

Change in groundwater chemistry as a consequence of suppression of floods: the case of the Rhine floodplain

J.M. Sánchez-Pérez^{a,*}, M. Trémolières^b

^aCentre d'Ecologie des Systèmes Aquatiques Continentaux (CESAC UMR 5576 CNRS), 29 rue Jeanne Marvig,
F-31055 Toulouse Cedex 04, France

^bCentre d'Ecologie Végétale et d'Hydrologie, CEVH, UMR MA 101 ULP/ENGEES, Institut de Botanique, 28 rue Goethe,
F-67083 Strasbourg Cedex, France

Abstract

Spatio-temporal variations of nitrogen, phosphorus and base cation concentrations in groundwater were related to the drastic change in hydrological conditions of the Rhine alluvial floodplain (Eastern France), which has been disconnected from the river by canalisation. The Groundwater chemistry was studied in two alluvial forests with contrasting hydrological conditions: one in a sector unflooded for 30 years, the second one in a sector still subject to flooding. Nutrient concentrations were measured at two levels, in the root zone (1.5 m depth) and in the gravel below the root layer (4.5 m depth).

In the unflooded sector, the average nitrate concentration was significantly lower in the shallow groundwater ($2.06 \text{ mg l}^{-1} \text{ NO}_3^-$) than in the deeper layer ($5.84 \text{ mg l}^{-1} \text{ NO}_3^-$). In contrast, in the flooded sector the nitrate concentrations in the shallow groundwater ($5.02 \text{ mg l}^{-1} \text{ NO}_3^-$) were not significantly different from those in the deep groundwater ($3.98 \text{ mg l}^{-1} \text{ NO}_3^-$). The concentration of phosphate was similar in shallow and deep groundwater in the unflooded sector (46 and $35 \text{ } \mu\text{g l}^{-1}$, respectively) but significantly lower in the deep groundwater of the flooded sector ($47 \text{ } \mu\text{g l}^{-1}$), than in the shallow groundwater ($58 \text{ } \mu\text{g l}^{-1}$). The major elements (cations: Ca^{2+} , Mg^{2+} , Na^+ and associated anions: HCO_3^- , SO_4^{2-} , Cl^-) concentrations were significantly higher in the groundwaters than in the surface water.

The results are discussed in terms of changes that accompanied suppression of floods, and processes that take place during the transfer of nutrients through the groundwater–soil–plant compartments. The reduction of groundwater fluctuations in the unflooded sector modified the transfer of nitrate by reducing the resolubilisation of locally produced nitrate, and/or denitrification. The transfer of phosphate was affected to a lesser extent, because of precipitation and adsorption. Base cation concentrations reflect exchange between groundwater and the calcareous gravel.

Keywords: Alluvial floodplain; Hydrological regime; Nitrate; Phosphate; Base cations; River Rhine

1. Introduction

Riparian and alluvial forests as ecotones play an important role in the regulation of the fluxes of energy and nutrients between surface water and groundwater. The nutrient retention capacity of these systems

* Corresponding author. Tel.: +33-5-62-26-99-85; fax: +33-5-62-26-99-99.

E-mail address: sanchez@ecolog.cnrs.fr (J.M. Sánchez-Pérez).

depends on the rate of transfer through the soil to the groundwater (Pinay and Décamps, 1988; Gregory et al., 1991; Correll et al., 1992) and the effect of traps in waterbodies (Cooper, 1990; Fustec et al., 1991; Jansson et al., 1994). The alluvial forest with a groundwater level close to the soil reduces the phosphate and nitrate levels in the surface layer of the groundwater (Sánchez-Pérez et al., 1991a). Moreover, in the flooded zones the infiltration of flood water provides the groundwater with water with low concentrations of nitrate and phosphate, despite the relatively high nutrient level of the river water (Sánchez-Pérez et al., 1991b). The nutrient depletion results from well-known processes, i.e. reduction of nitrate by denitrification (Lowrance, 1992; Lowrance et al., 1995; Simmons et al., 1992), plant uptake (Sánchez-Pérez et al., 1991b; Haycock and Pinay, 1993) and immobilisation in soils (Groffman et al., 1992), retention on colloids for cations and phosphate and precipitation of phosphate in calcareous soils (Reddy and Rao, 1983; Patrick, 1990). However, riparian forests can also be a source of nitrogen and phosphorus or act as a nutrient sink depending on the dissolved oxygen concentrations in groundwater (Mulholland, 1992; Patrick, 1994), which create favourable or unfavourable conditions for the elimination of certain nutrients.

Flooding largely controls nutrient dynamics in wetlands ecosystems (Brüsch and Nilsson, 1993; Cristofor et al., 1993; Neill, 1995). The flood duration and the alternation of dry and wet periods influence nutrient retention by the stimulation of biological processes. A long wet period trends to favour nitrate reduction and limits nitrification, which occurs during the dry periods (Leonardson et al., 1994). Thus a wetland is more efficient in the elimination of nitrate than a well-drained upland (Zak and Grigal, 1991). Moreover, links have been established between seasonal flooding and functions such as emergent plant production, nitrogen biochemistry and plant uptake (Neill, 1995; Sánchez-Pérez et al., 1991b).

The river Rhine was subjected to drastic environmental changes, such as the regulation of the river bed in the 19th century, canalisation during 1930–1977, and discharges of agricultural and industrial wastewater. The consequences were reduction of the area of alluvial floodplains, reduction of hydrological connectivity (i.e. disconnection of the former lateral arms

and of the alluvial forests, reduction of groundwater fluctuations) and a deterioration of water quality. At present, only small areas (400 ha of alluvial forests on the French bank) are still subject to annual floods. The new hydrological conditions greatly influenced the chemistry of the groundwater and of associated groundwater-fed water-bodies (former lateral arms of the river, Trémolières et al., 1993). The nitrate concentration in the river Rhine increased by about $4 \text{ mg l}^{-1} \text{ N}$ from 1960 ($2 \text{ mg l}^{-1} \text{ N}$) to 1985 (Malle, 1988). After the Sandoz accident in Basel in 1986, a program of ecological rehabilitation of the river Rhine was carried to counteract flooding and to improve water quality. Flood retention areas (polders) are about to be built along both sides of the Upper Rhine. Besides the aim of retaining floods, restoration of floodplain forests, mainly hardwood forests, and improvement of water quality are major issues for the polders. Since 1986, the nitrate and phosphorus concentrations of the Rhine waters decreased significantly (Van Dijk et al., 1995). However, the high nitrate load of the Rhine due to the high discharge of this river remains a problem affecting the lower Rhine and the North Sea (Howarth et al., 1996; Caraco and Cole, 1999). Nitrogen and phosphorus elimination in the Rhine floodplain would be a means to reduce the nutrient load of the Rhine, especially in the light of the present plans to restore alluvial forests on a large scale in the Upper Rhine valley (Dister et al., 1990).

The purpose of this study was to analyse the change in groundwater chemistry after suppression of floods and to specify the role played by the hydrological conditions on the groundwater quality. Our working hypothesis was that groundwater quality deteriorates, when fluctuations of groundwater level decrease. We compared the groundwater chemistry, more particularly the concentrations of phosphate, nitrate and ammonium, base cations (calcium, magnesium, sodium and potassium) and major anions (bicarbonate, sulphate and chloride), between two alluvial forests of the upper Rhine valley in France. The first one has been subjected to flooding without interruption flooded while in the other flooding has been prevented by levees since 1970 (unflooded). We monitored the chemical composition over several hydrological years in order to analyse the impact of flood episodes on groundwater chemistry.

2. Study area

Two forested sectors were investigated in the French Rhine floodplain: one is connected to the river Rhine and still subject to annual flood with summer high waters (the Rhinau forest), the other is disconnected from the river and has not been flooded since 1970 (the Erstein forest), (Fig. 1).

The dominant hydrological regime of the River Rhine is characterised by high water in summer (May to July) and low water in winter (December to January). However, winter floods (in February) can occur depending on climatic conditions. The alluvial deposit is calcareous (with around 25% CaCO₃) with spots of oxido-reduction in the layer where the groundwater level varies. The texture of the top soil is sandy-silty (USDA classification) in the unflooded sector (35% sand, 45% silt, less than 20% clay) and silty-clayey (10% sand, 60% silt and 30% clay in the surface horizon) in the flooded sector (Table 1). The topsoil described is underlain by gravel found at a depth of 1–3 m below the soil surface in both sectors. Since the groundwater is connected to the River Rhine, the groundwater table level is controlled by the Rhine level in the two sectors. In the flooded sector, groundwater fluctuations result from fluctuations in the Rhine water level and the overflow conditions. In the unflooded sector, the groundwater level varied only with the Rhine water level. Groundwater level fluctuates by 2 m in the flooded sector but by only 0.5 m in the unflooded sector. In the unflooded sector, the groundwater is drained by former side arms of the Rhine. The vegetation composition of the forest is similar in both sectors and corresponds to the hardwood stage (*Quercus-Ulmetum*) of the alluvial forest succession, with oak, elm and ash as dominant species.

3. Materials and methods

3.1. Groundwater sampling design

Groundwater samples were collected in a network of piezometers installed at two depths: one in the soil root zone (shallow groundwater) and the second in the gravel layer at 4.5 m depth (deep groundwater). In the flooded sector, four shallow piezometers installed in

1988 and four deep piezometers installed in June 1995 were sampled. In the unflooded sector, seven shallow (soil-root) wells and 12 deep wells installed in February 1994 were sampled.

Samples were taken monthly in both sectors. In the flooded sector, shallow groundwater was sampled from December 1993 to July 1995 and March 1996 to June 1997, and deep groundwater from March 1996 to June 1997. Flood waters were sampled daily during the flood period and groundwater was sampled 2 days, 4 days, 1 week and 2 weeks after the infiltration of flood waters. In the unflooded sector, the deep and shallow groundwater were sampled between April 1994 and June 1995.

In parallel, surface water was collected from the river Rhine in the flooded sector and in the disconnected side arm in the unflooded sector ('drainage water'). The water samples were collected in polyethylene bottles after pumping, filtered in the laboratory and stored in the dark at 4 °C until chemical analyses were performed. The sampling procedure was detailed by Sánchez-Pérez et al. (1991b).

3.2. Water chemistry

Water temperature, electrical conductivity (EC) and pH were measured in the field at the time of sample collection. Samples were analysed within 4 days of collection. Concentrations of NO₃⁻, NO₂⁻, NH₄⁺, PO₄³⁻, SO₄²⁻ and Cl⁻ were analysed using standard colorimetric methods with a microflux autoanalyser for N and P and macroflux for the others (ALLIANCE Instruments). Ca²⁺ and Mg²⁺ were analysed by atomic absorption spectroscopy (Varian), Na⁺ and K⁺ by flame emission spectroscopy (Varian). HCO₃⁻ was determined by titration to end point pH of 4.3 with sulphuric acid (0.04 N). The procedures used are specified by APHA (1985): ammonium by the indophenol blue method, nitrate by the cadmium reduction method, phosphate by the ascorbic acid method, sulphate by the methylthymol blue method and chloride by the automated ferricyanide method. Analytical detection limits were 5 µg l⁻¹ for NO₂⁻, NH₄⁺, and PO₄³⁻, 0.01 mg/l for NO₃⁻.

The data concerning the discharge of the river Rhine were provided by Electricité de France (EDF). The groundwater level was monitored every 10 min

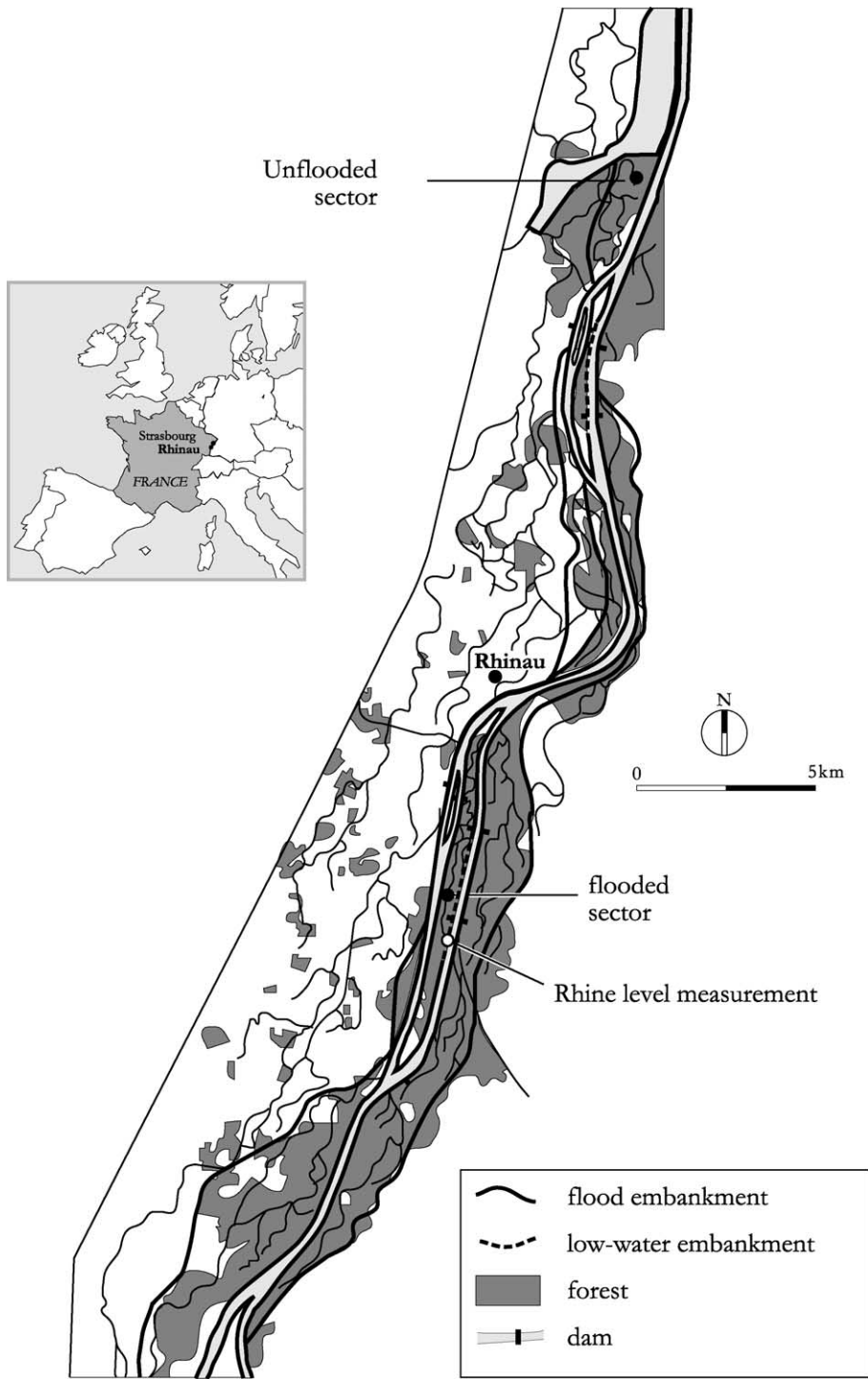


Fig. 1. Location of the two study sites in the upper Rhine floodplain (Eastern France).

Table 1
Major characteristics of the two alluvial forest sectors in hydrology, soil and vegetation

	Flooded sector	Unflooded sector
Hydrological regime	High water in summer, low water in winter Still flooded	High water in summer, low water in winter Unflooded
Granulometry	Silty–clayey (sand < 10% and clay around 30%)	Silty–sandy (sand > 30%, clay < 20%)
Gravel depth (m)	1–2	1–3
Chemistry of alluvial deposits	Highly carbonated, (CaCO ₃ > 20%)	Highly carbonated, (CaCO ₃ > 20%)
Vegetation type	Hardwood forest (oak, ash and poplar)	Hardwood forest (oak, ash and maple)
Groundwater fluctuations (m)	2.0	0.5

with a pressure probe (PDCR 850 Druck) recorded by a Campbell CR10 data logger in the flooded sector and every hour with a MADOSOLO pressure probe in the unflooded sector.

3.3. Statistical methods

Analysis of variance (ANOVA) was chosen to test for differences between the different compartments (shallow groundwater, deep groundwater and surface water), between the two sites for each compartment and between two periods in one compartment at one site. The statistical tests were performed on raw data for temperature, pH, EC, sulphate and chloride and on log transformed data (Ln) for dissolved oxygen, nitrate, nitrite, ammonium and phosphate. When the standardised residual of raw data and transformed data did not follow a normal distribution, we used the non parametric Kruskal–Wallis test.

In all the statistical methods, differences were considered significant at $p < 0.05$. All statistical calculations were made using MINITAB computer package (Minitab Inc., USA).

4. Results

We compared the data of the period 1994–1995 to those of 1996–1997 in the shallow groundwater of

the flooded stand. The means of nutrient concentrations for the two periods were not significantly different (Table 2), although the standard deviation and standard error were high. The chemistry of deep groundwater fluctuated less than the shallow groundwater (StDev 4.28 and 8.08, respectively). This led us to assume that in the flooded sector, the quality of deep groundwater did not change between the two periods, and we compared the shallow groundwater sampled from May 1994 to June 1995, with the deep groundwater sampled the following year. We also compared also concentrations of both shallow and deep groundwater in the two sectors over the whole sampling period.

The mean pH of Rhine water was 8.03, some that higher than that of groundwater (7.20–7.66, Table 3). In Rhine water, the EC ($565 \mu\text{S cm}^{-1}$) was lower than in the deep groundwater ($671\text{--}788 \mu\text{S cm}^{-1}$) and shallow groundwater ($890\text{--}1005 \mu\text{S cm}^{-1}$). The dissolved oxygen concentration was higher in surface waters (10.7 mg l^{-1}) than in deep groundwater (around 2 mg l^{-1}) and shallow groundwater ($2.4\text{--}3.0 \text{ mg l}^{-1}$). The mean nitrate and phosphate concentrations were significantly lower in the groundwater in the two sectors (less than $5.02 \text{ mg l}^{-1} \text{ NO}_3^-$ and less to $58 \mu\text{g l}^{-1} \text{ PO}_4^{3-}$, respectively) as compared to the surface water ($8.33 \text{ mg l}^{-1} \text{ NO}_3^-$ and $224 \mu\text{g l}^{-1} \text{ PO}_4^{3-}$, Table 4).

Nitrate, ammonium and phosphate concentrations in the deep groundwater differed widely according to the site. Mean nitrate concentrations were lower in the flooded sector than in the unflooded sector, whereas the reverse was the case for ammonium. In the shallow groundwater, nitrate was higher in the flooded than in the unflooded sector. Phosphate and ammonium levels were relatively similar in the two sites. The mean concentrations of most of the major elements (cations and anions) were significantly higher in the groundwater than in the river Rhine (Table 5).

In Table 6, we give the significance of differences between compartments and between sites. In the flooded sector, there was no significant difference between the two compartments, shallow and deep groundwater, for nitrate, but there was a difference for phosphate. In contrast, in the unflooded sector, nitrate levels in the shallow groundwater ($2.06 \text{ mg l}^{-1} \text{ NO}_3^-$) were significantly lower than in the deep groundwater

Table 2

Comparison of the shallow groundwater data for two periods (period 1 = 1/12/93–1/7/95 and period 2 = 13/3/96–29/5/97) in the flooded sector (Rhinau Island). Number of non missing values, number of missing values, mean, median, trimmed mean (mean after removal of the smallest 5% and the largest 5% of the values), standard deviation, standard error of mean, minimum, maximum, first quartile, third quartile and *p*-value (Each variable were tested for a Shapiro–Wilk test for normal distribution to the standardised residual of the ANOVA), * = (*p* > 0.05)

Variable	Serie	<i>N</i>	<i>N</i> *	Mean	Median	TrMean	StDev	SEMean	Min	Max	<i>Q</i> ₁	<i>Q</i> ₃	<i>p</i>
<i>T</i> (°C)	1	118	13	10.9	9.8	10.9	3.0	0.3	4.7	16.8	8.6	13.7	
	2	62	1	11.8	11.5	11.8	3.4	0.4	4.7	19.2	9.9	13.7	*(0.354)
pH	1	113	18	7.16	7.10	7.15	0.23	0.02	6.72	7.76	6.99	7.30	
	2	58	5	7.28	7.31	7.29	0.22	0.03	6.69	7.79	7.18	7.43	*(0.055)
EC (μS/cm)	1	113	18	899	891	899	258	24	444	1438	690	1126	
	2	62	1	873	866	872	113	14	660	1120	799	950	*(0.782)
O ₂ (mg/l)	1	102	29	2.5	1.6	2.3	2.2	0.2	0.2	11.2	1.0	3.3	
	2	47	16	4.0	3.8	4.0	2.1	0.3	0.2	7.8	2.2	6.1	(0.002)
NO ₃ ⁻ (mg/l)	1	131	0	5.41	2.08	3.96	8.84	0.77	0.04	62.44	0.75	6.16	
	2	63	0	4.21	1.99	3.31	6.19	0.78	0.18	30.20	0.89	3.76	*(0.334)
NO ₂ ⁻ (μg/l)	1	131	0	93	39	66	163	14	16	1249	16	95	
	2	63	0	85	23	65	141	18	16	555	16	66	*(0.737)
NH ₄ ⁺ (μg/l)	1	131	0	212	91	165	335	29	6	2301	18	316	
	2	63	0	152	46	104	283	36	6	1341	23	127	*(0.218)
PO ₄ ⁻³ (μg/l)	1	131	0	62	33	46	102	9	15	993	18	66	
	2	63	0	49	18	37	78	10	15	546	15	63	*(0.317)
SO ₄ ⁻² (mg/l)	1	130	1	106.2	101.5	102.9	53.8	4.7	27.5	276.0	61.6	141.3	
	2	63	0	87.2	89.1	87.2	18.6	2.3	48.1	126.0	80.6	93.0	*(0.418)
Cl ⁻ (mg/l)	1	131	0	55.7	56.1	55.5	21.8	1.9	14.9	103.2	38.0	72.1	
	2	45	18	49.4	48.9	48.9	13.4	2.0	17.4	87.1	39.5	54.9	*(0.203)

(5.84 mg l⁻¹ NO₃⁻) whereas phosphate concentrations were not different. The nitrate composition of deep groundwater in unflooded sector was similar to that of the drainage water, collected in the disconnected side arm (5.84 mg l⁻¹ and 6.58 mg l⁻¹ NO₃⁻, respectively).

Regarding major elements, only potassium concentrations were not significantly different in the shallow groundwater of both sectors compared to Rhine water concentrations (Table 6). In the unflooded sector, the concentrations of potassium were significantly higher in the deep groundwater than in the root layer, whereas the other major elements (except Na) were significantly lower in the deep groundwater as compared to the shallow groundwater. In the flooded sector, sulphate was not different between the two levels of groundwater, whereas chloride was.

The standard deviations for nitrogen forms and phosphate were higher in the flooded than in the unflooded sector, thus indicating large spatial and

temporal fluctuations over the year (Fig. 2). The concentrations in the flooded sector varied between 0.04 and 62.44 mg l⁻¹ for NO₃⁻, 5 and 1249 μg l⁻¹ for NO₂⁻, 5 and 2301 μg l⁻¹ for NH₄⁺, and 5–993 μg l⁻¹ for PO₄⁻³ (Table 3). The highest levels were measured during the flood episode(s). After floodwater infiltrated through the soil, the concentrations decreased rapidly to the low levels measured before the flood. In the unflooded sector, the variations of phosphate and nitrate over the sampling period were low. In the same way, anions showed lower temporal fluctuations in the unflooded forest than in the flooded area, where the concentrations varied widely with flood periods (Fig. 3). Thus during flooding, the base cation and associated anion concentrations decreased in groundwater and became close to those of Rhine water. We also observed a decrease of cations in spring 1994, which occurred in both flooded and unflooded sectors. However, standard deviations for major cations and anions were similar in both types of sector.

Table 3

Physico-chemical characteristics in groundwater and surface water in the two stands (1 = flooded sector, shallow groundwater; 2 = flooded sector, deep groundwater, 3 = Rhine river; 4 = unflooded sector, shallow groundwater; 5 = unflooded sector, deep groundwater; 6 = unflooded sector, drainage water). Number of non missing values, mean, median, trimmed mean, standard deviation, standard error of mean, minimum, maximum, first quartile and third quartile

Variable	SP	N	Mean	Median	TrMean	StDev	SEMean	Min	Max	Q ₁	Q ₃
T (°C)	1	180	11.2	10.8	11.2	3.2	0.2	4.7	19.2	8.7	13.7
	2	63	11.7	11.8	11.7	2.0	0.3	7.0	15.7	10.3	12.8
	3	47	12.3	12.8	12.2	5.6	0.8	3.4	25.2	7.6	15.5
	4	76	10.9	10.4	10.8	2.0	0.2	7.9	16.2	9.3	12.1
	5	86	12.8	12.6	12.7	1.5	0.2	9.8	16.1	11.8	13.9
	6	21	12.7	12.3	12.5	1.4	0.3	11.1	16.8	11.7	13.3
pH	1	171	7.20	7.18	7.19	0.23	0.02	6.69	7.79	7.04	7.36
	2	60	7.35	7.40	7.37	0.32	0.04	5.83	8.03	7.22	7.53
	3	44	8.03	8.06	8.04	0.29	0.04	7.39	8.60	7.89	8.19
	4	72	7.22	7.20	7.22	0.22	0.03	6.76	7.60	7.05	7.42
	5	86	7.61	7.65	7.61	0.25	0.03	6.94	8.43	7.48	7.74
	6	21	7.66	7.70	7.62	0.37	0.08	7.14	8.90	7.40	7.77
EC (µS/cm)	1	175	890	882	889	218	17	444	1438	739	1050
	2	62	788	790	788	30	4	711	872	766	809
	3	46	565	544	555	165	24	304	1015	424	651
	4	73	1005	973	997	237	28	571	1660	816	1132
	5	87	671	665	669	88	10	484	916	615	735
	6	21	668	679	657	106	23	518	1010	593	697
O ₂ (mg/l)	1	149	3.0	2.4	2.8	2.3	0.2	0.2	11.2	1.2	4.3
	2	53	2.3	2.0	2.1	1.8	0.3	0.2	9.7	1.0	3.2
	3	40	10.7	10.7	10.7	2.7	0.4	5.0	16.1	8.7	12.6
	4	71	2.4	2.0	2.1	2.0	0.2	0.5	9.4	0.9	2.8
	5	87	2.2	1.9	2.1	1.4	0.2	0.2	7.5	1.3	2.7
	6	19	3.77	3.3	3.8	1.1	0.2	2.0	5.7	2.9	4.6

5. Discussion

The alluvial floodplain presents a high temporal variability of the concentrations of inorganic constituents in groundwater, as a consequence of the large fluctuations in hydrological conditions (Takatert et al., 1999). In the flooded stand of the Rhine floodplain, nitrogen and phosphorus fluctuated considerably (compare the mean and the median) over a period of 4 years, whereas major cations and anions fluctuated less. Moreover, comparison of the chemical composition of the shallow groundwater between the two periods in the flooded sector revealed no significant differences. The variations of inorganic constituents in the deep groundwater were also less than in the shallow groundwater. The average values over the whole sampling period were similar to those calculated over the common period of reference in the two

studied sectors. For this reason, we decided to use all the information to characterise each compartment in the comparison of the flooded and unflooded sites.

The higher EC of the shallow groundwater, as compared to deep groundwater and surface water, corresponded to the highest concentrations of dominant ions, which were the result of exchange and solubilisation in the calcareous gravely aquifer. No significant difference appeared in the shallow groundwater between the two sectors, in the absence of flooding. In addition the EC and ionic composition of the deep groundwater were intermediate between shallow groundwater and Rhine water. This can be explained by the horizontal seepage of Rhine water through its bed or banks and dilution of the deep groundwater, as has been already shown by Trémolières et al. (1993). Moreover the less concentrated surface water dilutes the groundwater during

Table 4

Chemical characteristics (biogenic elements) in groundwater and surface water in the two stands (1 = flooded sector, shallow groundwater; 2 = flooded sector, deep groundwater, 3 = Rhine river; 4 = unflooded sector, shallow groundwater; 5 = unflooded sector, deep groundwater; 6 = unflooded sector, drainage water). Number of non missing values, mean, median, trimmed mean, standard deviation, standard error of mean, minimum, maximum, first quartile and third quartile

Variable	SP	N	Mean	Median	TrMean	StDev	SEMean	Min	Max	Q ₁	Q ₃
NO ₃ ⁻ (mg/l)	1	194	5.02	1.99	3.73	8.08	0.58	0.04	62.44	0.88	5.25
	2	64	3.98	3.10	3.33	4.28	0.54	0.44	29.23	1.96	4.21
	3	50	8.33	7.86	8.24	2.51	0.36	3.28	13.86	6.20	9.98
	4	76	2.06	0.93	1.68	2.49	0.29	0.22	12.05	0.53	2.91
	5	88	5.84	5.89	5.78	2.32	0.25	0.62	11.56	4.09	7.39
	6	22	6.58	6.47	6.57	1.48	0.32	4.43	9.03	5.13	7.78
NO ₂ ⁻ (μg/l)	1	194	90	30	64	156	11	16	1249	16	89
	2	64	48	28	37	69	9	5	391	13	49
	3	50	86	51	67	114	16	5	641	21	109
	4	73	53	28	45	61	7	5	343	10	78
	5	88	27	21	23	29	3	5	179	12	32
	6	23	53	30	37	93	19	5	435	13	43
NH ₄ ⁺ (μg/l)	1	194	193	60	144	320	23	6	2301	22	242
	2	64	62	35	44	108	13	5	784	20	63
	3	50	193	102	170	206	29	5	775	52	281
	4	76	158	68	142	173	20	5	649	31	290
	5	88	28	20	23	45	5	5	408	7	41
	6	23	53	51	51	39	8	8	149	18	74
PO ₄ ³⁻ (μg/l)	1	194	58	27	43	95	7	15	993	15	64
	2	64	47	15	24	131	16	5	990	9	33
	3	50	224	114	154	438	62	15	3060	56	266
	4	76	46	34	39	50	6	5	304	15	56
	5	87	35	27	33	29	3	5	135	14	48
	6	23	28	26	27	21	4	5	69	9	48

the vertical flood infiltration, which explains the decrease of certain major cation concentrations during a flood period. The similar large standard deviations of dominant ionic concentrations in both sectors seemed to indicate, in addition to temporal variations, spatial variations due to geomorphologic conditions, which are still preserved in the unflooded sector, i.e. juxtaposition of former channels and terraces differing in grain size composition, as has been shown by Pinay et al. (1995) for nitrate. In the unflooded forest, the ionic concentrations were similar in the two compartments, the drainage water of the former channel of the river and the deep groundwater, which shows the lateral flow of the groundwater at a depth of around 5 m.

In contrast, over a period of 4 years the concentrations of biogenic compounds, nitrate and phosphate, were lower in deep and shallow groundwater in

the flooded sector than in Rhine water, which demonstrates both the efficient capacity of retention and elimination by the soil–root system (Sánchez-Pérez et al., 1991b) and the role of river bank filtration for these nutrients (Trémolières et al., 1993; Doussan et al., 1997). In the shallow groundwater, the average concentrations of nitrate were significantly higher in the flooded than in the unflooded sectors. It should be noted that this calculation includes the periods of flooding; in fact the fluctuations of nutrient concentrations over the whole year were higher in the flooded sector in both shallow (1.5–2 m deep) and deep groundwater (4–4.5 m). The floods contributed to regular nutrient inputs and to high fluctuations of groundwater level. However, the comparison of the seasonal means during the study period, showed that there were no significant differences between summer and winter (December to March) in both flooded and

Table 5

Chemical characteristics (major elements) in groundwater and surface water in the two stands (1 = flooded sector, shallow groundwater; 2 = flooded sector, deep groundwater, 3 = Rhine river; 4 = unflooded sector, shallow groundwater; 5 = unflooded sector, deep groundwater; 6 = unflooded sector, drainage water). Number of non missing values, mean, median, trimmed mean, standard deviation, standard error of mean, minimum, maximum, first quartile and third quartile

Variable	SP	N	Mean	Median	TrMean	StDev	SEMean	Min	Max	Q ₁	Q ₃
HCO ₃ ⁻ (mg/l)	1	130	367.6	369.7	370.0	95.4	8.4	116.6	594.7	311.1	439.2
	2	0	-	-	-	-	-	-	-	-	-
	3	34	169.5	176.0	171.0	22.8	3.9	107.8	203.3	154.2	184.8
	4	76	422.9	394.1	414.8	135.2	15.5	209.8	843.3	325.1	497.2
	5	87	226.0	223.5	223.3	49.6	5.3	136.2	404.6	199.6	244.5
	6	23	220.4	213.5	220.5	21.9	4.6	175.0	263.5	205.0	236.7
Ca ²⁺ (mg/l)	1	131	102.1	96.5	101.4	40.4	3.5	30.0	213.8	66.5	136.0
	2	0	-	-	-	-	-	-	-	-	-
	3	34	46.3	48.6	46.6	10.3	1.8	25.5	61.1	36.9	53.9
	4	74	99.4	93.6	97.6	37.7	4.4	43.5	192.0	65.0	128.4
	5	86	63.6	63.9	62.2	24.7	2.7	28.0	150.5	44.0	77.3
	6	23	64.2	57.4	63.7	16.3	3.4	33.0	104.5	53.3	79.8
K ⁺ (mg/l)	1	130	3.83	3.60	3.76	1.04	0.09	2.10	7.10	3.12	4.50
	2	0	-	-	-	-	-	-	-	-	-
	3	34	4.15	4.10	4.09	1.22	0.21	2.40	7.10	3.13	5.15
	4	76	2.88	2.57	2.67	1.97	0.23	0.60	11.73	1.38	3.72
	5	87	5.28	5.35	5.20	1.77	0.19	1.80	17.20	4.41	6.00
	6	23	4.80	5.12	4.65	1.88	0.39	2.30	10.60	3.00	5.39
Na ⁺ (mg/l)	1	130	59.6	60.5	58.6	26.2	2.3	13.5	123.0	38.9	75.3
	2	0	-	-	-	-	-	-	-	-	-
	3	34	35.4	33.5	34.4	16.3	2.8	11.0	82.5	21.4	47.1
	4	75	57.8	49.0	55.0	37.0	4.3	6.9	197.0	26.4	82.0
	5	87	54.4	54.0	54.2	19.1	2.1	12.4	103.0	41.9	66.8
	6	23	45.7	47.6	46.3	11.9	2.5	10.6	69.0	38.8	51.96
Mg ²⁺ (mg/l)	1	130	13.3	13.5	13.3	4.2	0.4	3.7	21.4	10.0	16.4
	2	0	-	-	-	-	-	-	-	-	-
	3	34	7.3	7.5	7.3	1.4	0.2	3.9	9.8	6.1	8.5
	4	76	18.7	16.4	17.8	9.5	1.1	6.3	68.3	12.0	22.1
	5	87	8.9	8.1	8.5	2.6	0.3	5.9	25.1	7.6	9.3
	6	23	8.7	8.5	8.7	0.7	0.1	8.1	10.8	8.2	8.9
SO ₄ ⁻² (mg/l)	1	193	100.0	91.3	97.1	46.2	3.3	27.5	276.0	65.3	134.5
	2	64	94.8	92.9	96.2	14.4	1.8	27.0	118.0	91.6	98.0
	3	50	71.4	62.2	67.9	41.4	5.9	18.3	194.0	41.3	92.7
	4	76	50.1	40.9	49.4	25.2	2.9	6.9	114.0	32.9	69.4
	5	88	37.5	37.8	37.4	8.6	0.9	12.0	63.5	34.2	41.2
	6	23	37.9	37.0	37.7	4.5	0.9	29.8	48.6	35.2	40.1
Cl ⁻ (mg/l)	1	176	54.1	52.5	53.8	20.1	1.5	14.9	103.2	39.3	67.3
	2	43	47.8	48.0	48.1	3.2	0.5	31.9	52.2	46.6	49.6
	3	46	31.4	31.0	31.1	6.3	0.9	21.2	48.1	26.9	33.9
	4	75	120.1	101.0	113.8	78.8	9.1	10.0	380.0	55.9	160.0
	5	88	84.4	86.0	84.7	19.6	2.1	30.5	133.0	71.6	97.7
	6	23	84.2	84.6	84.1	5.9	1.2	75.5	96.0	79.0	89.8

Table 6

Significance of differences between compartments and between sites. p -values from the non parametric Kruskal–Wallis, K-sample test. * = $p < 0.05$ (statistical significant) the two compartments were different. $p > 0.05$ = statistical not significant, the two compartments were not different. – = non tested. (1 = comparison surface water to shallow groundwater; flooded sector; 2 = comparison shallow groundwater to deep groundwater, flooded sector; 3 = comparison shallow groundwater to deep groundwater, unflooded sector; 4 = comparison flooded sector to unflooded sector, shallow groundwater; 5 = comparison flooded sector to unflooded sector, deep groundwater)

Variable	1	2	3	4	5
T	0.290	0.149	*	0.735	*
pH	*	*	*	0.493	*
C	*	*	*	*	*
O ₂		0.083	0.936	0.085	0.959
NO ₃ ⁻	*	0.074	*	*	*
NO ₂ ⁻	0.490	*	*	*	*
NH ₄ ⁺	*	*	*	0.609	*
PO ₄ ³⁻	*	*	0.220	0.819	*
HCO ₃ ⁻	*	–	*	*	–
Ca ²⁺	*	–	*	0.606	–
K ⁺	0.195	–	*	*	–
Na ⁺	*	–	0.727	0.239	–
Mg ²⁺	*	–	*	*	–
SO ₄ ²⁻	*	0.499	*	*	*
Cl ⁻	*	*	*	*	*

unflooded forests, even though the flooded forest was regularly enriched in nutrients by floodwaters usually in summer.

The response of inorganic constituents to water level fluctuations differ according to the element, thus nitrogen and phosphorus increase greatly during the flood periods. The flood or the rising of groundwater levels allows nitrate and phosphate produced in soils during the low water period to be solubilised (Sánchez-Pérez and Trémolières, 1997). In fact, we measured in the first 40 cm of the soil (soil solution sampled with ceramic cups) the highest concentrations of nitrate, up to 24 mg l⁻¹ in a soil sampled in a former channel, and up to 53 mg l⁻¹ NO₃⁻ in a sandy profile of a terrace soil, which showed the high nitrification capacity of the soils in the flooded sector, since the Rhine water contained low concentrations of nitrate. The coarse porous substrate favours this process (McDowell et al., 1992). The low level of nitrate measured after the water infiltration was the result of processes, which are activated by high

groundwater level, such as denitrification (Leonardson et al., 1994; Davidsson and Leonardson, 1998) or dissimilative reduction (Fazzolari-Correa and Geron, 1991). In parallel with the decrease of nitrate, we measured a high level of ammonium, sometimes even higher than that of the River Rhine which is often highly contaminated by ammonium.

In the flooded sector, we measured high, potential denitrification especially in the topsoil, and the redox potential used as an indicator of denitrification, decreased considerably during the flood period (Brettar et al., 2002). These particular conditions could explain the similar low nitrate concentrations in deep and shallow groundwater in the flooded site. Thus, nitrate is produced by nitrification in the soil surface, then denitrified in the saturated zone during dry periods, the floods increasing the denitrification rate in the whole saturated soil profile (Davidsson and Leonardson, 1998). Thus the alternation of wet and dry cycles stimulated biochemical transformations of nitrogen, as demonstrated for example, by nitrous oxide emissions, which result from both nitrification and denitrification (Maag and Vinther, 1996; Davidsson and Leonardson, 1997).

That was no longer the case in the unflooded sector where there were significant nitrate differences between deep and shallow groundwater. The higher concentrations of nitrate in the deep groundwater could be the result of suppression of floods and consequently limited fluctuations of groundwater level. The working hypothesis was that the nitrate is only provided by mineralisation of organic matter, then highly absorbed by vegetation in the summer which would explain the low concentration in the shallow groundwater (root layer). The denitrification process did not occur in the deep horizon, as was the case in the flooded sector. In fact mineralisation, nitrification and denitrification are regulated not only by soil water content which affects the oxygen status in the soil (Reddy and Patrick, 1984), but also by nitrate content and organic input (Jordan et al., 1998). There are neither permanent reducing soil conditions, because of the very porous sandy–silty substrate, nor a temporary hydromorphic horizon because of the absence of flooding.

In the flooded sector phosphate decreased faster than nitrate after a flood and remained at the same low concentrations as in the unflooded sector, except during a flood period. This result is explained by

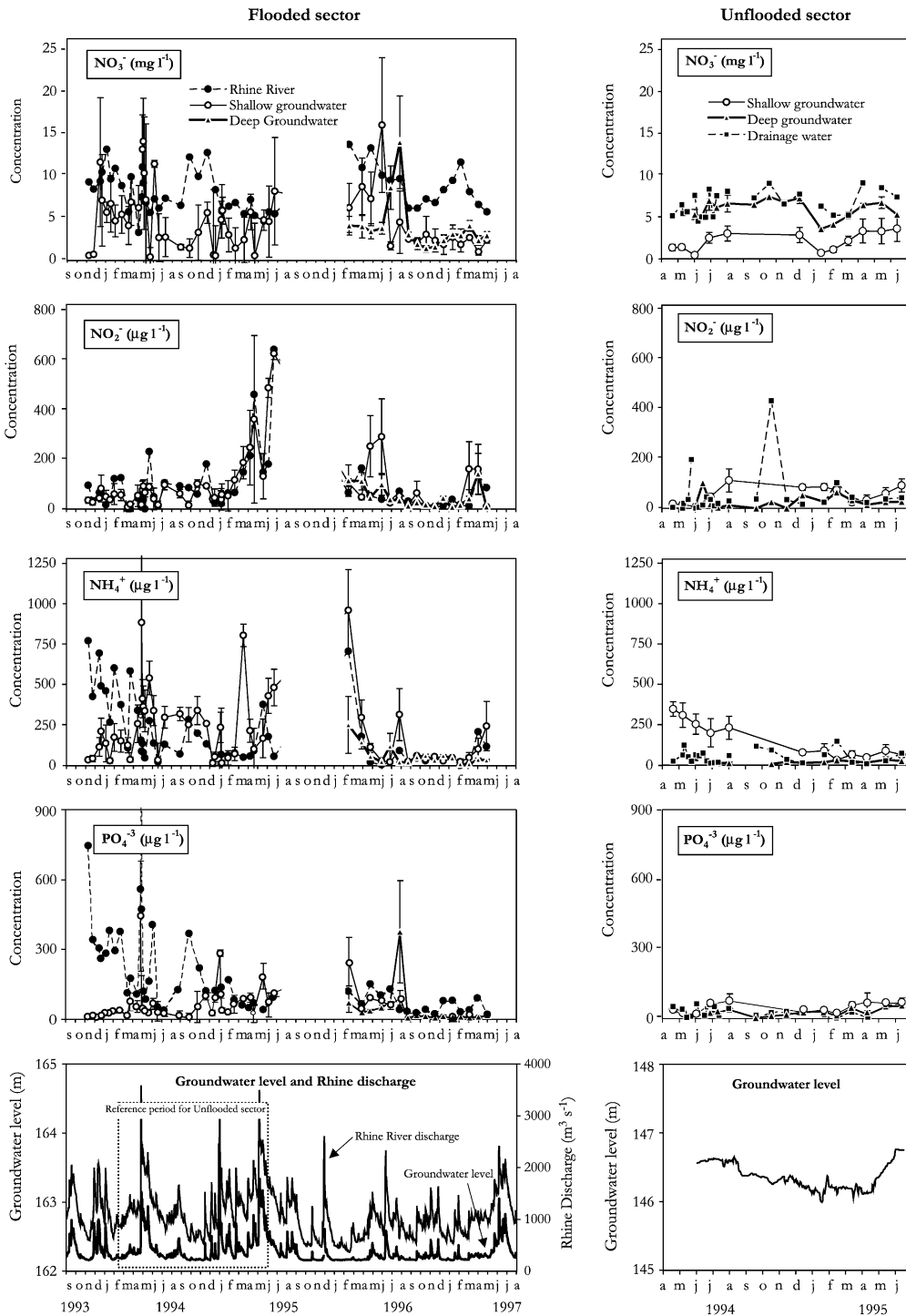


Fig. 2. Changes in NO_3^- , NO_2^- , NH_4^+ and PO_4^{3-} , concentrations in deep and shallow groundwater and Rhine water over the whole sampling period in the flooded sector (1993–1997) and the unflooded sector (1994–1995) in relation to the hydrology (mean \pm SE).

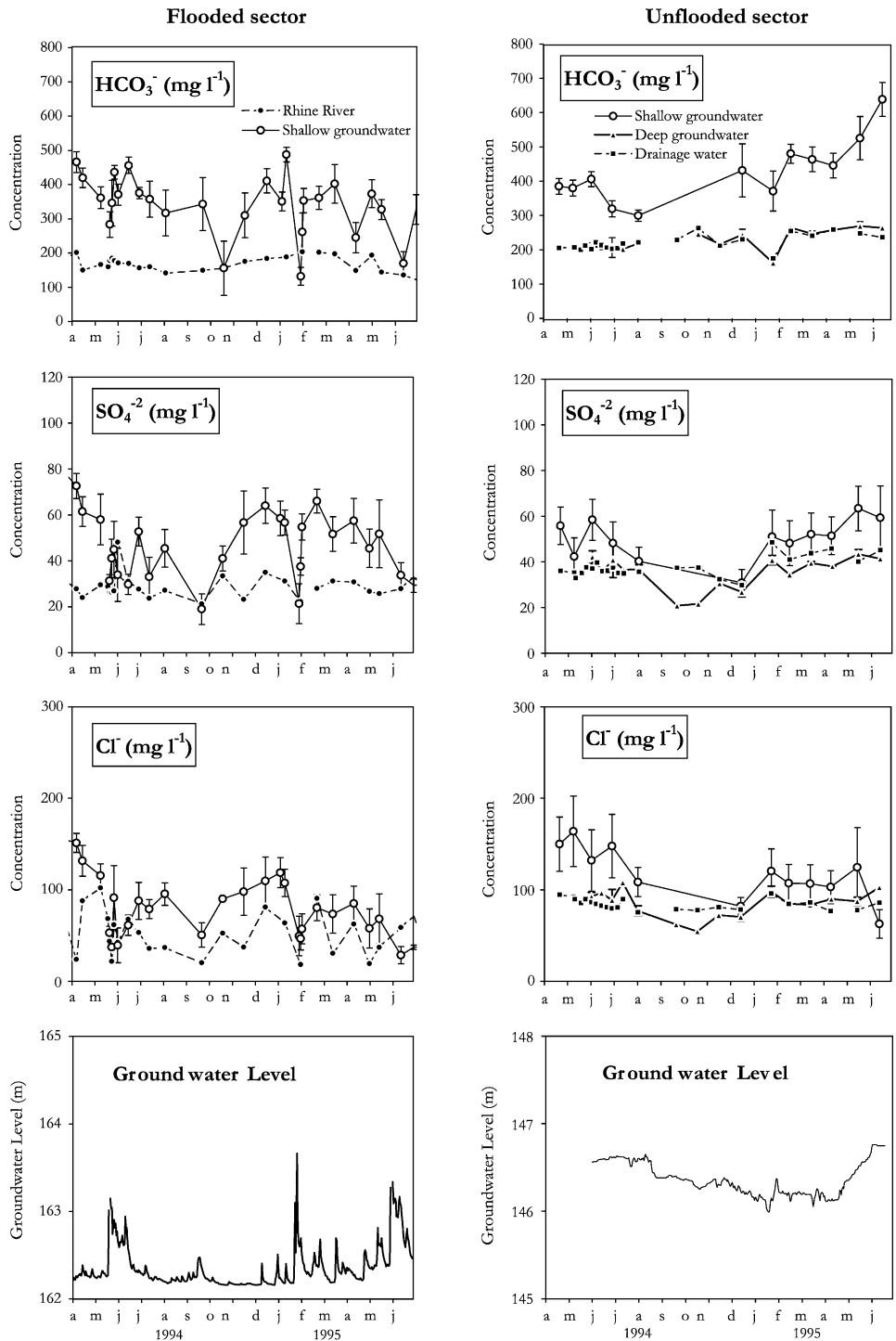


Fig. 3. Change in anions (HCO_3^- , SO_4^{-2} and Cl^-) and base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) concentrations in deep and shallow groundwater and Rhine water over a hydrological year (1994–95) in the flooded and unflooded sectors in relation to the hydrology (mean \pm SE).

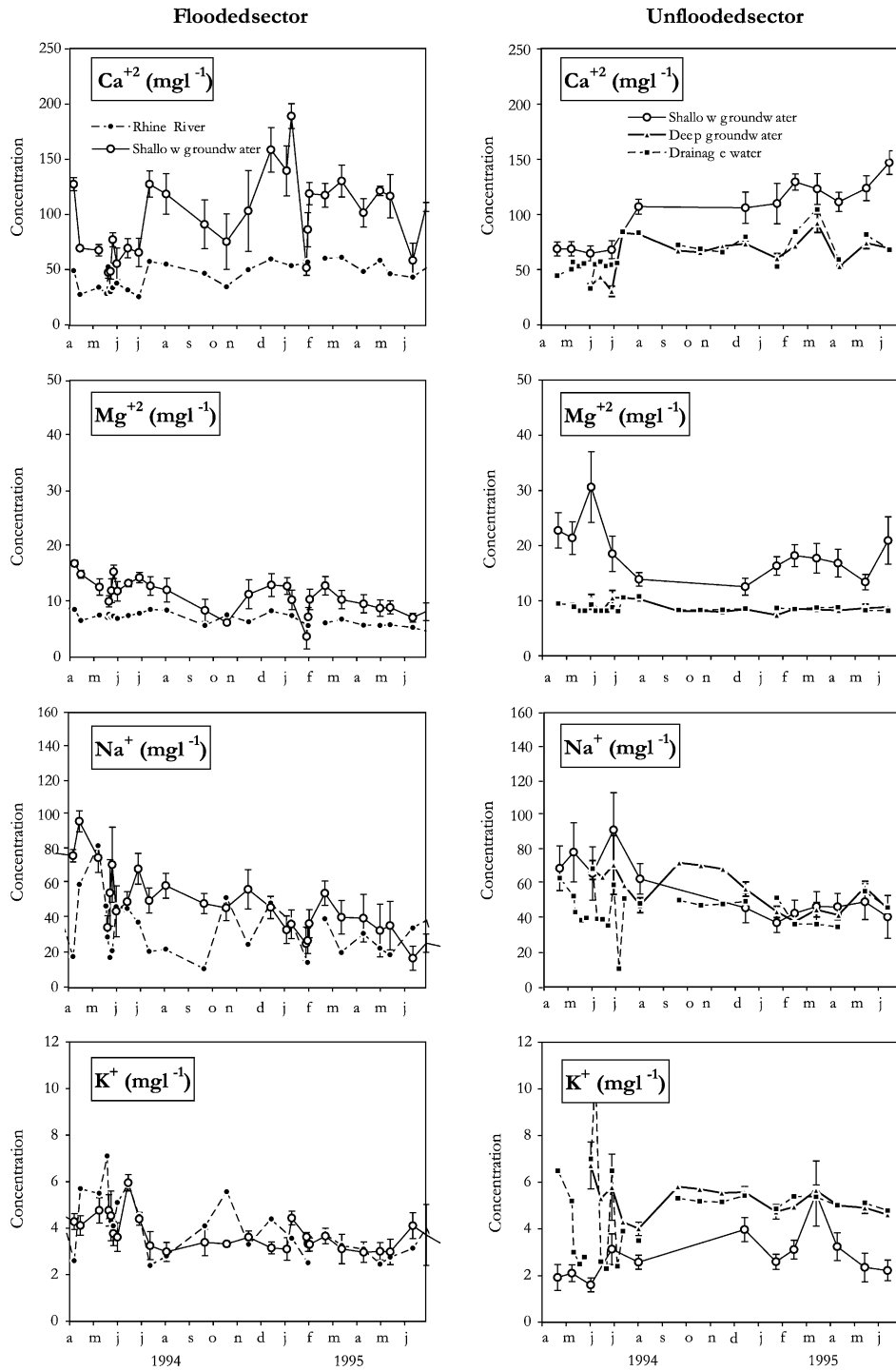


Fig. 3 (continued)

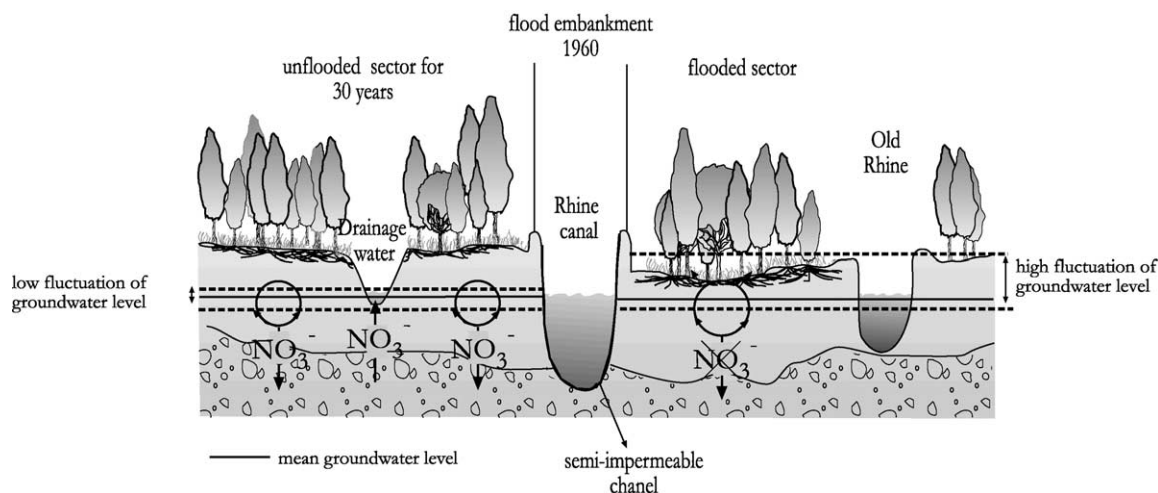


Fig. 4. Conceptual scheme of change in the transfer of nitrate after elimination of floods, in an alluvial forest site.

precipitation in the calcareous soils (Patrick, 1990), and/or adsorption on the clayey substrate. The fluctuations of the water level also ensure phosphate solubilisation (Arvieu, 1980; Masscheleyn et al., 1992), hence its large fluctuations in both levels of groundwater in the flooded sector. However, the same calcareous substrate in both sectors which precipitates the phosphate, explains the very low concentrations in shallow and deep groundwater of both sites.

6. Conclusion

The concentrations of major cations and associated anions are the result of exchange between the aquifer and groundwater and the dilution effect by surface water after riverbank filtration or flood infiltration. The similarity in their variations at both sites (coefficient of variation of around 20–40%) shows that these fluctuations can be explained more by the spatial geomorphic variations, which are relatively similar at both sites, than by temporal variations due to flood episodes. In contrast, flooding plays a more important role in the biochemical cycles of nitrogen and phosphorus, as has been already shown by Reddy and Patrick (1984), Sánchez-Pérez and Trémolières (1997), Takatert et al. (1999). Flooding creates alternating wet–dry periods favourable to bacterial activity and solubilisation processes and thus to alternating nitrification–denitrification. In the unflooded sector, this regulation is reduced and

the soil–root filter is less efficient during the vertical transfer of nutrients provided by mineralisation and nitrification. A conceptual scheme is proposed for the change in the transfer of nitrate with the suppression of flood and thus the reduction of groundwater movement (Fig. 4). Nitrate removal from the flooded forest is high, whereas the elimination of floods reduces the efficiency of the soil–root filter for nitrate, which could contribute to contamination of the surface water by the drainage of the deep groundwater, as has been shown in the unflooded sector. However, more research is needed for a better understanding of the biochemical transformation of nitrate in the soil during its vertical transfer to the groundwater under both types of condition, flooding and elimination of floods. Moreover the restoration of ‘polders’ could be an interesting model to test the resilience capacity of the floodplain, i.e. the capacity to restore some functions such as the filtering efficiency of alluvial forests.

Acknowledgements

This work was supported by the PIREN Eau-Alsace/CNRS-Région Alsace, IFARE (Institut Franco-Allemand de Recherche sur l’Environnement) and PNRH a research program on hydrology. The authors wish to thank O. Atteia and three others anonymous referees for their valuable comments and the Editor of the Journal (P. Van Cappellen) for checking the manuscript.

References

- APHA, 1985. Standard Methods for the Examination of Water and Wastewater, 16th ed., American Public Health Association, p. 1268.
- Arvieu, J.C., 1980. Relations des phosphates minéraux en milieu calcaire: conséquences sur l'état et la solubilité du phosphore. *Science du sol* 3, 179–190.
- Brettar, I., Sánchez-Pérez, J.M., Trémolières, M., 2002. Nitrate elimination by denitrification in hardwood forest soils of the Upper Rhine floodplain—correlation with redox potential and organic matter. *Hydrobiologia* 469, 11–21.
- Brüsch, W., Nilsson, B., 1993. Nitrate transformation and water movement in a wetland area. *Hydrobiologia* 251, 103–111.
- Caraco, N.F., Cole, J.J., 1999. Human impact on nitrate export: analysis using major world rivers. *Ambio* 28 (2), 167–170.
- Cooper, A.B., 1990. Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. *Hydrobiologia* 202, 12–36.
- Correll, D.L., Jordan, T.E., Weller, D.E., 1992. Nutrient flux in a landscape: effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. *Estuaries* 15, 431–442.
- Cristofor, S., Vadineanu, A., Ignat, G., 1993. Importance of flood zones for nitrogen and phosphorus dynamics in the Danube delta. *Hydrobiologia* 251, 143–148.
- Davidsson, T.E., Leonardson, L., 1997. Production of nitrous dioxide in artificially flooded and drained soils. *Wetlands Ecol. Manage.* 5, 111–119.
- Davidsson, T.E., Leonardson, L., 1998. Seasonal dynamics of denitrification activity in two water meadows. *Hydrobiologia* 363, 189–198.
- Dister, E., Gomer, D., Obrdlik, P., Peterman, P., Scheider, E., 1990. Water management and ecological perspectives of the Upper Rhine's floodplains. *Regul. River: Res. Manage.* 5, 1–15.
- Doussan, C., Poitevin, G., Ledoux, E., Detay, M., 1997. River bank filtration: modelling of the changes in water chemistry with emphasis on nitrogen species. *J. Contam. Hydrol.* 25, 129–156.
- Fazzolari-Correa, E., Germon, J.C., 1991. Dissimilative nitrate reduction to ammonium in different soils in waterlogged conditions. In: Berthelin, J., (Ed.), *Diversity of Environmental Biogeochemistry*, Elsevier, Amsterdam, pp. 295–308.
- Fustec, E., Mariotti, A., Grillot, X., Sajus, J., 1991. Nitrate removal by denitrification in alluvial groundwater. Role of former channels. *J. Hydrol.* 123, 337–354.
- Gregory, S.V., Swanson, F.J., McKee, W.A., Cummins, K.W., 1991. An ecosystem perspective of riparian zones. *BioScience* 41, 540–551.
- Groffman, P.M., Gold, A.J., Simmons, R.C., 1992. Nitrate dynamics in riparian forests: microbial studies. *J. Environ. Qual.* 21, 666–671.
- Haycock, N.E., Pinay, G., 1993. Nitrate reduction in grass and poplar vegetated riparian buffer strips during the winter. *J. Environ. Qual.* 22, 273–278.
- Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., Zhao-Liang, Z., 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainage to the North Atlantic Ocean: natural and human influences. *Biogeochemistry* 35, 75–139.
- Jansson, M., Leonardson, L., Fejes, J., 1994. Denitrification and nitrogen retention in a farmland stream in Southern Sweden. *Ambio* 23, 326–331.
- Jordan, T.E., Weller, D.E., Correll, D.L., 1998. Denitrification in surface soils of a riparian forest: effects of water, nitrate and sucrose additions. *Soil Biol. Biochem.* 30, 833–843.
- Leonardson, L., Bengtsson, L., Davidsson, T., Persson, T., Emanuelsson, U., 1994. Nitrogen retention in artificially flooded meadows. *Ambio* 23, 332–341.
- Lowrance, R., 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *J. Environ. Qual.* 21, 401–405.
- Lowrance, R., Vellidis, G., Hubbard, R.K., 1995. Denitrification in a restored riparian forest wetland. *J. Environ. Qual.* 24, 808–815.
- Maag, M., Vinther, F.P., 1996. Nitrous oxide emission by nitrification and denitrification in different soil types and at different soil moisture contents and temperatures. *Appl. Soil Ecol.* 4, 5–14.
- Malle, K.G., 1988. Die Nitratbelastung des Rheins. *Z. Wasser-Abwasser-Forschung* 21, 83–85.
- Masscheleyn, P.H., Pardue, J.H., DeLaune, R.D., Patrick, W.H. Jr., 1992. Phosphorus release and assimilatory capacity of two lower Mississippi valley freshwater wetland soils. *Water Resour. Bull.* 28, 763–773.
- McDowell, W.H., Bowden, W.B., Asbury, C.E., 1992. Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forests watersheds: subsurface solute patterns. *Biogeochemistry* 18, 53–75.
- Mulholland, P.J., 1992. Regulation of nutrient concentrations in a temperate forest stream: roles of upland, riparian and in-stream processes. *Limnol. Oceanogr.* 37, 1512–1526.
- Neill, C., 1995. Seasonal flooding, nitrogen mineralization and nitrogen utilization in a prairie marsh. *Biogeochemistry* 30, 171–189.
- Patrick, W.H. Jr., 1990. Microbial reactions of nitrogen and phosphorus in wetlands. *The Utrecht Plant Ecol. News Reports* 11, 52–63.
- Patrick, W.H., 1994. Phosphorus biogeochemistry of wetlands. *Phosphorus, Life Environ., Res. Appl.*, 199–205.
- Pinay, G., Décamps, H., 1988. The role of the riparian wood in regulating nitrogen fluxes between the alluvial aquifer and surface water: a conceptual model. *Regul. River* 2, 507–516.
- Pinay, G., Ruffinoni, C., Fabre, A., 1995. Nitrogen cycling in two riparian forest soils under different geomorphic conditions. *Biogeochemistry* 30, 9–29.
- Reddy, K.R., Patrick, W.H., 1984. Nitrogen transformations and loss in flooded soils and sediments. *CRC Crit. Rev. Environ. Control* 13, 273–309.
- Reddy, K.R., Rao, P.S.C., 1983. Nitrogen and phosphorus fluxes from a flooded organic soil. *Soil Science* 136, 300–307.
- Sánchez-Pérez, J.M., Trémolières, M., 1997. Groundwater nutrient levels in the Rhine alluvial forest ecosystems depending on the

- hydrological regime and the soil texture. *Global Ecol. Biogeographical Lett.* 6, 211–217.
- Sánchez-Pérez, J.M., Trémolières, M., Carbiener, R., 1991a. Une station naturelle d'épuration des phosphates et des nitrates apportés par les eaux de débordement du Rhin: la forêt alluviale à frêne et orme. *C. R. Acad. Sci., Paris* 112, 395–402.
- Sánchez-Pérez, J.M., Trémolières, M., Schnitzler, A., Carbiener, R., 1991b. Evolution de la qualité physico-chimique des eaux de la frange superficielle de la nappe phréatique en fonction du cycle saisonnier et des stades de succession des forêts alluviales rhénanes. *Acta Oecologica* 12, 581–601.
- Simmons, R.C., Gold, A.J., Groffman, P.M., 1992. Nitrate dynamics in riparian forests: groundwater studies. *J. Environ. Qual.* 21, 659–665.
- Takatert, N., Sánchez-Pérez, J.M., Trémolières, M., 1999. Spatial and temporal variations of nutrients concentration in the groundwater of a floodplain: effect of hydrology, vegetation and substrate. *Hydrol. Processes* 13, 1511–1526.
- Trémolières, M., Eglin, I., Roeck, U., Carbiener, R., 1993. The exchange process between river and groundwater on the central Alsace floodplain (Eastern France): I. The case of a canalised river. *Hydrobiologia* 254, 133–148.
- Van Dijk, G.M., Martejn, E.C.L., Schulte-Wülmer-Leidig, A., 1995. Ecological rehabilitation of the river Rhine: plans, progress and perspectives. *Regul. River: Res. Manage.* 11, 377–388.
- Zak, D.R., Grigal, D.F., 1991. Nitrogen mineralization, nitrification and denitrification in upland and wetland ecosystems. *Oecologia* 88, 189–196.