SPECIAL ISSUE-CURRENT EVIDENCE

Stoichiometry of carbon, nitrogen, and phosphorus through the freshwater pipe

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Scientific Significance Statement

Freshwaters play a critical role in changing the quantity, quality, and rates of carbon inputs from land to the ocean. This role has been captured in the "freshwater pipe" concept, which has improved our understanding of freshwater carbon cycling. However, the freshwater pipe concept has not been applied to macronutrients such as nitrogen and phosphorus, and has not considered these nutrients jointly with carbon. Here, we synthesize the important drivers of freshwater carbon-nutrient biogeochemistry within the freshwater pipe and develop a conceptual model for the coupled fate of carbon, nitrogen, and phosphorus from land to the ocean.

Abstract

The "freshwater pipe" concept has improved our understanding of freshwater carbon (C) cycling, however, it has rarely been applied to macronutrients such as nitrogen (N) or phosphorus (P). Here, we synthesize knowledge of the processing of C, N, and P together in freshwaters from land to the ocean. We compared flux estimates into and out of the N and P "pipes" and showed the net removal rates of N and P by inland waters were less than those for C. The C : N : P stoichiometry of inland water inputs vs. exports differed due to large respiratory C and N losses, and efficient P burial in inland waters. Residence time plays a critical role in the processing of these elements through the pipe, where higher water residence times from streams to lakes results in substantial increases in C : N, C : P, and N : P ratios.

Stoichiometry of the freshwater pipe: The challenge

Our understanding of freshwater systems in the context of the global carbon (C) cycle has benefited greatly in the past decade from the development of the "pipe model" (Cole et al. 2007; Tranvik et al. 2009) and a concerted research effort to understand C biogeochemistry in inland waters. The main objective of that model was to determine whether internal C biogeochemical processing in freshwaters

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was relevant in a global context with the null model being that freshwaters are simply passive pipes that carry all of the allochthonous C loaded into them downstream to the oceans. The important conclusion drawn from the original synthesis, and subsequent studies, was that freshwaters are far from a passive pipe and serve as active C reactors. Indeed inorganic and organic C are extensively processed internally, resulting in significant net losses of terrigenous organic material along the way either through atmospheric flux or sediment burial.

Most of these studies, however, paid little attention to the accompanying fluxes and processing of other elements such as nitrogen (N) and phosphorus (P), that critically influence C biogeochemistry either as limiting nutrients to primary production or in how they facilitate decomposition, including anaerobic processing such as denitrification and methanogenesis among others. Similar to C, the abundance and flow of both of these elements have significantly increased in the last 200 yr due to human activities, primarily through land-use changes, human population growth, and the industrialization of agriculture (Vitousek et al. 1997; Galloway et al. 2004). The increased application of chemically synthesized nitrogenous fertilizers and of mined phosphate rock to agricultural lands particularly during the great acceleration (Bennett et al. 2001; Galloway et al. 2003; Steffen et al. 2015) has dramatically impacted loading into freshwaters in many regions of the world (Smith et al. 1999). Therefore, if we think of the freshwater pipe globally, not only have the absolute amounts of these elements entering aquatic networks changed, but their stoichiometric ratios, relative to C, have likely also changed.

Although considering the stocks and fluxes of C, N, and P are at the foundation of aquatic ecosystem science, explicit consideration of the stoichiometric ratios of these elements in freshwaters has almost exclusively been at community and organismal scales. For example, we know that changes in the total N : P availability influence phytoplankton composition and their biomass elemental stoichiometry (Watson et al. 1997; Downing et al. 2001). For grazers, their stoichiometric composition is influenced both by the ratio of elements available in their prey as well as the relative excretion rates of those elements (Sterner 1990). Despite the inherent interlinking of C, N, and P through photosynthesis, how these foundational elements are processed together and the effects on stoichiometry have not been fully addressed at ecosystem and broader spatial scales in inland waters. Indeed, some studies have looked at the detailed stoichiometric changes of N and P using mass balance approaches at ecosystem scales for reservoirs (Vanni et al. 2011; Grantz et al. 2014), and assessed the influence of hydrology on nutrient stoichiometries in streams (Green and Finlay 2009). However, linking carbon processing to nutrient stoichiometry has been largely restricted to streams (Rosemond et al. 2015), with primarily a focus on the influence of net

metabolism on nutrient ratios (Schade et al. 2011). A framework for characterizing changes in ecosystem level C : N : P stoichiometry in terrestrial environments has been proposed (Schade et al. 2005), and to some degree tested (Vitousek 2003), but doing so for the entirety of inland waters presents a different challenge. Given that C, N, and P enter in different forms predominantly from their watersheds and interact via a multitude of physical, chemical, and biological mechanisms within aquatic ecosystems, we argue that the integrated stoichiometric changes along the freshwater pipe have not yet received appropriate consideration.

In contrast to previous aquatic work that quantified the stoichiometry of organisms, populations, and communities, defining the C : N : P stoichiometry of an aquatic ecosystem is more complex. The bulk C : N: P stoichiometry of an organism can be readily quantified but ecosystems contain particulate and dissolved as well as inorganic and organic forms of C, N, and P. Often these elements are quantified at the ecosystem scale individually with little work focused on bulk stoichiometry. In the oceans, ecosystem stoichiometric approaches are often compared to the Redfield ratio (molar ratio of 106C : 16N : 1P). Although there are many papers demonstrating deviations from this ratio in specific basins or at different latitudes (Martiny et al. 2013), it remains a benchmark in marine systems, likely due to the long residence times of the oceans (thousands of years), as well as more constrained biomass and physiologies of plankton due to low nutrient availability. In freshwaters, where contact with the terrestrial landscape is more direct and residence times are more variable and shorter (days to hundreds of years), stoichiometric ratios are also much more variable (Hecky et al. 1993). The challenge when considering how stoichiometry is regulated at the ecosystem scale requires untangling the way these elements enter, whether they are processed together or independently, and what the avenues for loss from the ecosystem are. Therefore, we propose a framework that focuses on the relative importance of transport, metabolism, evasion, and burial of C, N, and P along the freshwater pipe in order to develop expectations for the role of inland waters in regulating the stoichiometry exported to global oceans.

Coupling and uncoupling the cycles

The importance of downstream transport of C, N, and P echoes the key question raised by initial investigations of inland waters in processing terrestrial carbon (Cole et al. 2007; Tranvik et al. 2009). We learned from these previous studies that C is actively processed within the pipe, with a large fraction of the organic C pool being metabolized to CO_2 and lost to the atmosphere and a smaller fraction being buried in sediments (Mendonça et al. 2017) or lost as methane (Tranvik et al. 2009; Stanley et al. 2016). But, unless organic N and P are processed very similarly to organic C,

we should expect that the stoichiometry of these elements could change significantly, leading to very different export ratios to the ocean relative to what is loaded into freshwaters.

A critical process that couples all three biogeochemical cycles is primary production. Although N and P are not directly part of the biochemical process of C-fixation, these essential macronutrients are required by primary producers to generate biomolecules such as nucleotides, proteins, and lipids. It is worth noting that past discussions of the role of freshwaters in the global carbon cycle have essentially ignored the role of primary production because they have focused on the net effect of these systems on export of C to the oceans. However, because in situ primary production is important in coupling C to N and P, we have included it here. Primary production is often constrained by the availability of P in freshwaters but can also be limited by N, and frequently by both (Elser et al. 2007). Cyanobacteria and bacteria capable of N-fixation can further facilitate coupling of C, N, and P by accessing atmospheric N although this process is energetically expensive and the ability to correct ecosystem deficits are not common (Paerl et al. 2016).

A number of catabolic processes could also act to shift C, N, and P stoichiometry, particularly as they relate to atmospheric losses. These biogeochemical processes can have extreme stoichiometric signatures relative to the composition of organisms and therefore could significantly alter the stoichiometry of inland waters at the ecosystem scale. The two most important catabolic processes to consider along these lines are C respiration and denitrification. Inorganic C is produced through respiration and this process decreases the organic C concentration within systems while increasing the permanent loss of CO_2 to the atmosphere if concentrations are saturating. N and P are also remineralized in the process, primarily as ammonium and phosphate, which can be recycled within the systems. However, the conversion of ammonium to nitrate through nitrification in sediments can have two fates. One is nitrate flux from the sediment to the water column whereas the other is the conversion of nitrate to gaseous N (N_2 or N_2O) via denitrification (and to a lesser extent anammox), which also results in permanent N loss to the atmosphere. Nitrification and denitrification also influence C metabolism, through chemosynthesis and nitrate respiration, respectively (Zehr and Ward 2002). Contrary to C and N, P biogeochemistry does not produce a gaseous end product (Schlesinger and Bernhardt 2013). Previous work has shown that the net losses of C and N gases from inland waters to the atmosphere are meaningful emissions at the global scale (Raymond et al. 2013; Soued et al. 2016). Furthermore, the relatively independent loss of C and N via these processes represents an additional mechanism by which high inland water C : P and N : P ratios are decreased.

Using a framework that considers the relative importance of transport and metabolism with subsequent burial and/or atmospheric exchange, we attempted to couple global inland water C, N, and P biogeochemical cycles by examining their inputs, standing stocks, and outputs, as well as their stoichiometry along the freshwater pipe. In this article, we address three important questions: (1) Are inland waters an "active pipe" stoichiometrically, meaning that they export C, N, and P at ratios distinct from what is imported from the terrestrial landscape?; (2) What are the ranges of the C : N : P stoichiometry of inland waters?; and (3) How have human activities altered inland water C : N : P stoichiometry and changed the role of inland waters in modifying the stoichiometry of terrestrial exports as they are transported to the ocean?

Question 1: Are inland waters a stoichiometrically "active pipe"?

To investigate the degree to which the biogeochemistry of global inland waters alters the C : N : P stoichiometry of terrestrial inputs prior to their delivery to the ocean, we gathered available information on inputs to freshwaters of C, N, and P from their watersheds as well as outputs of C, N, and P from inland waters to the global oceans. Our conceptual framework described above suggests metabolism, burial and/or atmospheric exchange should have a large impact on altering the C : N : P ratios along the aquatic continuum. In contrast, if we observe little freshwater-mediated change in stoichiometry, it is likely that transport is the dominant process or that the multitude of biogeochemical processes that make up inland water metabolism, burial, and atmospheric exchange are balanced and yield no net change in stoichiometry.

Terrestrial inputs vs. oceanic outputs

In order to examine the stoichiometry of inputs and outputs from the freshwater pipe and assess processing, we compiled current estimates of C, N, and P loads and exports (Table 1; Fig. 1A–C). Terrestrial inputs of carbon into freshwaters have been estimated at about 2900 Tg yr^{-1} (Tranvik et al. 2009). This includes contributions of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and particulate organic carbon (POC), of which the organic components are less well constrained at the global scale. If we consider the lake budgets presented by Tranvik et al. (2009) as being potentially representative of different C forms, we estimate that ~ 55% of terrestrial carbon export is DIC, ~ 4% is POC, and the remainder enters inland waters as DOC (Fig. 1A). For the purposes of evaluating the relative inputs and outputs of whole ecosystem stoichiometry of inland waters, we focus on organic C inputs because the transformations of this pool to inorganic C vs. burial is important to our understanding of the role of freshwaters in the global carbon cycle and climate change. Indeed much of the terrestrial DIC load that enters the pipe is quickly vented to the atmosphere (McDonald et al. 2013). Furthermore, the most abundant gaseous form of N (N_2), which also enters at high concentrations, is typically not accounted for in ecosystem

Table 1. Estimates of C, N, and P terrestrial inputs, atmospheric inputs and losses and loss to burial through the freshwater pipe as well as export to the coastal ocean. Molar ratios from different terms also provided; only organic carbon estimates are used in ratios. See Supporting Information Material for details of data sources and calculations.

		Tg yr^{-1}				Molar ratio			
		DOC	POC	DIC	N	P	C : N	C : P	N : P	C : N : P
Watershed inputs		1189	116	1595	98	9	15.5	374.6	24.1	375 : 24 : 1
Atmospheric flux*	Input	—	2288	—	10	0.04	266.9	—	—	—
	Output	1018	2056	—	49	0.04	73	—	—	—
	Net	−786*	−1064†	−39	—	—	—	—	—	—
Total burial		—	150	—	16	5	11	77.5	7	78 : 7 : 1
Coastal exports		171	198	531	43	4	10	238.3	23.8	238 : 24 : 1
Reservoirs processing‡		—	60	38.6	6.5	1.3	10.8	119.2	11.1	119 : 11 : 1

*Calculated as the difference between gross primary production (atmospheric inputs to POC) minus respiration of DOC and POC (DOC and POC atmospheric flux output).
†Calculated as the difference between watershed inputs of DIC and DIC coastal exports.
‡POC and P is burial; DIC is CO_2 respiratory losses; N is both denitrification and burial; C : N ratios are sum of losses to atmosphere and burial.

exchanges or stoichiometry. Similarly, we excluded particulate mineral P from our analysis, although it is a large part of the P flux into freshwaters, it is largely unreactive and is either buried in the sediments or transported to the ocean without being biogeochemically transformed (Smil 2000; Schlesinger and Bernhardt 2013).

Omitting DIC, we estimated that a total 1305 Tg C yr^{-1} is loaded to inland waters as allochthonous DOC and POC. Getting an accurate estimate for N was a bit more problematic. The estimated amount of N loaded into inland water varies widely, from 67 Tg N yr^{-1} (Beusen et al. 2016) to 129 Tg N yr^{-1} (Galloway et al. 2004). Both estimates were derived from previous literature values as well as models to determine the export of N to freshwaters and coastal ecosystems. Rather than picking one or the other, we opted for the mean of these divergent values and estimated total N input at 98 Tg N yr^{-1} (Table 1). But it should be noted that given these widely divergent values for N loading into freshwaters, future work to refine our estimates of terrestrial N export to freshwaters would be beneficial. There was more consensus for the amount of P that entered freshwaters, at around 9 Tg P yr^{-1} (Smil 2000; Beusen et al. 2016) (Table 1). Therefore, in terms of inputs, these values gave a molar terrestrial export C : N : P ratio of about 375 : 24 : 1 suggesting an export of C-rich and P-poor materials into freshwaters, which is consistent with many observations of P-limited freshwaters (Table 1) (Schindler 1977; Hecky and Kilham 1988, Elser et al. 2007).

For oceanic export, we used 900 Tg C yr^{-1} (Cole et al. 2007; Tranvik et al. 2009). However similar to the terrestrial loads, we partitioned the carbon terms into DIC, DOC, and POC (59%, 19%, and 22%, respectively) based upon Stets and Striegl (2012), McDonald et al. (2013), and Seitzinger et al. (2005), thus resulting in an estimated 369 Tg C yr^{-1} for combined DOC and POC export (Fig. 1A). Values used

for N and P delivery to the ocean from freshwaters were 43 Tg N yr^{-1} (Seitzinger et al. 2010) and 4 Tg P yr^{-1} (Beusen et al. 2016), respectively (Fig. 1B,C). Thus, our final export numbers yield a molar ratio of 238 : 24 : 1 representing a 36% decrease in the C : N and C : P ratios of export relative to import (Table 1). Somewhat surprising was the fact that the N : P molar ratio did not change relative to the input ratio suggesting that these elements are processed similarly in freshwaters. Although N and P losses through the pipe are proportionately similar, the fate of those losses is very different where 75% of N loss is as gas to the atmosphere (N_2 and to a lesser extent N_2O) while all P loss is via sediment burial (see below).

Based upon our global estimates of terrestrial loads and freshwater exports of C, N, and P, inland waters clearly process a considerable amount of the material they receive from the terrestrial landscape, thus inland waters serve as an active pipe for all three elements. One way to express the effects of freshwaters on these biogeochemical cycles is to assess their relative removal rates, the quantity of each element that is either buried or released into the atmosphere in relation to terrestrial loading (Finlay et al. 2013). Using this approach, we estimate that 72% of C (organic C only), 56% of N, and 56% of P is removed through the pipe (Table 1). The differential removal rates of C relative to N and P highlight why we see such dramatic differences in the C : N and C : P stoichiometry of inland water loads and exports. Furthermore, the biogeochemical mechanisms by which removals occur are clearly different for each element and may occur at different locations along the continuum, thus influencing the stoichiometry among sub-components of inland waters (i.e., streams vs. rivers vs. lakes vs. reservoirs).

Removal of C and N through the pipe is dominated by atmospheric fluxes, but proportional losses of C via this pathway are considerably higher than losses of N. We
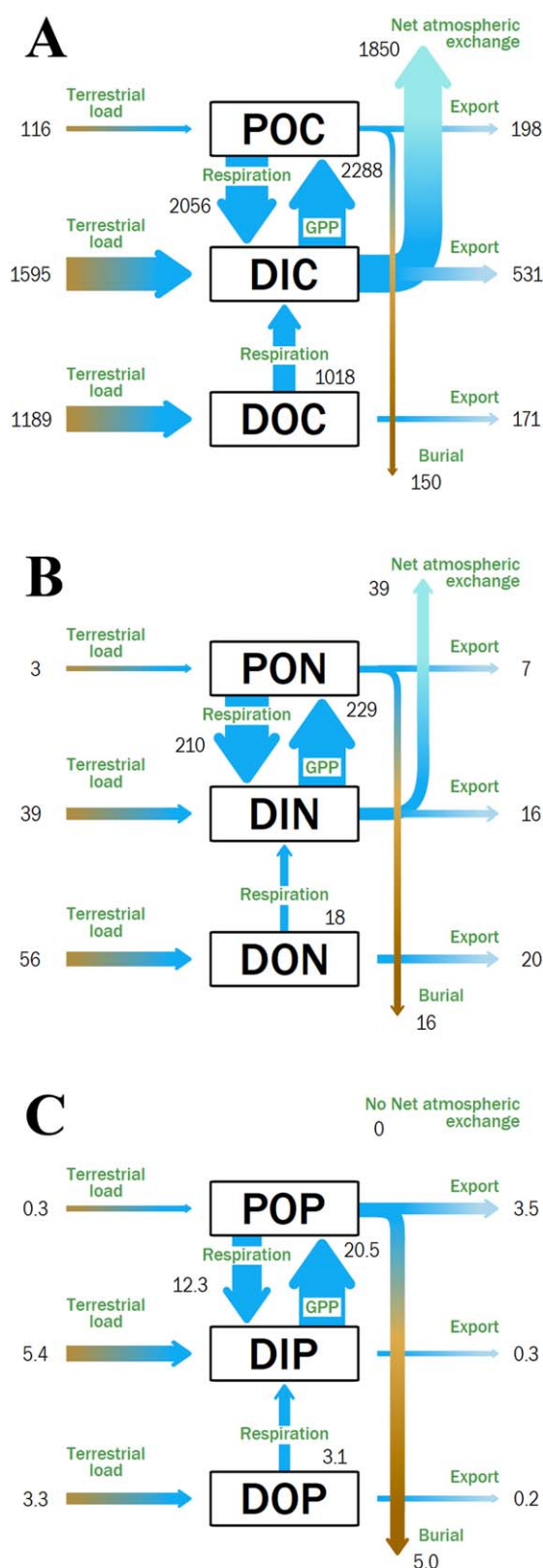
Fig. 1. Inputs, transformations, and outputs of different (**A**) carbon, (**B**) nitrogen, and (**C**) phosphorus forms through the freshwater pipe. All values are in Tg yr^{-1}.

estimate that nearly 86% of total organic C inputs, including gross primary production, are lost to the atmosphere whereas only 45% of total N input is removed via this mechanism (Fig. 1B). Indeed the C : N of terrestrial inputs is 16 while the stoichiometry of exchange with the atmosphere is much higher at 73 (Table 1). While gaseous loss of N and C are both mediated by different microbial transformation pathways, C loss can also be facilitated via photochemical oxidation (Koehler et al. 2014), but that is usually less than 10% of total oxidation to CO_2. Gaseous loss of N via denitrification is much higher than inputs from in situ N fixation, so that on average most of the N that is lost to the atmosphere enters from the watershed (around 90%), whereas around 67% of the C exchanged can be derived from in situ primary production (Table 1; Fig. 1A,B). Global N fixation in freshwaters is estimated to be approximately 10 Tg N yr^{-1} (Cleveland et al. 1999) whereas denitrification is estimated at 49 Tg N yr^{-1} (Table 1), which is similar to a previously accepted estimate of 66 Tg N yr^{-1} for denitrification proposed by Seitzinger et al. (2006). Given the widely different delta G's between nitrogen fixation and denitrification, (i.e., Gibb's free energy required to fuel the reaction), where denitrification is much more negative, the capacity of freshwaters to "inhale" N$_2$ gas to achieve stoichiometric balance is limited energetically. Although N-fixation can be an important component in the N-balance in some primarily unperturbed N-limited systems (Smith 1990), there is an inherent energetic bias toward N "exhalation" (Paerl et al. 2016) that is evident at the global scale.

In contrast to C and N, essentially all P removal through the pipe is lost via burial to the sediments (Table 1). Atmospheric losses of P as phosphine gas (PH$_3$) are not well understood nor quantified, but compared to C and N, it is negligible at less than 0.04 Tg P yr^{-1} globally (Schlesinger and Bernhardt 2013). As a result, burial of P in freshwater sediments is the only meaningful loss, representing 56% of terrestrial P inputs into freshwaters (Fig. 1C; Table 1). Burial of organic C in freshwaters has recently been revised to 150 Tg C yr^{-1} (Mendonça et al. 2017) and is substantially lower than the previous estimate of 600 Tg C yr^{-1} (Tranvik et al. 2009). Burial therefore represents a loss of only 4% of total organic C inputs. For N, freshwaters appear to bury around 15% of terrestrial inputs (16 Tg N yr^{-1}, Table 1), however as outlined above, this number is based on the difference of a relatively imprecise loading estimate. Although nearly all P losses are through burial, some of this buried P is bound to Fe and Al hydroxides that are solubilized when bottom waters become anoxic and can result in a significant P input term through internal loading (Nürnberg 1984). Indeed, all of the elements can be returned to the water column through sediment processing but given that P does not have an atmospheric loss term, and it often limits primary production, internal P loading may have greater consequences

on internal ecosystem level stoichiometry than internal fluxes of C and N from the sediment (discussed below).

The disproportionate loss of P via assimilation and/or sorption followed by sedimentation relative to C and N is clear when the C : N : P stoichiometry of terrestrial loads (375 : 24 : 1), freshwater exports (238 : 24 : 1) and sediment burial (78 : 7 : 1) are compared (Table 1). Presumably, the limited burial of C is driven by high rates of decomposition/respiration, and/or selective burial of low C : P and C : N plankton biomass, whereas for N, limited burial and high export ratios are the result of a combination of denitrification losses rather than long term storage as well as an 8–10 orders of magnitude greater solubility of nitrate relative to phosphate that favors its downstream export. Indeed, although the proportion of export of N and P total inputs are more or less the same at 44%, the dominant forms exported to the oceans reflects the differential importance of solubility of these two nutrients. Modeled particulate N and P exported by rivers to the oceans differed substantially in that only 31% of N was in particulate form while 77% of P was in particulate form (Fig. 1B,C) (Seitzinger et al. 2010).

The processing and fates of the different elements can occur in either the fluvial network (streams and rivers) or in lentic waterbodies (lakes and reservoirs). The relative retention and permanent loss of C, N, and P is apparently spatially distinct through the freshwater pipe. Burial of P occurs primarily in lentic waterbodies (Sorrano et al. 2015), and reservoirs are particularly effective at settling P (see below). By comparison to P, N and C are more heavily processed in streams and rivers. Denitrification losses throughout streams and rivers account for over half of gaseous losses (Seitzinger et al. 2006; Mulholland et al. 2008) where lower order streams tend to remove proportionally more N than higher order ones due to higher relative sediment contact. However, in highly eutrophic systems, excess N can lead to saturation of sediment transformation sites (Alexander et al. 2009) resulting in reduced removal efficiency and greater downstream export. For C, it remains unclear where along the continuum and what portion of the 2100 Tg C yr^{-1} lost to the atmosphere (Raymond et al. 2013) originates from in situ respiration or is a result of vented inputs from the watershed (McDonald et al. 2013; Raymond et al. 2013). Recent work suggests that 28% of the DIC emitted from streams and rivers is locally produced (Hotchkiss et al. 2015) and that the relative proportion of in situ respiration increases with stream size, reflecting reduced connectivity with the terrestrial landscape. Small ponds, however, which also have high relative sediment contact and are more terrestrially connected, are hotspots of locally produced C emissions, at 583 Tg C yr^{-1} (Holgerson and Raymond 2016). Therefore, much like N, approximately half of C that is internally catabolized through the freshwater pipe is lost from fluvial networks and half from small lakes and ponds. Thus, shallow freshwater systems, with their relatively high sediment

reactivity, are playing a crucial role in removing both C and N permanently from the pipe whereas deeper lentic bodies are where permanent P losses occur.

It should also be noted however, that efforts to understand C processing have been heavily influenced by studies focused primarily on boreal and temperate systems (Raymond et al. 2013). This may skew our overall interpretation of C processing dynamics through the freshwater pipe. Indeed, some studies suggest that the biogeochemical loading and processing in tropical inland waters may be behaving quite differently than temperate and boreal systems (Huszar et al. 2006). Regarding N, there has been strong focus on denitrification N losses in flowing waters, but the large majority of this work has been conducted in temperate regions with the most concrete measures on low order streams (Mulholland et al. 2008; Schade et al. 2011; Rosemond et al. 2015), again reflecting geographic and ecosystem bias in our overall understanding of processing. So, our current understanding of coupled biogeochemical cycling through inland waters would profit from a broader geographical assessment, with a focus on tropical and subtropical regions with rapid population growth and land-use development changes.

Question 2: What is the C : N : P stoichiometry of inland waters?

Because the stoichiometry of inputs to and outputs from freshwaters differ from the Redfield ratio, we wanted to know what expectations for inland water stoichiometry should be. Although Elser et al. (2000) and Hecky et al. (1993) examined the stoichiometry of particles in freshwater, no studies to our knowledge have examined the stoichiometry of the combined dissolved and particulate components (including C) at large scales. National surveys of streams, rivers, lakes, and reservoirs across the United States (2007 U.S. EPA National Lakes Assessment, U.S. Environmental Protection Agency 2010; 2007–2017 stream/river chemistry data, U.S. Geological Survey 2016) provide a picture of inland water stoichiometry for a geographically diverse set of systems (Table 2; *see* Supporting Information Material for methods). These observations corroborate a non-Redfield stoichiometry in freshwaters that closely reflects the stoichiometry of terrestrial source material. The median C : N : P ratios in streams and rivers (167 : 25 : 1), reservoirs (417 : 38 : 1), and lakes (963 : 62 : 1) differed strongly from the Redfield ratio and commonly observed ocean stoichiometry (Martiny et al. 2013).

It should be noted, however, that there really should be no expectation of Redfield-like stoichiometry in these measurements for a number of reasons. First, the stoichiometry of primary producers and organic matter on terrestrial landscapes is not particularly close to the Redfield ratio (McGroddy et al. 2004) with C : N : P ratios of trees > 1000 : 25 : 1 and soils at 186 : 13 : 1 (Cleveland and Liptzin 2007).

Table 2. Median and ranges in molar stoichiometric ratios of streams/rivers, reservoirs, and lakes in the United States. Values based on total organic C, total N, and total P concentrations across systems. See Supporting Information Material for methods.

	C : N (25th, 75th)	C : P (25th, 75th)	N : P (25th, 75th)
U.S. streams and rivers 2007–2017 (N = 7275)	7.1 (3.9, 12.4)	166.6 (82.6, 351.4)	24.7 (13.6, 44.6)
U.S. reservoirs 2007 (N = 636)	11.4 (7.9, 15.5)	416.7 (191.0, 798.8)	38.0 (22.7, 59.1)
U.S. lakes 2007 (N = 521)	13.0 (9.2, 18.2)	963.2 (372.2, 1854.8)	61.8 (35.4, 109.1)

Furthermore, in contrast to the oceans where terrestrial inputs are extremely low and the inorganic and plankton nutrient pools mirror each other (Redfield 1958), freshwater systems are open, with relatively short residence times of days to years, which means that it is more likely that the dissolved and particulate stoichiometry diverges from each other as we discussed above due to active processing (They et al. 2017). This is reflected in our comparisons of the stoichiometry of streams/rivers, reservoirs, and lakes.

Simple comparisons of streams/rivers, reservoirs, and lakes indicate that residence time and the magnitude of interactions with sediment surfaces appears to be important in dictating inland water stoichiometry. As residence times increase across inland water sub-components, the total C : P and C : N stoichiometry also increases. Perhaps this reflects increased burial of P through settling of particles with low C : P and N : P ratios, likely due in part to enhanced water column primary production. It may also represent higher C losses with increased sediment contact, as would be the case in shallow streams, rivers, and reservoirs relative to deeper lakes. The N : P stoichiometry also showed an increase with residence time (25 : 1, 38 : 1, and 62 : 1 in streams/rivers, reservoirs, and lakes, respectively). Lower ratios in streams could be due to elevated rates of N loss through denitrification whereas for reservoirs, it is likely a combination of both denitrification as well as high P burial (see below).

Question 3: Anthropogenic alterations to inland water stoichiometry and processing
Freshwater pipes: Changes in inputs and changes in plumbing

Humans have exerted tremendous control on the supply of N and P to inland waters. Urban and industrial point sources have enhanced N and P supply, but P inputs from point sources have been controlled in many regions of the developed world (Carpenter et al. 1998), whereas treatments to remove point source N lag behind (Conley et al. 2009). Municipal wastewaters as point sources of pollution remain a major concern particularly in the developing world due to rapid urbanization. Despite increasing regulation, 40% of municipal wastewater remains untreated globally (Mateo-Sagasta et al. 2015).

Agricultural non-point sources of N and P, however, are pervasive and have far surpassed historical point-source inputs in many areas of the globe (Carpenter et al. 1998). For example, a global surplus of 25 Tg of P is created by the mobilization of mined phosphate rock used as fertilizer for agricultural activities each year (Cordell et al. 2009), and between 20% and 100% of this surplus is thought to enter surface waters via leaching and erosion (MacDonald et al. 2011). P fertilizer use has doubled the reactive P concentrations in rivers worldwide (Smil 2000). In terms of N, massive amounts of N fertilizer, currently synthesized through the Haber-Bosch process, double the amount of bioavailable N to the terrestrial biosphere annually (Vitousek et al. 2013). This has resulted in what is termed the N cascade where N fertilizer use is inefficient and most N is lost to various other environmental compartments including surface and groundwaters (Galloway et al. 2003). Over the last few decades, NH_4-NO_3 synthesis has been replaced by the chemical synthesis of urea, making this dissolved organic nitrogen form now the most widely used nitrogenous fertilizer (Glibert et al. 2014). Furthermore, the N : P ratio of global fertilizer use has increased, likely altering the N : P ratios of what is entering surface waters (Glibert et al. 2014).

The role of sediments in both the processing and storage of nutrients through the freshwater pipe will become increasingly more important as more nutrients enter inland waters. Indeed, the C : N, C : P, and N : P ratios for our estimates of sediment burial are radically different from those that enter from terrestrial landscapes (Table 1). Furthermore, P that accumulates in sediments over time results in a legacy P effect whereby sediments can retain and act as a buffer against P loads but only to a certain point (Haygarth et al. 2014). Once this threshold of buffering has been met, accumulated P will be more chronically available to the entire system, or its downstream export will be promoted. Increased P loading onto landscapes along with selective burial of P suggests that we are globally enhancing internal P recycling through legacy P, potentially sustaining eutrophication for the long term (Carpenter 2005), as well as changing ecosystem level stoichiometry for many generations.

Humans have also directly altered the "piping" of inland waters through channelization of streams, removal and creation of wetlands, and perhaps most dramatically through the

construction of reservoirs. Reservoir surface area is currently estimated at 11% of the global lentic surface (Lehner et al. 2011) and there is an anticipated growth of 3700 large dams in the coming decades (Zarfl et al. 2015). Reservoirs and natural lakes are geomorphometrically and hydraulically quite different from each other (Hayes et al. 2017). Compared to natural lakes, reservoirs have much higher drainage ratios (catchment area to surface area) and thus receive more material from their catchments on an areal basis. Furthermore, reservoirs have higher settling velocities but also higher throughput due to relatively shorter water residence times and process significantly more material per unit area than natural lentic waterbodies (Harrison et al. 2009; Clow et al. 2015). Thus, this change in "piping" will likely influence the biogeochemistry of C, N, and P as well as their stoichiometry. One obvious implication is that the global export C : P and N : P ratios should increase due to increased residence times.

Relative to other surface waters, reservoirs disproportionately serve as settling basins for all elements. They retain a huge amount of sediment, so much so that they have reduced the accretion of several major coastal deltas (Syvitski et al. 2009). In terms of C burial, reservoirs bury 60 Tg C yr^{-1} (Mendonça et al. 2017) (Table 1), which is 40% of the total global C burial while for P, they bury 1.3 Tg P yr^{-1} (Maavara et al. 2015) or 26% of overall burial, despite only covering 11% of the global lentic surface. Per unit area, reservoirs are considered to be much more efficient at removing N than lakes (Harrison et al. 2009). The N retained in reservoirs is estimated at 6.5 Tg N yr^{-1} and is mostly lost to the atmosphere through denitrification (Harrison et al. 2009; Beusen et al. 2016). C from reservoirs is also lost to the atmosphere as both CO_2 through oxic respiration and CH_4 through methanogenesis, estimated at 36.8 Tg C yr^{-1} and 13.3 Tg C yr^{-1}, respectively (Deemer et al. 2016). In order to be consistent with other C respiratory loss terms, only CO_2 loss is represented in Table 1. Although CH_4 emissions contribute greatly to the global warming potential from inland waters, from a total C processing point of view, C lost through CH_4 emissions from freshwaters is relatively minor (Tranvik et al. 2009). For this reason, it was not included in our overall output terms. However, it should be noted that current estimates for methane emissions from reservoirs represent 12% of their total C loss, proportionally much higher than inland waters overall.

Given these global alterations in inputs and plumbing, we wanted to assess the relative influence of land use and water residence time on changes in inland water stoichiometry. In order to do so, we compared the distributions of C : N, C : P, and N : P ratios of reference vs. impacted lakes and reservoirs using the same set of lentic systems described above (Fig. 2; U.S. Environmental Protection Agency 2010; *see* Supporting Information Material for methods). For C : P ratios, impacted reservoirs had lower ratios than reference reservoirs, which had lower ratios than impacted lakes, with reference lakes
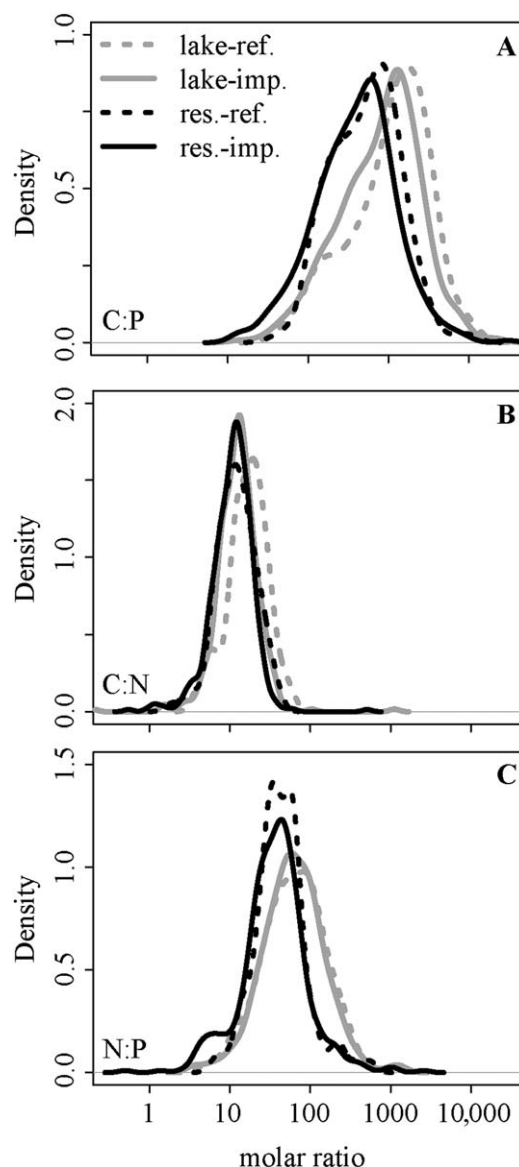

Fig. 2. Kernel density plots of stoichiometric (**A**) C : P, (**B**) C : N, and (**C**) N : P molar ratios of reference lakes and reservoirs vs. impacted lakes and reservoirs included in the 2007 U.S. Environmental Protection Agency National Lakes Assessment (U.S. Environmental Protection Agency 2010).

having the highest C : P ratio on average (Fig. 2A). Therefore, land use loading apparently impacted stoichiometry in both lakes and reservoirs, but residence time represented a stronger relative shift given that ratios for reference reservoirs were lower than those of impacted lakes. One possible explanation for this, in addition to residence time, is that reservoirs have greater internal P load brought on by an increased incidence of anoxia (Müller et al. 2012) combined with higher inputs. Another possibility is that increased P load enhances C loss in reservoirs. In fact, more eutrophic reservoirs tend to produce more methane and emit more CO_2 (Deemer et al. 2016; Harrison et al. 2017).

In terms of C : N, the mean ratios in impacted lakes and both categories of reservoirs were similar and lower than reference lakes (Fig. 2). It is possible that different mechanisms are responsible for this similar outcome. For impacted lakes, this lower ratio may simply be a function of higher N load and a signature of eutrophication. Alternatively, lower C : N ratios in reservoirs relative to reference lakes may be a function of relatively higher C loss due to burial and respiration but is more likely due to less N loss as a function of shorter residence times relative to lakes. In impacted reservoirs, however, one possible explanation for why land use did not result in lower C : N ratios relative to reference reservoirs is that relatively more N may be lost via denitrification as a function of additional P (Finlay et al. 2013). For N : P, although reservoir ratios were systematically lower than lakes, it was surprising to see no distinction between reference and non-reference systems in reservoirs and lakes for these ratios (Fig. 2C). This could potentially suggest that water residence time overrides relatively higher inputs, however, we do not have information on the relative loads of the different nutrients between reference and impacted systems. It is also possible that internal processing maintains the relative ratios of nutrients between impacted and referenced systems likely as a function of the strong coupling through metabolism. Indeed, there is a strong coupling of N and P within the sediments where processing time is relatively longer, which tends to result in sediment ratios that are similar even across land use gradients (Vanni et al. 2011). However, the absolute amounts stored among these systems likely differ across input gradients.

Nonetheless, the C : N and N : P ratios of the water were the same between reference and impacted reservoirs but the C : P ratios were lower in impacted systems (Fig. 2). The differential fate of N and P could explain this discrepancy. Indeed, the reference reservoirs were almost 2 m deeper on average than the impacted reservoirs (mean depth ref-res = 10.5 m vs. imp-res = 8.7 m), which could settle more P (Collins et al. 2017) and decrease resuspension. Furthermore, the shallower, impacted reservoirs may eliminate more N due to increased sediment to water contact resulting in increased denitrification and similar ratios for nutrients for both types of systems.

Summary

One of the important conclusions from this effort is the realization that, not surprisingly, a great deal more effort has been expended to understand the processing of C than understanding the fates of N and P throughout aquatic networks since the seminal Cole et al. (2007) paper. Nonetheless, in this first attempt to consider coupled biogeochemical cycles of inland waters and their ecosystem level stoichiometry at the global scale, we find that input and export stoichiometry of these elements differ due to differences in
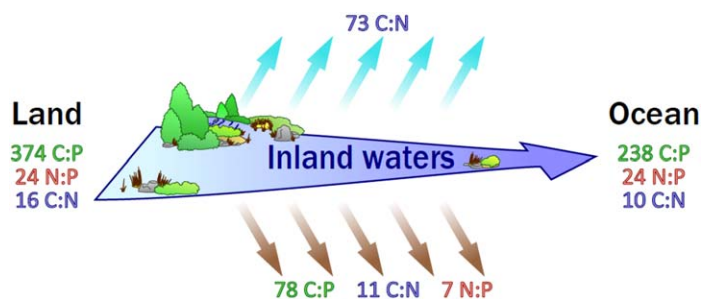

Fig. 3. Global estimates of stoichiometry of the freshwater pipe. C : P, N : P, and C : N molar ratios of estimated inputs from terrestrial systems, loss to burial and the atmosphere and export to the ocean. Figure adapted from Cole et al. (2007, fig. 1).

retention among the elements through the freshwater pipe. Furthermore, the fate of the retained elements differs due to their biogeochemistry. More C is retained relative to N and P (Table 1; Fig. 3) due to tight coupling of primary production and ecosystem respiration, which means that most of the "retention" is actually lost from freshwaters primarily as CO_2 (Raymond et al. 2013). Conceptually, this suggests that organic carbon pools are rapidly turning over in freshwater systems with rapid production being compensated by similarly rapid decomposition. P and N are retained at equivalent proportions through the pipe, but with very different fates, often in different locations along the aquatic continuum. Most P retention ends up in the sediments of lentic waterbodies, in a large part due to limited solubility of inorganic P relative to C and N. However, most of the N retained ends up in the atmosphere due to an imbalance between N-fixation and denitrification with the latter process dominating, particularly in small order streams and shallow lentic systems with high sediment contact.

Another important conclusion from this effort is that residence time plays a critical role in the processing of these elements through the pipe. There were profound differences in the stoichiometry of streams, reservoirs, and lakes in the USGS and NLA surveys. Moving from streams to lakes, there are large increases in residence times with substantial increases in C : N, C : P, and N : P ratios. Certainly, settling of particles likely plays a role along this continuum, but increased light availability may also be important to support the coupled settling of elements through primary production (Urabe et al. 2002; Elser et al. 2003). Once algal particles reach the sediments, respiratory C losses of this autochthonous organic matter and subsequent denitrification-mediated N losses decouples C from N from P.

Knowledge gaps

We have identified three critical knowledge gaps for freshwater scientists to consider in order to better characterize coupled elemental cycling along the aquatic continuum. First, although we have synthesized the best available

information to date on various components of C, N, and P, none of these biogeochemical cycles are well constrained at the global scale. The best estimates for global fluxes come from the Global NEWS Project and subsequent iterations (Seitzinger et al. 2005; Mayorga et al. 2010; Beusen et al. 2016) but these syntheses were primarily focused on the exports from freshwaters rather than quantifying the materials loaded into them. Consequently, there is a huge gap in our understanding of what actually is happening inside the pipe because we do not have a good understanding of what is entering it in the first place. For example, in the case of C, recently revised estimates suggest a 75% increase in terrestrial loading to the pipe, upscaling it to 5100 Tg C yr^{-1} (Drake et al. 2018). Our inability to constrain terrestrial inputs results from those values most often being estimated as the sum of atmospheric exchange, sediment burial, and export to the ocean. Increased observations of terrestrial C, N, and P inputs at watershed and larger scales, as well as process-based modeling efforts should increase our ability to constrain this important, but highly uncertain, aspect of inland water biogeochemistry.

Second, nitrogen remains the most poorly constrained of the three elements, likely due to the mechanistic complexity of the cycle, a bias at understanding P limitation in freshwaters, and the concerted effort to understand C cycling since the seminal Cole et al. (2007) paper. There seems to be good agreement on nitrogen exports to coasts but, as described above, there is a wide discrepancy as to what is believed to be going into the freshwater pipe (Galloway et al. 2004; Beusen et al. 2016). Global efforts at estimating exports are suggesting downscaling N inputs, however, efforts at estimating N loading to freshwaters at more regional scales suggest inputs are increasing at a rapid pace (Howarth et al. 1996; Gao et al. 2015; Goyette et al. 2016). Furthermore, although there has been a great amount of work done to understand N processing in streams (Mulholland et al. 2008; Schade et al. 2011; Rosemond et al. 2015), recent denitrification and burial estimates modeled by Beusen et al. (2016) were only 27 Tg N yr^{-1} whereas the previous estimate is around 66 Tg N yr^{-1} (Seitzinger et al. 2006). Indeed simple mass balance budgets cannot capture the more complex nature of N cycling through the pipe. Nitrification may be more ubiquitous in freshwaters than previously thought (Botrel et al. 2017) and N-fixation remains poorly constrained (Scott and McCarthy 2010). There is certainly a need improve our estimates of N loading to the pipe well as a greater understanding of what influences N processing in different aquatic compartments.

Finally, it is clear that where, when, and how terrestrial inputs are processed along the freshwater continuum is rapidly changing due to human activities. Land use alterations, the growing use of fertilizers, rapid urbanization, the lack of wastewater treatment, and increased eutrophication are all factors that have the potential to change freshwater stoichiometry at regional and global scales. These alterations of inputs are occurring in parallel with alterations to the hydrological features of the network, including increased reservoir construction as well as shifting precipitation and runoff patterns as a function climate change. Future work must consider the direct and interactive effects of hydrology on human-driven alterations in C, N, and P inputs from catchments, and how elements are processed together through different aquatic sub-components. We must also expand our understanding of coupled cycles in the freshwater ecosystems of the rapidly developing regions of the global south for a more complete portrait of the role of the freshwater pipe.

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