Citation	Stijn Baken, Peter Salaets, Nele Desmet, Piet Seuntjens, Elin Vanlierde, Erik Smolders (2015) **Oxidation of iron causes removal of phosphorus and arsenic from streamwater in groundwater-fed lowland catchments** Environmental Science & Technology, 49, 2886-2894.
Archived version	Author manuscript: the content is identical to the content of the published paper, but without the final typesetting by the publisher
Published version	http://pubs.acs.org/doi/full/10.1021/es505834y
Journal homepage	http://pubs.acs.org/journal/esthag
Author contact	stijn.baken@ees.kuleuven.be *+ 32 (0)16 321761*
IR	Klik hier als u tekst wilt invoeren.

Oxidation of iron causes removal of phosphorus and arsenic from stream water in groundwater-fed lowland catchments

STIJN BAKEN[1]*, PETER SALAETS[2], NELE DESMET[3], PIET SEUNTJENS[345], ELIN VANLIERDE[6], ERIK SMOLDERS[1]

[1] KU Leuven, Department of Earth and Environmental Sciences, Kasteelpark Arenberg 20 bus 2459, 3001 Leuven, Belgium

[2] KU Leuven, Faculty of Bioscience Engineering, Expertise Unit on Educational Provision, Kasteelpark Arenberg 21 box 2302, 3001 Leuven, Belgium

[3] VITO, Boeretang 200, 2400 Mol, Belgium

[4] University of Antwerp, Department of Bioscience Engineering, Groenenborgerlaan 171, 2020 Antwerp, Belgium

[5] Ghent University, Department of Soil Management, Coupure Links 653, 9000 Ghent, Belgium

[6] Flanders Hydraulics Research, Berchemlei 115, 2140 Antwerp, Belgium

* Corresponding author, phone +32 16 32 17 61, e-mail stijn.baken@ees.kuleuven.be

Abstract

The fate of iron (Fe) may affect that of phosphorus (P) and arsenic (As) in natural waters. This study addresses the removal of Fe, P, and As from streams in lowland catchments fed by reduced, Fe-rich groundwater (average: 20 mg Fe L^{-1}). The concentrations of dissolved Fe (<0.45 µm) in streams gradually decrease with increasing hydraulic residence time (travel time) of the water in the catchment. The removal of Fe from stream water is governed by chemical reactions and hydrological processes: the oxidation of ferrous iron (Fe(II)) and the subsequent formation of particulate Fe oxyhydroxides proceeds as the water flows through the catchment into increasingly larger streams. The Fe removal exhibits first-order kinetics with a mean half-life of 12 hours, a value in line with predictions by a kinetic model for Fe(II) oxidation. The Fe concentrations in streams vary seasonally: they are higher in winter than in summer, due to shorter hydraulic residence time and lower temperature in winter. The removal of P and As is much faster than that of Fe. The average concentrations of P and As in streams (42 µg P L^{-1} and 1.4 µg As L^{-1}) are one order of magnitude below those in groundwater (393 µg P L^{-1} and 17 µg As L^{-1}). This removal is attributed to fast sequestration by oxidizing Fe when the water enters oxic environments, possibly by adsorption on Fe oxyhydroxides or by formation of ferric phosphates. The average P and As concentrations in groundwater largely exceed local environmental limits for freshwater (140 µg P L^{-1} and 3 µg As L^{-1}), but in streams, they are below these limits. Naturally occurring Fe in groundwater may alleviate the environmental risk associated with P and As in the receiving streams.

Introduction

Eutrophication adversely affects water quality in many countries worldwide. In most cases, eutrophication of freshwater is related to increased concentrations of phosphorus (P)[1]. The major sources of P to freshwaters include point sources, such as sewage discharge, and diffuse inputs caused by excessive application of fertilizer or animal manure to agricultural land. The transfer of P from agricultural land to streams often occurs in the form of overland particulate P transport during rainstorm events[2]. However, in lowland areas with acid sandy soils and shallow groundwater tables, leaching of P to the groundwater is the principal pathway for P transfer from agricultural land to streams. Arsenic (As) is a major source of impaired water quality at various locations worldwide[3,4]. In lowland streams fed by shallow, reduced groundwater, the transfer of P and As from groundwater to streams is not necessarily conservative. Upon exfiltration (seepage) of groundwater, P and As may interact with redox-active elements, most notably iron (Fe)[5–7].

The fate of Fe may profoundly impact the speciation and mobility of nutrients and trace elements. The reduced ferrous iron (Fe(II)) is mobile in submerged environments[8]. Reductive dissolution of iron oxyhydroxides may release associated elements to the sediment pore water[9]. As reduced Fe(II) is transported from sediments to oxic environments, it is oxidized either abiotically or biotically, and subsequent precipitation yields particulate (>0.45 µm) authigenic (or diagenetic) Fe oxyhydroxides which have been characterized as ferrihydrite and lepidocrocite[10]. Such precipitates may bind other elements by adsorption or coprecipitation, including As, Cu, Ni, P, Pb, and Zn[11–14]. The coupling of reductive dissolution and oxidative precipitation may lead to Fe cycling, which has been observed in a variety of environments including sediments, groundwater seeps, and lakes[15–17]. Streams generally contain low dissolved (<0.45 µm) concentrations of Fe, *i.e.* in the order of 0.01—1 mg Fe L^{-1} [18]. The Fe speciation in streams is usually dominated by Fe(III), which may be present as organic complexes or as Fe oxyhydroxides of particular or colloidal dimensions[19–21]. The Fe(III) may affect the fate of trace elements in streams through competition with cationic trace metals for binding on organic matter[22], or through binding of trace elements on colloidal[23] or particulate[24] Fe-rich phases.

The kinetics of Fe(II) oxidation can in a first approach be approximated by a simple first order kinetic model[25]. Ligands such as chloride, bicarbonate, and natural organic matter may affect the oxidation rate, mostly at concentrations below 1 mg Fe L^{-1} [26,27]. The biological Fe(II) oxidation may outpace the chemical oxidation under acidic[28] or micro-oxic conditions[29,30]. The oxidation of Fe(II) and the production of Fe oxyhydroxides at circumneutral groundwater seeps has been studied extensively, both from a microbiological [31,32,16] as well as from a chemical perspective [27,33,34], and a large number of elaborate models for the chemical oxidation of Fe(II) have been developed. The fate of Fe(II) derived from acid mine drainage has also been widely investigated[35,36]. Burns et al.[37] have developed predictive models for the Fe oxidation rate and applied these models to stream water sampled at various locations of a catchment. Van der Grift et al.[5] have recently studied oxidation rates of naturally occurring Fe and removal of P from drainage water in reservoirs. They found that Fe oxidation is much slower in winter than in summer, but that removal of P by oxidizing Fe(II) was at all times highly efficient. However, the combined effect of Fe(II) oxidation and hydrological processes has rarely been addressed. After exfiltration of groundwater, Fe(II) may persist temporarily if oxidation kinetics are slow, and the oxidation reaction proceeds as the Fe(II) is transported by the stream water. The oxidation half-life of Fe(II) is predicted to range between a few hours and a few days under conditions typical for streams fed by circumneutral Fe-rich groundwater[25]. This range is comparable to the hydraulic residence time of water in the headwater streams of lowland river catchments. The above suggests that spatial and seasonal trends in hydrological properties and chemical characteristics might explain the fate of Fe in catchments and, hence, govern the dynamics of other elements such as P and As in these systems.

The goal of this study was to determine the fate of high Fe(II) inputs in catchments, and to address how this affects the fate of P and As. We selected the four Belgian catchments, the Kleine Nete catchment and three northern tributaries to the Demer river, as study sites. These lowland catchments are well suited to study such processes due to their hydrogeological setting. They are mainly fed by Fe-rich groundwater from the shallow, permeable, glauconite-containing aquifers of the Central Campine groundwater system[38,39]. Their flat topography limits erosion processes and the contribution of overland runoff to streamflow. Previous work showed that oxidation of Fe(II) in these streams yields authigenic ferrihydrite particles[19,39]. A key objective of this follow-up study was to relate spatial and temporal trends in Fe concentrations in the streams of these catchments to chemical (Fe(II) oxidation) and hydrological processes (the travel time or hydraulic residence time of water in the streams). In addition, we determined whether and how fast P and As are removed from the dissolved fraction of stream water through sequestration by the authigenic ferrihydrite particles.

Materials and methods

Study sites

Two study sites in northeastern Belgium with a similar setting were selected: the Kleine Nete catchment upstream of the town of Grobbendonk, and three major tributaries to the Demer river. The geography, hydrogeology, hydrology, and the water balances of the area are extensively discussed in other work [38,40–44]; the essentials are summarized here with additional figures are shown in the SI (section 1). The Kleine Nete catchment is located in the Belgian Campine region and drains a mostly agricultural lowland area of approximately 800 km^2, of which 590 km^2 are upstream of Grobbendonk. The studied part of the Demer catchment is mostly located in the Belgian sandy loam belt and includes its three main northern tributaries Mangelbeek, Zwartebeek, and Winterbeek, each of which drain an area of approximately 100 km^2. The topography of both study areas is flat, with the exception of a few limonite ridges which separate the three tributaries to the Demer. Common soil types in both study areas include podzols, plaggic anthrosols (organic matter accumulation in the topsoil), and soils with fluvic or gleyic properties in the valleys[45].

The lithology of both study areas is similar and consists of Miocene and Pliocene sands (up to 150 m thick), deposited on top of an impermeable Oligocene clay (Boom clay), and overlain by a thin layer of Pleistocene deposits. Hydrogeologically, two groundwater systems are present in the study area: the upper Central Campine system is separated from the underlying Brulandkrijt system by the Boom clay aquitard[41,42] (SI, section 1). Therefore, the Central Campine system is the only unconfined (phreatic) groundwater system which discharges into the streams of the study area[38]. The groundwater flow direction in this system is varied, and its recharge is mostly by percolation of rainwater (240—360 mm yr^{-1})[42]. Within the Central Campine system, the Diestiaan aquifer likely contributes most to stream flow, due to its thickness and high permeability[40]. The Diestiaan consists of glauconitic sands which supply large amounts of Fe(II) to the groundwater[39]. The streams in the study area are predominantly fed by groundwater: the year-averaged groundwater contribution to the total discharge has been estimated by various studies; estimates range between 62 and 87% (see also SI, section 1) [40,43,46]. Groundwater transfer to the streams occurs directly by exfiltration through the hyporheic zone of streams, or indirectly by seepage of excess groundwater in drains and ditches.

Field campaign and data acquisition

In a field campaign, 56 sampling locations were selected near the streams of both study areas. The locations were chosen in order to reflect the trajectory of the water in the streams from the headwaters to the major rivers, *i.e.* to reflect the gradual increase in contact time with atmospheric oxygen as the water moves downstream. At each location, fully screened groundwater monitoring wells were installed at 3—4 m depth and at close distance (< 5 m) to streams. The monitoring wells and the nearby streams were sampled on four occasions throughout the year (April – June – September – November 2013), hereinafter referred to as "sampling moments". The water temperature, O_2 concentration, electrical conductivity (EC), and pH were measured in the field. Groundwater and surface water samples were membrane filtered in the field (0.45 µm Chromafil Xtra PET 45/25 filters), and the dissolved concentrations of major elements (ICP-MS), anions (ion chromatography), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and Fe(II) and Fe(III) (colorimetric reaction with ferrozine reagent[47]) were determined (SI, section 2). All reported concentrations refer to the dissolved (<0.45 µm) fraction, 'Fe(II)' refers to concentrations measured with ferrozine, whereas 'Fe' refers to ICP-MS measurements, which includes both Fe(II) and Fe(III). At selected locations, suspended sediment was sampled and the Fe, P, and As concentrations were determined (SI, section 2).

Additional data were obtained from permanent monitoring programs. The water flow velocity was recorded by flow velocity loggers at selected locations throughout the study area. The O_2 concentration, stream water temperature, and pH in the Kleine Nete were measured at 5-min intervals by a multiparameter probe (YSI 6600) installed near the outlet of the catchment. The discharge was monitored at the same location based on permanent water level measurements, which were converted to discharge in accordance with the ISO748 and ISO/TS24154 protocols [48]. All data are publicly available (http://www.waterinfo.be) and were downloaded for a 3-year period (2011—2014).

Calculations

The hydraulic residence time or travel time of the stream water in the catchment was calculated for each stream water sample that was collected, *i.e.* for each of the 56 sampling locations and for each of the four sampling moments. The residence time estimates the average travel time of the water from the moment of its exfiltration to the moment it was sampled. Calculations were based on the hydrographic atlas of the Flanders region, which includes GIS information on the location and length of each stream stretch[49]. For each stream stretch, the water flow velocity at each sampling moment was estimated based on data from eight permanent flow velocity loggers installed at selected locations throughout the studied catchments (details: SI, section 2). At each stream node, the relative contribution of each of both tributaries to the total discharge was estimated using the groundwater recharge in the area drained by each tributary. The groundwater recharge was retrieved from the WetSpass model for the Kleine Nete catchment[44,50], and from the regional MODFLOW model of the central Campine groundwater system for the northern tributaries to the Demer river[41]. Finally, the average hydraulic residence time of each water sample was calculated by integration of all stream stretches upstream of the sampling location. This method for residence time calculation has limitations: it relies on water flow velocity data at selected locations only, and the method is less reliable during dynamic peak flow events. The method was sufficiently detailed for the purpose of this study. More detailed residence time calculations would require a catchment model which includes the smallest headwater streams, and flow velocity measurements at more locations, but such was beyond the scope of this study.

The Fe(II) oxidation rate constants in streams were derived by fitting a simple first order kinetic model to plots of Fe concentrations in streams versus hydraulic residence time, which is a proxy for the reaction time. When water containing an initial Fe concentration, defined as $Fe(II)_0$, reaches oxic environments, the Fe(II) concentration decreases with time (t) due to chemical oxidation, according to[25]

$$Fe(II) = Fe(II)_0 \cdot \exp(-k_1 \cdot t). \qquad \textit{(Equation 1)}$$

The rate constant of the pseudo first order chemical oxidation (k_1), which may also be expressed as a half-life ($t_{1/2}$), is given by

$$k_1 = k \cdot pO_2 \cdot (OH^-)^2, \qquad \textit{(Equation 2)}$$

where k is a ‘universal’ rate constant of approximately $2 \cdot 10^{13}$ M^{-2} atm^{-1} min^{-1} (uncertainty range 1.5—$3 \cdot 10^{13}$ M^{-2} atm^{-1} min^{-1}), pO_2 is the O_2 concentration in the water expressed as a partial pressure, and (OH^-) is the activity of the hydroxyl ion[25]. The (OH^-) is calculated from pH and from the temperature-dependent dissociation constant of water[51], and therefore k_1 depends on pH, temperature and the O_2 concentration.

All reported means and standard deviations are based on untransformed data. Regression analyses were performed using untransformed data and a least-squares algorithm. For correlation analyses, variable clustering, comparison of means (Student’s t-test), and ANOVA tests, all variables except pH, hydraulic residence time, and temperature were log-transformed. Based on a visual inspection of QQ-plots, the distribution of all variables appeared to be well approximated by a lognormal distribution, and Shapiro-Wilk tests confirmed that lognormal distributions were preferable to normal ones in nearly all cases. Correlation analyses, ANOVA tests, and nonlinear least-squares fitting were carried out in JMP Pro 11 (SAS Institute, Cary, United States). Variable clustering analyses were carried out by the VARCLUS procedure in SAS 9.3 (details in the SI, section 4).

Results and discussion

Groundwater: the source of dissolved Fe(II)

The characteristics and composition of filtered groundwater samples are shown in the SI, section 3. The groundwater is generally reduced, as evidenced by low O_2 and NO_3 concentrations and by the pale grey color of the material which was recovered upon installation of the monitoring wells. This may be due to large inputs of DOC, originating from animal manure or from peat accumulated in plaggic soil horizons which are common in the area. The groundwater is strongly enriched in Fe, which is entirely present as reduced Fe(II). The Fe concentrations average 20 mg L^{-1} and range over two orders of magnitude (Figure 1). The P concentrations (average 393 µg L^{-1}) and As concentrations (average 17 µg L^{-1}) range over three orders of magnitude.

The variable clustering analysis and the correlation analysis (SI, section 4) indicate that the concentrations of Fe in groundwater are positively correlated with those of As ($r = 0.48$), P ($r = 0.42$), and Mn ($r = 0.31$). This hints at a reductive dissolution mechanism which supplies these elements to the groundwater[3,4,39], even though no clear correlation with DOC (a plausible reductant) is observed. The P in groundwater mainly originates from fertilizer leaching from the excessively fertilized acid sandy soils of the region[52,53], whereas the As likely originates from weathering of As containing glauconite[6]. The large variability in groundwater Fe concentrations is neither explained by pH, EC, water temperature, nor by the concentration of any other measured element. Seasonality does not affect the groundwater Fe concentrations much: at four moments throughout the year, the average Fe concentrations range only between 16 and 24 mg L^{-1}. Analysis of variance confirms that the groundwater Fe concentrations vary spatially, whereas temporal effects are comparably small (SI, section 5). The relationship between the local lithology and groundwater Fe concentrations is further examined (SI, section 5). The groundwater Fe concentrations likely vary due to the heterogeneity of the greensand parent material[38]. This may be due to local differences in glauconite content of the parent material, in hydraulic conductivity, in glauconite weathering rate, or in the presence of electron donors which reductively dissolve Fe oxyhydroxides.

Chemical processes occurring after exfiltration of groundwater

The characteristics and composition of filtered (0.45 µm) stream water samples are presented in the SI, section 3. The meteorological and flow conditions at the moment of sampling are discussed in the SI, section 8. Some samplings occurred during dry spells, whereas others coincided with rainfall events of low or moderate intensity. This may to some extent affect stream water composition and chemistry due to dilution of baseflow by faster, more dilute components of stream flow. Separation of the baseflow from the total hydrograph using the WETSPRO numerical filtering procedure[54] shows that, during sampling, baseflow contributed between 65 and 91% to the total stream flow of the Kleine Nete. No discharge data are available for the Demer tributaries, but given its nearby location, similar daily rainfall, and similar geographic hydrogeological setting, baseflow contributions to stream flow during the sampling moments are likely similar. In addition, the mean and median Ca concentrations and EC in stream water do not differ much between different sampling moments (SI, section 8). This shows that dilution of baseflow by faster, more dilute components of stream flow was likely limited in most samples.

Given the large baseflow contribution, a comparison of the composition of groundwater and streams may yield information about chemical processes occurring at the groundwater-surface water interface (Figure 1 and SI, section 6). Contrary to the Ca concentration and the EC, the concentrations of dissolved O_2, Fe, As, and P differ considerably between groundwater and streams. The O_2 concentration increases strongly from groundwater to streams due to contact with the atmosphere. The dissolved concentrations of Fe concomitantly decrease: upon exfiltration of Fe(II)-rich groundwater, the Fe(II) is oxidized and precipitated as insoluble Fe oxyhydroxides. The concentrations of many cationic trace metals, including Ni, Cu, Cd, Zn, and Co, increase from the groundwater to the streams. We speculate that this may reflect anthropogenic inputs through wastewater discharge, or it may be the result of oxidation and mobilization of metals sulphides from streambed sediments which contain known legacy contaminations of trace metals (e.g. Zn and Cd[55]). The concentrations of P and As in streams are almost one order of magnitude lower than those in groundwater. These elements commonly occur as oxyanions and are known for their high affinity for fresh Fe oxyhydroxides[56]. The concentrations of Fe, P, and As in suspended matter are far above the typical concentration range of these elements in soils in the region (SI, section 10). These data therefore strongly suggest that the P and As are sequestered throughout the studied catchments by freshly formed hydrous ferric oxide precipitates.

Oxidation of Fe(II) and removal of Fe from the dissolved phase

The dissolved Fe concentrations in streams range between 0.1 and 70 mg L^{-1}. In streams containing Fe concentrations more than 3 mg Fe L^{-1}, the Fe redox speciation is dominated by Fe(II). Conversely, in streams with lower Fe concentrations, the Fe consists of a mixture of Fe(II) and Fe(III) in varying proportions. The median hydraulic residence time of the water in the streams is 27 hours (10th—90th percentile: 7—105 hours). A plot of the Fe concentrations versus Strahler stream order (Figure 2A) shows that the small headwater streams (order 1 and 2) may contain up to 70 mg Fe L^{-1}, but this drops to below 3 mg Fe L^{-1} in the streams of order 4 and 5. If plotted against the hydraulic residence time of the water in the streams, a similar trend is observed (r = -0.54): the Fe concentrations decrease with increasing residence time, which reflects the exposure time of water to oxic environments (Figure 2B). Similar trends emerge if Fe(II) instead of Fe concentrations are plotted (SI, section 7). The Fe(II) supplied by the groundwater is increasingly oxidized and removed from the dissolved fraction as water flows through the catchment into increasingly larger streams. This process results in the observed Fe concentration gradient which decreases from the smallest headwaters to the receiving streams.

A catchment-scale Fe(II) oxidation rate is derived based on measured Fe concentrations in streams and on the first order kinetic model (Equation 1). Previous laboratory studies have shown that this model is appropriate for oxidation of Fe(II) in the study area[19]. The first order rate constant for oxidation of Fe(II) at the catchment scale is estimated at $k_1 = 0.056 \pm 0.015\ \mathrm{h}^{-1}$, corresponding to a half-life of 12 hours, and the initial Fe concentration is 13.7 ± 2.5 mg Fe L^{-1} (error estimates are standard errors). The fitted catchment-scale oxidation rate agrees with theoretical predictions (Equation 2): it corresponds to the 42nd and 82nd percentile of the predicted oxidation rates in the samples from the Kleine Nete catchment and Demer tributaries, respectively (Table 1). The fitted initial Fe concentration is significantly ($P<0.05$) below the average groundwater Fe concentration (20 mg L^{-1}). This suggests that only part of the Fe(II) supplied by the groundwater is oxidized in the streams, whereas the remainder is oxidized and precipitated before it enters the streams, e.g. in open drainage ditches, drainage tubes, or in the hyporheic zone. The fitted kinetic model is visualized in Figure 2B. The groundwater-derived Fe is largely removed from the dissolved fraction of streams within approximately 50 hours. After that, the dissolved Fe concentrations in streams no longer decrease. The remaining Fe in samples with long residence times is a mixture of Fe(II) and Fe(III). In these samples, the Fe(III) likely occurs as complexes with organic matter or as colloidal Fe oxyhydroxides; the residual Fe(II) (around 0.3 mg L^{-1}) may be protected against oxidation through complexation with organic matter[57].

The concentrations of Fe and Fe(II) in streams exhibit pronounced seasonal variability (Figure 3A). During the sampling in late summer (September), the median Fe and Fe(II) concentrations were 5-fold and 7-fold lower than those measured in early spring (April) and late autumn (November). Due to the meteorological and flow conditions, this variability was even more pronounced in the Kleine Nete catchment than in the Demer tributaries (SI, section 9), and therefore the discussion below is focused on the Kleine Nete catchment. We set out to determine whether the rate of Fe(II) oxidation or the reaction time (hydraulic residence time) can explain this seasonal variability.

Based on permanent monitoring data recorded near the outlet of the Kleine Nete, the predicted rate of Fe oxidation varies widely throughout the year (predictions based on Equation 2; SI, section 9). The oxidation rate in summer is up to 50-fold faster than in winter, mainly caused by higher summer pH and temperature. Stream pH strongly and significantly decreases with increasing discharge (r = 0.75; Figure 3B). Stream pH is governed by degassing of CO_2 which is kinetically limited: lower discharge in summer than in winter causes increased hydraulic residence times, CO_2 degassing, and pH. The oxidation rates in the streams of the Kleine Nete catchment, predicted with Equation 2 using locally measured pH, O_2 concentrations and temperature, exhibit seasonal trends similar to those near the outlet of the catchment (Table 1; SI, section 9). In order to quantitatively relate the predicted seasonal variability to actual measurements of Fe concentrations, oxidation rates in the Kleine Nete catchment were derived for each sampling moment (SI, section 9). For the June and September samplings, the oxidation rate cannot be estimated: all Fe was already oxidized before it reached the headwaters. For the April and November sampling, the first-order rate constants are estimated at 0.06 ± 0.02 h^{-1}, and 0.06 ± 0.01 h^{-1}, respectively (error estimates are standard errors). Given the uncertainty generally associated with determining the oxidation rate of Fe(II)[25], these fitted rate constants agree relatively well with the median predicted oxidation rate constant (respectively 0.06 and 0.02 h^{-1}; Table 1). The theoretical predictions and the measured Fe concentrations both illustrate that the Fe oxidation rate varies seasonally. The theoretical predictions do not take into account microbially catalyzed Fe(II) oxidation, which may outpace the chemical oxidation reaction under specific circumstances at circumneutral pH[58]. If the rate of microbial Fe(II) oxidation exceeds that of chemical Fe(II) oxidation, it is expected to do so under conditions where the chemical oxidation reaction is slow, *i.e.* in winter[58]. This process may therefore to some extent counteract the seasonal trends discussed above.

The hydraulic residence times of the field campaign samples from the Kleine Nete catchment are shown in Table 1; data represent averages across 31 sampled locations. The average hydraulic residence time differs seasonally by factors of up to 5, and long residence times are associated with low discharge. The residence times during sampling of the Kleine Nete catchment are a good indication of typical seasonal variability and trends: the flow velocities recorded at the sampling moments cover the 3rd – 85th percentile range of the annual flow velocity, and flow velocities were lower in summer than in winter. A numerical example illustrates the effect of hydraulic residence time on the oxidation of Fe(II) and the resulting Fe concentration gradient: if in a hypothetical scenario 50% of the Fe(II) has already been oxidized at a certain location in the catchment, then a 5-fold longer residence time results in 97% oxidized Fe at this location. Clearly, the observed seasonal differences in Fe oxidation gradients can be ascribed to effects on both the oxidation rate and on the hydraulic residence time.

Taken together, our results show that oxidation of groundwater-borne Fe(II) in a catchment creates a Fe concentration gradient which decreases from the headwaters to the major streams. The fate of high Fe(II) inputs in catchments is governed by water temperature, pH, and hydraulic residence time. These findings are in line with previous studies. Spiteri et al.[59] showed that a pH gradient in a subterranean estuary created a Fe concentration gradient through its effect on the Fe oxidation rate. Van der Grift et al.[5] showed that the Fe oxidation rate and residence time in drainage reservoirs exhibit seasonal variations similar to those observed in this study. However, to the best of our knowledge, this study is the first to document the oxidation gradient of naturally occurring Fe in river catchments at circumneutral pH. Some previous studies have addressed the fate of naturally occurring Fe(II)-rich water entering circumneutral streams, but they concluded that most of the Fe(II) is already oxidized and removed from solution before it enters the streams[5,60]. Our observation of continued oxidation of Fe(II) in the receiving streams of a catchment can be ascribed to the combination of two factors. First, in the studied catchments, elevated concentrations of Fe(II) enter the streams across a geographically large area. Second, stream pH and temperature are such that the half-life of chemical Fe(II) oxidation is in the same range as the hydraulic residence time of the water in the catchment.

Removal of P and As by freshly formed Fe(III) minerals

The measured concentrations of dissolved P and As in streams are, on average, an order of magnitude lower than those in the groundwater that feeds these streams. If plotted against the hydraulic residence time of the water, the P and As concentrations do not exhibit the same trend as observed for Fe (Figure 2). This is confirmed by the correlation analysis which shows that the concentrations of P and As in streams are much less related to the hydraulic residence time than those of Fe (SI, section 4). Furthermore, the P and As concentrations in streams exhibit only minor seasonal variations: their means across different sampling moments differed less than a factor of two. Whereas Fe is gradually oxidized and removed, the removal of P and As occurs much faster after exfiltration of reduced groundwater. The removal of P is complete before the water reaches the smallest headwater streams: the average P concentration in streams with residence times below 10 hours does not exceed the average of all streams. The average As concentration in streams with short residence times (2 $\mu g\ L^{-1}$) is somewhat larger than that in the other streams (1 $\mu g\ L^{-1}$), which may indicate that As removal is to a small extent still going on in the headwater streams. Nevertheless, the removal of P and As from groundwater occurs predominantly before the water reaches the headwater streams, most likely in the hyporheic zone, in small unmapped streams, or in drainage systems. The local environmental limits for freshwaters are 3 µg As L^{-1} (measured in filtered samples), and 140 µg P L^{-1} (measured in unfiltered samples). In this study, the average concentrations of P and As in groundwater exceed these limits by factors of 2.8 for P and 5.5 for As, but in streams, they are more a factor of 2 below these limits. In the absence of high Fe concentrations in groundwater, there may have been a risk for eutrophication or As toxicity in these catchments. Clearly, the observed removal of P and As by oxidizing Fe has implications for surface water quality.

The removal of As upon oxidation of Fe(II) has been widely studied in the context of drinking water production[61]. At the catchment scale, it has been shown that As concentrations in particulate matter are related to the Fe concentrations[62], and that As removal in a catchment may occur through adsorption on suspended Fe oxyhydroxides[7]. A more recent study in a setting similar to this study confirmed that As in such systems may be sequestered by Fe[6]. Based on these previous studies, the observed As removal in this study is likely due to Fe-As interactions, and the As is bound by freshly formed Fe oxyhydroxides.

The fast immobilization of P in the presence of oxidizing Fe(II) has already been observed in synthetic systems[63–66], in aerated groundwater[19,67], and in natural waters[68,11,5,69]. It has also been observed in drainage ditches in the same study area[70]. Upon oxidation of Fe(II) in the presence of phosphate, ferric phosphate minerals are formed, with molar Fe:P as low as unity. After time, ferric phosphates may be converted into hydrous ferric oxides with surface-adsorbed P[66]. At low Fe:P ratios, this may result in release of P to the solution[64]. However, in the groundwater feeding the studied catchments, Fe is present in large excess: the molar Fe:P ratio in groundwater ranges between 8 and 218 (10th and 90th percentile), and the average molar Fe concentration in groundwater exceeds the average molar P concentration by a factor of 28. At such high Fe:P ratios, binding of P by Fe oxyhydroxides is highly efficient, and no release of P is expected.

The fate of particulate (>0.45 µm) P-containing Fe oxyhydroxides is most likely governed by the chemical boundary conditions in the receiving streams. The Kleine Nete and the Demer are ultimately only minor contributors to the suspended sediment load of the major receiving stream, the Scheldt (e.g. 4% for the Kleine Nete catchment)[71]. However, due to the high molar Fe:P ratio in the authigenic material[19], it may be able to sequester additional P: it has been shown that ferric phosphates are a major sink for P in the freshwater portion of the Scheldt[72]. If the settled particles reach anoxic sediments, reductive dissolution may release the P. Perhaps this does not increase the eutrophication risk: P and Fe(II) are released simultaneously to the sediment pore water, and if such water reaches oxic environments again, the P may again be sequestered by the oxidizing Fe[73]. The fate of P-containing authigenic material may be of greater environmental concern if it reaches brackish water. The large concentrations of sulphate cause the presence of sulphide in bottom sediments, which promotes conversion of Fe from oxyhydroxides and phosphates to sulphides, causing a release of P[72]. However, the processes governing P binding and release in the bottom sediments of brackish water are poorly understood[2]. Release of P from Fe-containing phases in bottom sediments is likely governed by the availability of electron donors, such as organic matter, and electron acceptors, such as sulphate or Fe. Further research should focus on the fate of Fe-P-minerals in receiving streams and estuaries, and on the risk of P-release from the bottom sediments of brackish waters.

Acknowledgements

Thanks to Daniel Wilczek, Karlien Cassaert, Kristin Coorevits, and Stefaan Dondeyne for assistance. S.B. thanks the FWO-Research Foundation Flanders for a PhD fellowship. Funding was provided by Flanders Hydraulics Research, a division of the Department of Mobility and Public Works of the Flemish Government - thanks to FHR staff, including Jan De Schutter, Bart De Maerschalck, Joris Vanlede, and Frank Mostaert.

Supporting Information (SI)

More detailed information on the study sites, Materials and Methods, Results and Discussion, and additional Figures and Tables. The Supporting Information (SI) is available free of charge via the Internet at http://pubs.acs.org/.

References

(1) Schindler, D. W. The dilemma of controlling cultural eutrophication of lakes. *Proc. Biol. Sci.* **2012**, *279*, 4322–4333.

(2) Ekholm, P.; Lehtoranta, J. Does control of soil erosion inhibit aquatic eutrophication? *J. Environ. Manage.* **2012**, *93*, 140–146.

(3) Rotiroti, M.; Sacchi, E.; Fumagalli, L.; Bonomi, T. Origin of arsenic in groundwater from the multilayer aquifer in Cremona (northern Italy). *Environ. Sci. Technol.* **2014**, *48*, 5395–5403.

(4) McArthur, J. .; Banerjee, D. .; Hudson-Edwards, K. .; Mishra, R.; Purohit, R.; Ravenscroft, P.; Cronin, A.; Howarth, R. .; Chatterjee, A.; Talukder, T.; et al. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Appl. Geochemistry* **2004**, *19*, 1255–1293.

(5) Van der Grift, B.; Rozemeijer, J. C.; Griffioen, J.; van der Velde, Y. Iron oxidation kinetics and phosphate immobilization along the flow-path from groundwater into surface water. *Hydrol. Earth Syst. Sci.* **2014**, *18*, 4687–4702.

(6) Barringer, J. L.; Reilly, P. A.; Eberl, D. D.; Blum, A. E.; Bonin, J. L.; Rosman, R.; Hirst, B.; Alebus, M.; Cenno, K.; Gorska, M. Arsenic in sediments, groundwater, and streamwater of a glauconitic Coastal Plain terrain, New Jersey, USA—Chemical "fingerprints" for geogenic and anthropogenic sources. *Appl. Geochemistry* **2011**, *26*, 763–776.

(7) Webster-Brown, J. G.; Lane, V. Modeling seasonal arsenic behavior in the Waikato river, New Zealand. In *Advances in Arsenic Research*; O'Day, P. A.; Vlassopoulos, D.; Meng, X.; Benning, L. G., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2005; Vol. 915, pp. 253–266.

(8) Kirk, G. *The biogeochemistry of submerged soils*; Wiley, Chichester, 2004; pp. 1–291.

(9) Weber, F.-A.; Voegelin, A.; Kretzschmar, R. Multi-metal contaminant dynamics in temporarily flooded soil under sulfate limitation. *Geochim. Cosmochim. Acta* **2009**, *73*, 5513–5527.

(10) Fortin, D.; Leppard, G.; Tessier, A. Characteristics of lacustrine diagenetic iron oxyhydroxides. *Geochim. Cosmochim. Acta* **1993**, *57*, 4391–4404.

(11) Gunnars, A.; Blomqvist, S.; Johansson, P.; Andersson, C. Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. *Geochim. Cosmochim. Acta* **2002**, *66*, 745–758.

(12) Tessier, A.; Fortin, D.; Belzile, N.; DeVitre, R. R.; Leppard, G. G. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter:

Narrowing the gap between field and laboratory measurements. *Geochim. Cosmochim. Acta* **1996**, *60*, 387–404.

(13) De Vitre, R.; Belzile, N.; Tessier, A. Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. *Limnol. Oceanogr.* **1991**, *36*, 1480–1485.

(14) Frierdich, A. J.; Hasenmueller, E. a.; Catalano, J. G. Composition and structure of nanocrystalline Fe and Mn oxide cave deposits: Implications for trace element mobility in karst systems. *Chem. Geol.* **2011**, *284*, 82–96.

(15) Davison, W. Iron and manganese in lakes. *Earth-Science Rev.* **1993**, *34*, 119–163.

(16) Blöthe, M.; Roden, E. E. Microbial iron redox cycling in a circumneutral-pH groundwater seep. *Appl. Environ. Microbiol.* **2009**, *75*, 468–473.

(17) Gault, A. G.; Ibrahim, A.; Langley, S.; Renaud, R.; Takahashi, Y.; Boothman, C.; Lloyd, J. R.; Clark, I. D.; Ferris, F. G.; Fortin, D. Microbial and geochemical features suggest iron redox cycling within bacteriogenic iron oxide-rich sediments. *Chem. Geol.* **2011**, *281*, 41–51.

(18) *Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps*; Salminen, R., Ed.; Geological Survey of Finland: Espoo, Finland, 2005; pp. 1–525.

(19) Baken, S.; Sjöstedt, C.; Gustafsson, J. P.; Seuntjens, P.; Desmet, N.; De Schutter, J.; Smolders, E. Characterisation of hydrous ferric oxides derived from iron-rich groundwaters and their contribution to the suspended sediment of streams. *Appl. Geochemistry* **2013**, *39*, 59–68.

(20) Sjöstedt, C.; Persson, I.; Hesterberg, D.; Kleja, D. B.; Borg, H.; Gustafsson, J. P. Iron speciation in soft-water lakes and soils as determined by EXAFS spectroscopy and geochemical modelling. *Geochim. Cosmochim. Acta* **2013**, *105*, 172–186.

(21) Lofts, S.; Tipping, E.; Hamilton-Taylor, J. The chemical speciation of Fe(III) in freshwaters. *Aquat. Geochemistry* **2008**, *14*, 337–358.

(22) Tipping, E.; Rey-Castro, C.; Bryan, S. E.; Hamilton-Taylor, J. Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation. *Geochim. Cosmochim. Acta* **2002**, *66*, 3211–3224.

(23) Stolpe, B.; Guo, L.; Shiller, A. M.; Hassellöv, M. Size and composition of colloidal organic matter and trace elements in the Mississippi River, Pearl River and the northern Gulf of Mexico, as characterized by flow field-flow fractionation. *Mar. Chem.* **2010**, *118*, 119–128.

(24) Cánovas, C. R.; Olías, M.; Sarmiento, A. M.; Nieto, J. M.; Galván, L. Pollutant transport processes in the Odiel River (SW Spain) during rain events. *Water Resour. Res.* **2012**, *48*, W06508.

(25) Davison, W.; Seed, G. The kinetics of the oxidation of ferrous iron in synthetic and natural waters. *Geochim. Cosmochim. Acta* **1983**, *47*, 67–79.

(26) Rose, A. L.; Waite, T. D. Kinetic model for Fe(II) oxidation in seawater in the absence and presence of natural organic matter. *Environ. Sci. Technol.* **2002**, *36*, 433–444.

(27) King, D. W. Role of Carbonate Speciation on the Oxidation Rate of Fe(II) in Aquatic Systems. *Environ. Sci. Technol.* **1998**, *32*, 2997–3003.

(28) Singer, P. C.; Stumm, W. Acidic mine drainage: the rate-determining step. *Science* **1970**, *167*, 1121–1123.

(29) Vollrath, S.; Behrends, T.; Bender Koch, C.; Van Cappellen, P. Effects of temperature on rates and mineral products of microbial Fe(II) oxidation by Leptothrix cholodnii at microaerobic conditions. *Geochim. Cosmochim. Acta* **2013**, *108*, 107–124.

(30) Kasama, T.; Murakami, T. The effect of microorganisms on Fe precipitation rates at neutral pH. *Chem. Geol.* **2001**, *180*, 117–128.

(31) Druschel, G. K.; Emerson, D.; Sutka, R.; Suchecki, P.; Luther, G. W. Low-oxygen and chemical kinetic constraints on the geochemical niche of neutrophilic iron(II) oxidizing microorganisms. *Geochim. Cosmochim. Acta* **2008**, *72*, 3358–3370.

(32) Duckworth, O. W.; Holmström, S. J. M.; Peña, J.; Sposito, G. Biogeochemistry of iron oxidation in a circumneutral freshwater habitat. *Chem. Geol.* **2009**, *260*, 149–158.

(33) Millero, F. J.; Sotolongo, S.; Izaguirre, M. The oxidation kinetics of Fe(II) in seawater. *Geochim. Cosmochim. Acta* **1987**, *51*, 793–801.

(34) Pham, A. N.; Waite, T. D. Oxygenation of Fe(II) in natural waters revisited: Kinetic modeling approaches, rate constant estimation and the importance of various reaction pathways. *Geochim. Cosmochim. Acta* **2008**, *72*, 3616–3630.

(35) Larson, L. N.; Sáanchez-España, J.; Kaley, B.; Sheng, Y.; Bibby, K.; Burgos, W. D. Thermodynamic Controls on the Kinetics of Microbial Low-pH Fe(II) Oxidation. *Environ. Sci. Technol.* **2014**, *48*, 9246–9254.

(36) Geroni, J. N.; Sapsford, D. J. Kinetics of iron (II) oxidation determined in the field. *Appl. Geochemistry* **2011**, *26*, 1452–1457.

(37) Burns, J. M.; Craig, P. S.; Shaw, T. J.; Ferry, J. L. Combinatorial parameter space as an empirical tool for predicting water chemistry: Fe(II) oxidation across a watershed. *Environ. Sci. Technol.* **2011**, *45*, 4023–4029.

(38) Vanlierde, E. Sediment concentrations, fluxes and source apportionment: methodology assessment and application in Nete and Demer, PhD thesis, Flanders Hydraulics Research, Antwerp, Belgium, 2013, pp. 1–328.

(39) Dekov, V. M.; Vanlierde, E.; Billström, K.; Garbe-Schönberg, C.-D.; Weiss, D. J.; Gatto Rotondo, G.; Van Meel, K.; Kuzmann, E.; Fortin, D.; Darchuk, L.; et al.

Ferrihydrite precipitation in groundwater-fed river systems (Nete and Demer river basins, Belgium): Insights from a combined Fe-Zn-Sr-Nd-Pb-isotope study. *Chem. Geol.* **2014**, *386*, 1–15.

(40) Vanlierde, E.; De Schutter, J.; Jacobs, P.; Mostaert, F. Estimating and modeling the annual contribution of authigenic sediment to the total suspended sediment load in the Kleine Nete Basin, Belgium. *Sediment. Geol.* **2007**, *202*, 317–332.

(41) Meyus, Y.; Severyns, J.; Batelaan, O.; De Smedt, F. *Ontwikkeling van regionale modellen ten behoeve van het Vlaams Grondwater Model in GMS/MODFLOW. Perceel 1: Het Centraal Kempisch model. Deelrapport 1: Basisgegevens en conceptueel model*; Report to the Flemish Government, Department of Environment and Infrastructure, 2004; pp. 1–126.

(42) Flemish Environment Agency VMM. *Grondwater in Vlaanderen: het Centraal Kempisch Systeem*; Aalst, Belgium, 2008; p. 110.

(43) Batelaan, O. Phreatology - Characterizing groundwater recharge and discharge using remote sensing, GIS, ecology, hydrochemistry and groundwater modelling, PhD thesis, Vrije Universiteit Brussel, 2006, pp. 1–332.

(44) Batelaan, O.; De Smedt, F. GIS-based recharge estimation by coupling surface–subsurface water balances. *J. Hydrol.* **2007**, *337*, 337–355.

(45) Dondeyne, S.; Vanierschot, L.; Langohr, R.; Van Ranst, E.; Deckers, S. *The soil map of the Flemish region converted to the third edition of the World Reference Base for soil resources*; Report to the Flemish Government, Department of Environment, Nature, and Energy, 2014; pp. 1–139.

(46) Van Der Beken, A.; Huybrechts, W. De waterbalans van het Vlaams gewest, een rationeel waterbeheer via kennis van de waterbalans. *Water* **1990**, *50*, 88–92.

(47) Viollier, E.; Inglett, P. W.; Hunter, K.; Roychoudhury, A. N.; Van Cappellen, P. The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Appl. Geochemistry* **2000**, *15*, 785–790.

(48) Willems, P.; Berlamont, J. *Doorlichting van de HIC methodologie voor de opmaak en het gebruik van Q-H verbanden*; Report, Flanders Hydraulics Research, Antwerp, Belgium, 2002.

(49) AGIV - Agentschap voor Geografische Informatie Vlaanderen. *Vlaamse Hydrografische Atlas*; accessible at http://www.geopunt.be; Ghent, Belgium, 2014.

(50) Batelaan, O.; De Smedt, F. WetSpass: a flexible, GIS based, distributed recharge methodology for regional groundwater modelling. In *Impact of human activity on groundwater dynamics*; Gehrels, H.; Peter, S. N.; Hoehn, E.; Jensen, K.; Leidundgut, C.; Griffioen, J.; Webb, B.; Zaadnoordijk, W. J., Eds.; International Association of Hydrological Sciences: Wallingford, U.K., 2001; pp. 11–17.

(51) Millero, F. J. Thermodynamics of the carbon dioxide system in the oceans. *Geochim. Cosmochim. Acta* **1995**, *59*, 661–677.

(52) Lookman, R.; Vandeweert, N.; Merckx, R.; Vlassak, K. Geostatistical assessment of the regional distribution of phosphate sorption capacity parameters (FeOX and AlOX) in northern Belgium. *Geoderma* **1995**, *66*, 285–296.

(53) Van der Zee, S. E. A. T. M. Transport of reactive contaminants in heterogeneous soil systems, PhD thesis, Agricultural University, Wageningen, the Netherlands, 1988.

(54) Willems, P. A time series tool to support the multi-criteria performance evaluation of rainfall-runoff models. *Environ. Model. Softw.* **2009**, *24*, 311–321.

(55) Van Laer, L.; Smolders, E. Does soil water saturation mobilize metals from riparian soils to adjacent surface water? A field monitoring study in a metal contaminated region. *Environ. Sci. Process. Impacts* **2013**, *15*, 1181–1190.

(56) Dzombak, D. A.; Morel, F. M. M. *Surface complexation modeling: Hydrous ferric oxide*; Wiley-Interscience: New York, 1990; p. 393.

(57) Gaffney, J. W.; White, K. N.; Boult, S. Oxidation state and size of Fe controlled by organic matter in natural waters. *Environ. Sci. Technol.* **2008**, *42*, 3575–3581.

(58) De Vet, W. W. J. M.; Dinkla, I. J. T.; Rietveld, L. C.; van Loosdrecht, M. C. M. Biological iron oxidation by Gallionella spp. in drinking water production under fully aerated conditions. *Water Res.* **2011**, *45*, 5389–5398.

(59) Spiteri, C.; Regnier, P.; Slomp, C. P.; Charette, M. A. pH-Dependent iron oxide precipitation in a subterranean estuary. *J. Geochemical Explor.* **2006**, *88*, 399–403.

(60) Hart, B. T.; Hines, T.; Coller, B. A. W. Geochemistry of Cu, Zn and Fe in the Tambo River, Australia II. Field investigation under low-flow conditions. *Mar. Freshw. Res.* **2008**, *59*, 80–88.

(61) Roberts, L. C.; Hug, S. J.; Ruettimann, T.; Billah, M. M.; Khan, A. W.; Rahman, M. T. Arsenic Removal with Iron(II) and Iron(III) in Waters with High Silicate and Phosphate Concentrations. *Environ. Sci. Technol.* **2004**, *38*, 307–315.

(62) Buzek, F.; Cejkova, B.; Dousova, B.; Jackova, I.; Kadlecova, R.; Lnenickova, Z. Mobilization of arsenic from acid deposition – The Elbe River catchment, Czech Republic. *Appl. Geochemistry* **2013**, *33*, 281–293.

(63) Voegelin, A.; Kaegi, R.; Frommer, J.; Vantelon, D.; Hug, S. J. Effect of phosphate, silicate, and Ca on Fe(III)-precipitates formed in aerated Fe(II)- and As(III)-containing water studied by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **2010**, *74*, 164–186.

(64) Mayer, T. D.; Jarrell, W. M. Phosphorus sorption during iron(II) oxidation in the presence of dissolved silica. *Water Res.* **2000**, *34*, 3949–3956.

(65) Kaegi, R.; Voegelin, A.; Folini, D.; Hug, S. J. Effect of phosphate, silicate, and Ca on the morphology, structure and elemental composition of Fe(III)-precipitates formed in aerated Fe(II) and As(III) containing water. *Geochim. Cosmochim. Acta* **2010**, *74*, 5798–5816.

(66) Voegelin, A.; Senn, A.-C.; Kaegi, R.; Hug, S. J.; Mangold, S. Dynamic Fe-precipitate formation induced by Fe(II) oxidation in aerated phosphate-containing water. *Geochim. Cosmochim. Acta* **2013**, *117*, 216–231.

(67) Griffioen, J. Extent of immobilisation of phosphate during aeration of nutrient-rich, anoxic groundwater. *J. Hydrol.* **2006**, *320*, 359–369.

(68) Lienemann, C.-P.; Monnerat, M.; Dominik, J.; Perret, D. Identification of stoichiometric iron-phosphorus colloids produced in a eutrophic lake. *Aquat. Sci.* **1999**, *61*, 133.

(69) Gunnars, A.; Blomqvist, S. Phosphate exchange across the sediment-water interface when shifting from anoxic to oxic conditions – an experimental comparison of freshwater and brackish-marine systems. **1997**, 203–226.

(70) Baken, S.; Verbeeck, M.; Verheyen, D.; Diels, J.; Smolders, E. Phosphorus losses from agricultural land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches. *Water Res.* **2015**, *in press*.

(71) Van Hoestenberghe, T.; Ferket, B.; De Boeck, K.; Vanlierde, E.; Vanlede, J.; Varwaest, T.; Mostaert, F. *Slibbalans Zeeschelde: deelrapport 2 - Sediment load for the river Scheldt and its main tributaries (1972-2009)*; Flanders Hydraulics Research, Antwerp, Belgium, 2009; pp. 1–71.

(72) Hyacinthe, C.; Van Cappellen, P. An authigenic iron phosphate phase in estuarine sediments: composition, formation and chemical reactivity. *Mar. Chem.* **2004**, *91*, 227–251.

(73) Zak, D.; Wagner, C.; Payer, B.; Augustin, J.; Gelbrecht, J. Phosphorus mobilization in rewetted fens: the effect of altered peat properties and implications for their restoration. *Ecol. Appl.* **2010**, *20*, 1336–1349.

Table 1: The abiotic Fe(II) oxidation rate (predicted using Equation 2) and hydraulic residence time of stream water in the Kleine Nete catchment at four sampling moments throughout the year. Averages, medians and percentiles refer to measurements obtained at 31 sampling locations. The discharge at the catchment outlet at the moment of sampling is also shown.

	Fe(II) oxidation rate				**hydraulic residence time**	**discharge**
	P_{10}	*median*	P_{90}	*average*	*average*	
	h^{-1}	h^{-1}	h^{-1}	h^{-1}	h	$m^3\ s^{-1}$
April 2013	0.01	0.06	0.40	0.13	26	4.3
June 2013	0.03	0.14	0.84	0.26	49	3.1
September 2013	0.01	0.12	3.18	0.93	106	1.4
November 2013	0.001	0.02	0.54	0.12	20	7.0

P_{10}: 10th percentile; P_{90}: 90th percentile

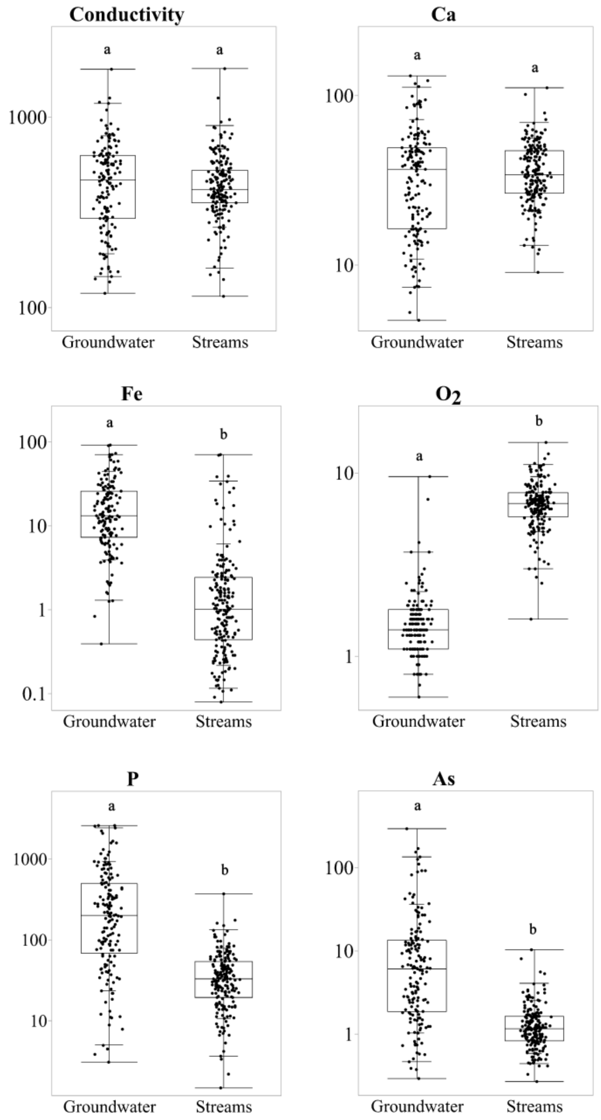

Figure 1: Comparison of the composition of groundwater and streams. Elements were measured after membrane filtration (0.45 µm). Units: µS cm^{-1} (electrical conductivity), mg L^{-1} (Ca, Fe, O_2), µg L^{-1} (P, As). Means followed by different characters are significantly different (Student's t-test performed on log-transformed data; $P < 0.05$).

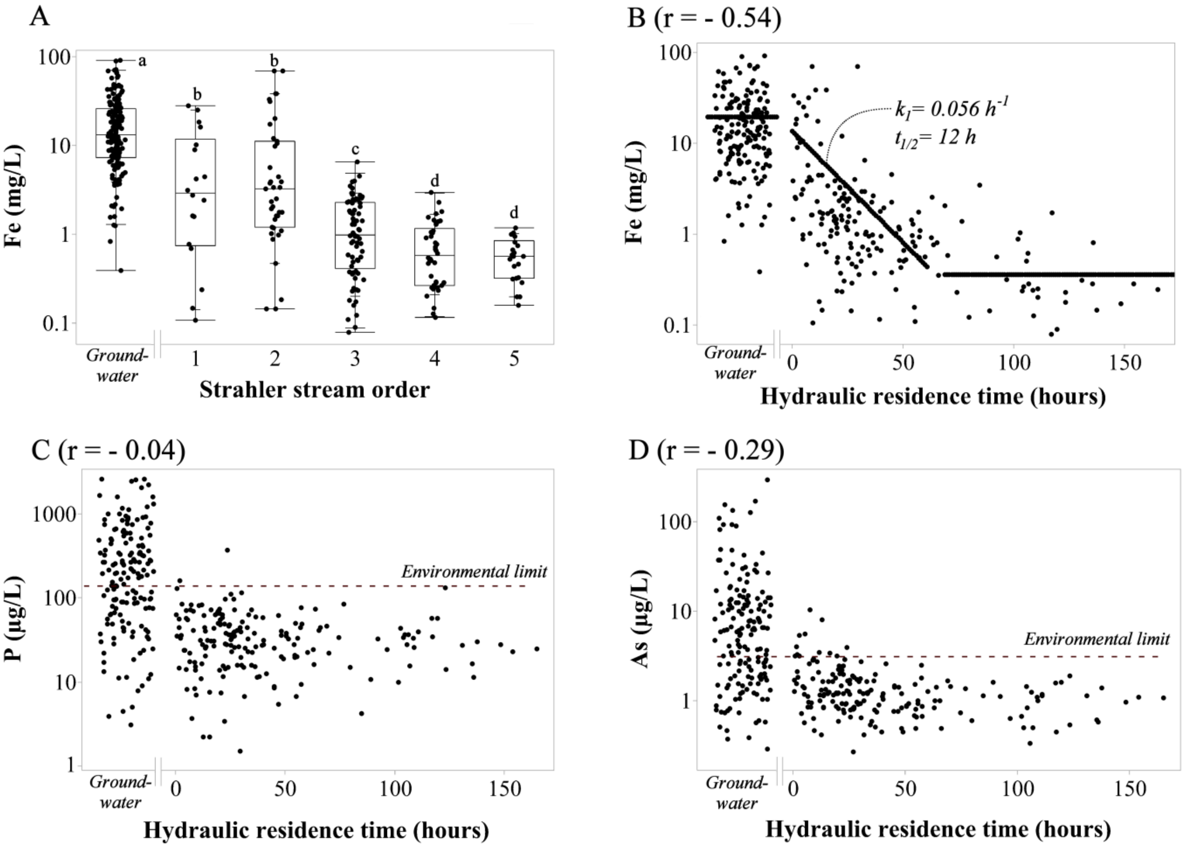

Figure 2: The concentrations of dissolved (<0.45 µm) Fe, P, and As in streams plotted against the Strahler stream order and against the hydrological residence time of the water in the catchment. The concentrations in groundwater are shown on the left for comparison, but the correlation coefficients refer to stream water samples only. A: Means followed by different characters are significantly different (Student's t-test on log-transformed data; $P < 0.05$). B: The decreasing line is the fitted first order model for catchment-scale Fe(II) oxidation (see text for details), and the horizontal lines indicate the average Fe concentration in groundwater and the average Fe(III) concentration in streams. C and D: The horizontal lines indicate local environmental limits for freshwater.

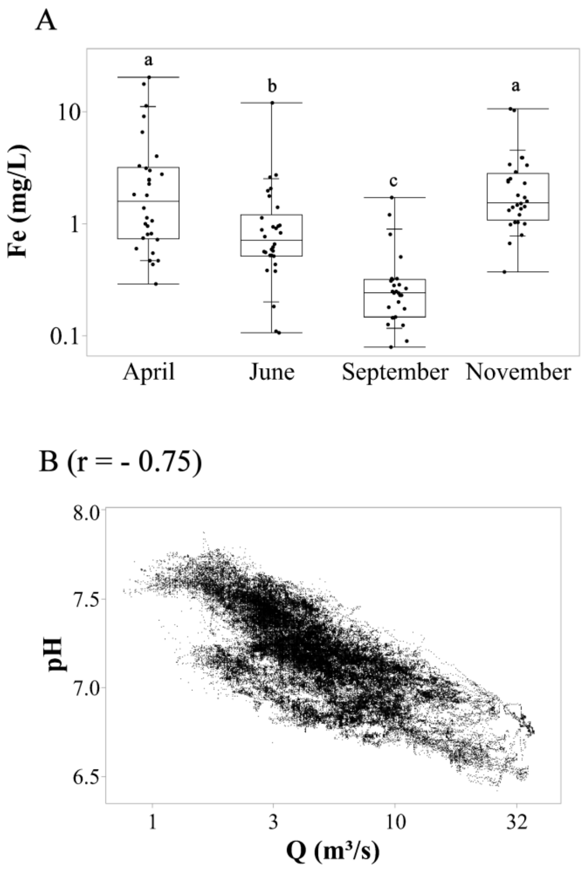

Figure 3: A: Seasonal variations of dissolved Fe concentrations in streams of the Kleine Nete catchment. Means followed by different characters are significantly different (Student's t-test performed on log-transformed data; $P < 0.05$). B: Plot of pH versus discharge (Q) near the outlet of the Kleine Nete catchment ($r = -0.75$).