Hydrogeology Journal – Electronic supplementary material

Fate of nitrate during groundwater recharge in a fractured karst aquifer in southwest Germany

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Piper plot

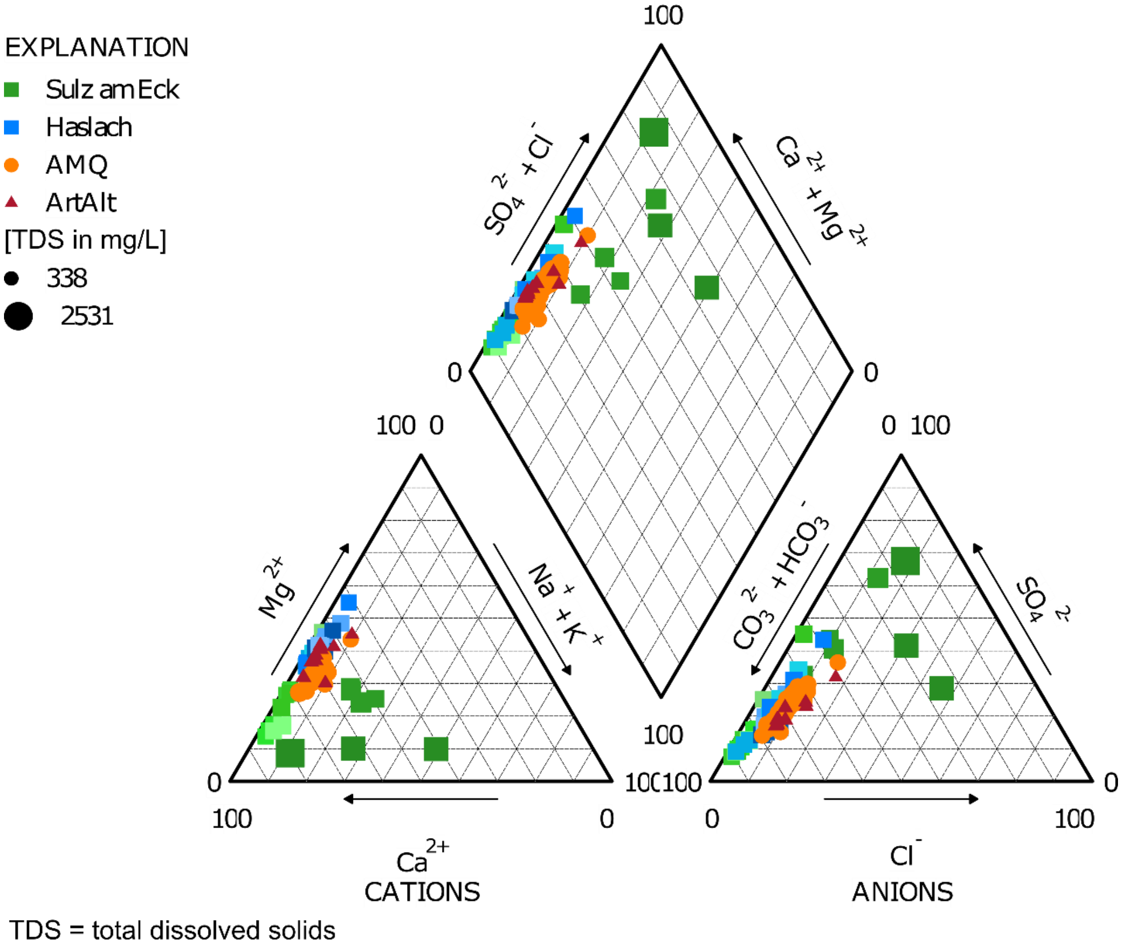

Figure S1: Piper diagram showing the hydrochemical facies of the groundwater within the Ammer catchment, Germany. Representative end-members are (I) Mg^{2+} - HCO_3^- type water; (II) Ca^{2+}-Cl^- type water and (III) mixed Na^+-Cl^-type.

Table hydrochemistry

Table S1: Averaged concentration in mg/l reflecting the hydrochemical composition of water samples from the four major field sites from 2005 to 2018.

Parameter	Ammer spring (AMQ)	Sulz am Eck (Sul)	Haslach (Has)	Artesian well (ArtAlt)
Major ions [mg/L]				
Na^+	15.6 ±0.3	41.7 ±15.7	6.3 ±0.8	7.7 ±0.6
K^+	2.4 ±0.1	4.6 ±1.8	2.0 ±0.2	2.6 ±0.2
Ca^{2+}	136 ±2.	172 ±24	111 ±2	128 ±4
Mg^{2+}	44.2. ±0.6	29.7 ±2.7	45.7 ±0.9	49.5 ±1.8
Cl^-	35.5 ±0.8	60.0 ±24.7	20.9 ±1.6	36.0 ±1.2
SO_4^{2-}	101 ±3	203 ±62	70 ±8	98 ±3
HCO_3^{2-}	428 ±7	410 ±10	422 ±10	462 ±3
Trace constitutes [µg/L]				
B	17.1 ±2.9	31 ±288	11.3 ±2.2	25 ±5
Fe	56.5 ±16.1	4.9 ±1.3	47.9 ±13.5	2.5
Li	6.0 ±1.0	47.4 ±19.0	10.3 ±1.6	10.0
Mn	8.1 ±7.4	7.1 ±3.3	4.8 ±1.0	78.3 ±36.8
Rb	1.8 ±x	2.4 ±1.2	2.1 ±0.2	3.0
Si	3230 ±30	3080 ±208	3716 ±69	3650 ±50
Sr	362 ±49	492 ±147	269 ±55	480 ±30
U	1.2 ±0.1	0.9 ±0.3	2.1 ±0.4	2.6 ±0.1

Table S2: Major ion concentrations in mg/l in groundwater samples from monitoring well Has2 before and after a major rain event (25.2 mm) on 21 March 2020.

Well/Date	Has2 07.02.2020	Has2 20.02.2020	Has2 25.03.2020
Precipitation P [mm] **Cumulative P (last 5 days before sampling)**	28.6	12.3	26.7
Hydraulic Head [m asl]	419.2	423.0	428.6
Major ions [mg/L]			
Na^+	3.7	3.8	4.6
K^+	1.5	1.4	0.8
Ca^{2+}	95.0	96.3	115.4
Mg^{2+}	38.5	35.8	39.9
Cl^-	4.4	7.6	7.8
SO_4^{2-}	50.4	32.6	22.2
HCO_3^-	403.9	396.2	496.7
NO_3^-	19.0	33.0	26.9

Temporal variability of nitrate

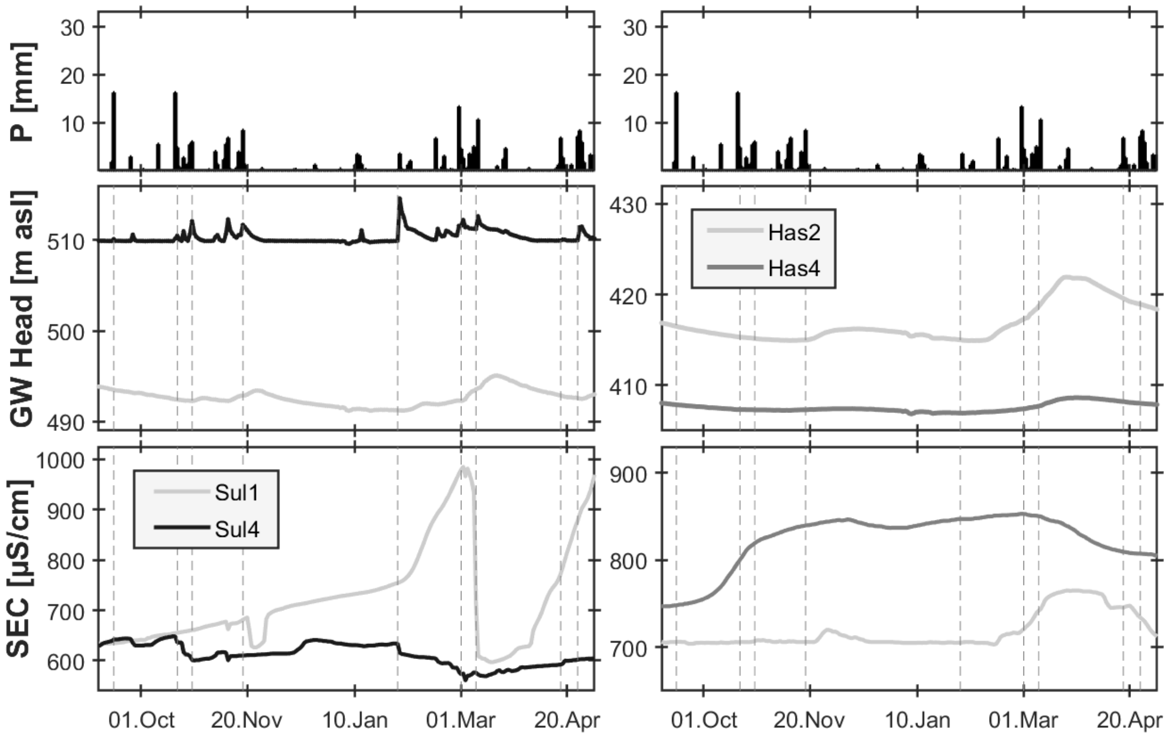

Figure S2: Time series of precipitation (*P*), hydraulic head (*H*) and specific electrical conductivity (SEC) at (**a**) Sulz am Eck (Sul1 and Sul4) and (**b**) Haslach (Has2 and Has4) for the period Jan 2016 to Jan 2019. Dashed grey lines (perpendicular to x-axis) indicate precipitation events larger than 20 mm within less or equal 2 days. Note that, *P* shown in (a)a and (b) is identical since the data depicted here were taken from the Bondorf station (Bundschuh et al. 2019).

Temporal variability of nitrate

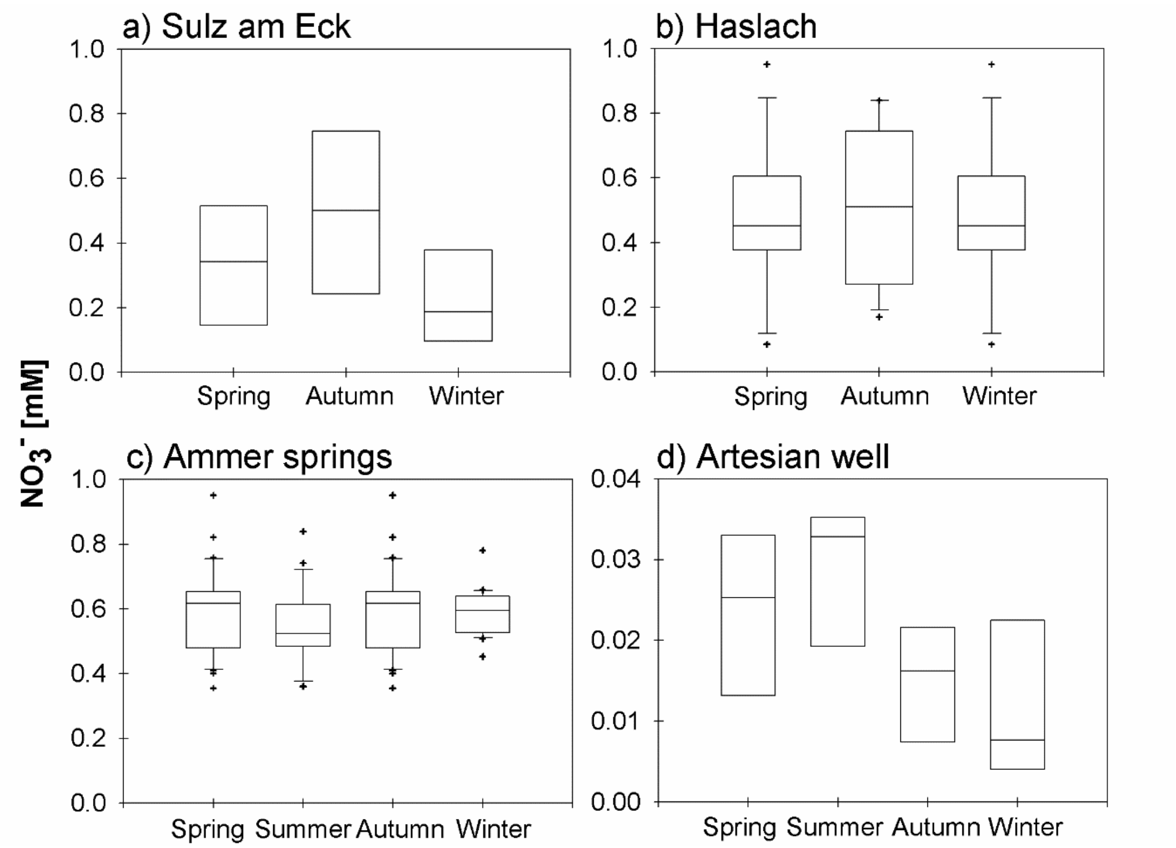

Figure S3: Whisker and box plot showing seasonal variability in nitrate concentrations over the years for wells located at Sulz am Eck, Sul (**a**), Haslach, Has (**b**), the Ammer spring, AMQ (**c**) and the artesian well at Altingen, ArtAlt (**d**). Dots mark the outliers, whereas the black lines represent the median.

Nitrate and nitrite concentrations

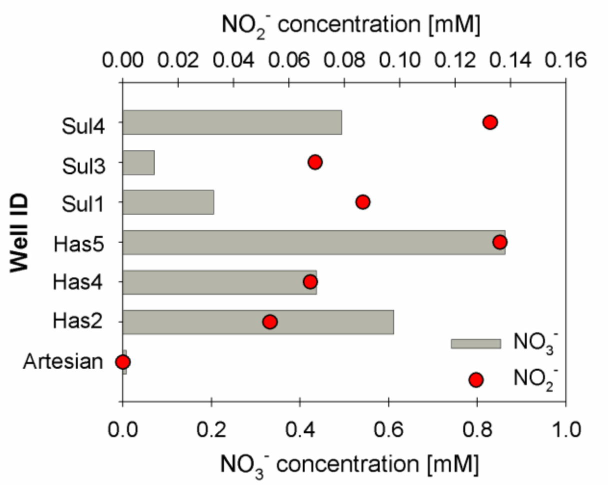

Figure S4: Nitrate and nitrite concentrations measured in selected wells in April 2016. Single samples were taken hence only technical replicates were measured (STD not included). Nitrite concentrations in samples taken in January 2018 were below detection limit and are therefore not shown here.

Land use in delineation areas of well capture zones

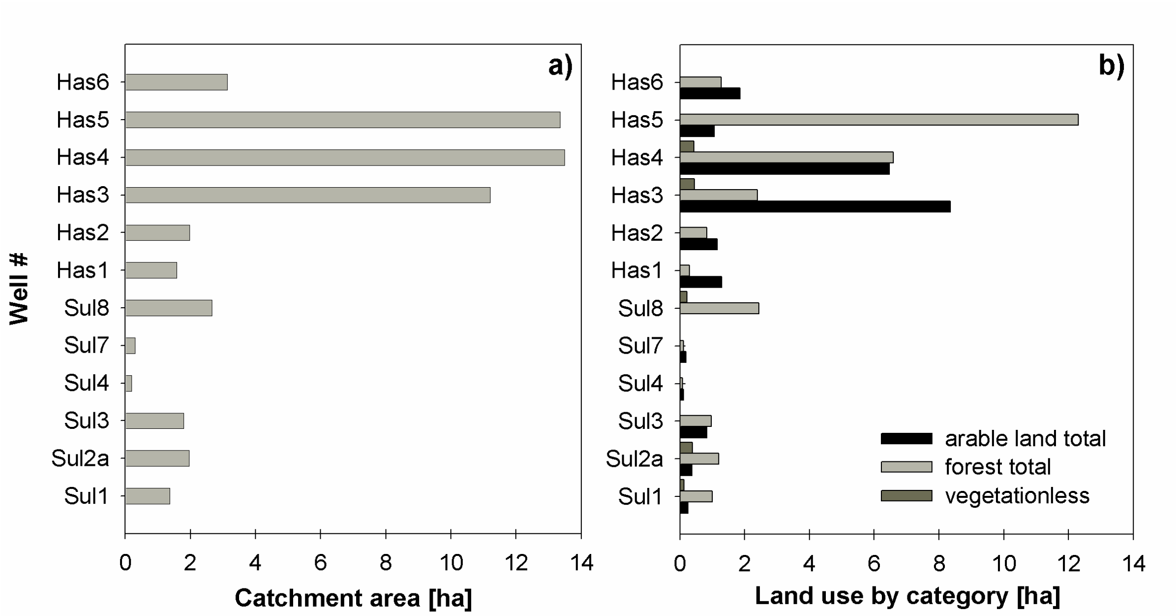

Figure S5: Estimates of total catchment area (**a**) and land use by category (**b**) based on the delineation of the well capture zones shown in Figure 7. Categories were chosen according to the maps provided by LUBW (LUBW Landesanstalt für Umwelt 2017). Categories shown in (**b**) include intensive grassland, meadow orchards and arable land (arable land total), broadleaf and mixed forest (forest total) and vegetation-less and sparsely populated areas (vegetation-less).

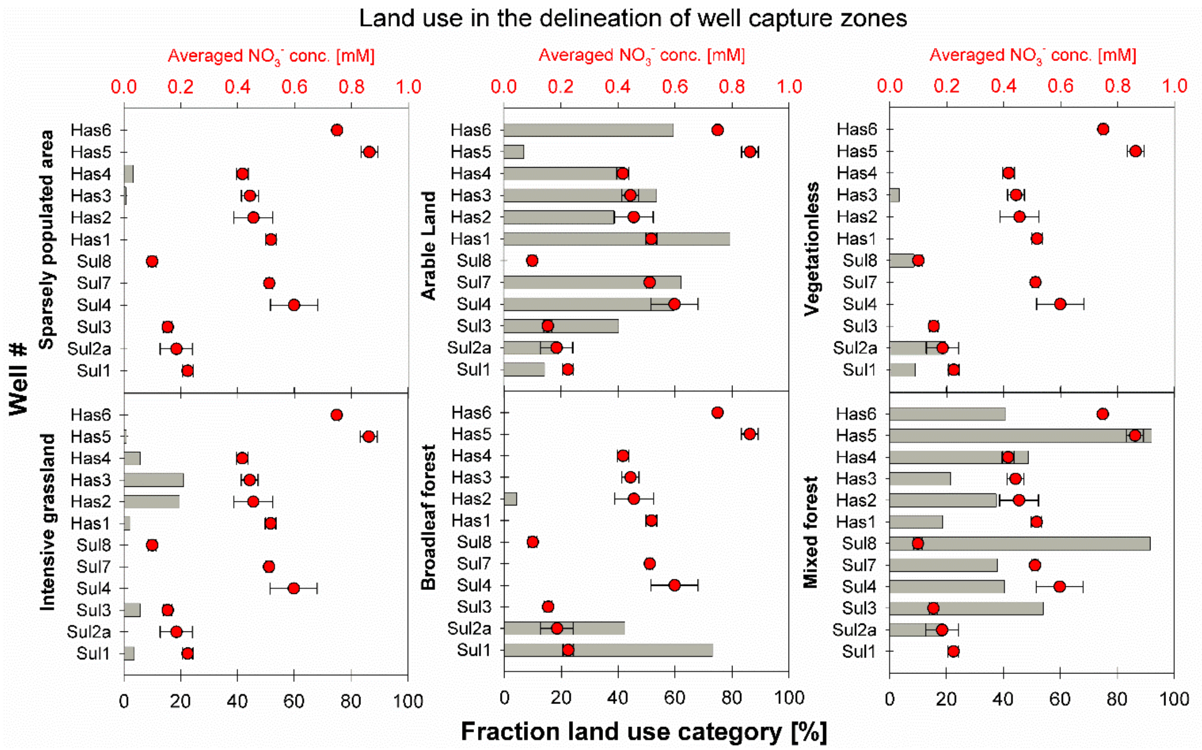

Figure S6: Detailed fractions [%] of the different land use categories for each monitoring well's catchment zone.

Sodium versus chloride ion concentrations

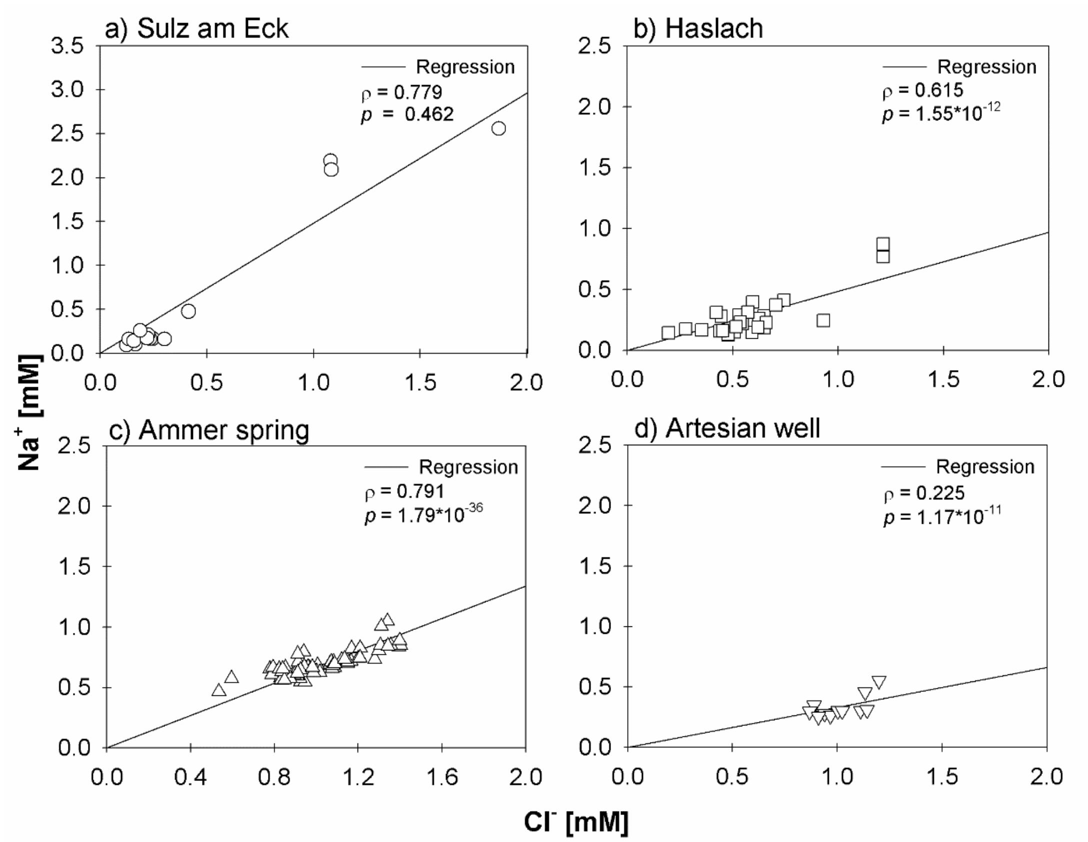

Figure S7: Correlation plots between sodium and chloride concentrations for wells located at Sulz am Eck, Sul (**a**), Haslach, Has (**b**), the Ammer spring, AMQ (**c**) and the artesian well at Altingen, ArtAlt (**d**). Plots include correlation value (ρ) calculated via Pearson test, p value calculated via ANOVA**.**

Spring discharge

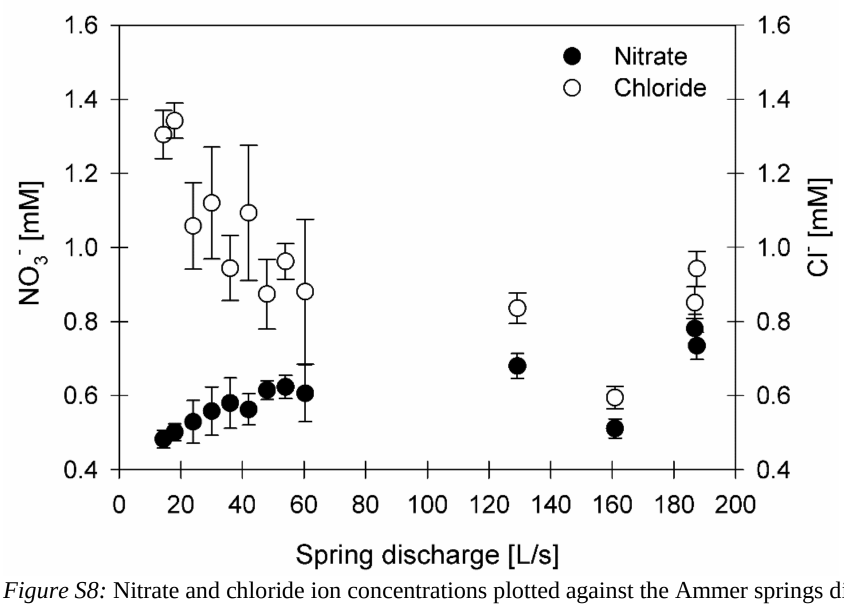

Figure S8: Nitrate and chloride ion concentrations plotted against the Ammer springs discharge from 2009 to 2018. Concentrations were averaged based on similar discharge values. Error bars represent standard deviation.

Nitrate versus SEC

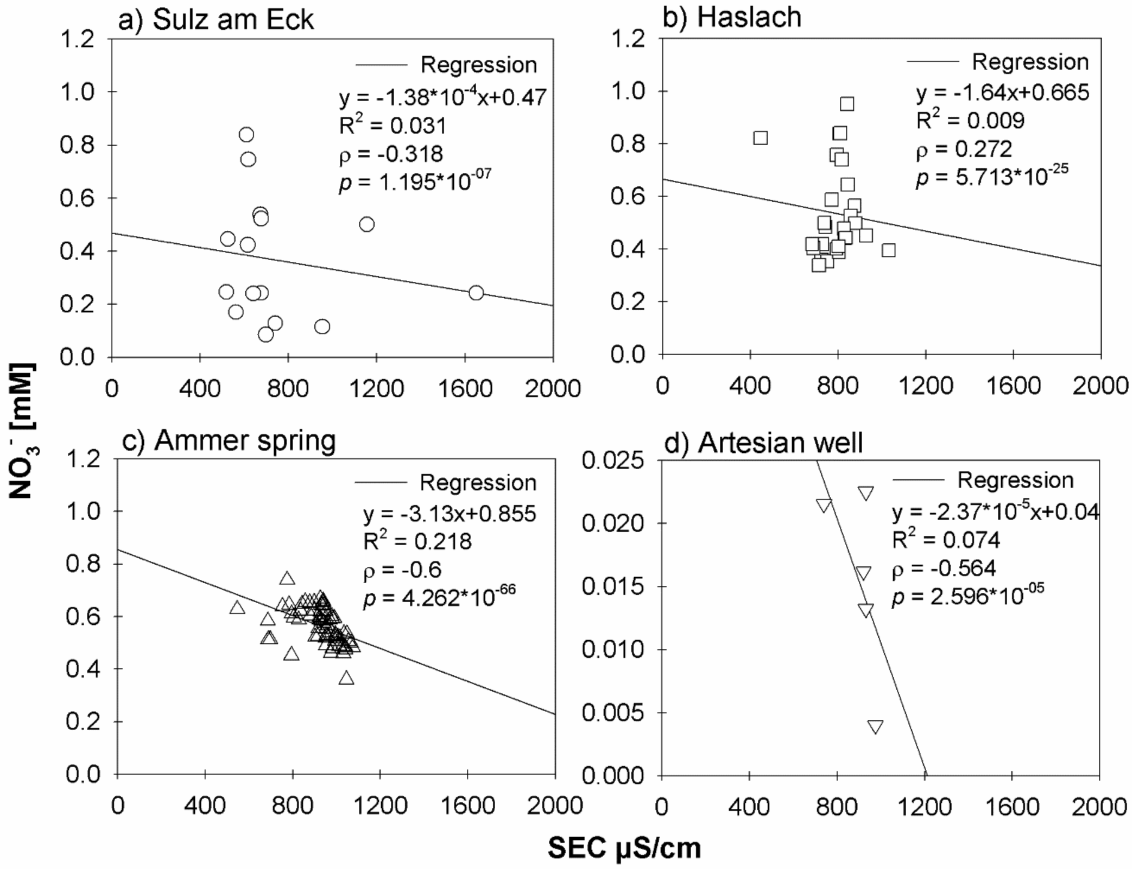

Figure S9: Correlation plot between nitrate and SEC for wells located at Sulz am Eck, Sul (**a**), Haslach, Has (**b**), the Ammer spring, AMQ (**c**) and the artesian well Altingen, ArtAlt (**d**). Plots include regression function, R^2, correlation value (ρ) calculated via Pearson test, p value calculated via ANOVA.

Previously published isotope value ranges for nitrate

Table S3: Simplified summary of previously published $\delta^{15}N$ and $\delta\ ^{18}O$-nitrate values with their corresponding nitrate sources. Most important references reporting these values are listed in the last column**.**

NO_3^- source	Resulting δ values for NO_3^-		Reference
	$\delta^{15}N$ [‰]	$\delta^{18}O$ [‰]	
Manure	+2 to +30 +10 to +20	-10 to +15	(Mariotti et al. 1988; Widory et al. 2004; Liu et al. 2006; Kendall et al. 2007; Di Lorenzo et al. 2012; Yue et al. 2017)
Ammonium fertilizer	-4 to +4	-5 to +15	
Nitrate fertilizer	-4 to +5 -7 to +3		
Artificial	+4.9 to 22.8 -1.4 to +14.9	+1.3 to +11 +2.8 to 18.2 +17 to +25	
Natural		+46 to +58	
Air		+18 to +22	
Sewage	+4 to +19 +7 to +25	-10 to +15	
Waste water	+8 to +20 *+5 to +42**		(Li et al. 2017)
Soil N_{org} DIN – $NO_3^-{}_{aqu}$	-10 to +15		(Kendall et al. 2007)

**mixed signal: waste water disposal and inorganic fertilizer*

Extreme observations in oxygen concentrations at Sul1

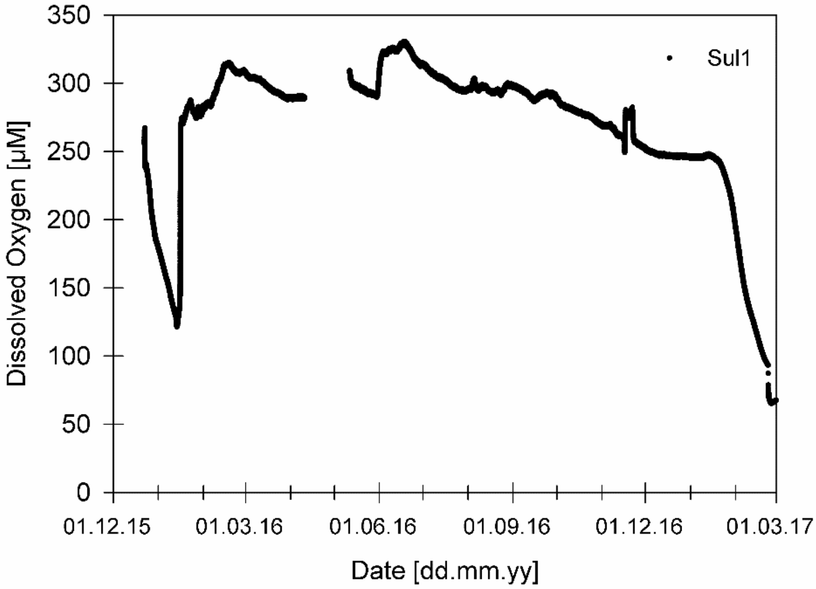

Figure S10: Exemplary time series of dissolved oxygen concentrations measured in situ in well Sul1 (Sulz am Eck) from December 2015 to March 2017. DO minima of the graph correlate with groundwater recharge time.

δ^{18}O versus δ^{15}N plots for nitrate and nitrite

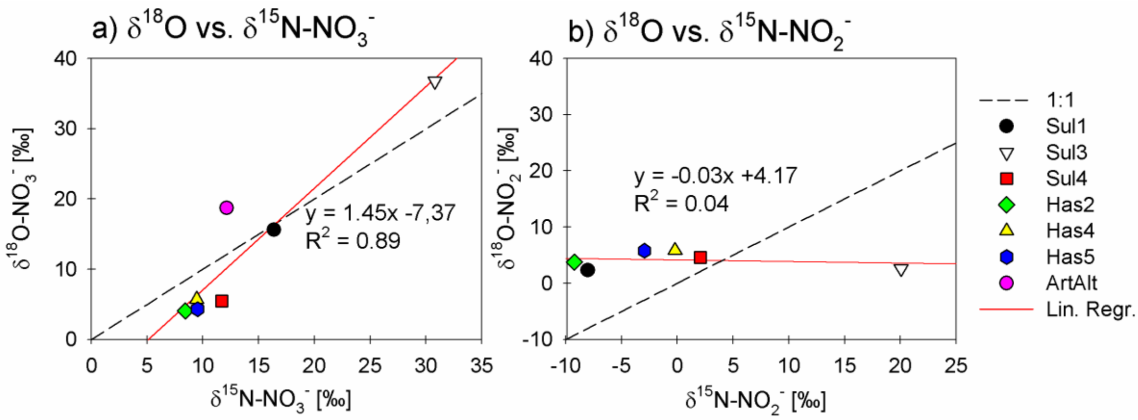

Figure S11: δ^{18}O versus δ^{15}N plots for nitrate (**a**) and nitrite (**b**). (**a**) strongly supports ongoing denitrification whereas (**b**) probably shows the effect of oxygen atom exchange with water, setting the δ^{18}O values to a constant value of ~4.2‰ independent of the original O isotopic composition of the nitrite.

DOC spatial and seasonal variability

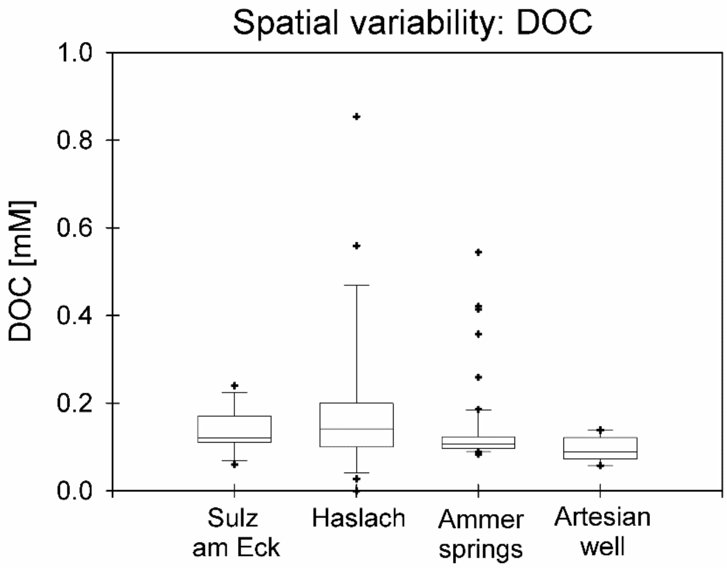

Figure S12: Whisker and box plot depicting the spatial variability of dissolved organic carbon concentrations (DOC) measured at the four major field sites. Dots mark the outliers, whereas the black lines represent the median.

Nitrate versus DOC concentrations

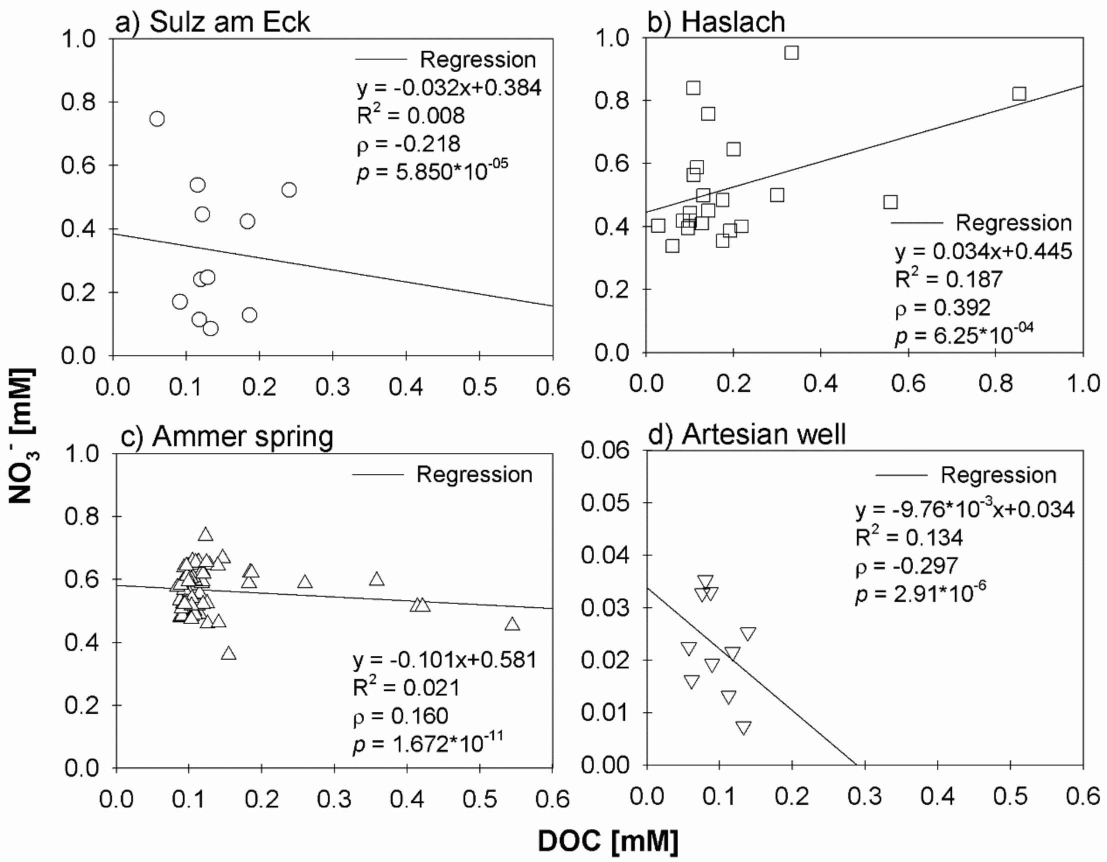

Figure S13: Correlation plot between nitrate and DOC concentrations for wells located at Sulz am Eck, Sul (**a**), Haslach, Has (**b**), the Ammer spring (**c**) and the artesian well Altingen, ArtAlt (**d**). Plots include regression function, R^2, correlation value (ρ) calculated via Pearson test, p value calculated via ANOVA.

Nitrate versus sulfate concentrations

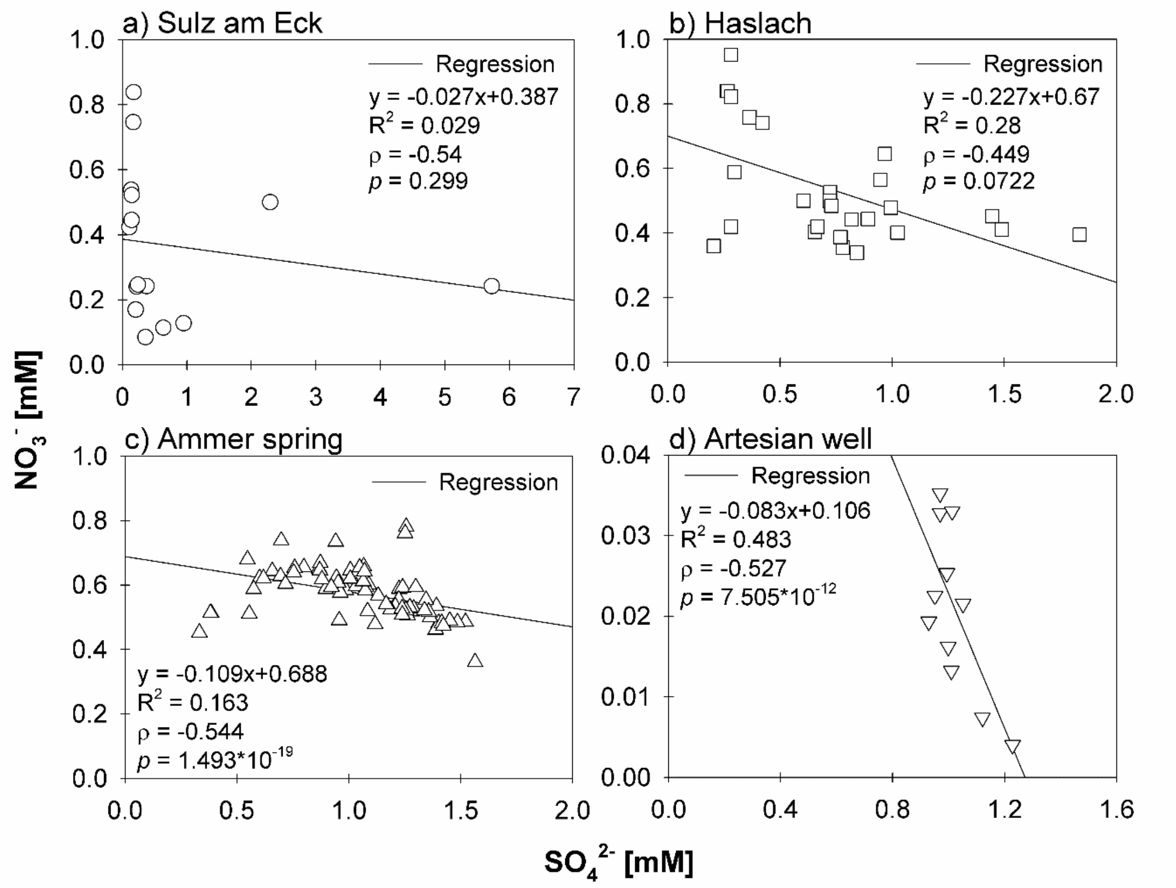

Figure S14: Correlation plot between nitrate and sulfate concentrations for wells located at Sulz am Eck, Sul (**a**), Haslach, Has (**b**), the Ammer spring, AMQ (**c**) and the artesian well Altingen, ArtAlt (**d**). Plots include regression function, R^2, correlation value (ρ) calculated via Pearson test, p value calculated via ANOVA.

Iron concentrations

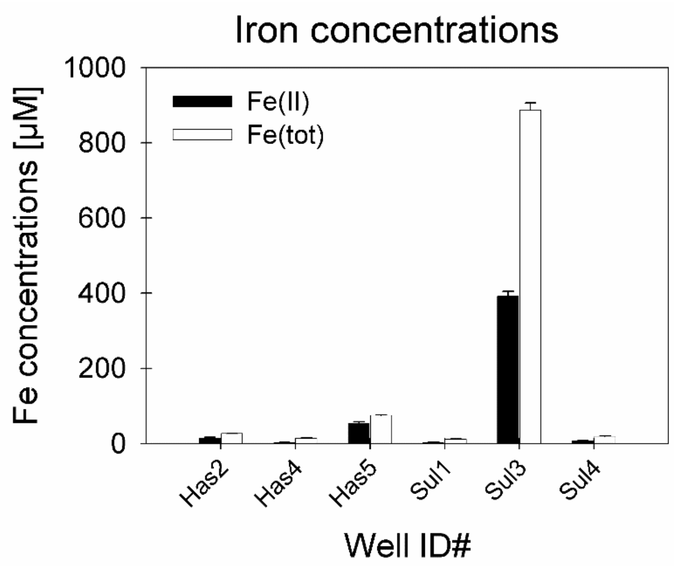

Figure S15: Concentrations of ferrous iron (Fe(II)) and iron total (Fe(tot)) measured via the ferrozine assay in selected wells for Haslach and Sulz am Eck. Standard deviation is represented by the error bars.

ESM References

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