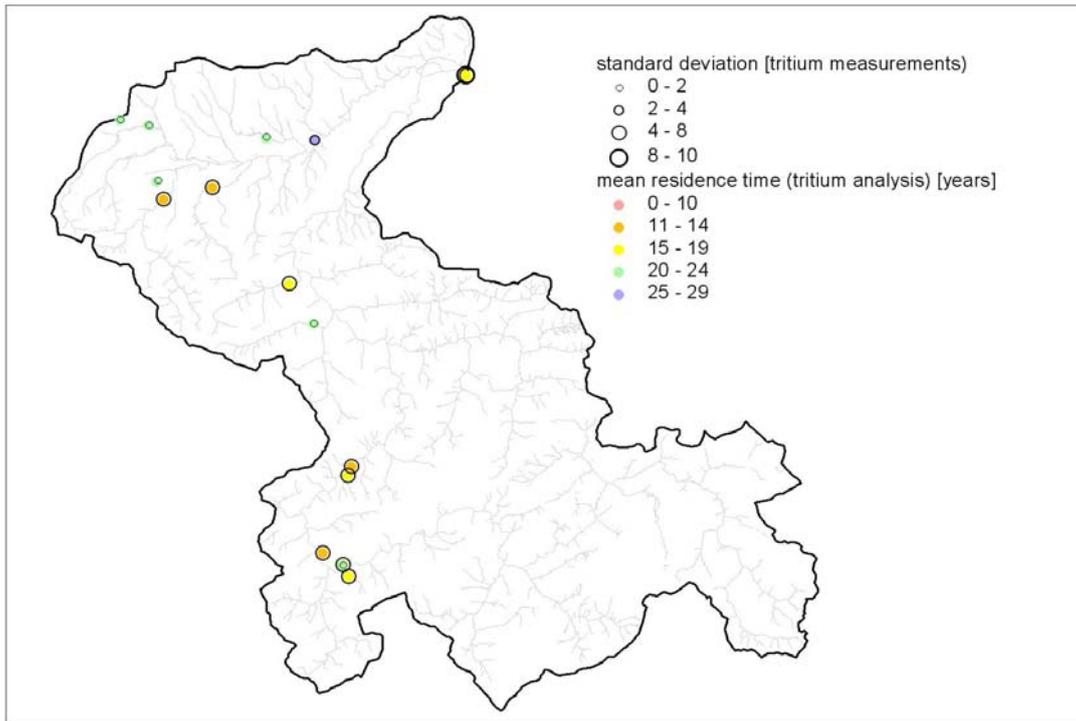


Figure 74: Residence time and standard deviation estimated based on tritium analysis in the Ybbs catchment

The Opponitz subcatchment is dominated by short groundwater residence times with high standard deviations. This subcatchment is dominated by consolidated rock (limestone and dolomite) with numerous springs. The groundwater residence times are short in these geological formations compared to unconsolidated deposits due to groundwater flow in fissures and channels.

The Krenstetten subcatchment showed significantly increased groundwater residence times with decreased standard deviations. This subcatchment is dominated by unconsolidated deposits and gravels comprising the aquifer. From tritium analyses and interpolated groundwater table information, a main groundwater flow direction can be expected for the Krenstetten subcatchment and the Ybbs catchment downstream of Kematen, which is directed from south-west to north-east parallel to the main rivers Url and Ybbs.

7.2.3 Conclusions

In both catchments, the small number of tritium samples resulted in considerable uncertainties in terms of estimated groundwater residence times using the tritium analyses.

The Wulka catchment showed near the Wulka river elevated groundwater residence times with low standard deviations. Near the catchment boundaries and particularly in most upstream catchment areas estimated groundwater residence times decreased similarly with increasing standard deviations. Short groundwater residence times with high standard deviations indicate short groundwater flow paths till the point of observation (young groundwater), they were observed mainly in the tributaries. Long groundwater residence times indicate long groundwater flow paths till the point of observation (old groundwater) and were observed close to the Wulka

river. From this analyses a main groundwater flow direction can be expected, which is directed from catchment boundaries towards the main river, the Wulka river.

The Ybbs catchment was dominated by tritium levels which indicated generally shorted groundwater residence times with bigger standard deviations in comparison to the Wulka catchment due to predominance of consolidated rock in large parts of the catchment. The Krenstetten subcatchment as well the Ybbs catchment downstream of Kematen showed elevated groundwater residence times, which were comparable to those of the Wulka catchment.

Despite the limited number of tritium samples and the limited expressiveness of estimated groundwater residence times in regard to spatial distributions, tritium analyses showed differences in terms of groundwater flow paths and involved geological formations between the catchments. They indicated that the Wulka catchment tends to show longer groundwater residence times in comparison to the Ybbs catchment.

7.3 Calculation of spatial distributions of the groundwater residence time using groundwater table observations

7.3.1 Development of the approach

Denitrification in groundwater has already been shown to be a significant process for the reduction of nitrogen concentrations in the groundwater of both catchments (chapter 5). Driven by hydrology, denitrification in the groundwater varied considerably between the Ybbs catchment and the Wulka catchment. Largely determined by average groundwater recharge rates, average groundwater residence times are assumed to vary considerably between both catchments. Tritium analyses revealed differences between the groundwater residence times of the catchments, but due to the high variability of the groundwater residence times (considerable oscillations in tritium reference concentrations in the atmosphere) which have been attributed to tritium estimates, these estimations were very uncertain and with limited expressiveness in terms of spatial distributions.

The consideration of denitrification processes in groundwater is essential even in modelling approaches, which focus at the estimation of nitrogen emissions at the catchment scale. Two modelling approaches were already presented with varying possibilities to consider denitrification processes in the groundwater. The empirical emission model MONERIS consider nitrate reduction via denitrification in the groundwater explicitly in dependency of the classification of catchment area to different geological classes. The SWAT 2000 model considers nitrate percolation to the groundwater (without a subsequent transport in the groundwater) as well as nitrate emission to the surface water directly by surface runoff and lateral runoff, but does not explicitly determine nitrate reductions via denitrification in the groundwater. Using a user-defined nitrate concentration for nitrogen emissions by groundwater runoff, the latter modelling approach takes into account nitrate reduction in the groundwater indirectly, and for steady state systems only. But it was shown in chapter 6.2 that particularly for catchments with dominant shares of the groundwater runoff the SWAT 2000 model significantly overestimates nitrate emissions to surface

waters due to insufficient consideration of denitrification processes for nitrogen emissions, which are contributed to surface water by lateral runoff.

However, from both modelling approaches information about the reduction of nitrate levels in the groundwater via denitrification can be obtained. Against the background of the reported model applications the question arises, to what extent it is reasonable to consider specific groundwater residence times, unless denitrification in groundwater is considered as area-weighted mean nitrate retention. Thus, the spatial resolutions of the modelling approaches are of central importance discussing these definitions. The MONERIS model takes into account spatial structures via the definition of subcatchments. Hence, the definition of empirically derived model parameters for certain hydrogeological classes for the consideration of mean groundwater travel times is absolutely sufficient, because every subcatchment is regarded as a lumped area with a certain (constant) segmentation of the area, but without a spatial relation. In the SWAT 2000 model the spatial structures are considered via definition of subcatchments and HRU's with a higher resolution, but similarly without a spatial relation of HRU's inside the subbasins. Thus, for both models only subbasin- or subcatchment- averaged mean groundwater residence time information is processed.

For consideration of spatial heterogeneities in nitrate reduction via denitrification it is therefore necessary to use fully-distributed spatial information in the form of grided data. Additionally, simple approaches using readily available, spatially distributed information would be desirable and more favourable for application than highly resolved flow models, which have to be calibrated first.

Since both applied models failed to provide information about denitrification in the groundwater of the Ybbs and the Wulka catchment with sufficient spatial or temporal resolution, an approach was developed for the estimation of fully distributed groundwater residence time distributions for each catchment based on mean observed groundwater flow directions. With the consideration of different hydraulic conductivities for changing geological formations, heterogeneities in the saturated zone were considered. From groundwater flow directions, groundwater flow paths were calculated assuming the groundwater infiltration into the surface water, when the river intersected the groundwater flow path. Thereby, the length of the groundwater flow path could be calculated. Using hydrogeological information about the hydraulic conductivities, a proper groundwater residence time could be obtained from calculated distances of each groundwater flow path. This approach enabled to allocate nitrogen surpluses of every grid cell to a specific travel time to the surface water. Using a half life time approach for the consideration of the denitrification in the groundwater, a specific nitrogen reduction along the flowpath due to the specific groundwater residence time could be considered resulting in a specific contribution of each grid cell to total diffuse nitrogen emissions to the surface water. As input, fully distributed information about the mean groundwater surface, geological conditions (digital maps) and location of the river network were used with varying grid resolutions and diverse boundary conditions for interpolation procedures.

A comparable approach was applied in order to calculate nitrogen emissions with consideration of denitrification in groundwater as function of groundwater residence time (DVWK et al. 1999). In contrast to that work, our approach aimed at the identification of management sensitive areas which are likely to be responsible for

most of the nitrogen emissions via groundwater to the surface water in the individual catchments.

For the estimation of the groundwater residence time distributions software (Tarbaton 1997) was modified based on algorithms for the calculation of flow directions from DEM (Digital Elevation Models) using slope vectors between each cell centre and its eight neighbours (Tarbaton 2000). The slope direction is then the resultant of two largest downwards slopes. The catchment area of each cell is added to two down slope cells proportional to the components of the steepest-slope vector (Burkhart et al. 2004a). A related approach was applied for the identification of riparian buffer locations in order to address water quality objectives derived from primary topographical attributes (Burkhart et al. 2004a, Burkhart et al. 2004b).

From prior interpolated grids of the mean groundwater surface groundwater flow directions were calculated in the following way:

1. Pit removal from the elevation information of the groundwater table (pits (depressions without discharge) were compared to the neighbouring cells and were elevated to the height of the neighbouring cells)
2. The flow directions (multiple) for every grid cell is calculated out of the interpolated groundwater table information
3. The upslope contributing area is estimated for every grid cell (for every grid cell in dependency of the flow direction the amount of water that contributes from upslope cells is calculated)
4. Calculation of the groundwater flow path by accumulation of the flow directions for every cell
5. The length of the flow path is calculated using a natural barrier (river network; groundwater infiltration into surface water is assumed only when groundwater flowpath intersects the river)
6. With division by the distance velocity (hydraulic conductivity from the geological maps) the potential travel time (groundwater residence time) is calculated from the flowpath length

The calculation of the distance velocity from hydraulic conductivities (k_f -Value) implies the knowledge of porosity, which is effectively used for groundwater flow. This information is very uncertain and changes significantly in respect to geological formations. Therefore, the porosity (n_f) for the calculation of the distance velocity was considered in different ways:

1. as constant: 0.2
2. calculated from the k_f -value using the relationship reported by DVWK et al. (1999):

$$\ln(n_f) = 0.182[\ln(k_f) - 2.1] \quad (\text{Equation 27})$$

Furthermore, the following input information was used and partly changed to identify sensitivities of the results in respect to the input information:

- Grids with different resolutions of the interpolated mean groundwater table (25m grid cell size, 150m grid cell size) calculated out of the measurements from the groundwater table observation wells.

- Shapes of the river network as barrier for the groundwater flow considering different orders of the rivers. Calculations were performed with the consideration of rivers belonging to the 3rd or higher order (order 1-3), the 4th or higher order (order 1-4) or the 5th or higher order (order 1-5)
- Geological maps for the provision of hydraulic conductivities. Maps of different spatial resolutions and different origins were used. For the geological formations ranges of k_f -values were defined for minimum (k_{fmin}) or maximum (k_{fmax}) values

Due to the limited number of groundwater observation wells and their limitation in spatial distribution within the Wulka catchment and the Ybbs catchment, the calculated groundwater residence time distributions are limited in spatial extent to the spatial distribution of the groundwater observation wells.

Nitrogen routing was realised using constant area-specific nitrogen surpluses on the groundwater surface, which were derived from long-term mean area-specific nitrogen surplus related to the catchment area with consideration of nitrogen losses via denitrification in the soil.

The nitrogen surplus on the soil amount to 40 kgN/ha*a and 75 kgN/ha*a according to Table 6 for the Wulka and the Ybbs catchment, respectively. Since most of the groundwater observation wells in the Ybbs catchment are situated in the Krenstetten subcatchment and Greimpersdorf subcatchment downstream of Kematen, the nitrogen surplus of Krenstetten subcatchment was used. Nitrogen losses by denitrification in the soil were defined based on own experiences to be 15 kgN/ha*a and 25 kgN/ha*a for the Wulka and the Ybbs catchment, respectively. Therewith, nitrogen surpluses on the groundwater surface of 25 kgN/ha*a and 50 kgN/ha*a were calculated for the Wulka catchment and the Ybbs catchment, respectively.

Already in chapter 2.3.1 denitrification kinetics were discussed being subject to first order reaction kinetics, when nitrate availability for denitrification is limited. So, nitrate degradation in the groundwater is subject to exponential decay and can be characterised by certain half life times.

Within this approach, denitrification in the groundwater was defined using two different half life times, which were reported by Wendland et al. (1999):

- $T_{1/2}=730$ days (2 years) or
- $T_{1/2}=1460$ days (4 years)

From the calculated groundwater residence times for each grid cell and the constant nitrogen surplus on the groundwater surface, the contribution of each grid cell to total diffuse nitrogen emissions via groundwater to the surface water was calculated with consideration of nitrate reduction in the groundwater by denitrification. Using different half life times characterising the denitrification rates in the groundwater resulted in different amounts of total nitrogen emissions to surface water. Calculated diffuse nitrogen emissions have been compared to calculated nitrogen emissions using the MONERIS model and to observations to evaluate the significance of the assumed half life times in terms of characterisation of denitrification processes in the groundwater of both catchments.

Since each grid cell is characterised by an individual groundwater residence time until the surface water, nitrate reduction in the groundwater by denitrification is dependent on the calculated groundwater residence time and can be related to the location of each cell within the catchment, what enables the identification of areas which are highly sensitive to large nitrogen releases by groundwater to the surface waters.

The application of this approach to both catchments is presented in this chapter. Differences between the catchments in terms of different geohydraulic conditions on groundwater residence times and thus, on the specific contribution of catchment areas to total diffuse nitrogen emissions to the surface water will be presented.

7.3.2 Application for the Wulka catchment

For the Wulka catchment calculations of groundwater residence time distributions have been performed using different input information.

First of all the calculations are based on groundwater table information, which have been observed in the Wulka catchment. The number of groundwater observation wells and their location within the catchment limited the spatial extent of the calculated groundwater residence time distributions, like shown in Figure 75.

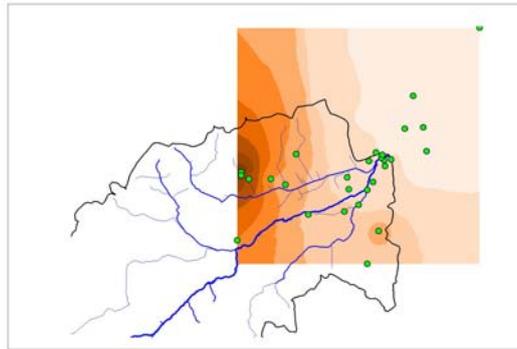


Figure 75: Spatial extent of the interpolated groundwater table information limited by the number of groundwater observation wells (stations: green points)

From the observed groundwater table information, mean groundwater table elevations have been calculated for the period 1970-2002. From the calculated means of the groundwater table elevation, grids of the mean groundwater surface were derived using the inverse distance weighted interpolator provided by the Spatial Analyst Vers. 2.0 for ArcView 3.2a with the following specifications:

- Interpolation of calculated mean groundwater elevations with 25m grid size
- Interpolation of calculated mean groundwater elevations with 150m grid size
- Interpolation of calculated mean groundwater elevations with 25m grid size with additional consideration of mean elevation of the river
- Interpolation of groundwater elevations from an appointed date with 25m grid size with additional consideration of mean elevation of the river
- Interpolation of groundwater elevations from an appointed date with 25m grid size with additional consideration of elevation of the river from a specific sampling date

To derive hydraulic conductivity for groundwater flow, the following geological maps were used with changing grid sizes and different resolution of geological information:

- Geological map of Austria (250m grid size, only rough information on geological formations)
- Geological map from Geological Survey of Austria (shapes converted to 25m grid size, detailed information on local geology; with Authorisation by the Geological Survey of Austria - ©GBA-2002-ZI.29/1/02)

From the digital maps hydraulic conductivities were evaluated using literature values from Spitz et al. (1996). For the detailed geological map ranges of the hydraulic conductivity were considered for the relevant geological formations, which are indicated by abbreviations **kfmin** (minimal hydraulic conductivity) and **kfmax** (maximum hydraulic conductivity) in Table 28.

For the calculation of distance velocity from hydraulic conductivity, the porosity of the aquifer which is used for groundwater flow has to be specified. Different assumptions were made for the consideration of the porosity:

- Constant porosity (0.2)
- Variable porosity as function of hydraulic conductivity

Table 28 gives a compilation of the diverse input data which have been used for the different calculations.

Table 28: Definitions for calculation versions in terms of variations of the different input information

Grid resolution of groundwater table	Groundwater surface interpolation	Geological map
- 25 m cell size - 150m cell size	- ... interpolation of mean groundwater level - f... interpolation of mean groundwater level and mean water level in river - f2... interpolation of mean groundwater level and water level in river from appointed day - f3... interpolation of groundwater level from appointed day and water level in river from appointed day	- geo... clip out of the geological map of Austria (rough information, 250m cell size) - kfmin... min. kf-value out of geol. map from geol. survey Austria; detailed information - kfmax... max. kf-value out of geol. map from geol. survey Austria - geo/kfmin/kfmax 2... distance velocity, constant porosity (min. J = 0,0001) - geo/kfmin/kfmax p2... distance velocity, variable porosity (min. J = 0,0001)

The nomenclature of the calculation versions was carried out in the following way and is important to understand the listed histograms and density distributions of the calculated groundwater residence times in the Appendix (chapter 10):

wu/25/_/geo/2 with

1. **wu...** abbreviation for ‚Wulka‘ catchment; **y...** stands for ‚Ybbs‘ (see chapter 7.3.3)
2. **25...** grid size of groundwater table information (**25m/150m**)
3. **_...** this replacement character was defined to consider changing input data for the groundwater surface interpolation (.../f/f2/f3)
4. **geo** abbreviation for geological maps, which were used for the calculations (**geo/kfmin/kfmax**)
5. **2...** abbreviation for consideration of constant or variable porosity for the calculations (**2/p2**)

Using the different input information according to Table 28, sensitivity analyses were performed to assess the influence of changes in input information on calculated groundwater residence time distributions.

Using groundwater surface information with 150m grid size resulted in noticeably shorter calculated average groundwater residence times in relation to a 25m grid cell size. Similar findings are reported by DVWK et al. (1999). The loss of information about spatial heterogeneities in the aquifer due to the aggregation (shapes with detailed geological information were transformed to 150m grid size too) results in a generalisation particular in geological information. Small parts of the catchment with low/high hydraulic conductivity may vanish due to aggregation and lead to considerable errors in estimations of the groundwater residence time. Additionally, the discretisation of the rivers is realised with the same grid size, what results in a river width according to the grid cell size (also 150m). This is likely to lead to significant underestimations of calculated groundwater residence times (see Figure 87 and Figure 88 in chapter 10.1). Further calculations were performed utilising the 25m grid cell size.

Furthermore, significant influences of the input data on calculated groundwater residence time distributions were obtained from:

- the considered geological maps
- utilisation of a constant or variable porosity

These influences on calculated groundwater residence time distributions are presented in Table 29. The consideration of elevations of the river for interpolation of the groundwater surface as well as utilisation of observations from sampling dates for both, the groundwater elevations and the elevation of the river, was not of significant influence on the calculated groundwater residence time distributions.

Table 29: Statistical values of the calculated residence times of selected versions [in years]

Calculation versions with 25m grid size	1st Quartile	Median	Mean	3rd Quartile	Max.
rough geo. Information (geo) with constant porosity	134	1362	3011	3815	47060
detailed geo. Information with maximal hydraulic conductivity (kfmax) and constant porosity	17	312	1845	1516	31640
detailed geo. Information with minimal hydraulic conductivity (kfmin) and constant porosity	34	608	2328	2429	35920
rough geo. Information (geo) with variable porosity	40	349	707	966	9367
detailed geo. Information with maximal hydraulic conductivity (kfmax) and variable porosity	10	100	670	388	22270
detailed geo. Information with minimal hydraulic conductivity (kfmin) and variable porosity	19	169	788	609	22320
Mean constant porosity	63	761	2395	2587	38207
Mean variable porosity	23	206	722	652	17986
Mean all	43	484	1559	1620	28097

The influence of the effective porosity is of significant importance on the calculated groundwater residence time distribution. The consideration of variable porosity calculated according to equation 38 resulted in significantly lower average

groundwater residence times compared to the calculations using a constant flow effective porosity.

In regard to Table 29 the calculated average groundwater residence time of the Wulka varies between 100...1362 years (median). Vertical heterogeneities were not considered in the calculations. The definitions of saturated conductivities in geological maps are based on literature values covering wide ranges for specific geological formations or textures. Additionally, spatial aggregations may lead to losses of information particularly eliminating small fractions of hydrologically significant different parts may result in complete different calculations in groundwater residence time distributions. And, the derivation of geological maps is based on point information as well. So uncertainties in input data are reflected in different groundwater residence time distributions using different input information.

Using the rough geological information (geo) the calculated mean groundwater residence times were obviously overestimated. As indicated by Figure 76, these input information resulted in groundwater residence time distributions with large fractions of areas with groundwater residence time < 10 years and marginal frequencies of areas with long groundwater residence times (see maximum values in Table 29), what results statistically in significantly larger average groundwater residence times.

The calculations using the more detailed geological information resulted in a larger fraction of areas with groundwater residence times < 50 years, but with more even distributed frequencies (see Figure 76). This resulted statistically in lower groundwater residence times. The calculations using maximal hydraulic conductivity resulted generally in average shorter groundwater residence times due to higher frequencies of areas with groundwater residence time < 50 years.

Generally, for each calculation version a larger frequency of areas with groundwater residence times of < 50 years was obtained using the variable porosity, what resulted in significantly shorter calculated groundwater residence times in comparison to the calculations using a constant porosity (see Figure 76).

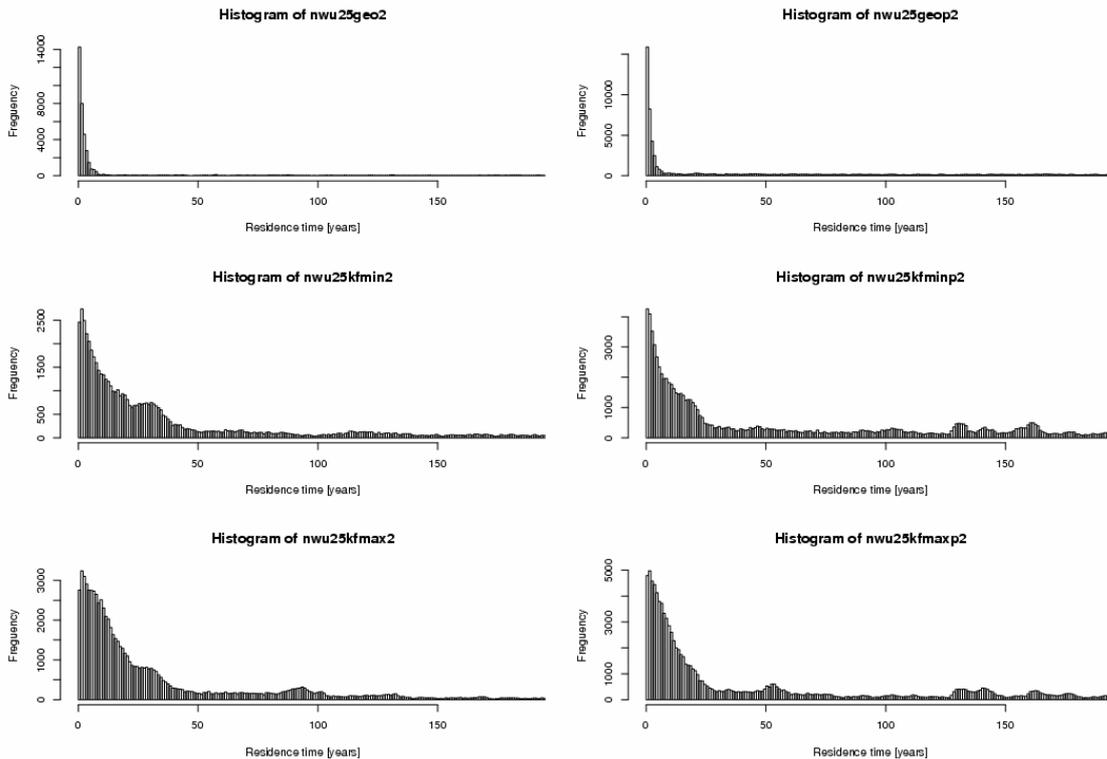


Figure 76: Comparison of histograms of groundwater residence time distributions using different geological input information with consideration of a constant (left) and a variable (right) porosity

Area-specific nitrogen emissions via groundwater to surface water were calculated using the calculated groundwater residence time distributions for the different input information. Differences in area-specific nitrogen emissions between the calculation versions are the result of varying distribution functions of the calculated groundwater residence times. A comparison of calculated area-specific nitrogen emissions is shown in Figure 77.

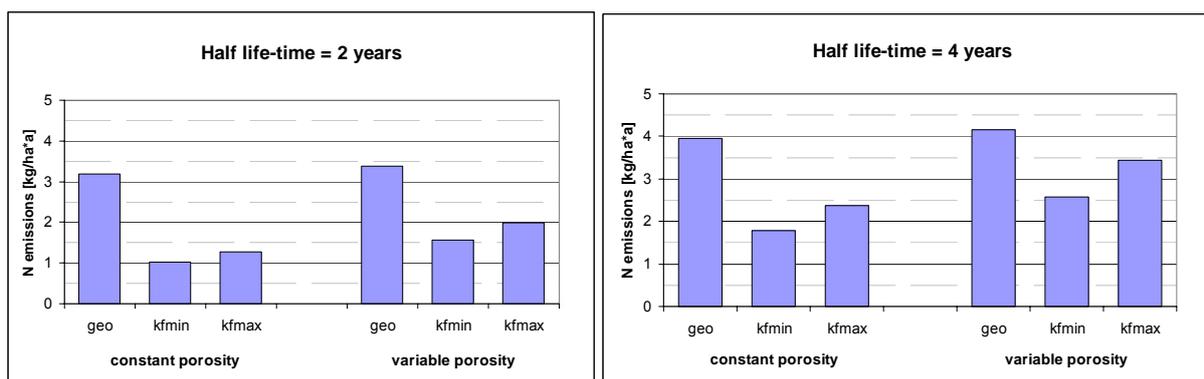


Figure 77: Area-specific nitrogen emissions via groundwater calculated from the residence time distributions of the different calculation versions with consideration of half-life-times of 2 years and 4 years, respectively (calculation area = 100.5 km²)

Generally, the calculated area-specific nitrogen emissions via groundwater using the more rough geological information (geo) were the highest compared to the more detailed geological information for both using the 2 years half life time as well as the 4 years half life time. This results from the comparably higher fraction of areas with only short groundwater residence time (see Figure 76) using the rough geological

information, but contradictory the higher average groundwater residence time using this information was obtained due to higher fraction of areas with extraordinary high groundwater residence time. With consideration of a variable porosity higher area specific nitrogen emissions were estimated compared to the consideration of a constant porosity. The comparison of the calculations using the variable porosity indicated higher calculated nitrogen emissions using the detailed geological information ($k_{fmin}/k_{fmax} \sim +50\%$) than using the rough geological information (geo $\sim +10\%$) in relation to the calculations using a constant porosity.

Using the 4 years half life time for characterisation of denitrification in the groundwater higher nitrogen emissions via groundwater were calculated compared to the calculations using the 2 years half life time. The calculated nitrogen emissions via groundwater using the MONERIS model fit quite well to the calculated nitrogen emissions using the half life time of 4 years (see Table 30). Additional comparison to observed nitrogen in-stream loads of the Wulka river indicated that the 4 years half-life time resulted in calculated nitrogen emissions to surface water, which are close to observations and that the selected half life time reflects denitrification activity in the groundwater of the Wulka catchment sufficiently. However, the assessment of the calculated nitrogen emissions via groundwater in terms of the most accurate estimation is not possible, since the definitions of the input data are highly uncertain and the spatial extent which was considered for these calculations does not match with total Wulka catchment area.

Table 30: Comparison of calculated area-specific nitrogen emissions via groundwater using the groundwater residence time distribution and changing half life times with calculated area-specific nitrogen emissions using the MONERIS model and observed in-stream nitrogen load

	[kgN/ha*a]
calculated N emissions via groundwater using the MONERIS model	2.0...3.6
calculated N emissions via groundwater using groundwater residence time distributions and half life time ($T_{1/2} = 2$ years)	1.6...2.0
calculated N emissions via groundwater using groundwater residence time distributions and half life time ($T_{1/2} = 4$ years)	2.6...3.4
observed in-stream nitrogen load	3.7

Using the calculated groundwater residence time distributions for the calculations of nitrogen emissions by groundwater to surface water enables one to account every grid cell for its contribution to total nitrogen loads via groundwater. Hence, the areas with certain calculated groundwater residence times were grouped and were related to their specific nitrogen emission to the calculated total nitrogen loads (see Figure 78). Naturally the most nitrogen emissions come from areas with the lowest groundwater residence time due to the lowest retention time, as Figure 78 definitely illustrates.

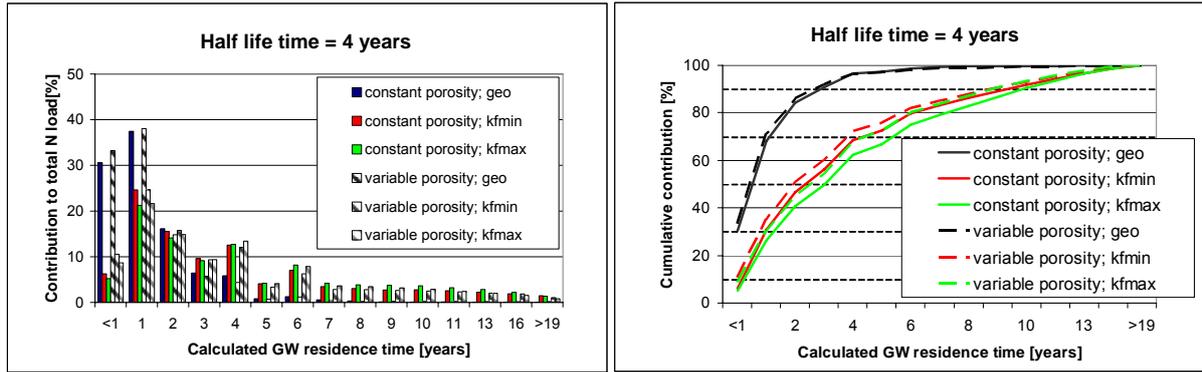


Figure 78: Contribution (relative and cumulative) of areas with certain groundwater residence times to total nitrogen emissions via groundwater using a half life time for denitrification of 4 years

In regard to the relative and cumulative contribution of nitrogen emissions to the total nitrogen loads from areas with a certain calculated groundwater residence time, significant deviations between the calculations in Figure 78 using different input information were obtained. With consideration of the more rough geological information (geo) for the calculations, 90% of the nitrogen emissions stem from areas with groundwater residence times of < 3 years. According to histograms (Figure 76) these calculation versions are characterised by large fraction of areas with extremely low groundwater residence time, what results in less effective denitrification activity in the groundwater and thus, in elevated area-specific nitrogen emissions to the surface water.

Using the more detailed more detailed geological information it was calculated that 90% of the nitrogen stem from areas with a calculated groundwater residence time of < 9 years. Due to the more even fractions of areas with groundwater residence time <50 years (see Figure 76) nitrogen emissions are contributed more evenly from larger fractions of areas with longer groundwater residence times.

From calculations it becomes apparent that 90% of the nitrogen emissions were contributed from areas with calculated groundwater residence times of <3...9 years. The fraction of these areas on the total area is shown in Figure 79.

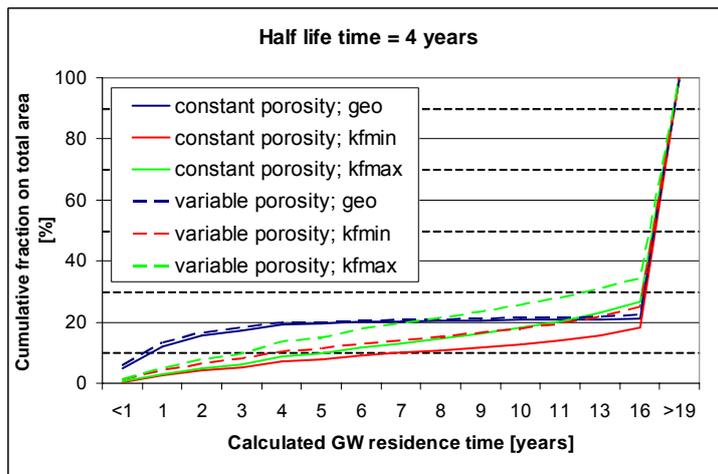


Figure 79: Cumulative distribution function of fractions of areas with a certain groundwater residence time on the total area

With consideration of different calculations using the detailed geological information, between 10-25% of the total area is characterised by a groundwater

residence time of <9 years and contribute to more than 90% of the total nitrogen load. Using the rough geological information about 20% of the total area is characterised by groundwater residence time of <3 years and contribute >90% of the total nitrogen emissions.

That means that from 75-90% of the total area <10% of the total nitrogen loads are contributed via groundwater to the surface water because of longer groundwater residence times and therefore higher nitrogen losses via denitrification in the groundwater.

Bringing these contributing areas in relation to their location within the catchment, it becomes apparent that these areas are located predominantly in very short distance to the surface waters (see Figure 80).

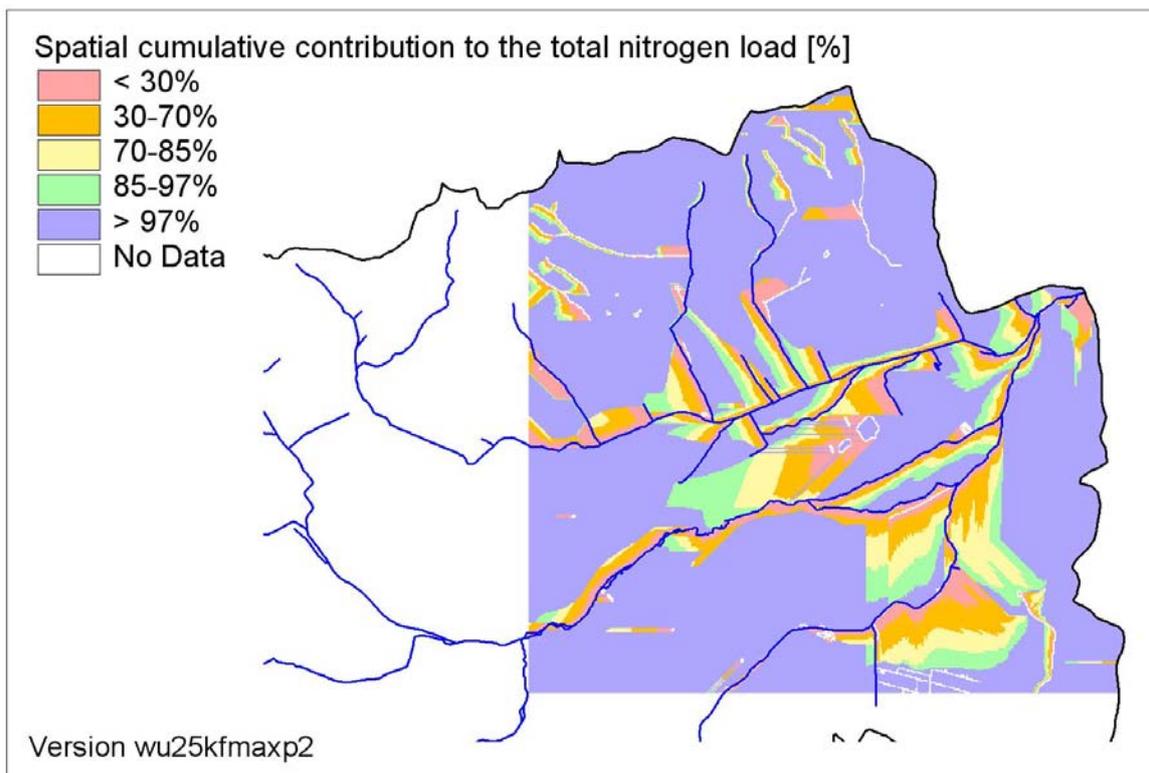


Figure 80: Location of areas related to specific cumulative contribution to the total nitrogen emissions via groundwater to surface waters (half-life time = 4 years)

Figure 80 shows the cumulative contribution of the areas to the calculated total diffuse nitrogen loads. In regard to the fraction of areas which are the source for most of the diffuse nitrogen emissions to the surface water, 97% of the nitrogen emissions are contributed by areas which are coloured pink to green and represent the areas with average groundwater residence times of ≤ 13 years. The remaining parts of the catchment area (blue coloured areas) have by far the highest fraction on total area, but contribute only the remaining 3% to the total nitrogen loads via groundwater to surface water.

That indicates the importance of the riparian areas near the river systems (<2000m distance to the surface water), because nitrogen loads from these areas via groundwater are emitted to surface water with only little reduction in nitrogen levels by denitrification. These areas are responsible for the majority of in-stream nitrogen

loads in the surface water, which have been emitted via groundwater. Areas, which produce most of the nitrogen due to agricultural activity, usually are located in larger distances to surface water and contribute to nitrogen load in surface water in reduced amount. The calculations reveal that particularly areas with large distances to surface water and with predominantly long groundwater residence times tend to show higher nitrate concentrations (according to the findings in chapter 5.2), but are of less significant importance in terms of contributions via diffuse nitrogen emissions to the total nitrogen loads of the surface water. Riparian zones form the interface between groundwater flow and surface water bodies and are areas where substances and flow are emitted, which are produced predominantly elsewhere. Due to short groundwater residence times these areas should be restricted from agricultural activity and elevated nitrogen exposition, they should be predominantly used as buffer zones to exploit their denitrification potential for groundwater flow.

Denitrification activity in the groundwater of the Wulka catchment could be confirmed using this approach, since calculated area-specific nitrogen emissions via groundwater coincided with calculated area-specific nitrogen emissions by groundwater using the MONERIS model. Additionally, using a half life time of 4 years calculated nitrogen emissions agreed with observed nitrogen in-stream loads of the Wulka river and confirmed the applicability of half life time approaches for the consideration of denitrification processes in the groundwater in modelling approaches.

7.3.3 Application for the Ybbs catchment

For the Ybbs catchment calculations of groundwater residence time distributions have been performed using different input information according to the definitions for the calculations for the Wulka catchment.

First of all the calculations are based on groundwater table information, which have been observed in the Ybbs catchment. The number of groundwater observation wells and their location limited the spatial extent of the calculated groundwater residence time distributions (see Figure 81). Additional information have been obtained from detailed observations of the groundwater surface using measurements from sampling dates, but with a less spatial extent.

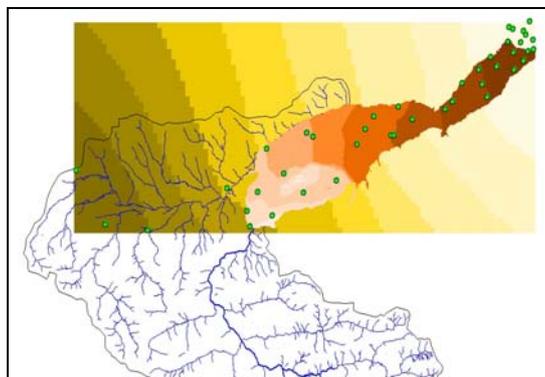


Figure 81: Spatial extent of the interpolated groundwater table information limited by the number of groundwater observation wells (yellow, stations green); additional information on groundwater surface was obtained from measurements using appointed dates (red-brown)

From the observed groundwater table information, mean groundwater table elevations have been calculated for the period 1970-2002. From the calculated

means of the groundwater table elevation, grids of the mean groundwater surface were derived using the inverse distance weighted interpolator provided by the Spatial Analyst Vers. 2.0 for ArcView 3.2a with the following specifications:

- Interpolation of calculated mean groundwater elevations with 25m grid size
- Interpolation of calculated mean groundwater elevations with 100m grid size
- Interpolation of the groundwater elevations from appointed dates with 25m grid size

To derive hydraulic conductivity for groundwater flow, the following geological maps were used with changing grid sizes and different resolution of geological information:

- Geological map of Austria (250m grid size, only rough information on geological formations)
- Geological map from Geological Survey of Austria (shapes converted to 25m grid size, detailed information on local geology; with Authorisation by the Geological Survey of Austria - ©GBA-2002-ZI.29/1/02)

From the digital maps hydraulic conductivities were evaluated using literature values (Spitz et al. 1996). For the detailed geological map ranges of the hydraulic conductivity were considered for the relevant geological formations, which is again indicated by abbreviations **kfmin** (minimal hydraulic conductivity) and **kfmax** (maximum hydraulic conductivity) in Table 31.

For the calculation of distance velocity from hydraulic conductivity, different assumptions were made for the consideration of the porosity:

- Constant porosity (0.2)
- Variable porosity as function of hydraulic conductivity

Additionally to the definitions, which were already presented for the calculations for the Wulka catchment, for the calculation of the groundwater residence time distributions of the Ybbs catchment different river orders were considered for the definition of the river network:

- Consideration of rivers of first 3 orders as barrier for groundwater flow
- Consideration of rivers of first 4 orders as barrier for groundwater flow
- Consideration of rivers of all river orders (5) as barrier for groundwater flow

Table 31 gives a compilation of the diverse input data which have been used for calculations.

Table 31: Definitions for calculation versions in terms of variations of the different input information

Grid resolution of groundwater table	Order of river network	Geological map
- 25 m cell size - 100m cell size	- ... interpolation of mean groundwater level - k3 ...consideration of rivers of the first, second and third order - k4 ...consideration of rivers of the first, second, third and fourth order - k5 ...consideration of rivers of all 5 orders	- geo ...clip out of the geological map of Austria (rough information, 250m cell size) - kfmin ...min. kf-value out of geol. map from geol. survey Austria; detailed information - kfmax ...max. kf-value out of geol. map from geol. survey Austria - geo/kfmin/kfmax2...distance velocity, constant porosity (min. J = 0,0001) - geo/kfmin/kfmaxp2...distance velocity, variable porosity (min. J = 0,0001)

The nomenclature of the calculation versions was carried out in the similar way like for the calculations for the Wulka catchment (see chapter 7.3.2).

Using the different input information according to Table 31, sensitivity analyses were performed. Using a grid size of 100m the calculated groundwater residence times were significantly lower compared to calculations using a 25m grid size, because the fraction of areas with short groundwater residence times (<10 years) was significantly higher using the 100m grid size (see Figure 92).

A significant decrease in calculated groundwater residence times was obtained, when the order of rivers which were considered as barrier for the groundwater flow, was increased (see Figure 90 and Figure 91). Due to additional consideration of smaller rivers as barrier for groundwater flow, flow paths were shortened significantly with adequate impacts on calculated groundwater residence time.

According to the calculations for the Wulka catchment, the detailed geological information resulted in significantly larger fractions of areas with short groundwater residence time, but with much larger difference in relation to the groundwater residence time distributions using the rough information compared to the calculations for the Wulka catchment.

For the observed groundwater table information using sampling dates (with considerably smaller spatial extent) the calculations using the rough geological information (geo) the histograms indicated less evenly distributed density functions for calculated groundwater residence times than for the calculations using the detailed geological information (kfmin/kfmax) (see Figure 92) due to the smaller spatial extent, whereby much less geological formations (geo) are located within this section and were considered for the calculations, what resulted in changed influence of considered geological information.

Main statistical values for the calculated groundwater residence time distributions are shown in Table 32.

Table 32: Statistical values of the calculated residence times of selected versions [in years]

version	1st Quartile	Median	Mean	3rd Quartile	Max.
rough geo. Information (geo) with constant porosity and consideration of rivers up to the 4 th order	157	800	1756	2192	88330
detailed geo. Information (kfmin) with minimal hydraulic conductivity, constant porosity and consideration of rivers up to the 4 th order	9.8	29	628	167	101600
detailed geo. Information (kfmax) with maximal hydraulic conductivity, constant porosity and consideration of rivers up to the 4 th order	6.2	15	222	36	101600
rough geo. Information (geo) with variable porosity and consideration of rivers up to the 4 th order	42	212	457	574	17160
detailed geo. Information (kfmin) with minimal hydraulic conductivity, variable porosity and consideration of rivers up to the 4 th order	5.4	15	184	67	19070
detailed geo. Information (kfmax) with maximal hydraulic conductivity, variable porosity and consideration of rivers up to the 4 th order	3.6	9	70	21	19070
Mean constant porosity	58	281	869	798	97177
Mean variable porosity	17	79	237	221	18433
Mean all	37	180	553	510	57805

According to Table 32 the rough geological information resulted in average calculated groundwater residence times, which are considerably higher, compared to calculations using the detailed geological information. Calculated groundwater residence time distributions using the rough geological information seem to be considerably overestimated and not realistic, even if groundwater residence times are expected to be lower than in the Wulka catchment, what was indicated also by tritium analyses.

The consideration of a variable porosity resulted in significantly shorter average groundwater residence times compared to the calculations using a constant porosity. In comparison to the calculated groundwater residence times of Wulka catchment, the calculated groundwater residence times are generally significantly lower for both the calculations using a constant as well as a variable porosity. This supports the assumption that was already concluded from water balance calculations using the SWAT 2000 model and from groundwater quality observations, that the Ybbs catchment is generally characterised by significant shorter groundwater residence times.

In regard to Table 32 the calculated average groundwater residence time of the Ybbs varies between 9...800 years (median) what indicates again consequences arising from the uncertainties in input data definitions.

The calculated groundwater residence time distributions using the rough geological information (**geo**) are dominated by considerable large fractions of areas with extremely long groundwater residence times (>200 years) and therefore

groundwater residence times seem to be significantly overestimated. The frequency distributions of the calculated groundwater residence times indicated the highest frequencies (counts of areas with certain estimated residence time) for areas with a groundwater residence time of <1 year (see Figure 82), but in addition a uniform distribution with small counts for areas with longer groundwater residence times leading to this large mean groundwater residence time.

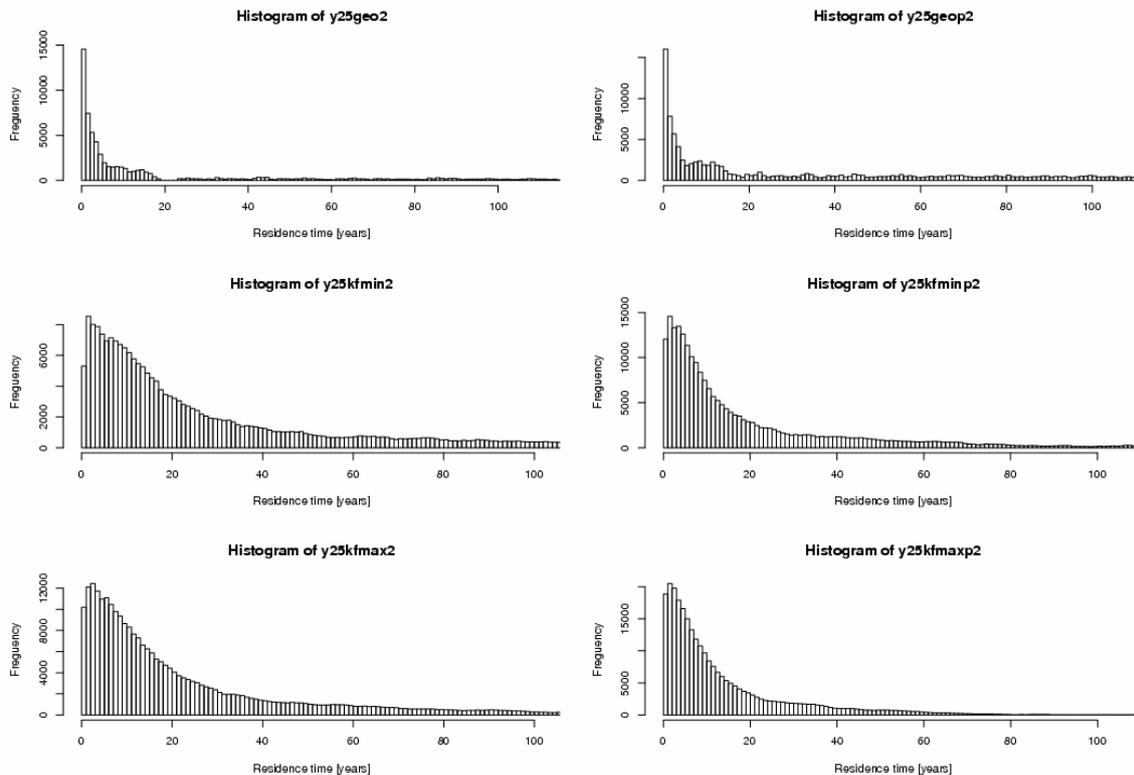


Figure 82: Comparison of histograms of groundwater residence time distributions using different input information with consideration of a constant (left) and a variable (right) porosity

In regard to the calculations using the detailed geological information (kfmin/kfmax) the calculated groundwater residence times were significantly shorter with approximately 50-90% of the calculated groundwater residence times of <50 years. Using the calculations with detailed geological information (kfmin/kfmax) more evenly distributed frequency distributions were obtained with high frequencies of areas with groundwater residence time of <50 years (Figure 82). The consideration of a variable porosity results in higher fractions of areas with shorter groundwater residence times compared to calculations with consideration of a constant porosity.

In comparison to Wulka catchment, the calculated groundwater residence time distributions of the Ybbs catchment show significantly higher fractions of areas with short groundwater residence times (<50 years) in relation to the total distributions.

According to definitions area-specific nitrogen emissions via groundwater to surface water were calculated using the calculated groundwater residence time distributions for the different input information. A comparison of the calculated area-specific nitrogen emissions via groundwater is shown in Figure 83.

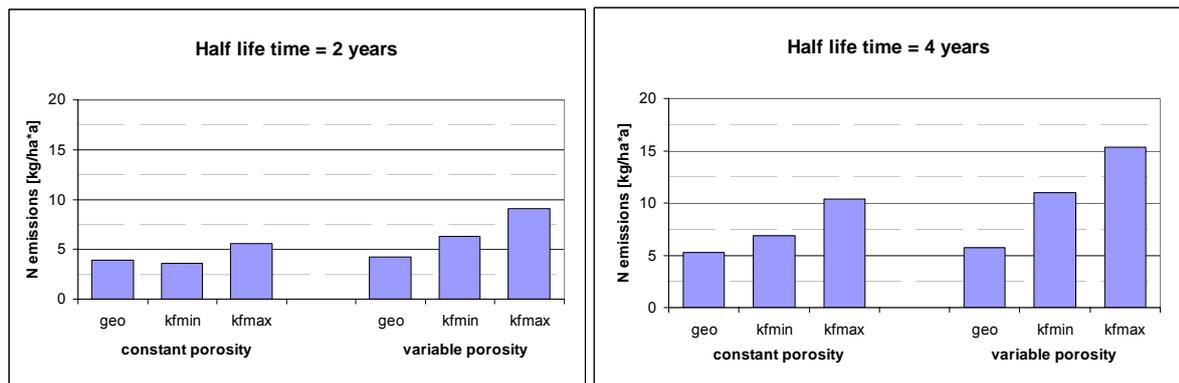


Figure 83: Area-specific nitrogen emissions via groundwater calculated from the residence time distributions of the different calculation versions with consideration of half-life-times of 2 years and 4 years, respectively (area=176 km²)

Generally, the calculated area-specific nitrogen emissions via groundwater using the rough geological information (geo) were the lowest compared to the calculations using the detailed geological information for both with 2 years half life time as well as with 4 years half life time. This results from the significant larger fraction of areas with long groundwater residence time, like indicated already by the histograms in Figure 82 using the rough geological information. With consideration of a variable porosity significantly higher area specific nitrogen emissions were calculated compared to the calculations with consideration of a constant porosity. The comparison of the calculations using the variable porosity indicated higher calculated nitrogen emissions using the detailed geological information (kfmin/kfmax ~ +50-60%) than using the rough geological information (geo ~ +10%) in relation to the calculations using a constant porosity.

Using the 4 years half life time for characterisation of denitrification in groundwater higher nitrogen emissions via groundwater were calculated in comparison to the calculations using the 2 years half life time. A comparison to the calculated nitrogen emissions via groundwater using the MONERIS model shows, that the calculated nitrogen emissions using the half life time of 4 years are less the nitrogen emissions from the MONERIS model (see Table 33). In comparison to the observed in-stream loads of the Ybbs river the calculated nitrogen emissions using a half life time of 4 years were noticeably lower. That reveals that denitrification in the groundwater of the Ybbs catchment is likely to be characterised by a half life time of >4 years, because the calculated mean groundwater residence time for the Ybbs catchment with the highest area-specific nitrogen emissions is considerably short with 9 years (median). Denitrification in the groundwater of the Ybbs catchment is likely to be lower in comparison to the Wulka catchment.

Table 33: Comparison of calculated area-specific nitrogen emissions via groundwater using the groundwater residence time distribution and changing half life time with calculated area-specific nitrogen emissions using the MONERIS model and observed in-stream nitrogen load

	[kgN/ha*a]
calculated N emissions via groundwater using the MONERIS model	17...18
calculated N emissions via groundwater using groundwater residence time distributions and half life time ($T_{1/2} = 2$ years)	6.3...9.7
calculated N emissions via groundwater using groundwater residence time distributions and half life time ($T_{1/2} = 4$ years)	11.0...15.4
observed in-stream nitrogen load	18.7

According to the analyses for the Wulka catchment, the areas with certain calculated groundwater residence times were grouped and were related to their specific nitrogen emission to the calculated total nitrogen loads (see Figure 84).

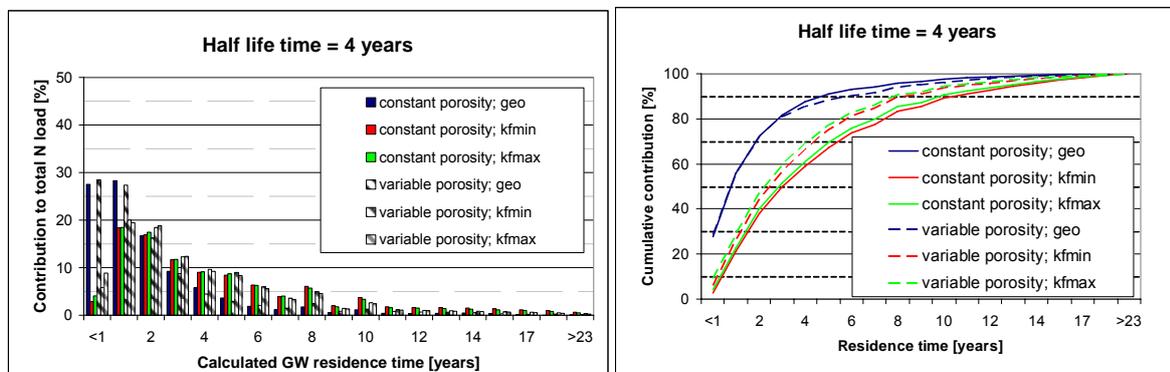


Figure 84: Contribution (relative and cumulative) of areas with certain groundwater residence times to total nitrogen emissions via groundwater using a half life time for denitrification of 4 years

In regard to the relative and cumulative contribution of nitrogen emissions to the total nitrogen loads from areas with a certain calculated groundwater residence time (Figure 84) again significant deviations between the calculations using different input information were obtained. With consideration of the rough geological information (geo) for the calculations, more than 90% of the nitrogen emissions stem from areas with groundwater residence times of <5 years. According to the histogram in Figure 82 the areas with groundwater residence time of ≤ 1 years have by far the highest fraction, and the areas with groundwater residence times of >5 years show a significantly smaller frequency. This results in contribution of nitrogen emissions predominantly by areas with long groundwater residence times and lower area-specific nitrogen emissions.

Using the detailed geological information it was calculated that more than 90% of the nitrogen emissions stem from areas with a calculated groundwater residence time of <10 years. The histograms show a larger fraction of areas with groundwater residence times <20 years, which contribute nitrogen emissions even more balanced, what results in higher area-specific nitrogen emissions by groundwater.

With consideration of detailed geological information, >90% of the nitrogen emissions were contributed from areas with a calculated groundwater residence time of <10 years. The fraction of these areas on the total area is shown in Figure 85. Taking into account the deviations between both calculations using detailed

geological information between 25-60% of the total area is characterised by a groundwater residence time of < 10 years and contribute to >90% of the total nitrogen load. In comparison to the calculations for the Wulka catchment, this fraction of the total area is significantly larger. For the calculations using the rough geological information, only about 10% of the total area contribute >90% of the total nitrogen emissions.

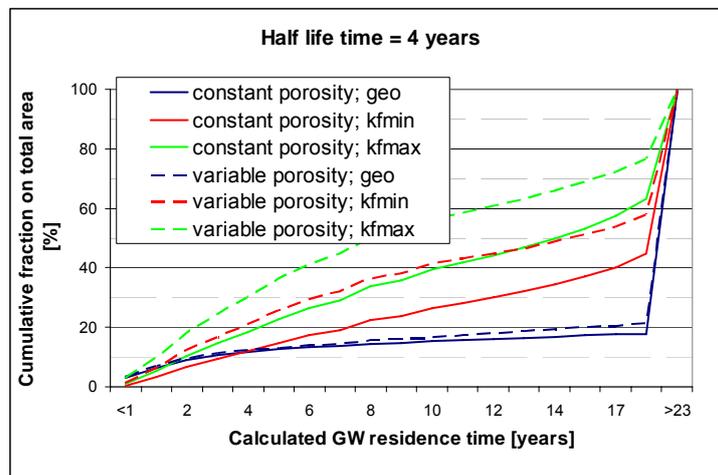


Figure 85: Cumulative distribution function of fractions of areas with a certain groundwater residence time on the total area

The areas with a calculated groundwater residence time of >10 years cover a fraction of 40-75% of the total area (for the calculations using the detailed geological information), but they contribute <10% of the total nitrogen loads via groundwater to surface water because of the longer groundwater residence times and therefore the higher nitrogen reductions via denitrification in the groundwater.

Bringing these contributing areas in relation to their location within the catchment, it becomes apparent that these areas are located predominantly in short distances (<2000m) to the surface waters, as indicated in Figure 86.

Figure 86 shows the cumulative contribution of the areas to the calculated total nitrogen loads. In regard to the fraction of areas which are the source of most of the nitrogen emissions, 97% of the nitrogen emissions are contributed by areas which are coloured pink to green and represent the areas with average groundwater residence times of ≤ 13 years. The remaining part of the catchment area (blue coloured areas) have by far the highest fraction on total area, but contribute only the remaining 3% to the total calculated nitrogen loads via groundwater to surface water.

The groundwater flow directions are, like indicated by Figure 86 mainly parallel to Ybbs river. Hence, contributions of nitrogen emissions via groundwater to surface water were considered from one side of the river only because of the definitions of this approach. Being more precise the infiltration of groundwater had to be considered from both sides of the river.

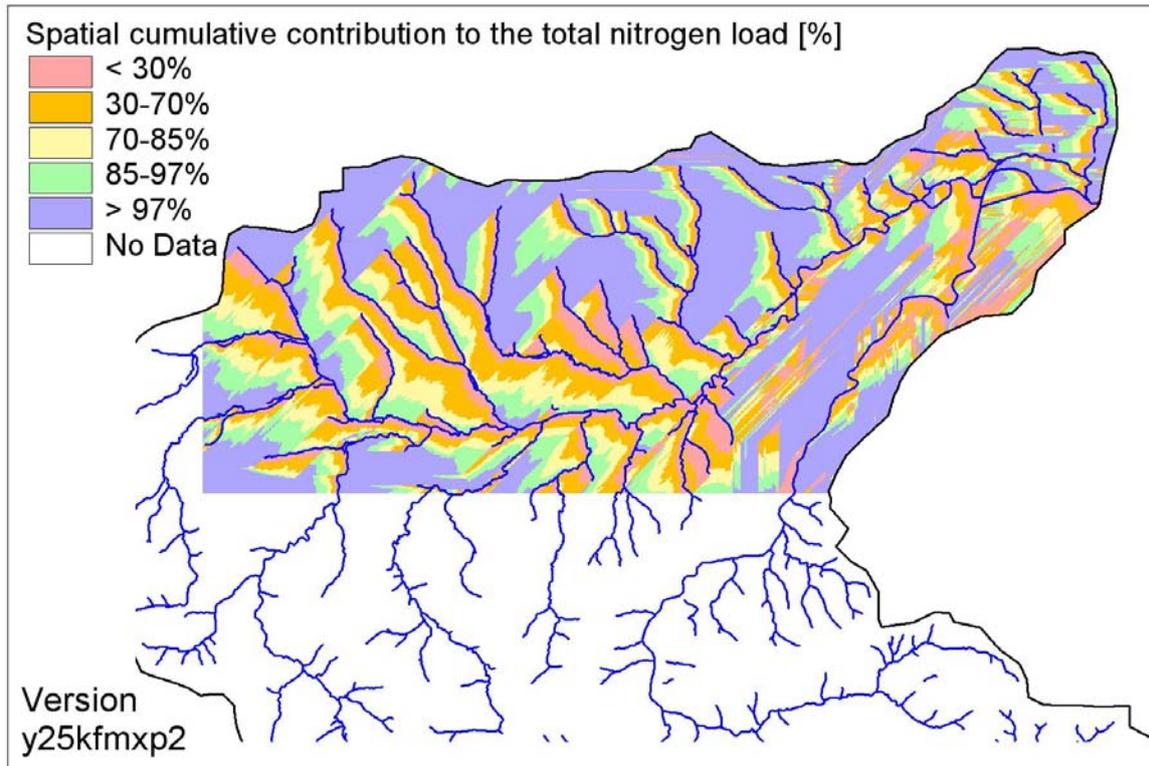


Figure 86: Location of areas related to specific cumulative contribution to the total nitrogen emissions via groundwater to surface waters (half-life time = 4 years)

Figure 86 indicates the importance of the zones near the river systems also in the Ybbs catchment (up to 2000m). The majority of nitrogen loads to the surface water, which were emitted by groundwater stem predominantly from riparian areas with only very short groundwater residence times. With increasing distances to the surface water the importance in terms of nitrogen contributions via groundwater from these areas to total nitrogen load in the surface water decreases significantly. These findings are well in line with results from chapter 5 concerning the observed decrease of nitrogen concentrations in groundwater with increasing distance to surface waters.

Under the management aspect the areas near the river system should be evaluated as sensitive in terms of nitrogen release due to a minor influence of denitrification in groundwater on nitrogen retention. Management strategies aiming at a reduction of diffuse nitrogen emission via groundwater to surface water should therefore be concentrated predominantly on areas with only small distances to surface waters and low groundwater residence times.

Denitrification in the groundwater of the Ybbs catchment could be confirmed using this approach. Using a half life time of 4 years for the characterisation of denitrification processes in the groundwater resulted in the underestimation of nitrogen emissions via groundwater in comparison to results, which were obtained by the MONERIS model. Calculations revealed significantly shorter groundwater residence times for the Ybbs catchments and denitrification in the groundwater, which is lower in comparison to the Wulka catchment.

7.4 Conclusions

The strengths of this new approach can be summarised in the following way:

- Simple approach, which is based on easily available data; model calibration is not needed, but the selection of the half life time characterising denitrification activity in groundwater significantly influences calculated nitrogen emissions to surface waters
- Differences in geohydraulic conditions and therefore in average groundwater residence times between both catchments, which have been already indicated as a result of the water balance calculations, could be confirmed
- Denitrification processes in groundwater were confirmed for the Wulka catchment and for the Ybbs catchment; Differences in denitrification in groundwater were indicated between the catchments, comparisons of calculated nitrogen emissions to surface water to results from the MONERIS model and to observed nitrogen in-stream river loads have been used to evaluate the selected half life times for characterising the catchment specific denitrification kinetics
- Denitrification in the groundwater was realised with consideration of heterogeneities in the groundwater due to geological conditions, nitrogen retention via denitrification in the groundwater could therefore be assessed fully-distributed for each grid cell as a function of geological conditions
- Connection could be established between the location of areas in the catchment and their specific nitrogen contributions via groundwater to total nitrogen loads in the surface water
- Assessment of the sensitivity of catchment areas in terms of their contribution of nitrogen emissions to surface waters could be undertaken

Due to the uncertainties in the input information the previously demonstrated calculations are highly uncertain concerning the quantitative conclusions. More precisely these are:

- Uncertainties due to interpolation of means of the groundwater surface; the interpolation method significantly impacts the spatial characteristics of the groundwater surface grids, the slope and groundwater residence time calculations
- Due to consideration of river network as barrier for groundwater flow the order of rivers taken into account significantly influence the calculated average groundwater residence times as well as calculated nitrogen emissions via groundwater to surface waters; digitalisation of river sections and their correct location may impact the calculated groundwater residence time distributions as well as the considered river order for the calculations; based on these investigations the consideration of rivers till the 3rd order can be recommended for the calculations
- Definition of saturated hydraulic conductivities depends mainly on experiences of the modeller as well as on values published in literature for certain texture classes; often considerable deviations are reported in literature mainly due to different grain size distributions, which are

summarised in one texture class; widespread ranges in conductivity and presence of preferential flow paths results in possibly wide ranges of calculated groundwater residence times

- The considered half life time used for the definition of denitrification considerably influences the calculated nitrogen emissions via groundwater to surface waters; spatial heterogeneities in half life time due to substrate limitation (nitrate, organic carbon, pyrite, dissolved oxygen) are not considered
- Consideration of nitrogen surplus as constant area specific nitrogen impulse; no deviations between agriculturally used and not agriculturally used areas is assumed, no dynamics or changes in nitrogen surpluses are regarded
- No vertical structure of aquifer was considered

The calculations clearly demonstrated the relation between constant nitrogen surpluses on the groundwater surface, the calculated groundwater residence time distributions and the contribution of each grid cell to nitrogen emissions via groundwater to surface water with consideration of denitrification processes in the groundwater.

From the application of the approach based on estimated groundwater residence time distributions the following statements can be derived:

- the order of rivers that are considered as groundwater flow barriers is of significant influence for the calculation of the groundwater residence time. Calculations with stepwise consideration of different river orders may allow the simulation of vertical structures in saturated zone estimating groundwater residence time distributions
- the grid cell size of the interpolated groundwater table affects the calculated groundwater residence time, with increasing grid sizes the uncertainty in groundwater residence time distribution increases due to aggregation of heterogeneities in geology and increase in assumed river width (due to same grid size); recommended are grid sizes of 25m
- resolution and information content (allocated saturated conductivity) of geological maps influence the estimation of the groundwater residence time distributions considerably
- calculations of groundwater residence time distributions using a variable porosity evaluating the distance velocity were assessed to be more appropriate than calculations using a constant porosity
- the estimation of nitrogen loads to surface waters considering a half life time of 4 years for characterisation of denitrification fit quite well with nitrogen emission calculations via groundwater using the MONERIS model as well as with measurements of in stream loads for the Wulka catchment; in the Ybbs catchment half life time for denitrification was likely to be >4 years
- almost all of the calculated nitrogen loads via groundwater to surface water stem from areas with a distance of <2500 m (for these calculation versions) to the river system and with relatively low calculated groundwater residence time (< 13 years), this indicates the importance of these areas in terms of

landuse management for reduction or maintenance of nitrogen emissions to surface water via groundwater

Possible advancements of this approach would concentrate first of all on the consideration of heterogeneities in nitrogen surpluses in order to differentiate between areas with and without agricultural activity. Also the consideration of varying denitrification activity using different half life times for diverse geological formations within a catchment may improve the significance of results of diffuse nitrogen emission calculations and could result in spatial distributions of denitrification activity in groundwater.

Using this approach it could be shown that diffuse nitrogen emissions to surface waters are not the result of land use practises and adequate nitrogen surpluses only. Land use practises do influence nitrogen loads to the groundwater by groundwater recharge to a large extent, and groundwater nitrogen concentrations are affected depending on the catchment-specific hydrology. Because of denitrification in groundwater, diffuse nitrogen emissions to surface waters depend beside specific nitrogen surpluses decisively on the location of the areas within the catchment, where the emissions come from, in respect to surface water bodies and on the hydrogeological conditions.

8 Summary and conclusions

Nitrogen leaching from soils to groundwater is seasonally and spatially dependent from fertilizer applications, plant growth, tillage practises and harvesting operations (Schachtschabel et al. 1992, Freudenthaler 1991). Moreover, nitrate content in leakage water is impacted by soil net mineralization processes and most critically, by the amount of soil percolation and groundwater recharge changing significantly throughout the year and with specific location (Rohmann et al. 1985, Pauwels et al. 2001).

Hence, catchment hydrology as consequence of climatic circumstances is of significant importance in terms of leaching potential for nitrate from soils to adjacent subsurface unsaturated and saturated zones. Convective transport of soluble nitrate in groundwater is predominantly the matter of lateral flow and groundwater flow (Wilkison et al. 2000). In this work it was shown, that groundwater flow is the major emission pathway for nitrogen emissions to surface waters in both Austrian case study areas, the Ybbs catchment and the Wulka catchment. Denitrification in groundwater is crucial for the reduction of nitrogen levels in the unsaturated and saturated zones and inheres to be of significant importance for the amount of total nitrogen loads, which are released from catchments to surface waters and transported to receiving seas (Zessner et al. 2004).

Nitrate concentrations in the groundwater are often considerably lower than theoretically can be expected from nitrogen surpluses on soil surface and long term groundwater recharge rates. Denitrification in unsaturated and saturated zones was subject of several studies, and significant differences in denitrification rates were reported between individual landscape positions, and between the unsaturated and saturated zone. Even if the highest denitrification potential can be found near the soil surface, denitrification rates are highly dependent on the presence of anoxic conditions and nitrate availability. Denitrification in soils under anoxic conditions is controlled by the supply of readily decomposable organic matter (Burford et al. 1975), but to ensure anoxic conditions in soil profile, soil saturation (soil water content) is of crucial importance regulating predominantly oxygen and nitrate diffusion. Upper soil horizons are almost rich in organic carbon and denitrification appears to operate effectively, but due to unsaturated conditions for most of the time denitrification rates will fall greatly below their potential maximum (Burt et al. 1999).

With increasing depths denitrification rates decrease considerably due to decreasing organic carbon contents in deeper soil horizons (Rolland 1996, Pavel et al. 1996, Strong et al. 2002, Willems et al. 1997). So denitrification in groundwater is slow compared to soil horizons (Well et al. 2005). Shallow aquifer sediments are oligotrophic environments low in organic carbon, and metabolic activity and growth rates of denitrifying bacteria in groundwater are lower compared to bacteria in surface soils and waters (Bengtsson et al. 1995). Seasonal water table fluctuations in shallow groundwater bodies are likely to interact with organic-rich surface soil horizons creating narrow zones of enhanced denitrification activity in the groundwater (Vidon et al. 2004). In deeper aquifer compartments organic matter intake from soils horizons by downwards DOC fluxes is much lower and is assumed to be insufficient to initiate dissolved oxygen and nitrate reduction. There, the likely source of degradable organic carbon for denitrification is the geological material

comprising the aquifer matrix (Hiscock et al. 1991), which largely determine solubilisation of groundwater humic substances, their composition and thus, their bioavailability.

Heterotrophic denitrifying bacteria are more abundant compared to autotrophic denitrifiers and are generally interpreted to be responsible for most observed cases of denitrification in groundwater. Due to limited availability of organic substances in groundwater, autotrophic denitrification may become the dominant process for nitrate reduction in groundwater with high levels of reduced inorganic (Mn^{2+} ; Fe^{2+} , S^{2-}) species obtained from aquifer material (Feast et al. 1998, Rolland 1996).

Since nitrate and electron donor availability determine denitrification activity in groundwater, enhanced groundwater flow rates may limit nitrate diffusion and favour transport of dissolved oxygen (Willems et al. 1997, Hefting 2003). The competition between dissolved oxygen and nitrate results in a diffusion limitation of denitrification. Aquifer heterogeneity may benefit the occurrence of denitrification "hot spots" (Vidon et al. 2004). Denitrification requires a considerable volume of groundwater flow and a high nitrogen flux through biologically active zones (Maitre et al. 2003), but in contrast a sufficient retention time or groundwater residence time is required since denitrification rates in groundwater reflect the limited availability of electron donors. Due to diffusion limitation denitrification in groundwater can be described using a Michaelis-Menton-model with first order decay (Strong et al. 2002), which can be characterised by certain half life times (Kreuzinger 2005). Ranges of reported half life times from several days (2-7d) (Clay et al. 1996) to years (2-10a) (Wendland et al. 1999, DVWK et al. 1999) and reflect the local environmental conditions in groundwater with (limited) availability of sources of electron donors, nitrate and dissolved oxygen.

Denitrification in the groundwater could be observed in both selected case study areas in a different extent. Observations in groundwater and surface water of the Ybbs catchment and the Wulka catchment indicated enhanced denitrification in the groundwater, and decreasing nitrate levels on the groundwater flow path towards the surface water. Considerable differences in denitrification in groundwater between the catchments have been observed in connection with significantly different concentrations levels. In average, nitrate reduction by denitrification was larger in the groundwater of Wulka catchment, where similarly significantly larger nitrate concentrations in the groundwater could be observed. Groundwater quality observations further indicated that heterotrophic denitrification is likely to be responsible for the reduction of nitrate levels in the groundwater of the Wulka catchment, whereas indications were found that nitrate reduction in the groundwater of the Ybbs catchment might be the result of autotrophic denitrification.

Water balance calculations were performed for the identification of main hydrological differences between the Ybbs catchment and the Wulka catchment, which are significantly related to nitrogen turnover at the catchment scale and in consequence to the level of nitrogen emissions to surface waters. Using the conceptual, distributed parameter, continuous time model SWAT 2000 (Arnold et al. 2000) water balances were calculated in detail indicating spatial and seasonal variations in catchment hydrology and in terms of runoff components contributing to total river discharge. The calculated annual average rates of precipitation, river discharge and groundwater recharge in the Ybbs catchment exceeded the annual

average rates in the Wulka catchment approximately by factor 2, 9 and 4 respectively. Higher fractions of surface runoff and lateral flow were obtained for the morphologically more heterogeneous Ybbs catchment in comparison to the Wulka catchment. Significantly larger groundwater recharge rates in the Ybbs catchment coincided with larger water fluxes through the aquifers and were expected to result in average shorter groundwater residence times compared to the Wulka catchment. The SWAT 2000 model was not able to close the long-term water balance for both catchments, but provided information about spatial variations and seasonal pattern in water balance and runoff components on the subcatchment level.

Using the SWAT 2000 model for nitrogen emission calculations resulted in significant overestimations in calculated nitrogen loads to the surface water particularly for the Wulka catchment. Calculated nitrogen loads to the surface water of the Ybbs catchment were in good correspondence with observed nitrogen river loads. The SWAT 2000 model indicated that from the three main runoff components the highest fraction of nitrogen was contributed by lateral runoff directly to the surface water. Since most of the lateral runoff 'naturally' infiltrates to the groundwater and stimulates groundwater flow, nitrogen loads by lateral runoff would be subject of denitrification in groundwater too. Due to model definitions the direct contributions of nitrogen emissions by lateral runoff to the surface water resulted in considerable overestimations in nitrogen emissions to surface water, particularly in catchments with predominant contributions of groundwater runoff to the total river discharge as for instance in the Wulka catchment. The highest nitrogen loads were leached by percolation from the soil to the groundwater. Nitrogen loads leached by percolation towards the groundwater surface were not considered for subsequent transport by groundwater runoff to surface water by the model due to model definitions. Nitrogen emissions by groundwater into the surface water were defined by the user based on surface water quality observations during low flow conditions. Thus, denitrification in groundwater is not modelled explicitly by the SWAT 2000 model, but the catchment-specific deficiency between nitrogen loads to the groundwater via percolation and nitrogen emissions by groundwater to surface water indicated the level of nitrate reductions in the groundwater, for which denitrification accounted for.

Main differences in catchment hydrology could be related to differences in concentration levels in groundwater, to differences in denitrification in groundwater between the catchments and to relative contribution of nitrogen loads by simulated runoff components to the surface water. Enhanced groundwater recharge rates of the Ybbs catchment resulted in low nitrate concentrations in groundwater and due to large water fluxes, in average shorter groundwater residence times. Therefore, shortened groundwater residence times and large water fluxes are likely to result in elevated nitrogen flow rates in groundwater and in less intensive denitrification in the groundwater of the Ybbs catchment in comparison to the Wulka catchment. The investigations revealed the comprehensive interrelations between the local environmental conditions characterised by specific hydrology, geology and land use and nitrogen reductions by denitrification in the groundwater, which deplete the fraction of nitrogen being emitted to surface waters to a large degree. Due to model definitions the SWAT 2000 model is unsuitable for nitrogen emission calculations at the catchment scale, because specific nitrogen surplus cannot be related to specific nitrogen emissions by groundwater runoff to surface waters.

Using the MONERIS model (Behrendt et al. 1999) the nitrogen emissions to surface waters for the two case study regions were calculated with consideration of the emission pathways. The groundwater was identified as the major emission pathway for nitrogen for both the Ybbs catchment and the Wulka catchment. The calculated area specific nitrogen emissions from the Ybbs catchment exceed the calculated emissions from Wulka catchment approximately by factor 4. Due to larger water fluxes in the Ybbs catchment considerably higher nitrogen emissions are contributed to the surface water in comparison to the Wulka catchment. It could be shown, that due to the dominant nitrogen contribution by the groundwater denitrification in groundwater is of high importance for the reduction of nitrogen loads to surface waters. Nitrogen loads which are reduced by denitrification in groundwater were shown to be significantly larger than nitrogen loads reduced by denitrification in the river. The MONERIS model was evaluated to be an appropriate tool for nitrogen emission estimations at the catchment scale. Individual emission pathways are considered as well as denitrification in groundwater as essential process quantifying nitrogen emissions to surface waters exactly. The required spatial resolution is provided by the calculation of emissions on subcatchment level.

Nitrogen retention in the groundwater via denitrification is considered in the MONERIS model using different hydrogeological formations. Fixed shares of catchment areas are assigned to hydrogeological classes with individual potential for denitrification in groundwater. But through this concept, no connections to the location within the catchment are possible to be established. Sensitivity analyses showed a significant influence of the allocation of catchment areas to hydrogeological classes on the calculated diffuse nitrogen emissions to surface waters (Zessner et al. 2004). Anyway, due to the spatial aggregation within the MONERIS model the consideration of denitrification in groundwater reflects a simple input-output-regression and does not allow process-oriented descriptions of nitrogen losses as it would be possible using a certain time or raster dependent descriptions for water routing.

Denitrification in groundwater is variable in dependency of local environmental conditions like hydrology, geology, nitrogen and organic carbon availability and the groundwater residence time. These conditions provide the facility for the characterisation of denitrification processes in various modelling approaches. Modelling nitrogen emissions to surface waters at the catchment scale should imply the consideration of denitrification in groundwater addressing catchment specific differences in denitrification potential as function of environmental conditions, which limit denitrification activity. Even if the groundwater residence time mainly impacts the reaction time for denitrification, the availability of carbon sources and of dissolved oxygen in groundwater due to microbial decomposition, groundwater recharge rates as well as hydrogeology considerably affect specific local groundwater residence times. In this respect the estimation of groundwater residence time distributions for selected groundwater bodies would create the precondition using half life time approaches for modelling denitrification in groundwater.

In literature, approaches are reported about the utilisation of half life time approaches for the characterisation of denitrification in groundwater as function of the hydrogeology (Wendland et al. 1999, Quast et al. 2001, DVWK et al. 1999), which concentrated on the estimation of nitrogen emissions by groundwater with consideration of denitrification processes. Within this work, an approach was

developed for the calculation of groundwater residence time distributions using distributed information about the groundwater surface, the geology and river location. Using a half life time of 2 and 4 years (Wendland et al. 1999) for the characterisation of denitrification in groundwater and constant, catchment specific nitrogen surpluses, the nitrogen loads via groundwater to surface waters as functions of calculated groundwater residence time were calculated for the Ybbs catchment and the Wulka catchment. This approach is innovative in respect to link the location of catchment areas to their specific contribution of diffuse nitrogen emissions to surface water. Using this approach, denitrification in groundwater could be considered for nitrogen emission calculations. Heterogeneities in groundwater flow due to geology have been considered for denitrification in groundwater via calculated groundwater residence time distributions.

Using this approach, the contributions of specific catchment areas to the total diffuse nitrogen load of the surface water were obtained. The calculated mean groundwater residence time for the Ybbs catchment was considerably lower in comparison to the mean groundwater residence time was obtained for the Wulka catchment. This is well in line with results from groundwater quality observations and conclusions from water balance calculations.

The calculated area specific nitrogen emissions by groundwater to surface water using the calculated groundwater residence time distributions were compared to calculated area specific nitrogen emissions by groundwater using the MONERIS model and indicated good coincidence of the results using the 4 years half life time for the Wulka catchment. Calculated nitrogen emissions were underestimated using the 4 years half life time for the Ybbs catchment, what indicated reduced denitrification in the groundwater of the Ybbs catchment. Calculations indicated that more than 90% of the calculated diffuse nitrogen emissions stem from areas with a groundwater residence times of <9 years and <10 years in the Wulka catchment and the Ybbs catchment, respectively. Quantifying the fraction of the areas contributing >90% of the total diffuse nitrogen emissions indicated a participation of 10-25% and 25-60% of the total area in the Wulka catchment and the Ybbs catchment, respectively.

Largest contributions of nitrogen emissions by groundwater to surface water were obtained from river-near (riparian) areas (with groundwater residence times < 10 years), which were located in almost <2000m distance to the surface water bodies in both catchments. Furthermore, the calculations indicated that particularly areas with large distances to surface water and with predominantly long groundwater residence times tended to show higher nitrate concentrations, but were of less importance for the total nitrogen loads to the surface waters. This underlined the importance of riparian areas and their sensitivity for contributing nitrogen emissions by groundwater with only little reduced nitrate levels due to denitrification. To restrain agricultural utilization with restrictions in nitrogen applications in these areas would be the consequence in terms of reducing diffuse nitrogen loads to surface waters.

Summarising the application of the different modelling approaches, uncertainties in modelling results have to be taken into account. All the modelling approaches focus on delivering information in a specific temporal and spatial resolution for catchments, which can't be provided by measurements basically due to their character being point information and being limited in availability, in time and space. The quantification

tools differ significantly in their model complexity and therefore, also in data requirements. Application of spatially or temporarily lumped or distributed models depends on data availability, the considered scale and determines the degree of consideration of changing environmental conditions. Consequently, results from modelling approaches will be aggregated to a certain extend in time and space as a function of model complexity and the regarded scale.

The higher the model complexity is the more data are necessary to run the model and the more uncertainties increase due to model parameter definitions and their impacts on model performance. More complex model are ambitious in terms of temporal and spatial resolution of model results, but regarding the previously mentioned uncertainties, the obtained model results are likely to be uncertain to a high extend too. Using more simple modelling approaches the resolution decreases significantly in time and space. Empirical approaches are based on regression analyses and therefore, data often are aggregated temporarily and sometimes also spatially balancing statistical dynamics in input data, what results in considerable losses in information. Data uncertainties consequently are generated because of the aggregation of distributed information in temporal and spatial aspects.

Thus, it appears correct to combine diverse modelling approaches for simultaneous applications and to use modelling results complementary in order to compensate weaknesses of each of the modelling approaches by the advantages of other quantification tools. A step forward in this direction was done in this work.

It was shown that even being aware of limitations of the modelling approaches, a combined model application of different modelling approaches resulted in a successful determination of hydrological circumstances, which are the result of catchment specific conditions and which are of significant importance for nitrogen emissions from catchments to surface waters, and which are considered in diverse modelling approaches variably delivering a comprehensive imagination about nitrogen sources, their relation to hydrology and retention processes coinciding with their spatial relevance.

Conclusions from this work are summarised as follows:

- Water balance calculations are a basic requirement for the estimation of nitrogen balances to account for the main transport pathways of individual nitrogen species; nitrogen emissions are largely determined by water fluxes at the catchment scale and hydrology decisively influences denitrification activity in the unsaturated and saturated zone.
- Beside common methods like acetylene inhibition or isotope fractionation denitrification activity in the groundwater at the (sub)catchment scale can be observed by nitrogen surplus calculations and groundwater and surface water quality observations.
- Nitrate is leached out from the soil to the groundwater in large quantities and is transported afterwards towards surface water bodies; therefore denitrification in groundwater is of crucial importance for the amount of nitrogen emissions, which are released by groundwater to the surface water.
- The groundwater is, beside local point sources, the major emitter of nitrogen to surface water bodies.
- Denitrification in soil and groundwater of both Austrian case study regions was significant and reduced the nitrogen loads to surface waters by 47% and 86% in the Ybbs catchment and the Wulka catchment respectively, in relation to the long-term area-specific nitrogen surplus.
- Nitrogen emissions to surface waters can be controlled by regulating nitrogen surpluses and nitrogen leaching with percolation by landuse practises; nitrogen transport by groundwater with specific denitrification activity can't be controlled anthropogenically and is predominantly a matter of local environmental conditions.
- The location of areas within the catchment in respect to surface water bodies decisively determines (beside the specific nitrogen surplus) the diffuse nitrogen loads to surface waters.
- Quantification tools for nitrogen emission estimations should consider all emission pathways and retention processes, prior to emission estimations the model complexity should be evaluated; process oriented complex models should be used for small scale investigations, where data availability does not limit model applicability; data oriented empirical models are suitable quantification tools for small scale and for large scale investigations to identify the average system status (i.e. nitrogen emissions) and to derive measures for a sustainable nitrogen management at the catchment scale.
- Estimation of groundwater residence time distributions is suitable to consider denitrification in groundwater using half life time approaches and with provision of fully distributed information about the contribution of catchment areas to total nitrogen emissions to surface waters.
- Since denitrification in groundwater could be described using half life time approaches, denitrification in groundwater is limited first of all by nitrate availability, while environmental conditions are reflected in the magnitude of the half life time

- A sufficient groundwater residence time is likely to encourage an effective removal of nitrogen from groundwater by denitrification.
- Areas with large distances to surface waters are dominated by high groundwater nitrate concentrations because of high nitrogen inputs to groundwater from agricultural and anthropogenic activity and may cause problems of groundwater utilisation for drinking water use, the diffuse nitrogen loads from these areas are significantly reduced by denitrification in groundwater due to long groundwater residence times and do not contribute significantly to nitrogen emissions to the surface waters.
- Areas with short distances to surface waters (<2000m in both Austrian case study regions) tended to show lower groundwater nitrate concentrations due to groundwater inflow from uphill areas, which was already subject of nitrate reduction by denitrification; diffuse nitrogen loads from these areas are subject of small nitrate reductions by denitrification due to short groundwater residence times and contribute the majority of the nitrogen emissions to the surface waters.
- The identification of areas, which are responsible for most of the diffuse nitrogen emissions to surface waters, gives possibilities to manage land utilisation and nitrogen applications by fertilizers in face of the maximum exploitation of natural denitrification processes in groundwater to moderate nitrogen emissions by groundwater as far as possible.
- Management of catchment areas is dependent on protection goals and may result in oppositional measures in respect to the regarded scale; local groundwater protection focuses on areas with high groundwater nitrogen concentrations, which were found to be located afar from surface waters, they are of marginal importance in regard to global management of nitrogen emissions to the surface waters and the receiving seas, sensitive areas for management of nitrogen emissions to surface waters are located near the surface waters and are not important for groundwater protection due to noticeably lower groundwater nitrate concentrations.

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10Appendix

10.1 Groundwater residence time calculations for the Wulka catchment

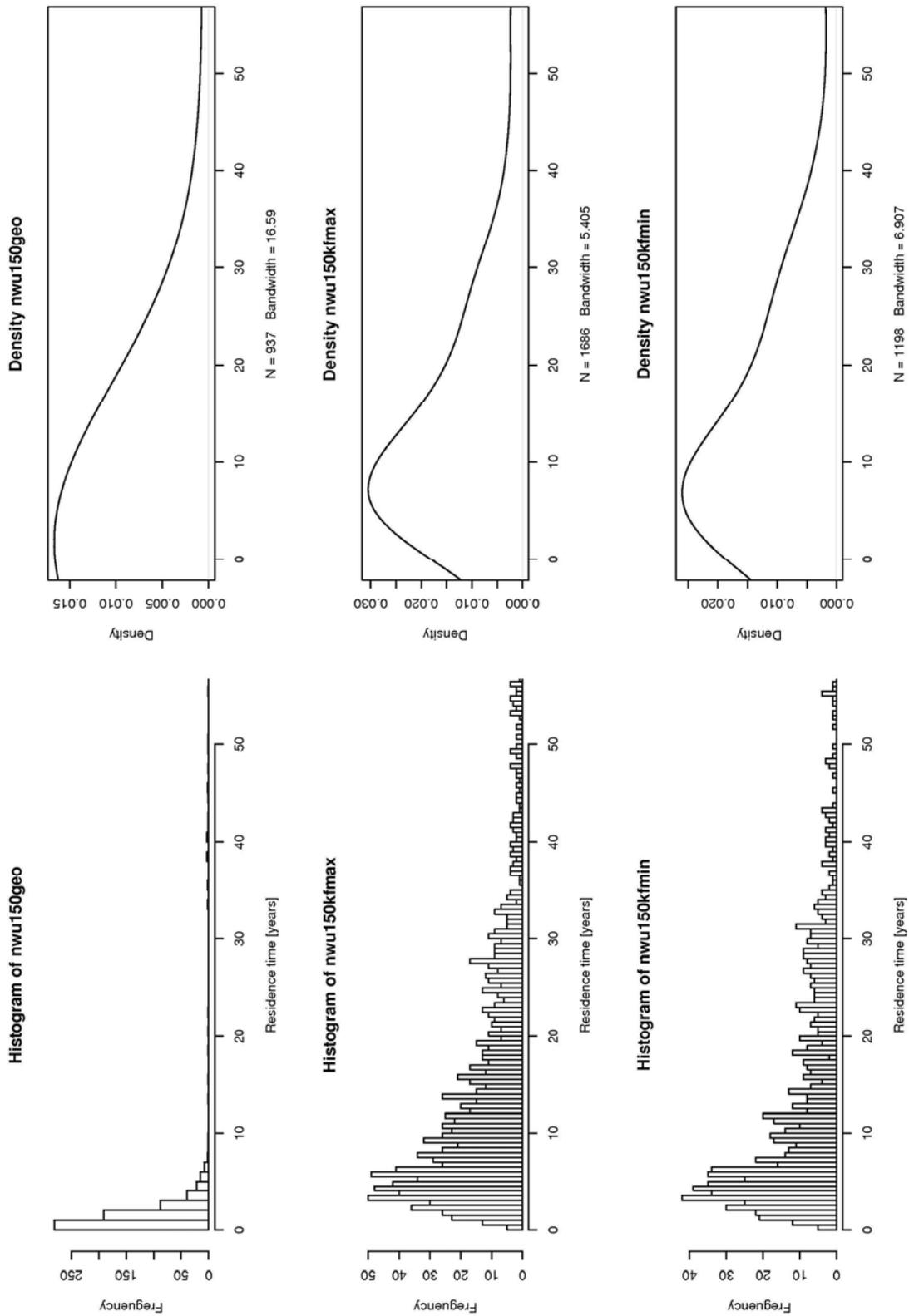


Figure 87: Histogram and density of calculated groundwater residence time distributions [years] of the Wulka catchment using interpolated groundwater surface grid with 150m cell size and varying geological information

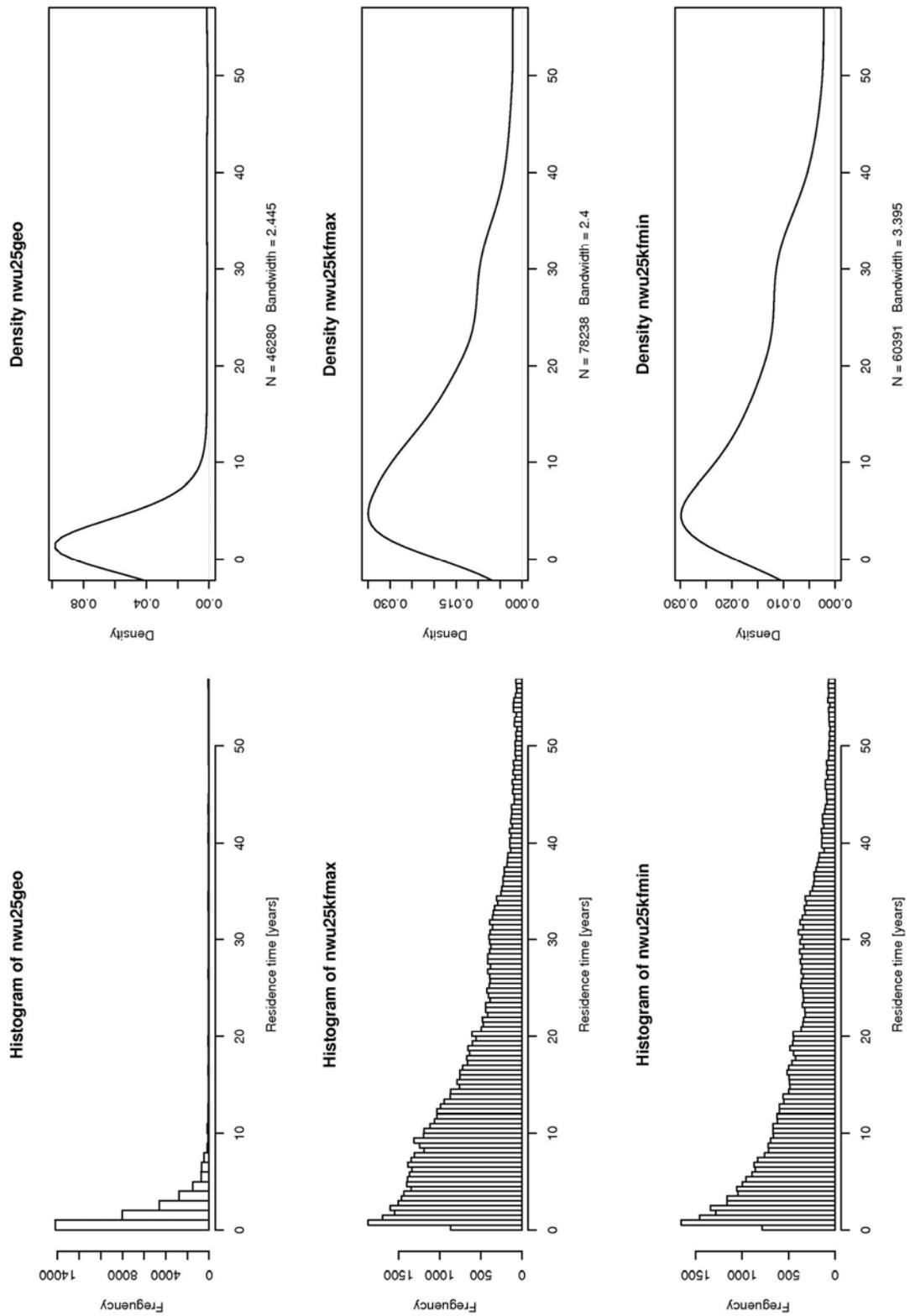


Figure 88: Histogram and density of calculated groundwater residence time distributions [years] of the Wulka catchment using interpolated groundwater surface grid with 25m cell size and varying geological information

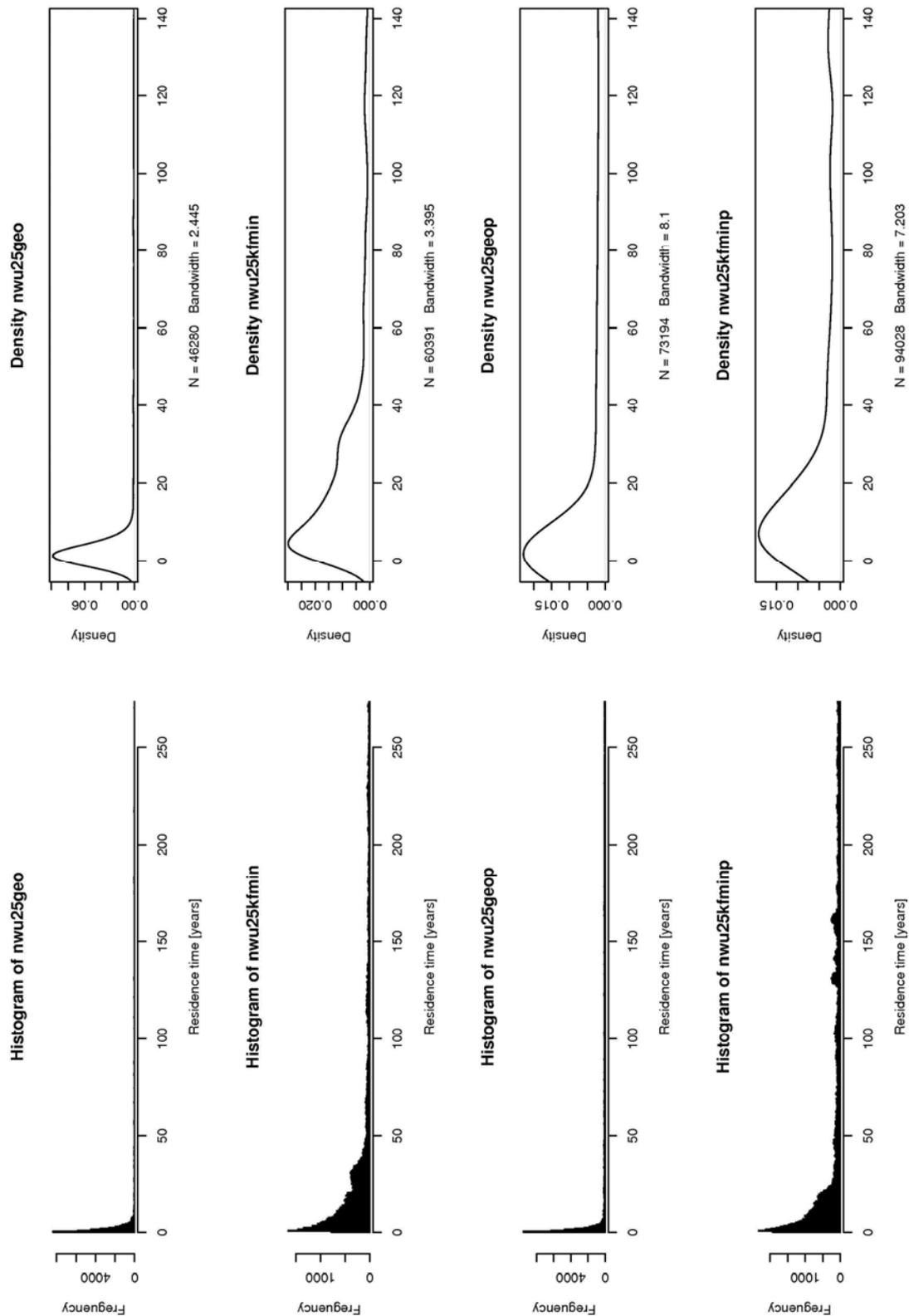


Figure 89: Comparison of histogram and density of calculated groundwater residence time distributions [years] of the Wulka catchment using interpolated groundwater surface grid with 25m cell size and varying geological information with a constant and variable porosity

10.2 Groundwater residence time calculations for the Ybbs catchment

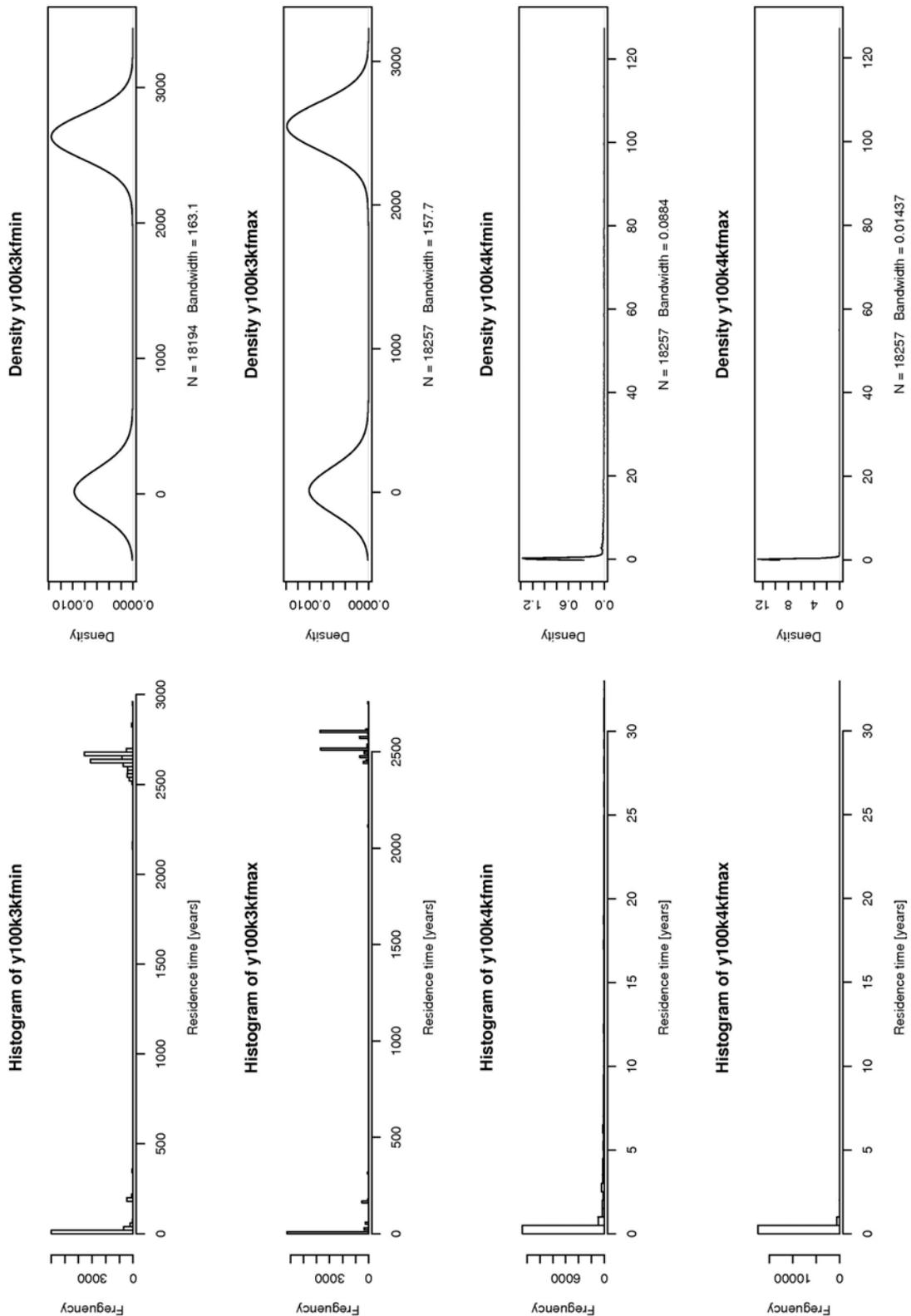


Figure 90: Histogram and density of calculated groundwater residence time distributions [years] of the Ybbs catchment using interpolated groundwater surface grid with 100m cell size, detailed geological information and with consideration of different orders of the rivers as barrier for groundwater flow

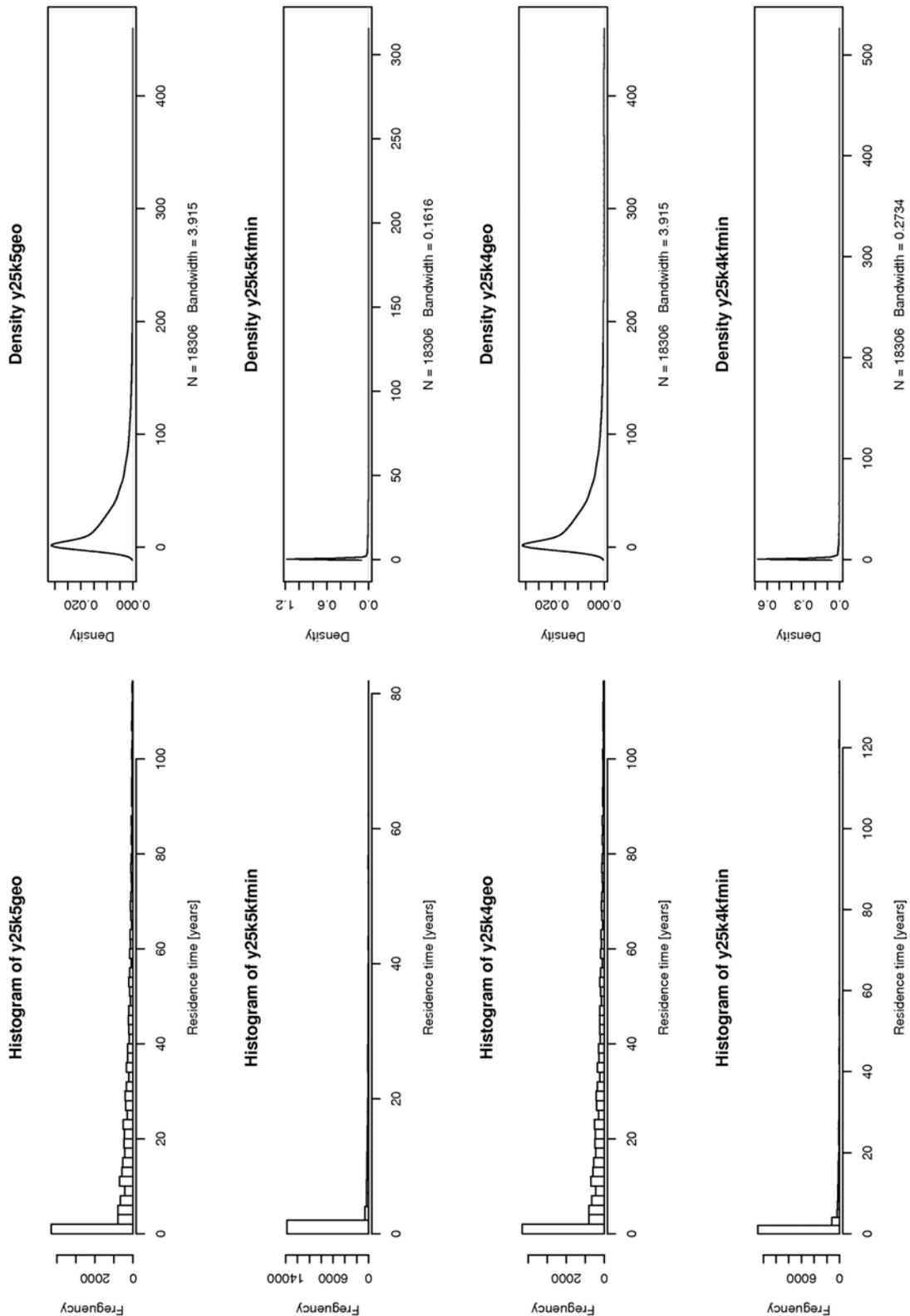


Figure 91: Histogram and density of calculated groundwater residence time distributions [years] of the Ybbs catchment using interpolated groundwater surface grid with 25m cell size with changing geological information and with consideration of different orders of the rivers as barrier for groundwater flow

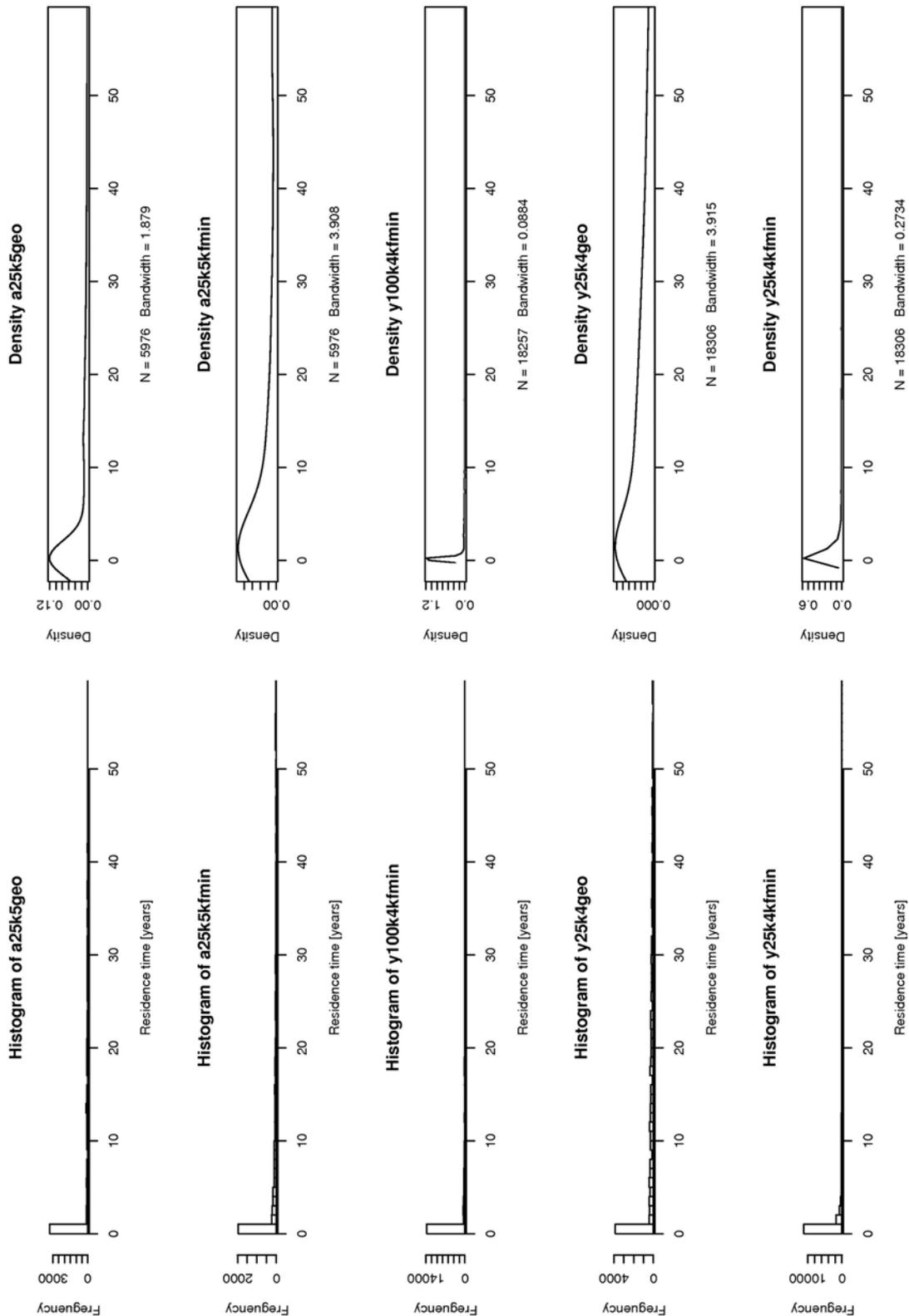


Figure 92: Histogram and density of calculated groundwater residence time distributions [years] of the Ybbs catchment using interpolated groundwater surface grid with different cell sizes, changing geological information, different spatial extent and with consideration of different orders of the rivers as barrier for groundwater flow