

**Carbon-nutrient
fluxes from
sediments in streams**

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Warming increases carbon-nutrient fluxes from sediments in streams across land use

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Abstract

Rising water temperatures due to climate and land-use change can accelerate biogeochemical fluxes from sediments to streams. We investigated impacts of increased streamwater temperatures on sediment fluxes of dissolved organic carbon (DOC), nitrate, soluble reactive phosphorus (SRP) and sulfate. Experiments were conducted at 8 long-term monitoring sites across land use (forest, agricultural, suburban, and urban) at the Baltimore Ecosystem Study Long-Term Ecological Research (LTER) site in the Chesapeake Bay watershed. Over 20 yr of routine water temperature data showed substantial variation across seasons and years, and lab incubations were conducted at 4 temperatures (4 °C, 15 °C, 25 °C and 35 °C) for 48 h. Results indicated: (1) warming consistently increased sediment DOC fluxes to overlying water across land use but decreased DOC quality via increases in the humic-like to protein-like fractions (2) warming consistently increased SRP fluxes from sediments to overlying water across land use (3) warming increased sulfate fluxes from sediments to overlying water at rural/suburban sites but decreased sulfate fluxes at urban sites likely due to sulfate reduction (4) nitrate fluxes showed an increasing trend with temperature but with larger variability than SRP. Sediment fluxes of nitrate, SRP and sulfate were strongly related to watershed urbanization and organic matter content. Using relationships of sediment fluxes with temperature, we estimate a 5 °C warming would increase the annual sediment release by 1.0–3.9 times. In addition to hydrologic variability, understanding warming impacts on coupled biogeochemical cycles in streams (e.g., organic matter mineralization, P sorption, nitrification, denitrification, and sulfate reduction) is critical for forecasting changes in carbon and nutrient exports across watershed land use.

1 Introduction

An improved understanding of coupled biogeochemical cycles is warranted in forecasting the interactive effects of climate and land-use change on water quality in streams

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and rivers (Chapin et al., 2011; Howarth et al., 2011; Schlesinger et al., 2011). In particular, the transformations of bioreactive elements (carbon, nitrogen, phosphorus and sulfur) are important processes for regulating biogeochemical cycles and water quality (Froelich, 1988; Seitzinger et al., 1988; Dail and Fitzgerald, 1999; Battin et al., 2008).

The role of sediments is particularly critical in small streams compared with larger rivers due to the greater potential for hydrologic interactions between surface water with sediments in response to channel morphology/geometry and hyporheic exchange (e.g., Alexandria et al., 2000). Stream sediments can act as “sources” or “sinks” of bioreactive elements, where they can be either transferred from the water column to sediments through abiotic adsorption and biotic uptake (Bowes et al., 2003; Arango et al., 2008; Kaplan et al., 2008) or released back to the water column via diffusing diagenetic products of organic matter decomposition or reduction reactions (Jensen and Andersen, 1992; Aguilar and Thibodeaux, 2005).

Temperature is an important variable influencing carbon, nitrogen, phosphorus and sulfur biogeochemical cycles in aquatic environments (House and Denison, 2002; Gudasz et al., 2010). There have been long-term warming water temperatures in streams and rivers due to interactive effects of climate and land-use change (e.g., Webb and Nobilis, 2007; Kaushal et al., 2010). In addition, there can be surges and increased variability in stream water temperatures due to urban runoff from impervious surfaces (Kim, 2007; Nelson and Palmer, 2007; Kaushal et al., 2010). Simultaneously, urbanization has been shown to also increase levels of labile organic matter, nutrients, sulfate concentrations (O’Driscoll et al., 2010 and references within). Increased water temperatures coupled with increased availability of carbon and nutrient sources can increase microbial activity in stream sediments (Imberger et al., 2008), and accelerate transformations of bioreactive elements.

Prior studies have commonly investigated the effects of warming on sediment fluxes and transformations of individual bioreactive elements, but little work has been done to improve our conceptual understanding of the interactive effects of land use and temperature on coupled biogeochemical cycles. The primary objective of the present study

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was to investigate the interactive effects of land use and potential climate change on fluxes of bioreactive elements and organic carbon quality influenced by stream sediments. We tested two hypotheses: (1) warmer temperature in stream water sequentially accelerates sediment transformations and fluxes of dissolved organic carbon (DOC), nitrate, soluble reactive phosphorus (SRP), and sulfate as a result of organic matter decomposition and, (2) sediment fluxes in urban watersheds are more sensitive to warming than rural watersheds. An improved understanding of the potential role of warming on fluxes of bioreactive elements in small streams and across the broader urban watershed continuum can contribute to our understanding of drivers of change in water quality, microbial communities, and ecosystem functions (Kaushal et al., 2010; Kaushal and Belt, 2012). It can also inform approaches for predicting alterations in the dynamics and fluxes of limiting nutrients in aquatic ecosystems and assessing potential impacts on downstream eutrophication in response to climate and land-use change.

2 Methods

2.1 Site description

Temperature-manipulation incubation experiments were conducted with stream sediments across 8 sites with varying land use (e.g., forest, agricultural, suburban and urban) at the US National Science Foundation supported Baltimore Ecosystem Study (BES) Long-term Ecological Research (LTER). The results of lab experiments were used to estimate annual sediment fluxes and predict changes in sediment fluxes with 5 °C warming. The BES LTER site in the Chesapeake Bay watershed provides access to extensive background information and long-term monitoring of nitrogen, phosphorus, sulfate, and carbon concentrations and fluxes in streams (www.beslter.org) (e.g., Groffman et al., 2004; Kaushal et al., 2008a, b, 2011). Long-term streamwater chemistry has been described extensively elsewhere (Groffman et al., 2004; Kaushal et al., 2005a, 2008a, 2011; Duan et al., 2012).

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Briefly, the main focal watershed of the BES LTER site is the Gwynns Falls, a 17 150 ha watershed in the Piedmont physiographic province that drains into the north-west branch of the Patapsco River that flows into the Chesapeake Bay (Fig. 1). The Gwynns Falls sites from Glyndon (GFGL), Gwynnbrook (GFGB), Villa Nova (GFVN) to Carroll Park (GFCP) traverse a rural/suburban to urban gradient (Fig. 1 and Table 1). MCDN is a small tributary to the Gwynns Falls draining a watershed dominated by row crop agriculture (corn, soybeans), while Dead Run (DRKR) is an urbanized tributary of the Gwynns Falls between the Villa Nova and Carroll Park stations. Samples were also taken from a small tributary to the Gwynns Falls (GFGR), approximately 700 m above GFCP, which was highly contaminated with sewage. Pond Branch (POBR) is a small forested watershed located in the nearby Gunpowder Falls watershed.

Long-term water temperature data from the Gwynns Falls at Villa Nova (GFVN) were acquired from the Chesapeake Bay Program (CBP) which is a co-operative effort between the US federal government and state and local governments in the Chesapeake Bay watershed for routine monitoring of water quality parameters. The station was sampled once a month from 1986–2006 and was used to characterize long-term temperature variability for the Gwynns Falls at the Baltimore LTER site. The records show strong seasonal signal with highest values in July–August and lowest in January–February, although the long-term trend is not clear during this 20-yr period (Fig. 2).

2.2 Sample collection and processing

Sediment and water samples were collected on 2 April 2010 from all 8 sites that were described above and in Table 1. Sediment samples at each site comprise material taken from 5–10 points along each stream that were randomly selected to make a composite sample. Three litres of stream water were collected simultaneously for later incubation experiments and water quality analyses. Water and sediment samples were kept cold on ice during transfer to the lab, where they were temporarily kept refrigerated. In the lab, sediments were sieved through a 2 mm sieve, and the fractions < 2 mm were homogenized and kept cold for incubations.

2.3 Sediment incubations

The sediments were incubated in 4 environmental control chambers with temperatures set at 4, 15, 25, and 35 °C, respectively. At each temperature, 200 g of wet sediment and 450 ml of unfiltered stream water were added to a 500 ml glass flask. The water and sediment were well-mixed by swirling the flasks to represent a high-flow event, and then the flasks were left stationary at 4 °C for two days to wait for particles to settle. Water samples without sediment additions were also prepared in 500 ml flasks at the same time as controls. Four sets of flasks (8 samples with 8 controls for each set) were placed in 4 environmental control chambers for incubation experiments for 48 h, during which the flasks were kept in the dark and gently stirred with a shaker table. During the 2-day incubations, 30 ml of water were collected at 0, 6, 12, 24, and 48 h increments and filtered immediately through 25 mm Whatman GF/F filters in a syringe filter. The filtrates were stored in combusted amber glass vials and stored in a refrigerator. Sediments were collected before incubations for size fractionation and chemical analyses to examine their effect on bioactive element fluxes and transformation. Sediment samples were dried at 40 °C for three days, and the dried sediments were fractionated into 5 size fractions with a set of sieves (0.5 mm, 0.25 mm, 0.125 mm and 0.0625 mm) and weighed for particle size analysis. The bulk sediments were grinded with a mortar and pestle, and the powder was saved for chemical analyses.

2.4 Chemical analysis

DOC concentrations were measured on a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN), by using high-temperature catalytic oxidation. HCl was added to remove dissolved inorganic carbon with a 1-min sparge time. Three injections (with maximum of 5) were run for each sample to obtain a standard derivation less than 0.2. Fluorescence spectroscopy was used in characterization of DOC composition and source. Fluorescence measurements were made on a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon, Edison NJ, USA) using a 1 cm quartz cuvette with slit widths set

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to 5 nm. Excitation emission matrix scans (EEMs) were obtained by collecting a series of emission wavelengths ranging from 300 to 600 nm (2 nm increments) at excitation wavelengths ranging from 240 to 450 nm (5 nm increments). Instrument biases such as excitation and emission monochromators (as well as bulb life and efficiency) were automatically corrected. After data acquisition on the spectrofluorometer, the raw data was exported into MATLAB for remaining corrections (e.g., inner filtering and scatter removal; Walker et al., 2009). The calibrated values of fluorescence intensities at excitation/emission = 275 nm/240 nm and 350 nm/480 nm were recorded as protein-like and humic-like fluorospores (Coble, 1996; Stolpe et al., 2010). Relative to the humic-like fluorospore, the intensity of the protein-like fluorospore is generally higher in labile DOC sources (e.g., wastewater; Hudson et al., 2007) and positively correlated with DOC bioavailability (Balcarczyk et al., 2009; Lønborg et al., 2010). So, the ratio of protein-like to the humic-like fluorospore (P/H) was calculated here as an index for organic carbon lability.

Nitrate, sulfate and chloride ion (Cl^-) concentrations were measured with a Dionex ICS-1500 ion chromatograph (ICS-1500, Dionex INC., USA). The instrument was equipped with an AS14 4-mm analytical column and an AG14 4-mm guard column. An eluent of 3.5 mM of Na_2CO_3 with 1.0 mM NaHCO_3 was used and a flow rate was set at 0.3 ml min^{-1} . An internal standard was run every 12 samples, and one check standard that was provided by Dionex was run for each set of samples. Chloride ion (Cl^-) was used as a conservative tracer to normalize the effect of evaporation during incubations, which may change the water volume and concentrations. We assumed that there was no Cl^- exchange between water and sediment. SRP was measured colorimetrically on a Thermo Fisher Scientific spectrophotometer (Duan et al., 2012), using the ascorbic acid-molybdate blue method (Murphy and Riley, 1962).

The grinded sediment samples were weighed in tin boats, and vapor-phase acidified overnight in a desiccator with HCl (fuming) to remove carbonates. The acidified samples were transferred back to the drying oven (60°C) again to remove HCl vapor residual, before being shipped to the Stable Isotope Facility at UC Davis for carbon

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and nitrogen isotope analyses. Carbon and nitrogen isotopic compositions ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) were determined by CF-IRMS and an elemental analyzer that converted organic N into N_2 gas and organic C into CO_2 gas. Precision was 0.3% for $\delta^{15}\text{N}$ and 0.2% for $\delta^{13}\text{C}$ for replicate analyses of reference standards. Sediment ash weight was calculated as the difference in weight before and after being combusted at 650°C for 4 h. Before combustion, sediments were dried at 90°C for 4 h to remove water. Ash weights were determined in triplicates.

2.5 Data analysis and statistics

Sediment fluxes per unit area were calculated by dividing the net changes in the masses of DOC, nitrate, SRP or sulfate with the area of water-sediment interface and the time of incubation period (48 h). The changes in the control flask (with water only), occurring in water without sediments, were subtracted to obtain the fluxes that were released from sediments. Positive and negative values represent net release from sediments or retention by sediments, respectively. Temperature effects on sediment fluxes and organic matter composition across varying land-uses were examined with one-way ANOVA in SPSS, by testing for differences among four groups – 4°C , 15°C , 25°C and 35°C with $p < 0.05$.

Relationships between sediment fluxes at the end of the incubations (48 h) and controlling parameters (temperature, impervious surface cover, and sediment characteristics) were tested using with linear or non-linear curves with $\alpha = 0.05$. For linear relationships, Spearman's correlation was used in cases where assumptions of normality were not met. For non-linear relationships, curve estimations were performed in SPSS and the best estimate (with lowest p-value) was selected.

The relationship between temperature and SRP flux at individual site was used to estimate the contributions of SRP loads from sediment to stream loads, as well as to predict an increase in sediment fluxes with warming by 5°C . Phosphorus is a common limiting nutrient and there is clear warming response for phosphorus, and it was used

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as a case study for prediction (Duan et al., 2012). Water temperature was measured monthly at all sites from July 2009 to June 2010 over an annual period at the 8 sites. The width of stream channel was also measured to estimate water-sediment interaction area, while stream length was estimated from a Geographical Information System map.

The buried length of stream channel of Gwynns Run (GFGR) was not included, given that many urban streams in Baltimore have been buried and placed into storm drains as a result of historical development (Elmore and Kaushal, 2008). For sediment loading calculations, the values of width and fluxes of each section of the Gwynns Fall were the averages of the beginning and the ending stations, while the average width of tributary channels was assumed to be 2/3 of the value measured each tributary site.

3 Result

3.1 Water and sediment chemistry

As expected, chemistry of streamwater that was used for incubations varied with land use (Table 2). DOC concentrations and protein-like to humic-like fluorescence (P/H) ratios increased with impervious surface cover (ISC), but the relationship was not significant ($R^2 = 0.29$ and 0.26 , $p = 0.17$ and 0.20). Concentrations of SRP and sulfate significantly increased with ISC ($R^2 = 0.72$ and 0.92 , $p = 0.007$ and 0.000). Nitrate concentrations were variable but higher at sites of the upper Gwynns Falls (GFGB, GFGL and MCDN) and an urban site with a sewage leak (GFGR) (Kaushal et al., 2011).

Sediment size fractionation varied with stream size and land use (Table 2), but showed an increase in particle size along the mainstem of the Gwynns Falls and with increasing watershed urbanization. The % ash weight and $\delta^{15}\text{N}$ increased from 1.3% and 0.63‰ at the forest site (POBR) to 3.8–6.7% and 1.95–1.89‰ at the degraded urban sites DRKR and GFGR, respectively. The % ash weight was positively correlated with impervious surface cover ($R^2 = 0.85$, $p = 0.001$). The $\delta^{13}\text{C}$, on the other hand, displayed the opposite pattern, and a depleted value was observed at urban GFGR.

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3.2 Temperature controls on sediment DOC fluxes and composition

Warming clearly altered the amount and quality of DOC fluxes from sediments. Increases in DOC concentration, humic-like fluorescence and protein-like fluorescence (not shown) and decreases in protein to humic (P/H) ratio occurred for all sites during the time course of the 48-h incubations at temperatures $\geq 15^\circ\text{C}$, with larger changes observed at higher incubation temperatures (Fig. 3). Changes in DOC concentration, humic-like fluorescence, protein-like fluorescence and P/H ratio during the 35°C incubation were 0.2–2.4, 1.0–3.0, 0.5–1.3 and 0.2–0.4 times that of their original values, respectively.

Sediment fluxes of DOC and changes in DOC composition (humic-like and protein-like fluorescence and their ratio) displayed significant differences among the 4 temperature groups ($p = 0.000$, one-way ANOVA). The mean fluxes of DOC, humic-like and protein-like matter showed positive nonlinear temperature effects, while the temperature effects on P/H ratio were consistently negative (Fig. 4).

3.3 Temperature controls on fluxes and concentrations of SRP, sulfate and nitrate

During the time course of the incubations, the effects of temperature on sediment fluxes differed for SRP, sulfate and nitrate concentrations. In general, SRP concentrations gradually increased during the incubations at temperatures $\geq 15^\circ\text{C}$, with larger increases observed at higher incubation temperatures (Fig. 5 left panels). The increases in SRP concentrations at 35°C were 2 to 15 times that of the original values. Sulfate concentrations also displayed a similar trend of change to that of SRP at rural (POBR and MCDN) and suburban (GFGL and GFGB) sites (Fig. 5 middle panels), although the increases ($< 2\text{ mg l}^{-1}$) were generally minor relative to stream sulfate levels ($2\text{--}54\text{ mg l}^{-1}$). Interestingly, sulfate concentrations at 3 urban sites (GFVN, GFGR and DRKR) showed substantial decreases during the later stage of the incubation at 25 and 35°C (e.g., up to 0.81 to 19.3 mg l^{-1} or 7% to 40% at 35°C). Incubations at the

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forest (POBR) and agricultural sites (MCDN) exhibited a linear increase or decrease in nitrate concentrations, respectively (Fig. 5 right panels). At suburban/urban sites, nitrate showed a gradual decrease in the beginning of the incubations followed by an increase during the later stage. The changes in nitrate were 0.3 to 2 times that of the original concentration.

There were also clear changes in fluxes of major bioreactive elements from sediments in response to warming (Fig. 6). SRP fluxes displayed a significant difference among the 4 temperature groups ($p < 0.001$, one-way ANOVA), and temperature effects on mean SRP fluxes was consistently positive, with values varying from retention or minor release at 4 °C to highest value at 35 °C. Sulfate fluxes displayed no significant difference among the 4 temperature groups ($p > 0.05$, one-way ANOVA); the difference was significant if only rural and suburban sites (POBR, MCDN, GFGL and GFGB) were included together, where a positive temperature effect could be observed ($p < 0.05$; Fig. 7). The difference in nitrate fluxes among the 4 temperature groups was also significant but there was more variability compared to SRP fluxes ($p = 0.03$, one-way ANOVA; Fig. 6). The temperature effect on mean nitrate flux was also positive, and the most apparent positive effect was observed at urban sites (Fig. 7).

3.4 Effect of land-use, sediment characteristics and water chemistry on sediment fluxes

Sediment fluxes also showed the influence of urban land use, indicated by the fraction of watershed impervious surface cover (ISC). For SRP and nitrate, sediment fluxes were negatively correlated with watershed impervious surface cover at 4 °C but positively correlated with watershed impervious surface cover at 35 °C (Fig. 8). In contrast, sulfate fluxes were positively correlated to watershed impervious surface cover at 4 °C and negatively correlated with watershed impervious surface cover at 35 °C. There was no strong correlation between DOC fluxes and watershed ISC (Fig. 6; $r^2 < 0.1$, $p > 0.05$).

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Sediment composition and water chemistry were potential explanatory variables for the fluxes. The fluxes of SRP and nitrate at 35 °C and sulfate at 15 °C were all positively correlated with sediment ash-weight ($r^2 = 0.65\text{--}0.80$, $p < 0.05$; Fig. 6), and stream water SRP ($r^2 = 0.53\text{--}0.90$, $p < 0.05$) and sulfate concentrations ($r^2 = 0.72\text{--}0.90$, $p < 0.05$). SRP flux was also positively correlated with with sediment $\delta^{15}\text{N}$ ($r^2 = 0.58$, $p < 0.05$). Sulfate flux at 35 °C, which showed sulfate retention, displayed an opposite (negative) correlation.

4 Discussion

4.1 Effects of temperature on transformation and fluxes of DOC, nitrate, SRP and sulfate

Temperature had substantial effects on biogeochemical fluxes in stream sediments across land use and indicated the importance of warming on influencing coupled biogeochemical cycles. The observed changes in DOC, nitrate, SRP and sulfate during the incubations were a result of temperature-dependent transformations of carbon, nitrate, phosphorus and sulfur that can also be described by previous sedimentary biogeochemical models (e.g., Middelburg and Levin, 2009). According to models that describe sedimentary diagenesis near the water-sediment interface, as sediment organic carbon decomposes along the sediment profile, dissolved oxygen (DO), nitrate, manganese/iron oxides ($\text{MnO}_2/\text{Fe}_2\text{O}_3$) and sulfate sequentially act as dominant electron acceptors. Because decomposition of sedimentary organic matter is a process that can be stimulated by warming (Arnosti et al., 1998; Gudasz et al., 2010), biogeochemical fluxes are enhanced at higher temperatures and may result in altered fluxes of SRP, sulphate, and nitrate in response to warming.

Bioreactive elements can cycle differently and undergo release or retention from sediments in response to warming and redox conditions. Dissolved organic carbon (DOC), the intermediate product of sedimentary organic carbon decomposition, can

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be released to the water column with increased temperature. Similarly, warming enhances the remineralization of organic N, P and S to nitrate, SRP and sulfate respectively. However, there can also be retention and recycling of nitrate and sulfate released to the overlying water column in response to warming because they can also service as electron receptors depending on redox conditions and oxygen availability. In contrast, SRP that is adsorbed onto $\text{MnO}_2/\text{Fe}_2\text{O}_3$ surfaces typically releases to stream water, as more MnO_2 and Fe_2O_3 are reduced at higher temperature with organic matter decomposition. Given that stream sediments are heterogeneous with respect to redox conditions, these reactions may also occur simultaneously in natural environments. Some further discussion of the temperature effects on fluxes of each element are provided below.

Consistent temperature-enhanced DOC fluxes across sites (Figs. 3 and 4) have been reported in lab experiments with sediments, soils and mor humus (Christ and David, 1996; Andersson et al., 2000; Marschner and Bredow, 2002) and field temperature manipulations of shallow aquifers (Wilson and Williams, 2006). Prior studies have shown that changes in air temperature may directly influence DOC export from peat soils by altering decomposition and mineralization of organic matter, both sensitive to changes in moisture and temperature (Freeman et al., 2001; Tranvik and Jansson, 2002; Worrall et al., 2003). Results of field temperature manipulations of shallow aquifers by Wilson and Williams (2006) showed significant increases in DOC with elevated temperatures (3.9–5.0 °C than ambient). DOC release from sediments or soils can be either abiotic (e.g., DOC dissolution and abiotic oxidation) and/or biotically mediated (via fungi and heterotrophic bacteria); both pathways are sensitive to temperature (e.g., White et al., 1991; Cheng et al., 2006). The former is generally considered to be far less important than the latter (Aguilar and Thibodeaux, 2005).

Our results indicate that increased temperatures also influence the composition and lability of sediment released DOC, with more humic substances than protein-like components at higher temperatures (Figs. 3 and 4). This change may be attributed to two possibilities: (1) sediment is enriched in humic substances (HS), and more HS is

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decomposed and release to water at higher temperatures and/or (2) the released labile (protein-like) fraction is preferentially used over the refractory (humic-like) component. In either case, DOC released from sediments will likely become more refractory with stream warming. This conclusion is similar to what has been found in soil warming experiments (Melillo et al., 2001, 2011) and decomposition of black carbon (Nguyen et al., 2010). Melillo et al. (2001, 2011) found over several years of soil warming 5 °C above ambient conditions, the labile soil carbon pool diminished and microbes adjusted to a more refractory carbon source. Nguyen et al. (2010) reported that decomposition of more refractory carbon was more sensitive to increased temperature than less stable materials.

Temperature-enhanced P transformations and SRP fluxes from sediments have been widely observed in lab incubations (House and Denison, 2002; Suplee and Cotner, 2002; James and Barko, 2004; Schulz and Herzog, 2004) and field temperature manipulations (e.g., Zhang et al., 2012). The consistent temperature dependence of SRP fluxes across sites is likely related to the fact that organic P mineralization and $\text{MnO}_2/\text{Fe}_2\text{O}_3$ reduction (two processes contributing to SRP release from sediments) can be enhanced at higher temperatures with organic matter (OM) decomposition. House and Denison (2002) found that equilibrium SRP concentrations under anoxic conditions (in response to organic matter decomposition) are an order of magnitude higher than in oxic environments. Because phosphate cannot act as an electron receptor (as nitrate and sulphate), there is no a decreased sink for released SRP under anoxic conditions. So, warmer temperatures can increase the water-sediment porewater SRP gradient, thereby facilitating the release SRP from sediment to water column (House and Denison, 2002).

In contrast to SRP, the role of sediment as a source or sink of nitrate and sulfate is the net result of organic N or S mineralization and/or nitrate and sulfate reduction. Denitrification (nitrate reduction) and nitrification (organic N oxidization) can both be increased as a function of temperature (Pfenning and McMahon, 1996; Saunders and Kalf, 2001; Carrera et al., 2003; Fdz-Polanco et al., 1994; Saidu, 2009). Thus, the

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effect of temperature on net nitrate release as a result of organic N mineralization may be partially counteracted by enhanced nitrate loss via denitrification and/or N immobilization. A few stream studies have shown that N immobilization into microbial cells occurs when labile carbon is present (Bernhardt and Likens, 2002; Kaushal and Lewis, 2005). Consequently, the patterns we observed for the changes in nitrate concentration were complicated (Fig. 5) and temperature effects on sediment nitrate fluxes were more variable than SRP and DOC (Figs. 6 and 7). We speculate that an initial decrease in nitrate followed by an increase in later stages of the incubations was likely attributed to denitrification and/or immobilization occurring at lower temperatures and nitrification at warmer temperatures well over 10 °C (Fdz-Polanco et al., 1994). More work is needed investigating the changing influence of temperature and redox conditions on the relative importance of nitrification vs. denitrification vs. N immobilization in stream sediments.

Compared to nitrogen and phosphorus, little is known regarding temperature effects on sediment sulfate fluxes. Our results suggest that there can be significant positive temperature effects on sulfate fluxes at rural and suburban sites (Figs. 5 and 7). As discussed earlier, this positive effect can be attributed to temperature-enhanced release of sulfate with organic sulfur mineralization. The mechanism for sulfate retention at higher temperatures at urban sites (Figs. 5 and 7) is likely due to sulfate reduction. Evidence from incubations suggests that sulfate retention occurred during later stages following the occurrence of nitrate retention (Fig. 5); this is consistent with the early diagenesis model showing that sulfate is used later than nitrate as an electron receptor. Additionally, sulfate retention occurred at urban sites with higher temperatures, under which the intensive decomposition of labile organic matter may decrease redox potential to the threshold level for sulfate reduction. Therefore, temperature effects on sulfate fluxes can be either positive or negative, depending on whether sulfate acts as an electron receptor. More work is necessary characterizing the cycling of sulfur in urban streams and determining the relative importance of sulfate reduction as a competing process with denitrification.

4.2 Response of sediment fluxes to warming across land use

Our results indicate that the effects of temperature on sediment fluxes of DOC, nitrate, SRP and sulfate can increase across a rural-urban gradient (indicated by watershed impervious surface cover, Fig. 8), with a greater warming effect in sediments from urban than rural sites. The mechanism for greater response of sediment biogeochemical fluxes in urbanized watersheds can be indicated by stream water chemistry and sediment composition. Table 2 and studies at the Baltimore LTER site have found that suburban and urban watersheds have higher concentrations of nitrogen, sulfur and phosphorus than forested watersheds (e.g., Groffman et al., 2004; Kaushal et al., 2008; Duan et al., 2012; Kaushal and Belt, 2012), which provide nutrients for growth of microbial communities. Prior studies have shown that the abundance and activity of bacteria and fungi, the organisms that transform organic C, N, P and S, are generally higher in urban watersheds than rural watersheds (e.g., Imberger et al., 2008). The supporting evidence for nutrient-stimulated microbial activities include that fluxes of SRP, nitrate and sulfate at 35 °C were all correlated with stream water SRP ($r^2 = 0.53\text{--}0.90$, $p < 0.05$) – a potential limiting nutrient and master variable for biological processes in many freshwater ecosystems.

Other work shows that biologically mediated transformation of C, N, P and S are highly dependent on organic matter quality because heterotrophic microbes require a carbon source (Arnosti et al., 1998; Schulz and Herzog, 2004; Kaushal and Lewis, 2005; Saidu, 2009; Zhang et al., 2012). In this study, we found significant relationships between fluxes of nitrate, SRP and sulfate retention with sediment % ash weight ($r^2 = 0.65\text{--}0.80$, $p < 0.05$) – an proxy for organic matter in sediments. SRP flux was also positively correlated with $\delta^{15}\text{N}$ – a tracer for organic matter from sewage and manure sources which are considered to be more labile than natural organic matter sources. Prior studies at the BES LTER site (e.g., Newcomer et al., 2012) show that organic matter composition or lability is an important variable influencing rate of denitrification. Because of increased availability of limiting nutrients and labile organic carbon,

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biotically mediated fluxes of nitrate, SRP and sulfate (retention or net release) may have increased with urbanization at both low (4 °C) and high (35 °C) temperatures (Fig. 8).

Sediment size, porosity, and composition may also play a role in the changes in sediment fluxes with land use. Larger porosity in coarse sediments may facilitate solute exchange between sediments and stream water and therefore may result in larger sediment fluxes. However, we did not observe a significant correlation between sediment fluxes and sediment size, suggesting less potential importance of particle size relative to other biogeochemical controls. Additionally, higher fluxes of DOC, SRP, nitrate and sulfate at urbanized sites can be directly attributed to higher contents of total organic carbon, nitrogen, phosphorus and sulfur in incubated sediments than those at the rural sites, but we did not account for all these variables. Future studies should examine these factors in urban watersheds, and possible relationships to microbial community composition and organic matter bioavailability across sites.

4.3 Predicting warming impacts in streams

The potential interactive effects of land use and temperature on biogeochemical fluxes from stream sediments can be depicted in a hypothetical conceptual model predicting DOC, SRP, nitrate and sulfate fluxes (Fig. 9). The effect can be further depicted with 2-variable linear regressions listed in Table 3. As shown in the conceptual model and slopes of the linear regression equation, DOC fluxes from sediments may increase initially with stream temperature and watershed urbanization (indicated by ISC) due to more organic matter decomposition and transformation. But, the quality of DOC lability can be considerably reduced reflecting products of increased microbial metabolism. SRP fluxes may increase with stream temperature and urbanization due to organic P mineralization and later on the desorption processes associated with reduction of magnesium/iron oxides and sulfate. Sulfate fluxes at rural sites may increase due to organic sulfur mineralization, but there may be sulfate reduction at urban sites with high organic matter content and low redox potential (Fig. 9 and Table 2). Although less clear, we hypothesize that nitrate fluxes can increase due to mineralization of

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organic nitrogen but are counteracted by a greater relative importance of denitrification and/or N immobilization at lower temperatures and/or reduced redox conditions. But, this hypothesis regarding the effects of warming on shifts in the N cycle requires further testing.

Another implication from the conceptual model is that the relative importance of nitrate may be replaced by sulfate as an electron receptor for organic matter mineralization in some urban streams with low redox conditions and high levels of organic matter. Prior studies have shown that ammonia oxidation is coupled to the reductions of Mn oxides, Fe oxides and sulfate under anaerobic conditions (e.g., Giray and King, 1997; Clément et al., 2005; Javanaud et al., 2011). This hypothesized replacement may occur due to increased labile DOC, low redox, and different microbial communities in urban environments. In particular, studies on sulfate reduction in hyporheic zones of urban streams are in need, because sulfate reduction can be related to geochemical cycles of mercury (e.g., mercury methylation; Gilmour et al., 1992) and other metals.

5 Conclusions

We found that warming water temperatures can increase stream SRP concentrations and influence the quantity and quality of DOC. An increase in SRP concentrations can influence downstream eutrophication potential and changes in carbon quality may impact foodwebs and microbial metabolism (e.g., Schindler et al., 1971; Godfrey and Mitchell, 1972). For example, using the regression curves describing the change in sediment fluxes with temperature (supporting material), we crudely estimate current sediment fluxes and their changes with a 5°C warming in stream temperature (Table 4). We predict that a 5°C warming would substantially increase the SRP flux from sediment by 96 % to 390 % which could influence downstream eutrophication potential.

Although there was no trend of increase in stream temperatures in the Gwynns Falls during the last 20 yr (Fig. 2), long-term temperature records in other streams and rivers show warming trends (e.g., Webb and Nobilis, 2007; Kaushal et al., 2010; Seekell and

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Pace, 2011; Isaak et al., 2012), and variability in extremes in water temperature are also important in urban streams (Kaushal et al., 2010). Warming may have the potential to influence net nitrogen mineralization in rural watersheds (Brookshire et al., 2011; Butler et al., 2012), but our results regarding warming effects on N fluxes show a larger variability than SRP if all land use type are included. Further work is necessary regarding the impacts of stream warming on microbial processes, sulfur cycling, and coupled impacts on carbon, nitrogen, phosphorus, and metals in sediments of streams and rivers.

Supplementary material related to this article is available online at:

<http://www.biogeosciences-discuss.net/9/11293/2012/bgd-9-11293-2012-supplement.pdf>

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References

- Aguilar, L. and Thibodeaux, L. J.: Kinetics of peat soil dissolved organic carbon release from bed sediment to water – Part 1: Laboratory simulation, *Chemosphere*, 58, 1309–1318, 2005.
- Andersson, S., Nilsson, S. I., and Saetre, P.: Leaching of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in mor humus as affected by temperature and pH, *Soil Biol. Biochem.*, 32, 1–10, doi:10.1016/S0038-0717(99)00103-0, 2000.
- Arango, C. P., Tank, L. J. L., Johnson, T., and Hamilton, S. K.: Assimilatory uptake rather than nitrification and denitrification determines nitrogen removal patterns in streams of varying land use, *Limnol. Oceanogr.*, 53, 2558–2572, 2008.

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- Arnosti, C., Jørgensen, B. B., Sagemann, J., and Thamdrup B.: Temperature dependence of microbial degradation of organic matter in marine sediments: polysaccharide hydrolysis, oxygen consumption, and sulfate reduction, *Mar. Ecol.-Progr. Ser.*, 165, 59–70, doi:10.3354/meps165059, 1998.
- 5 Balcarczyk, K. L., Jones, J. B., Jaffe, R., and Maie, N.: Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost, *Biogeochemistry*, 94, 255–270, doi:10.1007/s10533-009-9324-x, 2009.
- Battin, T. J. Kaplan, L. A., Findlay, S., Hopkinson, C. S., Marti, E., Packman, A. I., Newbold, D. J., and Sabater, F.: Biophysical controls on organic carbon fluxes in fluvial networks, *Nat.*
- 10 *Geosci.*, 1, 95–100, doi:10.1038/ngeo101, 2008.
- Bernhardt, E. S. and Likens, G. E.: Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream, *Ecology*, 83, 1689–1700, 2002.
- Bowes, M. J., House, W. A., and Hodgekinson, R. A.: Phosphorus dynamics along a river continuum, *Sci. Total Environ.*, 313, 199–212, doi:10.1016/S0048-9697(03)00260-2, 2003.
- 15 Brookshire, E. N. J., Gerber, S., Webster, J. R., Vose, J. M., and Swank, W. T.: Direct effects of temperature on forest nitrogen cycling revealed through analysis of long-term watershed records, *Global Change Biol.*, 17, 297–308, doi:10.1111/j.1365-2486.2010.02245.x, 2011.
- Butler, S. M., Melillo, J. M., Johnson, J. E., Mohan, J., Steudler, P. A., Lux, H., Burrows, E., Smith, R. M., Vario, C. L., Scott, L., Hill, T. D., Aponte, N., and Bowles, F.: Soil warming alters
- 20 nitrogen cycling in a New England forest: implications for ecosystem function and structure, *Oecologia*, 168, 819–828, doi:10.1007/s00442-011-2133-7, 2012.
- Carrera, J., Vicent, T., and Lafuente, F. J.: Influence of temperature on denitrification of an industrial high-strength nitrogen wastewater in a two-sludge system, *Water Sa*, 29, 11–16, 2003.
- 25 Chapin III, F. S., Power, M. E., and Cole, J. J.: Coupled biogeochemical cycles and Earth stewardship, *Front. Ecol. Environ.*, 9, p. 3, doi:10.1890/1540-9295-9.1.3, 2011.
- Cheng, C. H., Lehmann, J., Thies, J. E., Janice, E., Burton, S. D., and Engelhard, M. H.: Oxidation of black carbon by biotic and abiotic processes, *Org. Geochem.*, 37, 1477–1488, 2006.
- Christ, M. J. and David, M. B.: Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol, *Soil Biol. Biochem.*, 28, 1191–1199, doi:10.1016/0038-0717(96)00120-4, 1996.
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- Clement, J., Shrestha, J., Ehrenfeld, J., and Jaffe, P.: Ammonium oxidation coupled to dissimilatory reduction of iron under anaerobic conditions in wetland soils, *Soil Biol. Biochem.*, 37, 2323–2328, doi:10.1016/j.soilbio.2005.03.027, 2005.
- Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, *Mar. Chem.*, 51, 325–346, 1996.
- Dail, D. B. and Fitzgerald, J. W.: S Cycling in soil and stream sediment: influence of season and in situ concentrations of carbon, nitrogen and sulfur, *Soil Biol. Biochem.*, 31, 1395–1404, 1999.
- Duan, S. W., Kaushal, S. S., Groffman, P. M., Band, L. E., and Belt, K. T.: Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed, *J. Geophys. Res.-Biogeo.*, 117, G01025, doi:10.1029/2011JG001782, 2012.
- Elmore, A. J. and Kaushal, S. S.: Disappearing headwaters: patterns of stream burial due to urbanization, *Front. Ecol. Environ.*, 6, 308–312, doi:10.1890/070101, 2008.
- Fdz-Polanco, F., Villaverde, S., and Garcid, P. A.: Temperature effect on nitrifying bacteria activity in biofilters: activation and free ammonia inhibition, *Water Sci. Technol.*, 30, 121–130, 1994.
- Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B., and Fenner, N.: Export of organic carbon from peat soils, *Nature*, 412, 785–785, doi:10.1038/35090628, 2001.
- Froelich, P. N.: Kinetic control of dissolved phosphate in natural rivers and estuaries – a primer on the phosphate buffer mechanism, *Limnol. Oceanogr.*, 33, 649–668, 1988.
- Gilmour, C. C., Henry, E. A., and Mitchell, R.: Sulfate Stimulation of Mercury Methylation in Freshwater Sediments, *Environ. Sci. Technol.*, 26, 2281–2287, 1992.
- Giray, C. and King, G. M.: Effect of naturally occurring bromophenols on sulfate reduction and ammonia oxidation in intertidal sediments, *Aquat. Microb. Ecol.*, 13, 295–301, 1997.
- Godfrey, P. and Mitchell, D.: Eutrophication and Phosphate Detergents, *Science*, 177, 816–817, doi:10.1126/science.177.4051.816, 1972.
- Groffman, P. M., Law, N. L., Belt, K. T., Band, L. E., and Fisher, G. T.: Nitrogen fluxes and retention in urban watershed ecosystems, *Ecosystems*, 7, 393–403, 2004.
- Gudasz, C., Bastviken, D., Steger, K., Premke, K., Sobek, S., and Tranvik, L. J.: Temperature-controlled organic carbon mineralization in lake sediments, *Nature*, 466, 478–481, doi:10.1038/nature09186, 2010.
- House, W. A. and Denison, F. H.: Exchange of inorganic phosphate between river waters and bed-sediments, *Environ. Sci. Technol.*, 36, 4295–4301, doi:10.1021/es020039z, 2002.

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Howarth, R., Chan, F., Conley, D. J., Garnier, J., Doney, S. C., Marino, R., and Billen, G.: Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems, *Front. Ecol. Environ.*, 9, 18–26, doi:10.1890/100008, 2011.

Hudson, N., Baker, A., and Reynolds, D.: Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters – A review, *River Res. Appl.*, 23, 631–649, doi:10.1002/rra.1005, 2007.

Imberger, S. J., Walsh, C. J., and Grace, M. R.: More microbial activity, not abrasive flow or shredder abundance, accelerates breakdown of labile leaf litter in urban streams, *J. N. Am. Benthol. Soc.*, 27, 549–561, doi:10.1899/07-123.1, 2008.

Isaak, D. J., Wollrab, S., Horan, D., and Chandler, G.: Climate change effects on stream and river temperatures across the northwest US from 1980–2009 and implications for salmonid fishes, *Climatic Change*, 113, 499–524, doi:10.1007/s10584-011-0326-z, 2012.

James, W. F. and Barko, J. W.: Diffusive fluxes and equilibrium processes in relation to phosphorus dynamics in the Upper Mississippi River, *River Res. Appl.*, 20, 473–484, 2004.

Javanaud C., Michotey, V. D., Guasco, S., Garcia, N., Anschutz, P., Canton, M., and Bonin, P. C.: Anaerobic ammonium oxidation mediated by Mn-oxides: from sediment to strain level, *Res. Microbiol.*, 162, 848–857, 2011.

Jensen, H. S. and Anderson, F. O.: Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of four shallow eutrophic lakes, *Limnol. Oceanogr.*, 37, 577–589, 1992.

Kaplan, L. A., Wiegner, T. N., Newbold, J. D., Ostrom, P. H., and Gandhi, H.: Untangling the complex issue of dissolved organic carbon uptake: a stable isotope approach, *Freshwater Biol.*, 53, 855–864, doi:10.1111/j.1365-2427.2007.01941.x, 2008.

Kaushal, S. S. and Lewis, W. M.: Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA, *Biogeochemistry*, 74, 303–321, doi:10.1007/s10533-004-4723-5, 2005.

Kaushal S. S. and Belt, K. T.: The urban watershed continuum: evolving spatial and temporal dimensions, *Urban Ecosystems*, 15, 409–435, doi:10.1007/s11252-012-0226-7, 2012.

Kaushal, S. S., Groffman, P. M., Likens, G. E., Belt, K. T., Stack, W. P., Kelly, V. R., Weathers, K. C., Band, L. E., and Fisher, G. T.: Increased salinization of fresh water in the northeastern US, *P. Natl. Acad. Sci. USA*, 102, 13517–13520, 2005.

Kaushal, S. S., Groffman, P. M., Band, L. E., Shields, C. A., Morgan, R. P., Palmer, M. A., Belt, K. T., Fisher, G. T., Swan, C. M., and Findlay, S. E. G.: Interaction between urbanization and

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climate variability amplifies watershed nitrate export in Maryland, *Environ. Sci. Technol.*, 42, 5872–5878, doi:10.1021/es800264f, 2008a.

Kaushal, S. S., Groffman, P. M., Mayer, P. M., Striz, E., Doheny, E. J., and Gold, A. J.: Effects of stream restoration on denitrification at the riparian-stream interface of an urbanizing watershed of the mid-Atlantic US, *Ecol. Appl.*, 18, 789–804, 2008b.

Kaushal, S. S., Likens, G. E., Jaworski, N. A., Pace, M. L., Sides, A. M., Seekell, D., Belt, K. T., Secor D. H., and Wingate, R. L.: Rising stream and river temperatures in the United States, *Front. Ecol. Environ.*, 8, 461–466, doi:10.1890/090037, 2010.

Kaushal, S. S., Groffman, P. M., Band, L. E., Elliott, E. M., Shields, C. A., and Kendall, C.: Tracking Nonpoint Source Nitrogen Pollution in Human-Impacted Watersheds, *Environ. Sci. Technol.*, 45, 8225–8232, doi:10.1021/es200779e, 2011.

Kim, H. J.: Temperatures of urban streams: Impervious surface cover, runoff, and the importance of spatial and temporal variations, M.S. Thesis, Department of Civil and Environmental Engineering, University of Maryland Baltimore County, Maryland, USA, 2007.

Lønborg, C., Alvarez-Salgado, X. A., Davidson, K., Martinez-Garcia, S., and Teira, E.: Assessing the microbial bioavailability and degradation rate constants of dissolved organic matter by fluorescence spectroscopy in the coastal upwelling system of the Ria de Vigo, *Mar. Chem.*, 119, 121–129 doi:10.1016/j.marchem.2010.02.001, 2010.

Marschner, B. and Bredow, A.: Temperature effects on release and ecologically relevant properties of dissolved organic carbon in sterilised and biologically active soil samples, *Soil Biol. Biochem.*, 34, 459–466, 2002.

Melillo, J. M., Steudler, P. A., Aber, J. D., Newkirk, K., Lux, H., Bowles, F. P., Catricala, C., Magill, A., Ahrens, T., and Morrisseau, S.: Soil warming and carbon-cycle feedbacks to the climate system, *Science*, 298, 2173–2176, doi:10.1126/science.1074153, 2002.

Melillo, J. M., Butler, S., Johnson, J., Mohan, J., Steudler, P., Lux, H., Burrows, E., Bowles, F., Smith, R., Scott, L., Vario, C., Hill, T., Burton, A., Zhou, Y. M., and Tang, J.: Soil warming, carbon-nitrogen interactions, and forest carbon budgets, *P. Natl. Acad. Sci. USA*, 108, 9508–9512, doi:10.1073/pnas.1018189108, 2011.

Middelburg, J. J. and Levin, L. A.: Coastal hypoxia and sediment biogeochemistry, *Biogeochemistry*, 6, 1273–1293, doi:10.5194/bg-6-1273-2009, 2009.

Murphy, J. and Riley, J. P.: A modified single solution method for determination of phosphate in natural waters, *Anal. Chim. ACTA*, 27, 31–36, doi:10.1016/S0003-2670(00)88444-5, 1962.

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- Nguyen, B. T., Lehmann, J., Hockaday, W. C., Joseph, S., and Masiello, C. A.: Temperature sensitivity of black carbon decomposition and oxidation, *Environ. Sci. Technol.*, 44, 3324–3331, doi:10.1021/es903016y, 2010.
- O'Driscoll, M., Clinton, S., Jefferson, A., Manda A., and McMillan, S.: Urbanization Effects on Watershed Hydrology and In-Stream Processes in the Southern United States, *Water*, 2, 605–648, doi:10.3390/w2030605, 2010.
- Pfenning, K. S. and McMahon, P. B.: Effect of nitrate, organic carbon, and temperature on potential denitrification rates in nitrate-rich riverbed sediments, *J. Hydrol.*, 187, 283–295, 1996.
- Saidu, M.-G.: Ph.D. Dissertation, Temperature impact on nitrification and bacterial growth kinetics in acclimating recirculating aquaculture systems biofilters, Louisiana State University, Agricultural and Mechanical College, 2009.
- Saunders, D. L. and Kalf, J.: Denitrification rates in the sediment of Lake Memphremagog, Canada, USA, *Water Res.*, 35, 1897–1904, 2001.
- Schindler, D. W., Armstrong, F. A. J., Holmgren, S. K., and Brunskill, G. J.: Eutrophication of Lake 227, Experimental Lakes Area, Northwestern Ontario, by addition of phosphate and nitrate, *J. Fish. Res. Board Can.*, 28, 1763–1781, 1971.
- Schlesinger, W. H., Cole, J. J., Finzi, A. C., and Holland, E. A.: Introduction to coupled biogeochemical cycles, *Front. Ecol. Environ.*, 9, 5–8, doi:10.1890/090235, 2011.
- Schulz, M. and Herzog, C.: The influence of sorption processes on the phosphorus mass balance in a eutrophic German lowland river, *Water Air Soil Pollut.*, 155, 291–301, 2004.
- Seekell, D. A. and Pace, M. L.: Climate change drives warming in the Hudson River Estuary, New York, USA, *J. Environ. Monitor.*, 13, 2321–2327, doi:10.1039/c1em10053j, 2011.
- Seitzinger, S. P.: Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance, *Limnol. Oceanogr.*, 33, 702–724, 1988.
- Stolpe, B., Guo, L., Shiller, A. M., and 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.*, 118, 119–128, doi:10.1016/j.marchem.2009.11.007, 2010.

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Tranvik, L. J. and Jansson, M.: Climate change – Terrestrial export of organic carbon, *Nature*, 415, 861–862, 2002.

Walker, S. A., Amon, R. M. W., Stedmon, C., Duan, S. W., and Louchouart, P.: The use of PARAFAC modeling to trace terrestrial dissolved organic matter and finger-print water masses in Canadian Arctic surface waters, *J. Geophys. Res.-Biogeo.*, 114, G00F06 doi:10.1029/2009JG000990, 2009.

Webb, B. W. and Nobilis, F.: Long-term changes in river temperature and the influence of climatic and hydrological factors, *Hydrol. Sci. J.*, 52, 74–85, doi:10.1623/hysj.52.1.74, 2007.

White, P. A., Kalf, J., Rasmussen, J. B., and Gasol, J. M.: The effect of temperature and algal biomass on bacterial production and specific growth-rate in fresh-water and marine habitats, *Microb. Ecol.*, 21, 99–118, 1991.

Wilson, K. P. and Williams, D. D.: Response of dissolved organic carbon in a shallow ground-water ecosystem to a simulated global warming experiment, in: *Geo-Environment and Landscape Evolution II*, Institute of Technology Press Press, Southampton, UK, 163–174, 2006.

Worrall, F., Burt, T. P., and Shedden, R.: Long terms records of riverine carbon flux, *Biogeochemistry*, 64, 165–178, 2003.

Zhang, Z. J., Wang, Z. D., Holden, J., Xu, X. H., Wang, H., Ruan, J. H., and Xu, X.: The release of phosphorus from sediment into water in subtropical wetlands: a warming microcosm experiment, *Hydrol. Process.*, 26, 15–26, doi:10.1002/hyp.8105, 2012.

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S. S. Kaushal**Table 1.** Characteristics of study subwatersheds.

Sites	POBR	MCDN	GFGB	GFGL	GFVN	GFCP	DRKR	GFGR	
Type	forest	agriculture	suburban	suburban	suburban/ urban	urban	urban	urban	
Area (ha)	0.38	0.1	11	0.8	84.2	170.7	14.3	6.5	
Land Use ^a	%ISC ^b	0	0.1	15	19	17	24	45	61
	%Forest	100	26	17	19	24	18	5	1.6
	%agriculture	0	70	8	5	10	6	2	0
	Runoff (m)	0.57	0.35	0.41	0.34	0.42	0.45	0.58	0.5

^a Catchment land cover and impervious surface data are from Shields et al. (2008) and the National Land Cover Database (NLCD).

^b ISC refers to Impervious land use.

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Table 2. Water chemistry, sediment size and chemical composition prior to incubation experiments.

Site		POBR	MCDN	GFGB	GFGL	GFVN	GFCP	DRKR	GFGR
	Variables	forest	agriculture	suburban	suburban	suburban/ urban	urban	urban	urban
Water chemistry	DOC (mg l ⁻¹)	1.89	1.82	1.95	4.37	2.12	2.78	3.59	3.00
	P/H ratio	0.40	0.41	0.39	0.28	0.42	0.49	0.48	0.48
	NO ₃ -N (mg l ⁻¹)	0.01	1.37	1.92	1.18	1.16	0.89	0.56	2.23
	SRP (μg l ⁻¹)	1.15	1.67	2.97	4.48	3.28	4.85	7.93	33.5
	SO ₄ -S (mg l ⁻¹)	2.0	8.3	6.6	23.5	10.9	18.6	34.0	53.7
Sediment size fractions (%)	< 0.0625 mm	0.5	1.6	0.8	2.6	0.6	0.2	1.4	0.03
	0.0625–0.125 mm	0.6	1.8	1.0	2.5	0.9	0.2	1.7	0.03
	0.125–0.25 mm	3.3	11.4	7.6	11.8	4.7	1.1	8.5	0.6
	0.25–0.5 mm	9.5	46.4	19.7	37.5	13.8	4.8	15.6	2.8
	2–0.5 mm	37.1	34.9	36.9	37.0	25.5	41.2	21.8	21.2
	> 2 mm	49.0	3.9	33.9	8.6	54.5	52.4	51.0	75.4
Sediment chemistry	Ash wt (%)	1.3	2.0	1.4	2.7	1.8	2.7	3.8	6.7
	δ ¹³ C (‰)	-27.3	-25.5	-25.5	-25.6	-25.5	-21.4	-19.6	-27.3
	δ ¹⁵ N (‰)	0.63	1.50	1.30	1.20	2.24	1.70	1.95	1.89

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Table 3. Linear regressions of SRP, nitrate, sulfate and DOC fluxes with incubation temperature and watershed impervious surface cover (%ISC).

DOC ($\text{g m}^{-2} \text{d}^{-1}$) = $0.0707 \times t (^{\circ}\text{C}) + 0.0141 \times \% \text{ISC} - 0.78$	($R^2 = 0.514$, $F = 15.3$, $p = 0.000$)
SRP ($\text{mg m}^{-2} \text{d}^{-1}$) = $0.514 \times t (^{\circ}\text{C}) + 0.0984 \times \% \text{ISC} - 7.21$	($R^2 = 0.690$, $F = 32.3$, $p = 0.000$)
NO_3 ($\text{g m}^{-2} \text{d}^{-1}$) = $0.0097 \times t (^{\circ}\text{C}) + 0.0012 \times \% \text{ISC} - 0.23$	($R^2 = 0.278$, $F = 5.6$, $p = 0.009$)
SO_4^* ($\text{g m}^{-2} \text{d}^{-1}$) _{rural + suburban} = $0.0155 \times t (^{\circ}\text{C}) + 0.0049 \times \% \text{ISC} - 0.653$	($R^2 = 0.621$, $F = 13.9$, $p = 0.000$)
SO_4^* ($\text{g m}^{-2} \text{d}^{-1}$) _{urban} = $-0.148 \times t (^{\circ}\text{C}) - 0.0590 \times \% \text{ISC} + 4.003$	($R^2 = 0.531$, $F = 5.1$, $p = 0.033$)

* The regressions for SO_4 are divided into two groups – rural and suburban (POBR, MCDN, GFGL and GFGB), and urban (GFGR, DRKR, GFVN and GFCP).

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Table 4. Estimated SRP release from stream sediment without and with 5 °C-warming.

	Sediment release (kg yr ⁻¹)	Stream load ^a (kg yr ⁻¹)	Sediment Contribution %	$\Delta\text{Release}_{\text{warming}}^{\text{b}}$ (kg yr ⁻¹)	$\Delta\text{Release}_{\text{warming}}/\text{sediment release}$ %
GFGR	1.7	67	2.6	5.7	338
DRKR	14.2	85	16.6	17.1	120
GFVN	25.8	300	8.6	98.1	391
GFCP	82.9	763	10.9	135.5	175
GFGL	1.30	9.3	14.0	1.04	96
GFGB	5.8	49.9	11.6	12.1	232
MCDN	0.05	1.16	4.4	0.13	229
POBR	0.09	0.41	21.4	0.26	249

^a Data for annual SRP loads are from Duan et al. (2012).

^b $\Delta\text{Release}_{\text{warming}}$ are the changes in sediment SRP release with 5 °C-warming.

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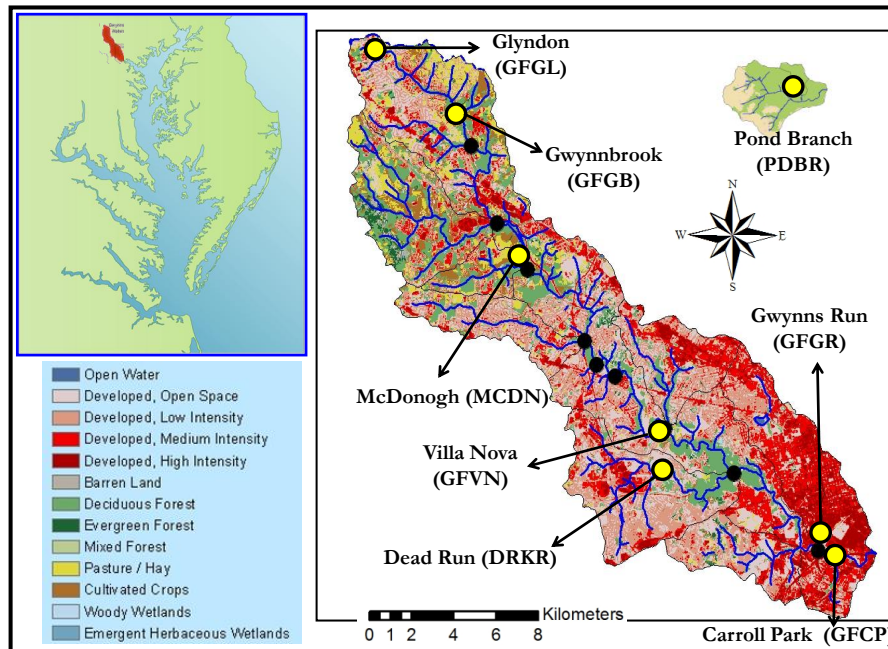


Fig. 1. Land use of the Gwynns Falls and Baisman Run watersheds, showing sites from which sediment and water were collected for sediment incubations.

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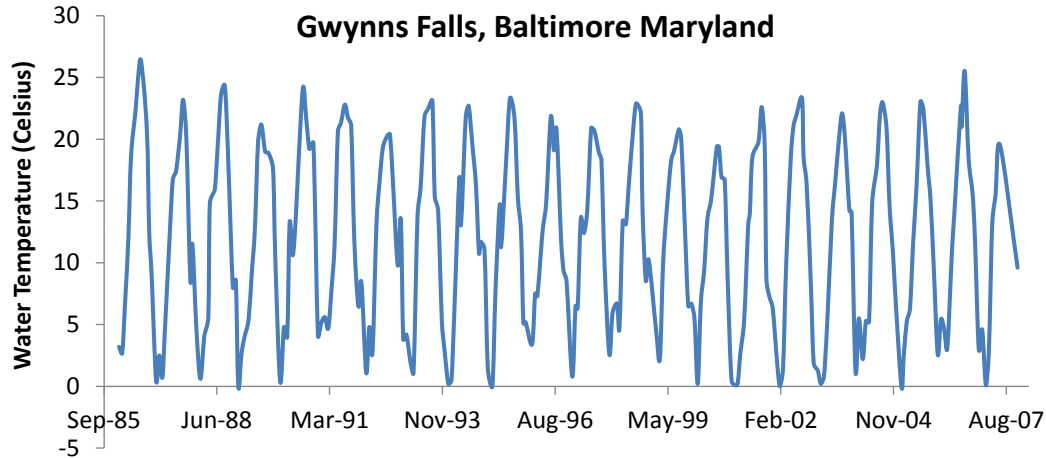


Fig. 2. Time series of water temperature at the Gwynns Falls at Villa Nova (GFVN).

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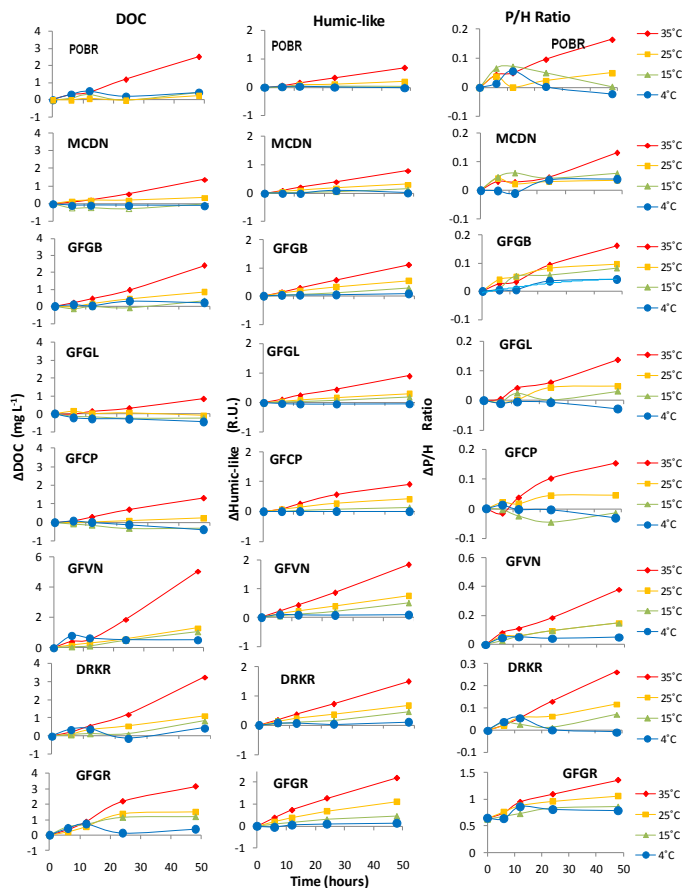


Fig. 3. Changes in DOC concentration, humic-like fluorescence and the ratio of protein-like fluorescence to humic-like fluorescence (P/H ratio) during the 48 h sediment incubations, relative to initial values before incubation. The scale of humic-like fluorescence is in Raman Unit (R.U.).

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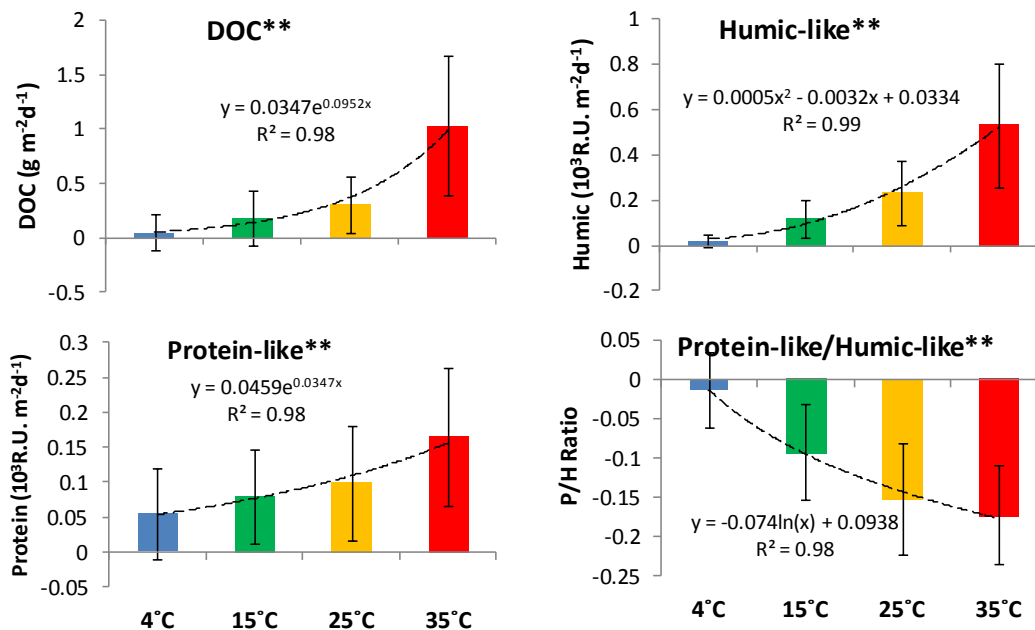


Fig. 4. Changes in DOC flux and composition (humic-like fluorescence and protein to humic or P/H ratio) with incubation temperature (all sites included). Means and standard errors are presented, and best fit regression lines are added to the averages. ** and * indicate significant level $p < 0.001$ and $p < 0.05$ of one-way ANOVA analysis for difference among 4 temperature groups, respectively.

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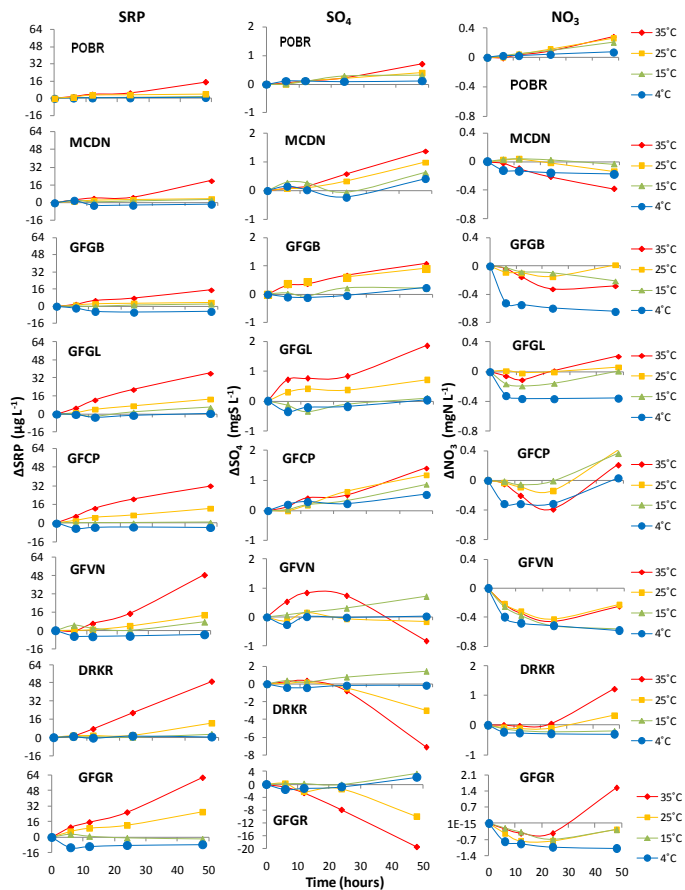
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Fig. 5. Changes in nitrate, SRP and sulfate concentrations during the 48 h sediment incubations, relative to initial values before incubation.

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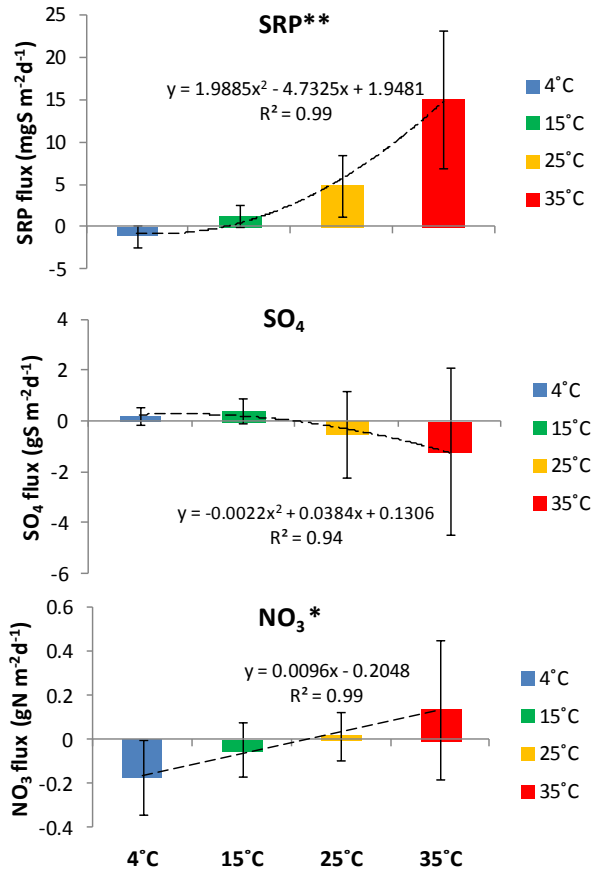


Fig. 6. Fluxes of SRP, sulfate and nitrate with incubation temperature. Means and standard errors are presented, and best fit regression lines are added to the averages. ** indicates significance level $p < 0.001$, and * indicates significance level $p < 0.05$ of one-way ANOVA analysis for differences among 4 temperature groups.

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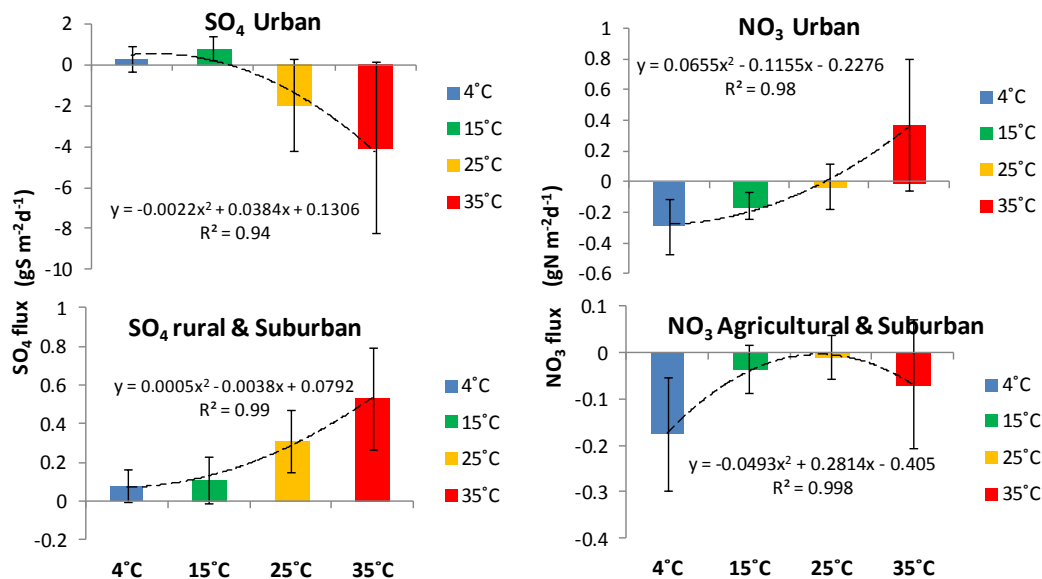


Fig. 7. Difference in temperature dependence of sulfate and nitrate fluxes between urban and suburban/rural sites. Urban sites include: GFGR, DRKR, GFCP and GFVN, whereas suburban and rural sites refers to: GFGL (suburban), GFGB (suburban), POBR (forest), and MCDN (agricultural). Means and standard errors are presented, and best fit regression lines are added to the averages.

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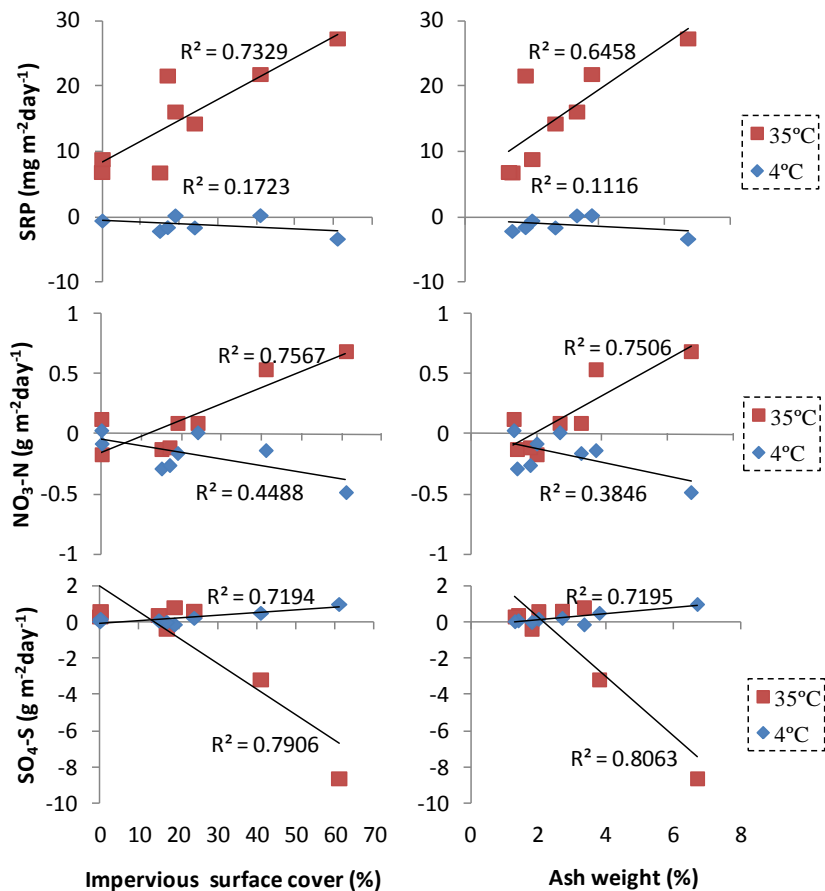


Fig. 8. Relationship of sediment fluxes of DOC, nitrate, SRP and sulfate at 4°C and 35°C with watershed impervious surface cover (ISC) and percent of sediment ash weight.

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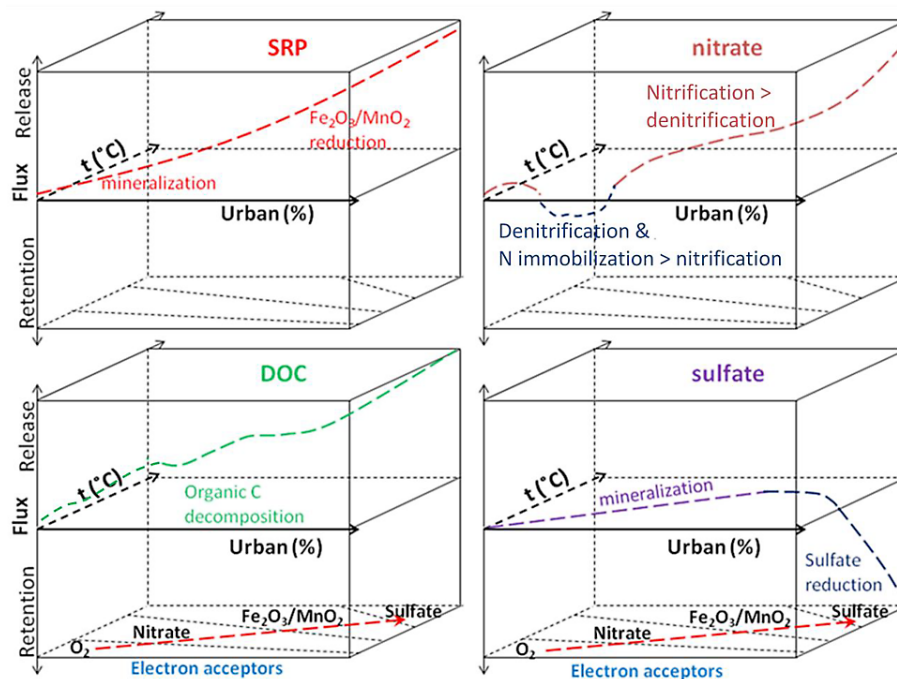


Fig. 9. Conceptual model of how temperature and land use impact C, N, S, P fluxes in stream sediments. Given that stream sediments are heterogeneous with respect to redox conditions, these reactions may occur simultaneously in streams in nature. Different colors are used to represent positive (release) and negative (retention) values for sediment fluxes.

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