Musolff, A., Selle, B., **Büttner, O.**, Opitz, M., **Tittel, J.** (2017):
Unexpected release of phosphate and organic carbon to streams linked to declining nitrogen depositions
Glob. Change Biol. **23** (5), 1891 – 1901

http://dx.doi.org/10.1111/gcb.13498

Received Date : 28-Apr-2016

Revised Date : 11-Aug-2016

Accepted Date : 04-Sep-2016

Article type : Primary Research Articles

Title: Unexpected release of phosphate and organic carbon to streams linked to declining nitrogen depositions

Running head: Release of phosphate and DOC to streams

Authors: Andreas Musolff[1,*], Benny Selle[2,*], Olaf Büttner[3], Michael Opitz[4], Jörg Tittel[5,*]

[1]Department Hydrogeology, Helmholtz-Centre for Environmental Research – UFZ, Permoserstr. 15, 04318 Leipzig, Germany.

[2]Institute of Earth and Environmental Science, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany, now at: Department of Civil Engineering and Geoinformation, Beuth University of Applied Sciences, Luxemburger Straße 10, D-13353 Berlin, Germany

[3]Department Aquatic Ecosystem Analysis, Helmholtz-Centre for Environmental Research – UFZ, Brückstr. 3a, 39114 Magdeburg, Germany.

[4]IDUS Biologisch-Analystisches Umweltlabor GmbH, Radeberger Str. 1, 01458 Ottendorf-Okrilla.

[5]Department Lake Research, Helmholtz-Centre for Environmental Research – UFZ, Brückstr. 3a, 39114 Magdeburg, Germany.

*These authors contributed equally to this work.

Author contribution: J.T. and A.M. formulated the hypotheses and analyzed and interpreted the data from the larger scale database. B.S. performed the GAM analysis, interpreted data and co-wrote the manuscript together with J.T. and A.M.. M.O. collected and compiled all data for the larger scale database from operators and authorities of drinking water reservoirs. O.B. structured the database, validated, aggregated, extracted specific data and conducted topographic data analysis.

Corresponding author: *Andreas Musolff, Department Hydrogeology, Helmholtz-Centre for Environmental Research – UFZ, Permoserstr. 15, 04318 Leipzig, Germany; Tel.: +49 341 235 1983; email: andreas.musolff@ufz.de

Keywords: carbon cycle, organic matter, nitrogen biogeochemistry, streamwater chemistry, atmospheric deposition, riparian zone

Type of paper: Primary research article

Abstract:

Reductions in emissions have successfully led to a regional decline in atmospheric nitrogen depositions over the past 20 years. By analyzing long-term data from 110 mountainous streams draining into German drinking water reservoirs, nitrate concentrations indeed declined in the majority of catchments. Furthermore, our meta-analysis indicates that the declining nitrate levels are linked to the release of dissolved iron to streams likely due to a reductive dissolution of iron(III) minerals in riparian wetland soils. This dissolution process mobilized adsorbed compounds, such as phosphate, dissolved organic carbon and arsenic, resulting in concentration increases in the streams and higher inputs to receiving drinking water reservoirs. Reductive mobilization was most significant in catchments with stream nitrate concentrations <6 mg l^{-1}. Here nitrate, as a competing electron acceptor, was too low in concentration to inhibit microbial iron(III) reduction. Consequently, observed trends were strongest in forested catchments, where nitrate concentrations were unaffected by agricultural and urban sources and which were therefore sensitive to reductions of atmospheric nitrogen depositions. We conclude that there is strong evidence that the decline in nitrogen deposition towards pre-industrial conditions lowers the redox buffer in riparian soils, destabilizing formerly fixed problematic compounds and results in serious implications for water quality.

Introduction

The human transformation of the global nitrogen cycle is considered as one of the most fundamental environmental issues (Galloway *et al.*, 2008). The emission of reactive nitrogen species (NOx, NHy) by fossil fuel combustion and biomass burning rose enormously from 34 Tg N yr^{-1} in 1860 to 116 Tg N yr^{-1} in 2000 (Duce *et al.*, 2008). Even in remote watersheds of the northern hemisphere isotopic traces of this process were detected

(Holtgrieve *et al.*, 2011). Although the world remains “awash” with nitrogen (Elser, 2011) and global inputs are larger than known sinks (Schlesinger, 2009), regional trends have reversed. After its peak in the 1980ies, nitrogen depositions declined in large parts of Europe and North America ((MSC-W, 2014; Vet *et al.*, 2014), Table S1) as a result of reduced emissions from vehicles and power plants. However, nitrate is a powerful redox-active substance. Declining abundance potentially affects the cycling of redox-sensitive elements such as iron, since the reduction of iron(III) is inhibited if nitrate is available (Sørensen, 1982). Particulate iron(III) hydroxides are known to sorb with a high affinity (oxy)anions (Dzombak & Morel, 1990) such as dissolved organic carbon (DOC) (Kaiser & Guggenberger, 2000; Tipping *et al.*, 2002), phosphate (Gunnars *et al.*, 2002; Hyacinthe & Van Cappellen, 2004; Jaisi *et al.*, 2010; Zak *et al.*, 2010) and metals (Young & Harvey, 1992) in soils, wetlands and aquatic sediments. The microbial reduction of iron(III) releases and mobilizes not only iron itself but also sorption partners as shown for DOC (Grybos *et al.*, 2007; Hagedorn *et al.*, 2000; Riedel *et al.*, 2013) and for phosphate (Chacon *et al.*, 2006). The inhibition of iron reduction under the presence of well available nitrate concentrations was shown to be the primary control for the release of phosphate from lake sediments (Andersen, 1982). Furthermore, nitrate-reducing bacteria are capable of oxidizing ferrous iron under anaerobic conditions, generating ferric iron which increases the sorption capacity of the sediment (Straub *et al.*, 1996). This was confirmed experimentally in lab with soil monoliths from black alder carrs (Lucassen *et al.*, 2004). A continuous supply of a nitrate-rich medium leads to a higher redox potential in the sediment accompanied by a significantly lower release of phosphate compared to a medium poor in nitrate. The authors conclude that the nitrate oxidizes reduced iron and thereby increase the amount of iron minerals capable of binding phosphate. A similar result was obtained in mesocosm experiments using peat (Cabezas *et al.*, 2013). Although added nitrate was reduced within the peat and did not prevent the production of phosphate as well as of DOC, the release of both solutes was suppressed due to available nitrate remaining in the peat surface layer. In sediment cores taken from reservoirs, the flux of DOC was found to be closely related to iron fluxes but negatively related with redox sensitive species such as nitrate concentrations (Dadi *et al.*, 2015).

Long-term increases of iron stream concentrations were reported from UK (Neal *et al.*, 2008), Sweden (Kritzberg & Ekstrom, 2012; Temnerud *et al.*, 2014) and Finland (Sarkkola *et al.*, 2013). Ekström *et al.* (2016) and Knorr (2013) hypothesize this is controlled by an increase of the reduction of ferric iron hydroxides in riparian wetland soils. The driver of that development is supposed to be related to increased wetness and increasing temperatures (Ekström *et al.*, 2016; Knorr, 2013). However, a potential control of iron reduction by nitrate as known from lab experiments and field observations was so far not considered to be a dominant process controlling iron mobilization at catchment scales.

Similar to iron, concentrations of DOC have been observed to increase over the last 25 years in surface waters of the northern hemisphere (Worrall *et al.*, 2003) causing problems in drinking water production by growth of pathogens (Ledesma *et al.*, 2012) and formation of carcinogenic disinfection by-products (Sadiq & Rodriguez, 2004). There is still a debate on the cause of this development (Clark *et al.*, 2010).The most-cited hypothesis is that declining depositions of sulfur increase the solubility of organic carbon compounds due to a higher pH and lower ionic strength of soil solution (Evans *et al.*, 2012; Monteith *et al.*, 2007). More recently, Knorr (2013) hypothesized that the long-term increase in the reductive dissolution of iron(III) hydroxides also controls the increased mobilization of DOC to the stream.

In this study, we combined previous observations and findings into a novel hypothesis: We hypothesized that declining nitrate abundance controls the rising iron exports to streams. We also expected that this mobilization process destabilizes not only DOC but also other adsorptive compounds such as phosphate at catchment scales. To explore the links between nitrate, iron and adsorbed compounds, we combine a detailed exploratory analysis of the temporal variability of stream water solutes for an individual catchment with the evaluation of long-term concentration changes in mountainous 110 streams draining into German drinking water reservoirs. We relate the results to findings from other studies and discuss implications for catchment nutrient management. The results let us conclude that minimizing nitrogen inputs in catchments which are less affected by agriculture and urbanization can destabilize soil phosphorus and increase the risk of eutrophication.

Materials and Methods

We compiled data from 110 streams and the associated catchments draining into 36 German reservoirs (locations in Fig. S1). Due to their use for drinking water purposes management in the catchment is restricted. The studied streams span wide ranges in catchment size (0.1-303 km^2), topography (1-20° mean slope angle), precipitation (660-1290 mm yr^{-1}), land use (0-100% forest, 0-100% agriculture, 0-25% urban area) and chemical characteristics (annual means) such as stream pH (4.1-8.3), ionic strength (chloride 1-124 mg l^{-1}, sulfate 6-122 mg l^{-1}, nitrate 1-107 mg l^{-1}) and DOC (1-19 mg l^{-1}). We did not consider streams flowing through reservoirs or lakes with an area of greater than 0.01 km^2 within a distance of 5 km upstream from the sampling station. Precipitations were recorded by the reservoir management authorities using rain gauges located downstream from the sampling stations and close to the reservoir dams. Samples were taken in the framework of routine monitoring programs conducted by the reservoir management authorities, mainly on the basis of a monthly interval. The results were not compiled and evaluated previously, although shorter time-series from 20 stations were also included in the study of (Sucker *et al.*, 2011). Samples were taken as grab samples and chemical analyses of water samples were performed using standard protocols (Wasserchemische Gesellschaft, 2014). DOC was measured by infrared gas analysis of CO_2. Phosphate concentrations were analyzed using the molybdate reaction as soluble reactive phosphorus (SRP). The dissolved fractions (DOC, SRP, iron) are defined by the fraction passing a 0.45 µm filter, except DOC (pre-combusted glass microfiber filter, ~0.7 µm). Overall, our analysis considered ~17,000 samples from the period between 1993 and 2013 with a mean sample frequency of 11 samples per year. Note that nitrate concentrations are always given as mass of nitrate while atmospheric depositions are given as mass of total or oxidized nitrogen.

Long-term and annual means of nitrate and phosphate for each catchment were estimated by transforming the data using the Box-Cox method (Box & Cox, 1964) to ensure a more normal-like distribution. Mean concentrations were computed on the basis of transformed variables and back-transformed to the original scale. The same method applies to the mean annual iron_d:DOC ratios that were computed on the basis of the iron_d:DOC ratio within each sample. Trends in water quality were quantified by the slope of a linear regression of concentrations over time of the entire time series. Significance of the trends was tested using the non-parametric Mann-Kendall test for monotonic trends frequently used in hydrology (Burn & Elnur, 2002).

For generalized additive models (GAM) in a selected catchment, dynamics of flow-corrected concentrations were represented as a linear combination of a non-linear long-term trend and a seasonal component (Morton & Henderson, 2008). Technically, GAM was applied as an extended multiple linear regression (Zuur *et al.*, 2009), for which predictor variables were replaced by smooth spline functions of decimal time, week of the year and discharge transformed by the natural logarithm. Due to spline smoothing, this technique can naturally deal with data gaps. In brief, data was first aggregated at weekly time steps, and then transformed by the natural logarithm (except for pH). GAMs were fitted using trend, season and discharge effects, after which model residuals were examined for structures including autocorrelation; finally we fitted autoregressive–moving-average type of models to residuals, out of which the model with the lowest Akaike information criterion was selected (Zuur *et al.*, 2009). The *mgcv* package (Wood, 2006) with the R environment (Team, 2015) was used to apply GAM.

Delineation of the catchment areas and analysis of land use were performed based on a digital elevation model (10 m raster size) and the German spatial database ATKIS, Basis-DLM (GeoBasis-DE/BKG 2012), respectively, using the software package ArcGIS 10.2 (ESRI).

Wet atmospheric deposition data for the Wilzsch Creek catchment were routinely monitored as part of a larger observational network (federal state agency LfULG Saxony). Deposition data for Germany and other European countries were provided by the Meteorological Synthesizing Centre – West (MSC-W, 2014).

Results and Discussion

Trends in nitrate, iron and adsorbed compounds for the Wilzsch Creek catchment

As first step we analyzed time series (1999-2013) for the Wilzsch Creek, which drains a forested headwater catchment of 1.7 km^2 and feeds the Carlsfeld drinking water reservoir (Ore Mountains, Germany). This drinking water reservoir was affected by increasing DOC concentrations over the last decades and had a suitable data set for a detailed, site-specific investigation. Generalized additive models (GAM) were applied to analyze stream water concentrations of DOC together with dissolved iron (iron$_d$), nitrate, as well as dissolved inorganic phosphorus (phosphate). For the analysis, it was assumed that stream water chemistry closely resembles conditions in the catchment's riparian wetland soils hydrologically connected to the stream (Burt, 2005; Ledesma *et al.*, 2015; Seibert *et al.*, 2009; Winterdahl *et al.*, 2011). The shallow topography (mean slope angle 3.5°) favor the formation of wetlands (Li *et al.*, 2015) and supports the assumption of a close link between soil water and stream water quality. Conceptually, in the GAM analysis temporal variability of concentrations was expressed as the sum of dynamics acting at three different temporal scales: a long-term trend, a seasonal pattern and short-term dynamics due to discharge variability (Fig. 1, left, middle and right column, respectively). While the first two scales are possibly associated with biogeochemical reactions, the latter gives insight into the mixing of water from different hydrological storage compartments with various concentrations contributing to stream flow. The analysis revealed that iron_d, DOC and phosphate concentrations behaved similarly with upward long-term trends and a concentration maximum in late summer. With increasing discharges, the concentrations of iron_d, DOC and phosphate increased as well. While we found no indication of a long-term increase in discharge or increase in the wetness of soils as triggers for increased iron_d export (see Supporting Information), nitrate concentrations mirrored the behavior of the former three solutes in all three components of the GAM analysis (downward trend, minimum in late summer, lower concentrations with higher discharge). We note that both pH level and sulfate concentrations behaved more ambiguously than DOC; although they exhibited upward (pH) and downward (sulfate) trends, they did not show a clear seasonal pattern and reacted inversely to changing discharge (Fig. 1).

The GAM analysis corroborates the central hypothesis and suggests that both DOC and phosphate were jointly released with iron_d under iron-reducing conditions from the same hydrological storage compartment. Nitrate has a higher redox potential than iron(III), making microbial nitrate reduction thermodynamically favorable compared to iron reduction (Zehnder & Stumm, 1988); iron reduction is therefore inhibited if nitrate is available

(Andersen, 1982; Lucassen *et al.*, 2004; Sørensen, 1982). We estimated that wet depositions of oxidized and reduced nitrogen in the Wilzsch catchment decreased by 36 mg N m^{-2} yr^{-1} between 1999 and 2013 (Fig. S2). The deposition of oxidized nitrogen decreased by 19 mg N m^{-2} yr^{-1}. Considering that wet depositions contribute 56 – 60% to total (wet plus dry) depositions (Jaworski *et al.*, 1997; Poor *et al.*, 2001), the decline in oxidized nitrogen was sufficient to explain the decrease in nitrate surface water yields of 23 mg N m^{-2} yr^{-1} referring to the Wilzsch Creek catchment area within the same period of time. Neither in the nitrogen depositions (R^2 = 0.02) nor in the discharge (R^2 = 0.12) there is a pronounced seasonality that could explain the strong seasonality in the stream nitrate concentrations (see methodology in SI Discussions H2).

The mobilization processes described above likely take place in riparian wetland soils, which favor the reducing conditions and a fast solute transfer to the stream. Here, the upper organic-rich soil horizon is the dominant source for DOC exports to the stream, while iron and nitrate are provided by upward groundwater flow from lower mineralic horizons and from the hinterland (Frei *et al.*, 2012; Knorr, 2013; Lambert *et al.*, 2013; Ledesma *et al.*, 2015). In the upper horizon, iron is oxidized and precipitated even under water-clogged anoxic conditions as long as nitrate is abundant (Cabezas *et al.*, 2013; Lucassen *et al.*, 2004). With rising temperatures during the growing season, nitrate will be microbially reduced and taken up by plants and thus more and more depleted. This allows the subsequent reduction of iron and its joint transfer with previously adsorbed constituents to the stream when precipitation rises groundwater levels (Frei *et al.*, 2012; Knorr, 2013). This relationship is obvious from the seasonality of iron_d, phosphate and DOC in the receiving stream as well as in decreasing nitrate but increasing iron_d concentrations with rising discharges (Fig. 1). Higher nitrate supplies in the past prevented the initiation of iron reductive conditions for longer timespans during the growing season. As there is no indication of a wetter climate (see above), we assume that the supplies of iron from deep mineralic horizons did not generally increase. The positive trends in stream iron$_d$ concentrations are therefore thought to be a consequence of decreasing storages or of decreasing generation rates of ferric iron hydroxides in the riparian soils.

Trends in nitrate, iron and adsorbed compounds across German catchments

To test if the results from the Wilzsch Creek may represent a dominant mechanism across a wider range of catchments, we investigated long-term trends for 110 streams by means of slopes of linear regressions of concentrations over time. It is assumed that processes responsible for differences between the catchments are congruent to the ones responsible for the relationship of temporal trends between DOC, iron$_d$, nitrate and phosphate in the individual catchments. Here, the principle of "trading space for time" is applied (Sivapalan, 2006; Wagener *et al.*, 2010).

For pH ≤6, significant DOC trends were all positive (mean of slopes 0.17, range 0.03 to 0.36 mg C l^{-1} yr^{-1}, n = 18). Here, the slopes of DOC trends were positively associated with the slopes of iron$_d$ trends (Fig. 2a). These results support our findings from Wilzsch Creek with an average pH of 4.5. On the other hand, at pH >6, positive (n = 23) as well as negative (n = 24) significant trends in DOC levels (mean of slopes 0.00, range -0.21 to 0.15 mg l^{-1} yr^{-1}) and no relationship to the slopes of iron$_d$ trends was observed. The pH dependency is expected as sorption of DOC on ferric iron minerals is most efficient under acidic conditions and decreases with higher pH (Tipping, 1981). This relationship is also confirmed by a compilation of field data from 10 studies in freshwater environments in (Neubauer *et al.*, 2013). In addition, reduction of iron(III) minerals consumes protons. Thus, at a lower pH, iron reduction already starts under less reductive conditions, i.e. at higher redox potentials compared to higher pH (Brookins, 1988). We used absolute instead of relative slopes because we hypothesized that iron reduction and DOC mobilization were linked quantitatively. The ratio between slopes of iron$_d$ and DOC (Fig. 2a) indicate that an increase of 0.12 mg l^{-1} iron$_d$ resulted in the mobilization of 1 mg l^{-1} DOC. As this was still below the sorption capacity of natural DOC (>45 mg DOC per mg iron$_d$, iron$_d$:DOC = 0.022 [mg mg^{-1}], (Neubauer *et al.*, 2013)), a link between iron$_d$ and DOC mobilization appears to be plausible. An additional, probabilistic assessment of the relationship between iron$_d$, DOC and phosphate trends (the phenomena) with nitrate trends, average nitrate concentrations as well as pH conditions (the possible stimuli) can be found in the Supporting Information.

To study the effect of iron$_d$ trends on phosphate mobilization, we selected catchments with a low fraction of urban and agricultural areas (<20%, see Table S2), as these catchments were less likely to be influenced by anthropogenic sources of phosphate. In contrast to DOC, sorption of phosphate to ferric iron minerals is also effective for a higher pH (Lopez-Hernandez & Burnham, 1974). We found a positive relationship between the slopes of phosphate and iron$_d$ (Fig. 2b), similar to the one for DOC and iron$_d$. Thus, we surmise that iron reduction mobilized not only DOC but also phosphate.

If nitrate availability induced positive trends for iron$_d$, two conditions would be required: low nitrate concentrations to facilitate the reduction of iron(III) and negative trends of nitrate concentrations to increase the rate of iron reduction. From our data we observed that strong positive trends (high slopes) of iron$_d$ were associated with low annual average nitrate concentrations of below ~6 mg NO_3^- l^{-1} (Fig. 3a). This value should not be mistaken as a precise threshold but rather as a transition zone below which - due to annual dynamics - it becomes increasingly likely that nitrate concentrations will fall below a value, which allows iron reduction. In addition, stream nitrate concentrations decreased significantly in 68% of all investigated streams and increased significantly in only 6%. We found that, with low average nitrate concentrations, even small negative trends are sufficient to cause relatively strong

iron_d trends (Fig. 3a). Overall, the analyses of trends and nitrate concentrations support our interpretation that declining nitrate concentrations governed the observed rising trends in iron_d, DOC and phosphate (Fig. 3b, c).

Alternatively, one could argue that iron_d is not the driver but rather the consequence of a mobilization of DOC without reductive processes involved. Iron (III) can be complexed to DOC molecules and transported without prior reductive dissolution along with the DOC to the stream. To pursue that issue we analyzed mean annual iron_d:DOC ratios of the studied catchments. If DOC and iron_d were not mobilized by reductive processes we expected that the iron_d:DOC ratios were a function of pH only as the sorption of DOC to iron is pH dependent (Tipping, 1981). However, a multiple regression revealed a significant predictive power of the mean annual nitrate concentrations, the mean annual pH, and the mean slope angle in the catchment (SI Discussion, Tab. S5). This means that low nitrate concentrations (Fig. 4), low pH and a shallow topography favored high iron_d:DOC ratios. Both, low nitrate concentrations and a shallow topography can be interpreted as indicators for a prevalence of reducing conditions. Here, we argue that low slope angle in a catchment facilitate the presence of riparian wetlands (Li *et al.*, 2015) rich in organic carbon as well as iron and thus to the susceptibility of a catchment to the dominance of riparian zone processes (Dillon & Molot, 1997; Laudon *et al.*, 2012; Tetzlaff *et al.*, 2013). Note that at lowest nitrate availabilities the iron_d:DOC ratios converged towards a value of ~0.1 mg mg^{-1} (Fig. 4). This value is close to the ratio of the long-term slopes of iron_d and DOC (0.12 mg mg^{-1}, Fig. 2a), which can be interpreted as the mass ratio, at which iron_d and DOC were mobilized in the process of reductive mobilization. The significance of pH in the multiple regression is in line with this interpretation: Due to the decreasing sorption of DOC to iron(III) minerals with increasing pH (see above, Fig. 2a) lower amounts of DOC can be released with iron reduction at circumneutral conditions. We conclude that the process of reductive mobilization was a dominant control of the observed strongest increases in iron$_d$, DOC, and likely phosphate. This process gain importance with lower nitrate concentrations, lower pH and shallow topography. An extended assessment of the reductive mobilization can be found in the SI Discussions.

Strongly rising trends for iron$_d$ were observed in predominantly forested catchments that were presumably uninfluenced by fertilizer applications or urban sources, and hence nitrate concentrations tended to be low (median 4.3, range 1.2-14.6 mg NO_3^- l^{-1}). For these forested catchments, absolute nitrate trends were small and predominantly negative (Fig. S3). We could not find indication that an increase in reductive mobilization may be related to increased soil wetness as proposed by Knorr (2013) and Lambert *et al.* (2013) (SI Discussion).

Traditionally, catchment management has been aimed at minimizing the aquatic input of phosphate and nitrate in order to limit algal growth and its potential impact on water quality. Agricultural and urban areas are important sources of both nutrients (Carpenter *et al.*, 1998). Consequently, a positive relationship between annual average nitrate and phosphate concentrations was observed for catchments with a significant proportion of agricultural and urban areas (>20%, Fig. 5b). In contrast, a negative relationship was observed for catchments dominated by forest (Fig. 5a). For these catchments, the low nitrate concentrations and typically negative nitrate trends imply that - with declining nitrate concentrations - more phosphate may become available. This unexpected result can be explained by mobilization of phosphate due to iron reduction. As nitrogen to phosphorus ratios are still below the Redfield ratio (Hillebrand & Sommer, 1999), the proportion with which algae incorporate these elements, the potential for algal growth will increase with decreasing nitrate but rising phosphate availability.

Our study does support the hypothesis that atmospheric deposition is the key control of DOC increase. However, with the reductive dissolution of iron and a subsequent release of DOC and phosphate we suggest a different mechanism that was not considered as dominant before. In the Supporting Information we discuss several alternative hypotheses for the controls of the long-term increase of DOC and iron_d concentrations. This includes the most cited hypothesis of a possible mobilization of DOC due to decreased depositions of sulfate and chloride and a subsequent increase of pH and reduced ionic strength (Monteith *et al.*, 2007). In contrast to the finding of Monteith *et al.* (2007) the strongest upward trends in DOC in the catchments presented here were connected to the weakest downward trends in sulfate while a significant relation to chloride was not found. Moreover, for pH ≤6 where highest DOC concentrations and strongest trends can be observed (see above) there was no correlation between DOC and pH trends (Fig. S5a). Therefore, the hypothesis of Monteith *et al.* (2007) cannot be applied here.

We argue that there is convincing evidence that the observed positive trends of phosphate and DOC concentrations resulted from a long-term decrease in the redox potential of the soils as a consequence of decreasing nitrogen input. Moreover, other sorption partners of ferric iron such as arsenic (Senn & Hemond, 2002), cadmium and lead (Benjamin & Leckie, 1981) may be mobilized by the same mechanism. An example of the long-term increase in arsenic concentrations in two of the studied streams can be found in the Supporting Information (Fig. S4).

Declining nitrogen depositions as the driver of reductive mobilization

As a close link between nitrogen depositions and nitrate export was previously demonstrated in catchments with a minor agricultural influence (Jaworski *et al.*, 1997), we believe that - for the studied catchments that were predominantly covered by forest - decreasing nitrate concentrations were most likely caused by decreasing atmospheric depositions of nitrogen. Germany was strongly affected by high inputs of nitrogen (MSC-W, 2014) (in 1990: 2.23 g N m^{-2} yr^{-1}). The depositions in nitrogen (oxidized plus reduced) decreased by 35 mg N m^{-2} yr^{-1} between 1990 and 2012 in Germany (Table S1). The reductions in oxidized nitrogen of 22 mg m^{-2} yr^{-1} alone were sufficiently high to explain the average decrease in nitrate yields of 14 mg N m^{-2} yr^{-1} from the studied, predominantly forested, catchments. Reduced nitrogen can be converted to N_2 or to nitrate in soil surface layers (Krupa, 2003; Patrick & Reddy, 1976). Ammonium has also the potential to reduce iron(III) under anaerobic conditions (Yang *et al.*, 2012). Decreasing depositions of reduced nitrogen would translate to lower rates of iron reduction and lower iron leaching. As there is a widespread increase in $iron_d$ concentrations in the catchment presented here, we do not consider this process to be significant.

Correlations between the exports of $iron_d$, phosphate and DOC from forested catchments in northern America (Dillon & Molot, 1997) as well as correlated positive trends for iron and organic carbon have been previously reported from Scandinavia and the UK (Neal *et al.*, 2008; Sarkkola *et al.*, 2013; Weyhenmeyer *et al.*, 2014). Recently, Ekström *et al.* (2016) found evidence that in two of three Swedish rivers seasonal variations and long-term trends in iron concentration are mainly driven by redox dynamics. However, there were no or only weak relationships with DOC concentration. This is in agreement with the data presented here, since the studied Swedish rivers exhibited circumneutral pH values (6.7-7.1), at which we do not expect significant adsorption of DOC to ferric iron hydroxides (see above). In a study comprising 62 Swedish streams, the concentrations of iron were related to those of arsenic in 59 streams, to vanadium, which is also adsorptive to iron, in 60 streams as well as to organic carbon in 53 streams (Wallstedt *et al.*, 2010). A nonlinear negative linkage between nitrate and DOC concentrations in surface waters were described before (Goodale *et al.*, 2005; Taylor & Townsend, 2010). Taylor & Townsend (2010) argue that resource stoichiometry couples DOC and nitrate concentrations in soil and surface waters. High DOC availability leads to a nitrogen limitation of microbial anabolism. In contrast a low DOC concentration leads to low nitrogen assimilation and promotes nitrification. Consequently, a tight non-linear negative relation between nitrate and DOC concentrations can be observed in a range of ecosystems. In contrast to Goodale *et al.* (2005) and Taylor & Townsend (2010), the DOC and nitrate concentrations from our catchments did not exhibit a clear negative relationship (based on annual mean concentrations, exponential model $R^2 = 0.006$, note that Fig. 3b shows DOC trends vs. nitrate concentrations). The reason might be that the nitrate availabilities reported here were much higher than in Taylor & Townsend (2010) and were not depleted to levels potentially limiting microbial DOC uptake and decomposition. This limiting nitrate availability may be different from the nitrate threshold above that nitrate abundance inhibits iron reduction. We conclude that the stoichiometric control of DOC and nitrate as proposed by Taylor & Townsend (2010) is not the process driving the relation seen in our dataset. The observations of correlated positive trends for iron, phosphate and organic carbon (Dillon & Molot, 1997; Neal *et al.*, 2008; Sarkkola *et al.*, 2013; Weyhenmeyer *et al.*, 2014) as well as nonlinear negative linkages between nitrate and DOC (Taylor & Townsend, 2010) were not interpreted as a reductive desorption of DOC and a depletion of nitrate buffers in soils. The nitrate depletion, as shown here for forested German catchments, is most likely explained by atmospheric depositions. They declined across large parts of North America and Europe since the 1990s as a consequence of reduced emissions of reactive nitrogen (Vet *et al.* (2014), Table S1). Altogether, these reports suggest that the relationships revealed from our analyses across a range of spatial and temporal scales may be of general significance for understanding water quality of surface water bodies in the northern hemisphere.

Implications

Elevated nitrate concentrations are commonly considered to pollute aquatic and terrestrial ecosystems. Our study suggests that decreasing nitrate concentrations to pre-industrial conditions can remove the redox buffer in soils and may deteriorate water quality by destabilizing other undesired compounds. There may be a trade-off between decreasing nitrate concentrations and increasing phosphate and DOC concentrations. This raises several questions: How do we want our streams and ecosystems to be? What are the historic pre-industrial pristine conditions we are referring to? As an example, Valinia *et al.* (2015) show that most Swedish lakes are now recovered to the same TOC concentrations as in 1860. However, Meyer-Jacob *et al.* (2015) point out that decreasing concentrations of organic carbon in Swedish lakes started already in the years 1450-1600 as a response to land use changes and thus present concentrations are far away from pristine conditions. Our data was derived from drinking-water producing catchments and a rise of DOC, phosphate and metal concentrations will negatively affect treatment options and costs. Here, we need a careful discussion on catchment nutrient management to balance the concentrations of nitrate with phosphate and DOC and on potential measures to improve the situation for drinking water production without interfering ecosystem functioning.

This study is of data-driven nature: From an integral signal in the stream we inferred dominant processes within the catchment. The strength of the analysis presented here is that we jointly interpreted solute patterns in space (differences between the catchments) and time (changes at different scales) using one common process. However, our hypotheses that nitrate abundance controls iron reduction and subsequently the mobilization of both DOC and phosphate has to be further tested using experimental field studies and/or process based modelling. Our study will help to focus these efforts on the above mentioned redox processes as well as on the location of these processes within the catchment, i.e. riparian wetland soils.

Acknowledgements

We thank the reservoir management authorities who made the chemical and hydrological data obtained within their monitoring programs available to us. The State Reservoir Administration Saxony, Germany (Landestalsperrenverwaltung) supplied the data for the Wilzsch and the State Authority for Environmental Protection, Agriculture and Geology (LfULG) Saxony provided the deposition data. Stefan Heider derived data on land use. We also thank Jan H. Fleckenstein, Matthias Koschorreck, Gunnar Lischeid, Marieke R. Oosterwoud, Marie J. Kurz and Thorsten Reemtsma for valuable discussions on this topic. The work was supported by the Federal Ministry of Education and Research Germany (BMBF, 02WT1290A). The authors declare no conflict of interest.

References

Andersen JM (1982) Effect of Nitrate Concentration in Lake Water on Phosphate Release from the Sediment. *Water Research*, **16**, 1119-1126.

Benjamin MM, Leckie JO (1981) Multiple-Site Adsorption of Cd, Cu, Zn, and Pb on Amorphous Iron Oxyhydroxide. *Journal of Colloid and Interface Science*, **79**, 209-221.

Box GEP, Cox DR (1964) An Analysis of Transformations. *Journal of the Royal Statistical Society Series B-Statistical Methodology,* **26**, 211-252.

Brookins DG (1988) *Eh-pH diagrams for geochemistry,* Berlin, Germany, Springer.

Burn DH, Elnur MaH (2002) Detection of hydrologic trends and variability. *Journal of Hydrology,* **255**, 107-122.

Burt TP (2005) A third paradox in catchment hydrology and biogeochemistry: decoupling in the riparian zone. *Hydrological Processes,* **19**, 2087-2089.

Cabezas A, Gelbrecht J, Zak D (2013) The effect of rewetting drained fens with nitrate-polluted water on dissolved organic carbon and phosphorus release. *Ecological Engineering*, **53**, 79-88.

Carpenter SR, Caraco NF, Correll DL, Howarth RW, Sharpley AN, Smith VH (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*, **8**, 559-568.

Chacon N, Silver WL, Dubinsky EA, Cusack DF (2006) Iron reduction and soil phosphorus solubilization in humid tropical forests soils: The roles of labile carbon pools and an electron shuttle compound. *Biogeochemistry*, **78**, 67-84.

Clark JM, Bottrell SH, Evans CD *et al.* (2010) The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of the Total Environment*, **408**, 2768-2775.

Dadi T, Friese K, Wendt-Potthoff K, Koschorreck M (2015) Benthic dissolved organic carbon fluxes in a drinking water reservoir. *Limnology and Oceanography*, **61**, 445–459.

Dillon PJ, Molot LA (1997) Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. *Water Resources Research,* **33**, 2591-2600.

Duce RA, Laroche J, Altieri K *et al.* (2008) Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science*, **320**, 893-897.

Dzombak DA, Morel FMM (1990) *Surface complexation modeling: hydrous ferric oxide,* New York, Wiley-Interscience.

Ekström SM, Regnell O, Reader HE, Nilsson PA, Löfgren S, Kritzberg ES (2016) Increasing concentrations of iron in surface waters as a consequence of reducing conditions in the catchment area. *Journal of Geophysical Research-Biogeosciences,* **121**, 479-493.

Elser JJ (2011) A World Awash with Nitrogen. *Science,* **334**, 1504-1505.

Evans CD, Jones TG, Burden A *et al.* (2012) Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology,* **18**, 3317-3331.

Frei S, Knorr KH, Peiffer S, Fleckenstein JH (2012) Surface micro-topography causes hot spots of biogeochemical activity in wetland systems: A virtual modeling experiment. *Journal of Geophysical Research-Biogeosciences,* **117**.

Galloway JN, Townsend AR, Erisman JW *et al.* (2008) Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science,* **320**, 889-892.

Goodale CL, Aber JD, Vitousek PM, Mcdowell WH (2005) Long-term decreases in stream nitrate: Successional causes unlikely; Possible links to DOC? *Ecosystems,* **8**, 334-337.

Grybos M, Davranche M, Gruau G, Petitjean P (2007) Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? *Journal of Colloid and Interface Science*, **314**, 490-501.

Gunnars A, Blomqvist S, Johansson P, Andersson C (2002) Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. *Geochimica et Cosmochimica Acta,* **66**, 745-758.

Hagedorn F, Kaiser K, Feyen H, Schleppi P (2000) Effects of redox conditions and flow processes on the mobility of dissolved organic carbon and nitrogen in a forest soil. *Journal of Environmental Quality,* **29**, 288-297.

Hillebrand H, Sommer U (1999) The nutrient stoichiometry of benthic microalgal growth: Redfield proportions are optimal. *Limnology and Oceanography,* **44**, 440-446.

Holtgrieve GW, Schindler DE, Hobbs WO *et al.* (2011) A Coherent Signature of Anthropogenic Nitrogen Deposition to Remote Watersheds of the Northern Hemisphere. *Science,* **334**, 1545-1548.

Hyacinthe C, Van Cappellen P (2004) An authigenic iron phosphate phase in estuarine sediments: composition, formation and chemical reactivity. *Marine Chemistry*, **91**, 227-251.

Jaisi DP, Blake RE, Kukkadapu RK (2010) Fractionation of oxygen isotopes in phosphate during its interactions with iron oxides. *Geochimica et Cosmochimica Acta,* **74**, 1309-1319.

Jaworski NA, Howarth RW, Hetling LI (1997) Atmospheric deposition of nitrogen oxides onto the landscape contributes to coastal eutrophication in the northeast United States. *Environmental Science and Technology,* **31**, 1995-2004.

Kaiser K, Guggenberger G (2000) The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Organic Geochemistry,* **31**, 711-725.

Knorr KH (2013) DOC-dynamics in a small headwater catchment as driven by redox fluctuations and hydrological flow paths - are DOC exports mediated by iron reduction/oxidation cycles? *Biogeosciences,* **10**, 891-904.

Kritzberg ES, Ekstrom SM (2012) Increasing iron concentrations in surface waters - a factor behind brownification? *Biogeosciences,* **9**, 1465-1478.

Krupa SV (2003) Effects of atmospheric ammonia (NH3) on terrestrial vegetation: a review. *Environmental Pollution,* **124**, 179-221.

Lambert T, Pierson-Wickmann AC, Gruau G, Jaffrezic A, Petitjean P, Thibault JN, Jeanneau L (2013) Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment. *Water Resources Research,* **49**, 5792-5803.

Laudon H, Buttle J, Carey SK *et al.* (2012) Cross-regional prediction of long-term trajectory of stream water DOC response to climate change. *Geophysical Research Letters,* **39**.

Ledesma JLJ, Grabs T, Bishop KH, Schiff SL, Kohler SJ (2015) Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. *Global Change Biology,* **21**, 2963-2979.

Ledesma JLJ, Kohler SJ, Futter MN (2012) Long-term dynamics of dissolved organic carbon: Implications for drinking water supply. *Science of the Total Environment,* **432**, 1-11.

Li MF, Del Giorgio PA, Parkes AH, Prairie YT (2015) The relative influence of topography and land cover on inorganic and organic carbon exports from catchments in southern Quebec, Canada. *Journal of Geophysical Research-Biogeosciences,* **120**, 2562-2578.

Lopez-Hernandez D, Burnham CP (1974) Effect of Ph on phosphate adsorption in soils. *Journal of Soil Science,* **25**, 207-216.

Lucassen ECHET, Smolders AJP, Van Der Salm AL, Roelofs JGM (2004) High groundwater nitrate concentrations inhibit eutrophication of sulphate-rich freshwater wetlands. *Biogeochemistry,* **67**, 249-267.

Meyer-Jacob C, Tolu J, Bigler C, Yang HD, Bindler R (2015) Early land use and centennial scale changes in lake-water organic carbon prior to contemporary monitoring. *Proceedings of the National Academy of Sciences of the United States of America,* **112**, 6579-6584.

Monteith DT, Stoddard JL, Evans CD *et al.* (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature,* **450**, 537-540.

Morton R, Henderson BL (2008) Estimation of nonlinear trends in water quality: An improved approach using generalized additive models. *Water Resources Research,* **44**.

MSC-W (2014) EMEP/Meteorological Synthesizing Centre - West (MSC-W). http://www.emep.int/mscw/index_mscw.html.

Neal C, Lofts S, Evans CD, Reynolds B, Tipping E, Neal M (2008) Increasing iron concentrations in UK upland waters. *Aquatic Geochemistry,* **14**, 263-288.

Neubauer E, Kohler SJ, Von Der Kammer F, Laudon H, Hofmann T (2013) Effect of pH and Stream Order on Iron and Arsenic Speciation in Boreal Catchments. *Environmental Science and Technology,* **47**, 7120-7128.

Patrick WH, Reddy KR (1976) Nitrification-Denitrification Reactions in Flooded Soils and Water Bottoms - Dependence on Oxygen-Supply and Ammonium Diffusion. *Journal of Environmental Quality,* **5**, 469-472.

Poor N, Pribble R, Greening H (2001) Direct wet and dry deposition of ammonia, nitric acid, ammonium and nitrate to the Tampa Bay Estuary, FL, USA. *Atmospheric Environment,* **35**, 3947-3955.

Riedel T, Zak D, Biester H, Dittmar T (2013) Iron traps terrestrially derived dissolved organic matter at redox interfaces. *Proceedings of the National Academy of Sciences of the United States of America,* **110**, 10101-10105.

Sadiq R, Rodriguez MJ (2004) Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review. *Science of the Total Environment,* **321**, 21-46.

Sarkkola S, Nieminen M, Koivusalo H *et al.* (2013) Iron concentrations are increasing in surface waters from forested headwater catchments in eastern Finland. *Science of the Total Environment,* **463**, 683-689.

Schlesinger WH (2009) On the fate of anthropogenic nitrogen. *Proceedings of the National Academy of Sciences of the United States of America,* **106**, 203-208.

Seibert J, Grabs T, Kohler S, Laudon H, Winterdahl M, Bishop K (2009) Linking soil- and stream-water chemistry based on a Riparian Flow-Concentration Integration Model. *Hydrology and Earth System Sciences,* **13**, 2287-2297.

Senn DB, Hemond HF (2002) Nitrate controls on iron and arsenic in an urban lake. *Science,* **296**, 2373-2376.

Sivapalan M (2006) Pattern, process and function: Elements of a unified theory of hydrology at the catchment scale. In: *Encyclopedia of Hydrological Sciences.* (ed Anderson MG), Hoboken, John Wiley & Sons, Ltd.

Sørensen J (1982) Reduction of Ferric Iron in Anaerobic, Marine Sediment and Interaction with Reduction of Nitrate and Sulfate. *Applied and Environmental Microbiology,* **43**, 319-324.

Straub KL, Benz M, Schink B, Widdel F (1996) Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. *Applied and Environmental Microbiology,* **62**, 1458-1460.

Sucker C, Von Wilpert K, Puhlmann H (2011) Acidification reversal in low mountain range streams of Germany. *Environmental Monitoring and Assessment,* **174**, 65-89.

R Core Team (2015) R: A language and environment for statistical computing. Vienna, Austria, R Foundation for Statistical Computing.

Taylor PG, Townsend AR (2010) Stoichiometric control of organic carbon-nitrate relationships from soils to the sea. *Nature,* **464**, 1178-1181.

Temnerud J, Hytteborn JK, Futter MN, Kohler SJ (2014) Evaluating common drivers for color, iron and organic carbon in Swedish watercourses. *Ambio,* **43**, 30-44.

Tetzlaff D, Soulsby C, Buttle J *et al.* (2013) Catchments on the cusp? Structural and functional change in northern ecohydrology. *Hydrological Processes,* **27**, 766-774.

Tipping E (1981) The adsorption of aquatic humic substances by iron-oxides. *Geochimica et Cosmochimica Acta,* **45**, 191-199.

Tipping E, Rey-Castro C, Bryan SE, Hamilton-Taylor J (2002) Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation. *Geochimica et Cosmochimica Acta,* **66**, 3211-3224.

Valinia S, Futter MN, Cosby BJ, Rosen P, Folster J (2015) Simple Models to Estimate Historical and Recent Changes of Total Organic Carbon Concentrations in Lakes. *Environmental Science and Technology,* **49**, 386-394.

Vet R, Artz RS, Carou S *et al.* (2014) A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmospheric Environment,* **93**, 3-100.

Wagener T, Sivapalan M, Troch PA *et al.* (2010) The future of hydrology: An evolving science for a changing world. *Water Resources Research,* **46**.

Wallstedt T, Bjorkvald L, Gustafsson JP (2010) Increasing concentrations of arsenic and vanadium in (southern) Swedish streams. *Applied Geochemistry,* **25**, 1162-1175.

Wasserchemische Gesellschaft FIDG (2014) *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung (German standard methods for the examination of water, wastewater and sludge),* Weinheim, Germany, Wiley-VCH.

Weyhenmeyer GA, Prairie YT, Tranvik LJ (2014) Browning of Boreal Freshwaters Coupled to Carbon-Iron Interactions along the Aquatic Continuum. *Plos One,* **9**, e88104.

Winterdahl M, Futter M, Kohler S, Laudon H, Seibert J, Bishop K (2011) Riparian soil temperature modification of the relationship between flow and dissolved organic carbon concentration in a boreal stream. *Water Resources Research,* **47**.

Wood SN (2006) *Generalized additive models: an introduction with R,* Boca Raton, USA, Chapman and Hall/CRC.

Worrall F, Burt T, Shedden R (2003) Long term records of riverine dissolved organic matter. *Biogeochemistry,* **64**, 165-178.

Yang WH, Weber KA, Silver WL (2012) Nitrogen loss from soil through anaerobic ammonium oxidation coupled to iron reduction. *Nature Geoscience,* **5**, 538-541.

Young LB, Harvey HH (1992) The relative importance of manganese and iron-oxides and organic matter in the sorption of trace-metals by surficial lake-sediments. *Geochimica et Cosmochimica Acta,* **56**, 1175-1186.

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

Zehnder AJB, Stumm W (1988) Geochemistry and biogeochemistry of anaerobic habitats. In: *Biology of anaerobic microorganisms.* (ed Zehnder AJB) pp 1-38. New York, John Wiley & Sons.

Zuur A, Ieno EN, Walker N, Saveliev AA, Smith GM (2009) *Mixed effects models and extensions in ecology with R,* New York, USA, Springer.

Supporting Information captions

Discussions: Addressing alternative hypotheses (H)

H1: Reduced ionic strength and increasing pH in soils mobilized organic compounds

H2: The coherent behavior of DOC and iron$_d$ was related to complexation of Fe(III) by DOC compounds

H3: Negative trends of nitrate are a consequence of a more efficient microbial nitrogen retention with rising DOC availabilities

H4: Reductive iron mobilization was induced by increased wetness

H5: Desorption of organic matter from soil minerals due to pH increase

H6: Mobilization of iron and DOC due to increased flushing of iron-rich deep soil layers

H7: High concentrations of sulfate instead of nitrate inhibited the reduction of iron(III) minerals

Discussions:Experimental nitrogen addition to forests and DOC export

Discussions: Probabilistic assessment of phenomena and possible stimuli

Table S1: Deposition of nitrogen in the EU and individual countries

Table S2: Regression between trends of iron$_d$ and phosphate: Impact of land use

Table S3: Regression statistics of long-term trends

Table S4: Evaluation of changes in the annual cycle to test hypothesis H2

Table S5: Multiple regression of iron$_d$:DOC ratio

Fig. S1:Location of the studied catchments within Germany

Fig. S2: Annual wet deposition of oxidized nitrogen, sulfate and chloride at Wilzsch Creek catchment

Fig. S3: Nitrate concentrations and nitrate trends as a function of land use

Fig. S4: Additional information to GAM analysis: Arsenic

Fig. S5: Trends in DOC and iron$_d$ and their dependence on trends in pH

Fig. S6: Example of the analysis of seasonality for one stream

Figure captions

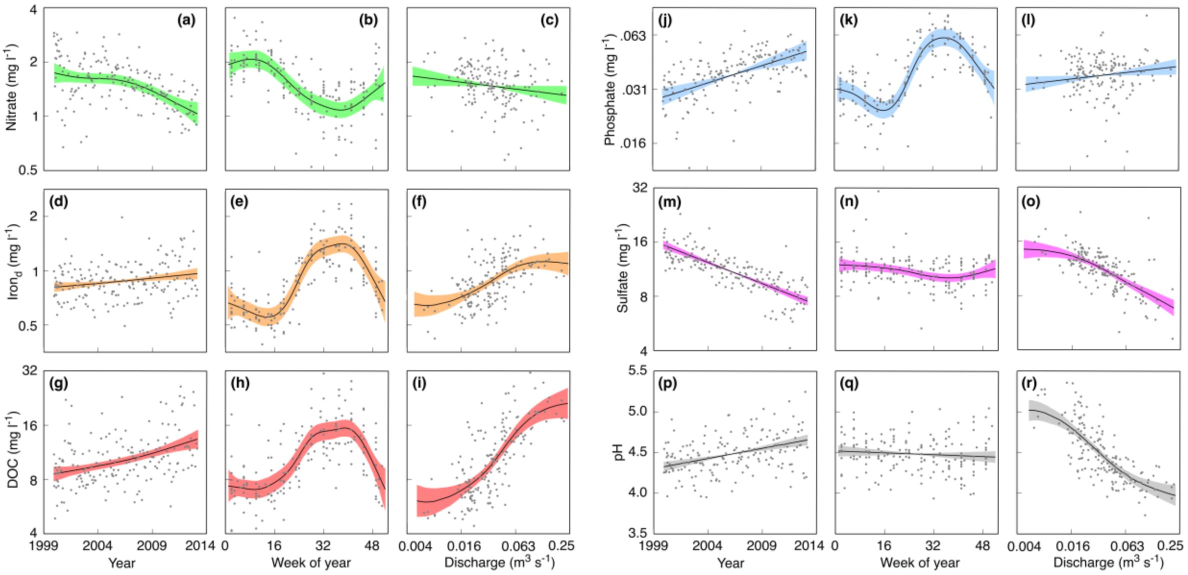
Fig. 1 Long-term, seasonal and discharge-dependent dynamics of DOC and other solutes in a selected stream (Wilzsch Creek). Results for the application of generalized additive models. Left, middle and right columns represent long-term trends, seasonal patterns and discharge effects, respectively. Each model component was graphed (solid black line) along with the observed data adjusted for the remaining model components (grey circles, *n* = 168-177). The 95% confidence intervals of the estimated model components are colored.

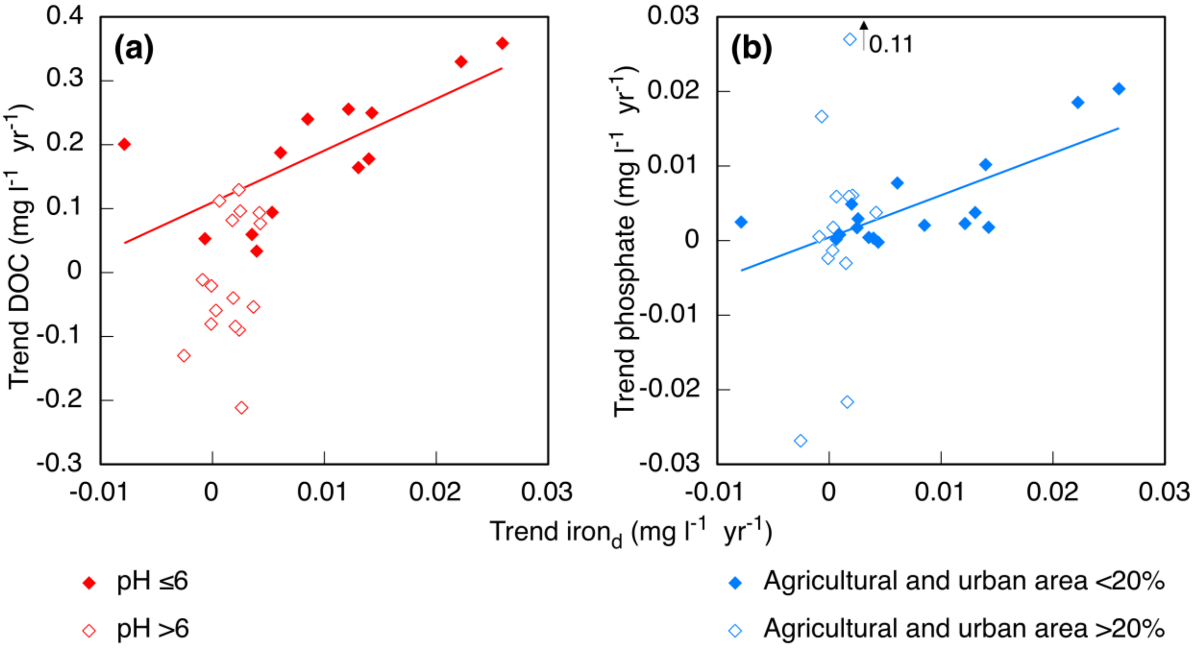
Fig. 2 Changes in DOC and phosphate concentration and their dependence on changes in iron$_d$ concentrations. (a): DOC, closed symbols represent streams with pH ≤6, R^2 = 0.51, *n* = 13, *P* < 0.01; open symbols: pH >6, R^2 = 0.03, *n* = 18, n.s. (b): phosphate, closed symbols denote forested catchments less influenced by agricultural or urban sources, R^2 = 0.60, *n* = 17, *P* < 0.001; this relationship is robust against moderate changes of the share of forested area (see Table S2); open symbols represent the remaining catchments with a fraction of agricultural and urban areas >20%, one outlying value not shown, R^2 = 0.13, *n* = 13, n.s. Only catchments with significant trends were considered.

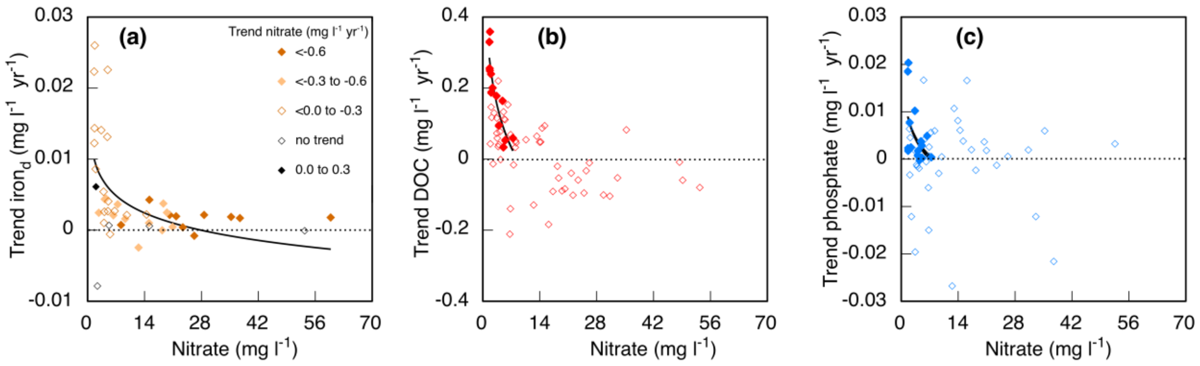
Fig. 3 The dependence of iron$_d$, DOC, phosphate trends and iron$_d$:DOC ratio on nitrate availability. (a): changes in iron$_d$ concentrations, R^2 = 0.28, *n* = 44, *P* < 0.001, colors refer to the observed long-term trend in nitrate concentrations, (b): changes in DOC concentrations, R^2 = 0.80, *n* = 13, *P* < 0.001, closed symbols characterize streams with pH ≤6, (c): phosphate, R^2 = 0.25, *n* = 16, *P* < 0.05, closed symbols denote catchments with a forest cover ≥80% (Six outlying values with forest cover <80% are not shown). Only catchments with significant trends were considered.

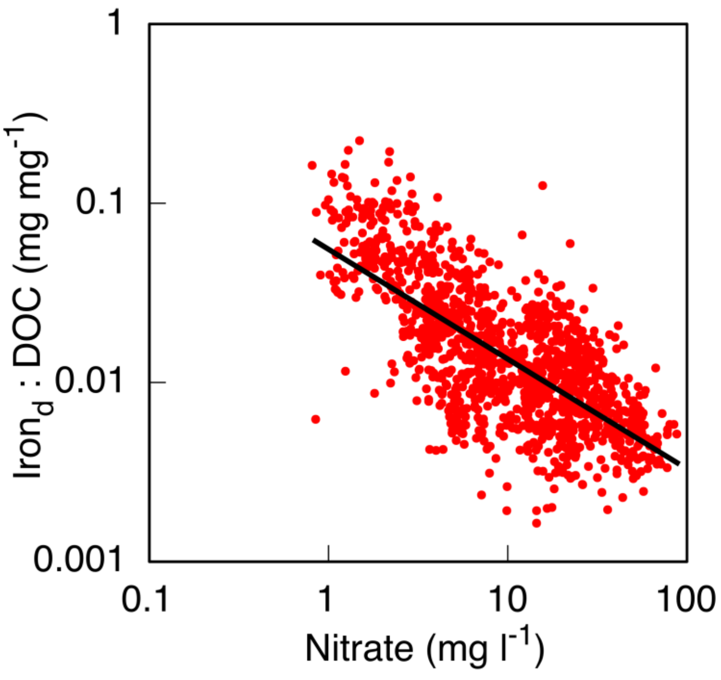
Fig. 4 Mean annual iron$_d$:DOC ratio as a function of mean annual nitrate concentration, R^2 = 0.52, *n* = 1231, *P* < 0.001.

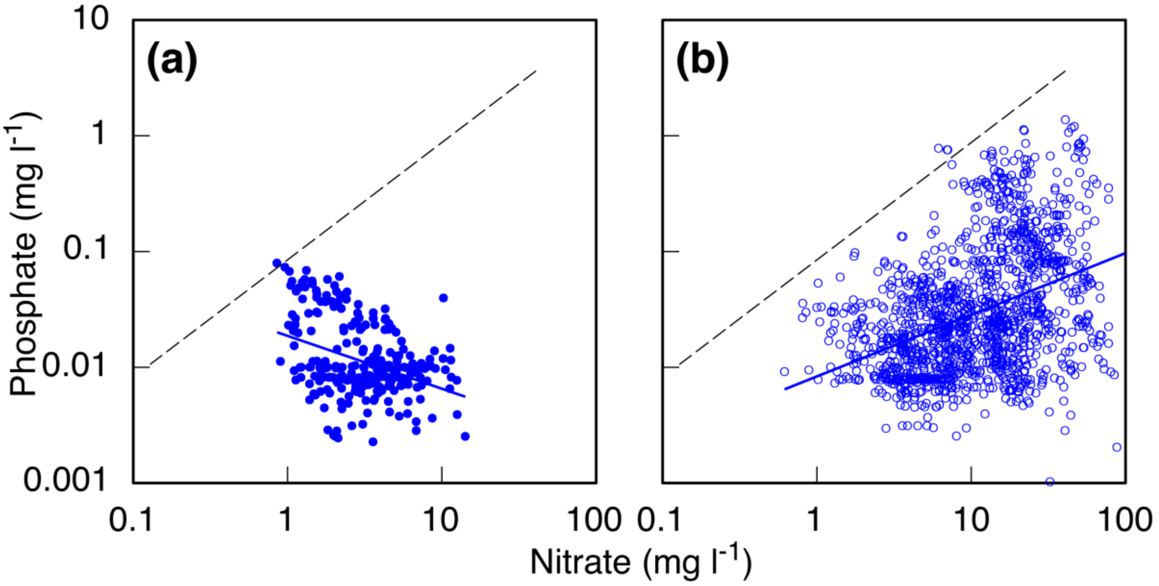
Fig. 5 Divergent relationship between nitrate and phosphate concentrations in streams with different land use. Symbols represent annual mean concentrations from individual streams. (a): catchments with forest cover ≥80%, less influenced by agricultural fertilization or urban wastewater release (R^2 = 0.16, *n* = 1449, *P* < 0.001), (b): catchments with forest cover <80% (R^2 = 0.14, *n* = 303, *P* < 0.001). The dashed lines show the proportion of both nutrients typically occurring in algal biomass (Redfield ratio).


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
(m)
(n)
(o)
(p)
(q)
(r)
Nitrate (mg l^{-1})
4
2
1
0.5
Iron$_d$ (mg l^{-1})
2
1
0.5
DOC (mg l^{-1})
32
16
8
4
Phosphate (mg l^{-1})
.063
.031
.016
Sulfate (mg l^{-1})
32
16
8
4
pH
5.5
5.0
4.5
4.0
3.5
1999
2004
2009
2014
Year
0
16
32
48
Week of year
0.004
0.016
0.063
0.25
Discharge (m^3 s^{-1})


(a)
Trend DOC (mg l^{-1} yr^{-1})
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
(b)
Trend phosphate (mg l^{-1} yr^{-1})
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
0.11
-0.01
0
0.01
0.02
0.03
Trend iron$_d$ (mg l^{-1} yr^{-1})
◆ pH ≤6
◇ pH >6
◆ Agricultural and urban area <20%
◇ Agricultural and urban area >20%


(a)
Trend iron$_d$ (mg l^{-1} yr^{-1})
0.03
0.02
0.01
0
-0.01
Trend nitrate (mg l^{-1} yr^{-1})
<-0.6
<-0.3 to -0.6
<0.0 to -0.3
no trend
0.0 to 0.3
0
14
28
42
56
70
Nitrate (mg l^{-1})
(b)
Trend DOC (mg l^{-1} yr^{-1})
0.4
0.2
0
-0.2
-0.4
0
14
28
42
56
70
Nitrate (mg l^{-1})
(c)
Trend phosphate (mg l^{-1} yr^{-1})
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
0
14
28
42
56
70
Nitrate (mg l^{-1})


Iron$_d$: DOC (mg mg^{-1})
1
0.1
0.01
0.001
0.1
1
10
100
Nitrate (mg l^{-1})


(a)
(b)
Phosphate (mg l^{-1})
10
1
0.1
0.01
0.001
0.1
1
10
100
0.1
1
10
100
Nitrate (mg l^{-1})