Biogeochemical decoupling: how, where and when?

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Abstract: Research has dealt with coupling of chemical element cycles and feedback in recent years. Sometimes, this biogeochemical coupling is reversed through abiotic or biotic (including man-made) processes. It is then called biogeochemical decoupling and is a disconnection between two chemical elements whereby transformations of one affect cycling of the other, and results in asynchronical behavior of chemical elements. It appears to be more important and widespread than earlier reports suggest, and gives rise to important changes in element stoichiometry of resources. These changes in turn modify organismal stoichiometry that, if great enough, can affect biodiversity and food webs, thus altering community structure and function. Biogeochemical decoupling then impinges on ecosystem dynamics and may impair ecosystem services.

Keywords: chemical elements, stoichiometry, biogeochemical processes, ecological effects.

Table 1. Glossary of terms.

Burial: storage of a given chemical element in either soils or sediments. It is also termed as "sequestration".

Chelation: a chemical process by which ions and molecules bind metal ions.

Ecological stoichiometry: how balance of energy and elements affects and is affected by organisms and their interactions in ecosystems.

Element cycling: the flow of a given chemical element and its compounds between living organisms and the abiotic environment.

Homeostasis: the ability of organisms to maintain constant element concentrations in their bodies despite changing concentrations in the environment and/or resource supply.

Limiting factor: a factor that limits the growth or development of an organism, population or process. According to the Justus von Liebig's law of the minimum, it is the factor being the scarcest resource.

Organism stoichiometry: a synonym of elemental composition, it is the element balance in components, interactions and processes in a given organism.

Redfield composition: a 106:16:1 ratio of elemental C:N:P in aquatic seston that enables autotrophs to grow at optimal rates. An updated ratio has recently been suggested (166:20:1 on average; Sterner et al. 2008).

Resiliency of biogeochemical coupling: rate of recovery of biogeochemical coupling after decoupling, if this has occurred.

Stoichiometrically-balanced ecosystem: one whose chemical element pools are approximately at Redfield composition.

Stoichiometrically-unbalanced ecosystem: one whose chemical element pools all are not approximately at Redfield composition.

Transient state: an ecosystem is said to be in a **transient** state when a process variable has been changed and the ecosystem has not yet reached a new steady-state.

Trophic cascade: it occurs when top predators in a food web suppress the abundance and/or alter traits (*e.g.* behavior) of their prey, thereby releasing the next lower trophic level from predation (or herbivory if the intermediate trophic level is a herbivore).

Box 1. Some instances of biogeochemical decoupling.

The most frequent reports of element decoupling are those of **C** and **N**. One has been ascribed to long-term drought of the US Great Plains with suggestions that environmental factors influence biogeochemical recoupling (Evans and Burke 2013) whereas the other relates to seasonal availability of water and results in lagged primary production of plants in the Patagonian steppe (Yahdjian et al. 2006). There is also a report in an Indiana stream (Johnson et al. 2012), where (de)coupling between C and N involves potentially complex interactions with sediment texture and organic matter, microbial community structure, and possibly indirect biogeochemical pathways.

C and **P** are decoupled in another Indiana, nitrate-rich stream when enriched with dissolved organic carbon (Oviedo-Vargas et al. 2013). Heterotrophs out-competed autotrophs for N and sediment-sorbed P sustained the heterotrophic community while P uptake from the water column was dominated by autotrophs. (De)coupling of C and P can be mediated by the availability of different forms of inorganic N.

In environments of Pacific Ocean (Hawaii) and the eastern Mediterranean **N** and **P** in the pelagial were decoupled as a result of dust (Herut et al. 2002) and freshwater inputs (Tanaka and Mackenzie 2005), Saharan dust was also responsible for decoupling N and P in the water environment of Southern Spanish high mountain lakes (Morales-Baquero et al. 2006). Soil N and P have also been suggested to be decoupled on a seasonal basis in a central Kenya semiarid savanna (Augustine and MacNaughton 2004).

Fe and **N** decoupling was observed in a modeling effort of N-fixing organisms in the world ocean (Ward et al. 2013), which was tested and confirmed by Southern Atlantic data.

In an estuary of Chesapeake bay, it has been reported the decoupling of **Fe** and **P** in sediments along a salinity gradient (Jordan et al. 2008). Phosphate is released from terrigenous sediments when they are deposited in saline portions of the estuary. Such release may contribute to the generally observed switch from phosphorus limitation in freshwater to nitrogen limitation in coastal marine water.

Defining biogeochemical decoupling

This new concept describes the opposite of coupling of biogeochemical cycles, a topic of growing interest nowadays. Coupled biogeochemistry relies upon metabolism, biomass and chelation of the Biosphere (Schlesinger et al. 2011). Coupling of element cycles and its feedback have received increasing attention in recent years (Ptacnik. *et al.* 2005, the whole issue 9 of *Frontiers of Ecology and the Environment* in 2011]. Schlesinger *et al.* (2011) have stated that "movements of about 30 chemical elements essential to life are coupled, so that the behavior of one element can often be used to predict the behavior of other elements". Element coupling in metabolism depends on biochemical processes that are coupled to each other through redox processes (Schlesinger et al. 2011). For example, photosynthetic C fixation results in lower C levels, which can be coupled to N nitrification that renders oxidized N in cellular metabolism. Thus, this assumption is based upon biogeochemistry and hence element coupling in biogeochemistry implies biogeochemical coupling of processes.

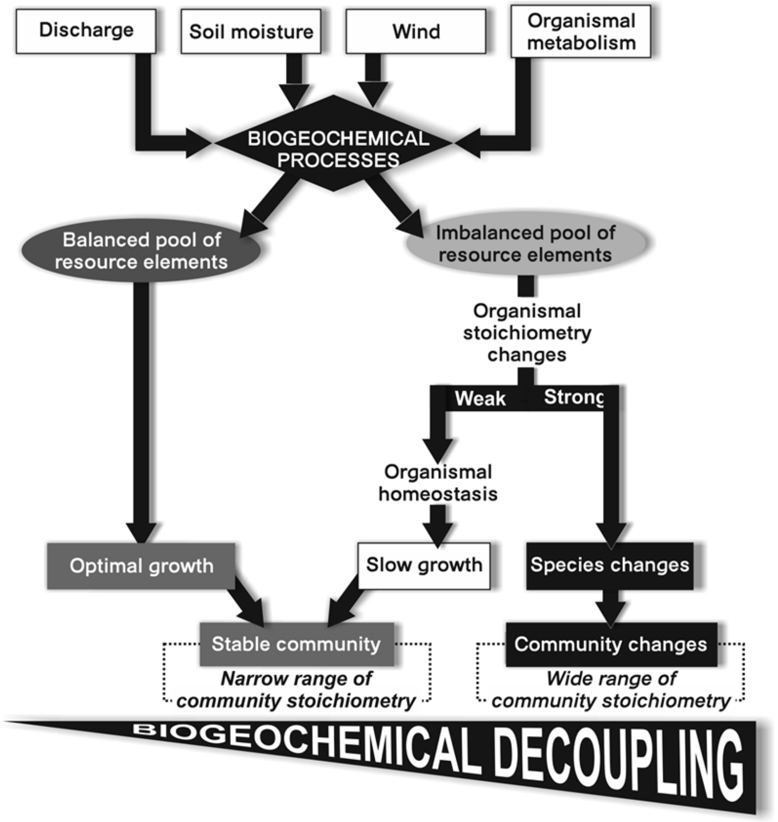

Figure 1. A conceptual model of the effect of biogeochemical decoupling on organisms and communities. The obvious simplification overlooks the fact that ecological communities are compounded systems of groups of organisms (taxonomic or functional groups), each having distinct stoichiometries, varying in magnitude and range as well. Hence, stoichiometric changes in resources arising from elemental decoupling in the environment might result in the disappearance (or not) of certain groups, depending upon their stoichiometric abilities. Organismal metabolism may also include that of Man and his products and by-products.

Abiotic or biotic agents may sometimes destroy the element coupling process, which is then termed biogeochemical decoupling. After the seminal paper by Asner et al. in the late nineties (Asner et al. 1997), this process came under scrutiny leading to a number of recent reports (Augustine and McNaughton 2004; Mackenzie and Lerman 2006; Oviedo-Vargas et al. 2013). So far, the elements reported to be involved in decoupling have been C and P (Oviedo-Vargas et al. 2013), C and N (Evans and Burke 2013; Johnson et al. 2012; Yahdjian et al. 2009), N and P (Augustine and McNaughton 2004; Herut et al. 2002; Morales-Baquero et al. 2006; Tanaka and Mackenzie 2005), Fe and N (Ward et al. 2013) and Fe and P (Jordan et al. 2008; Box 1). However, these reports do not define what element decoupling is or what its consequences are for ecosystem dynamics. An attempt to do so is undertaken here. While biogeochemical coupling is a connection between two chemical elements, by which the transformations of one affect the

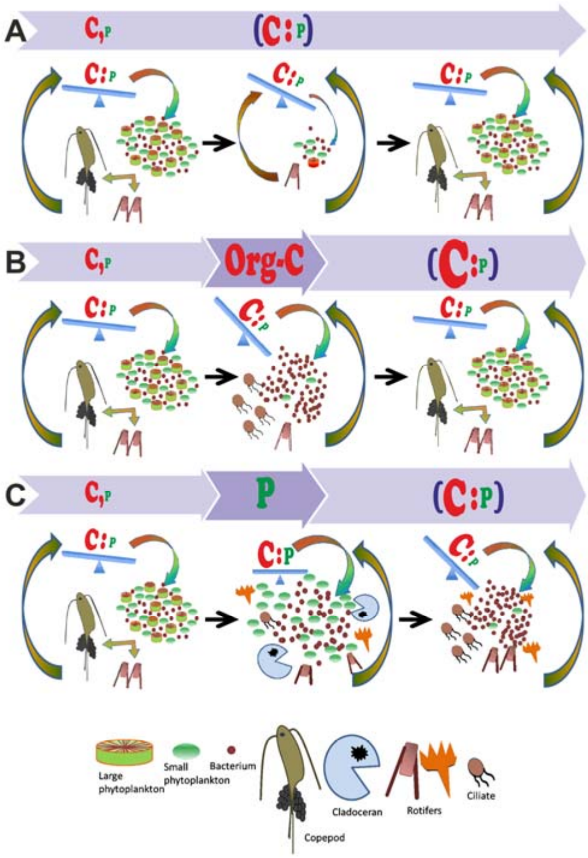

Figure 2. An sketchy example: biogeochemical coupling and decoupling of C and P in freshwater pelagial environments and their effects on plankton assemblages. The biogeochemical processes involved will be gross primary production (GPP) and P uptake. A) In an oligotrophic environment, there are low inputs of P whose uptake by primary producers fuels low GPP rates upon which the plankton community partly relies. B) It may occur that C:P ratios will increase as a result of increasing organic C inputs from the catchment, thereby promoting the growth of bacteria which are better competitors for P than phytoplankton. Then, GPP rates decrease and both they and the P uptake are temporary decoupled. However, zooplankton herbivory of bacteria and small phytoplankters will promote increased water column P cycling due to excretion by those animals, then putting more P at the disposal of phytoplankton to restore previous GPP rates again. This decoupling and later recoupling, thereby fluctuating C:P ratios around an average, do not result in changing structure of the ecological community involved. C) Now P inputs suddenly happen to be higher (i.e. the site experiences eutrophication). Therefore, P is no longer in shortage for phytoplankton, GPP dramatically increases and results in decoupling from P uptake. Hence, phytoplankton community structure changes towards fast growing species. Zooplankters change concomitantly because herbivory is impaired, and large zooplankton (mostly Cladocerans and Copepods) is substituted by smaller animals (mostly Rotifers and Ciliates). Bacteria also increase due to higher amounts of organic substrates available, which in turn benefit small zooplankters whose numbers also increase. Hence, a change in the processes of GPP and P uptake driven by higher inputs of P has decoupled C and P biogeochemistry in this model environment, diminishing C:P ratios and changing pelagic community structure.

cycling of the other chemical element, biogeochemical decoupling could be defined as the reverse process: a disconnection between two chemical elements, which does not allow transformations of one to affect the cycling of the other. Thus element decoupling results in the asynchronical behavior of elements.

Given the increase in studies showing biogeochemical decoupling, it would seem to occur more often than previously thought and appears to be a widespread phenomenon in Nature. Let us start by asking some important questions: How does biogeochemical decoupling affect organisms? How does this process change communities and ecosystems? We can only guess at the answers because none are reported. To gain insight into the effects of element decoupling on organisms, it may be useful to address the concept of organismal stoichiometry (Hessen et al. 2013). It is well known that external stoichiometric imbalances affect physiological processes underlying growth, reproduction and maintenance of organisms (Persson et al. 2010). Then, one can imagine (Fig. 1) an environment where there is a balanced pool of resource elements that enable organisms to grow at optimal rates. Suddenly, an abiotic or biotic agent (or both) starts operating and decouples biogeochemical processes, resulting in changing elemental ratios of resources (for instance, C:N, N:P, Fe:C). Thus, the resource environment turns into an imbalanced pool of elements and it is likely that, as a result, organismal stoichiometry changes too. If this change is weak, owing to biogeochemical plasticity (Arbačiauskas et al. 2013), organisms can adapt stoichiometrically (*i.e.,* a homeostatic process would take place within) and grow; hence, community structure would remain unaltered. However, if organismal stoichiometry undergoes strong (even severe) changes arising from external imbalances of resource elements, it is likely that the ecological community will change, giving rise to organisms with either a wider stoichiometric flexibility or a different elemental composition. Therefore, imbalances in elemental ratios, triggered by element decoupling in the environment, may result in ecological changes affecting community structure and function. An idealized example of element coupling/decoupling and its effects on freshwater ecological communities can be seen in Figure 2.

Element decoupling may have two main effects: 1) changing ecosystem dynamics (Asner et al. 1997), and 2) impairing ecosystem functions (Daily 1997). Thus, given the well known effects of biogeochemical cycles on ecosystems (Schlesinger 1997), we can speculate that, at the ecosystem and Biosphere level, the main processes resulting from element decoupling include: loss of biodiversity, increased element accumulation in soils and sediments, promotion of the detrital pathway (as opposed to herbivore) with the concomitant increase in greenhouse gases, lower rates of element recycling and entry of invasive species. As a corollary, some ecosystem services, such as nutrient cycling, waste decomposition, purification of water, etc., may be altered or even impaired.

The issue of how to measure decoupling is still in its infancy. Usually authors report rates of several biogeochemical processes over time to decide whether decoupling has taken place (Oviedo-Vargas et al. 2013; Evans and Burke 2013; Yahdjian et al. 2006) or not. But this is not always possible given the complexity involved in measuring several biogeochemical rates simultaneously in field conditions. Therefore, other simpler approaches will be useful to find out whether element decoupling is happening (Box 2).

Agents, processes and scales involved in biogeochemical decoupling

Agents can be either abiotic or biotic. The former include water discharge (Tanaka and Mackenzie 2005), wind transport (Herut et al. 2002; Morales-Baquero et al. 2006) and moisture limitation (Evans and Burke 2013). The latter agents relate to the metabolism of organisms other than man (bacteria, algae and fungi (Oviedo-Vargas et al. 2013; Johnson et al. 2012), lake plankton and/or benthos (Morales-Baquero et al. 2006; Ebise and Inoue 1991; Levine and Chindler 1992), ocean plankton (Herut et al. 2002; Marañón 2010), microorganisms and higher plants (Augustine and McNaughton 2004; Evans and Burke 2013) and anthropogenic effects on the Biosphere (fertilizer inputs (Asner et al. 1997), nitrogen and sulfur deposition (Driscol et al. 2001; Elser et al. 2009), eutrophication (Smith et al. 2003; Finlay et al. 2013), and global change (Mackenzie and Lerman 2006)).

Organisms may trigger decoupling through their metabolism. They uptake and transform elements following the law of the minimum (von Liebig 1843) and consequently deplete some elements more than others, which leads to a shortage of elements for other biogeochemical processes. Thus, element decoupling takes place.

There is even some evidence that the coupling/decoupling of two elements (C, P) may be mediated by different compounds of another element (N, Oviedo-Vargas et al. 2013). Decoupling of biogeochemical processes can also occur within the same element, such as that shown for C by

Box 2. The use of element ratios as surrogates of coupling/decoupling processes.

Since a variety of biogeochemical processes can be involved in biogeochemical decoupling (Schlesinger et al. 2011, Burgin et al. 2011), and it is not always easy to measure them all, a simpler approach to qualify decoupling is advisable. Some studies suggest that proportions between chemical elements (also called “element ratios”) change along with decoupling. Data gathered by Oviedo-Vargas et al. (2013) in a study of a stream draining an agricultural catchment enabled them to calculate average dissolved inorganic nitrogen:soluble reactive phosphorus- and dissolved organic carbon:dissolved inorganic nitrogen ratios in treatment- and control stream reaches; both ratios were statistically higher in the treatment areas with element decoupling. Also, data gathered by Augustine and McNaughton (2004) in semiarid soils show a seasonal increase in nitrogen:phosphorus ratios as biogeochemical decoupling proceeds. Furthermore, Wang et al. (2014) suggest the use of the labile organic carbon to soluble phosphorus ratio in sediment pore water of wetlands as a measure of microbial homeostatic regulation; it could also be an index of element decoupling. Thus changes in averaged element ratios can be used as a surrogate of element decoupling. To test their differences statistically, variance comparison of element ratios before and after decoupling is in order; when variances cannot be ascertained, permutation tests (Legendre and Legendre 2012) are useful to compute a statistic to compare average elemental ratios.

In addition, an index of the decoupling magnitude could be represented as ΔER, where this is the difference of the average element ratio of interest between treatment- and control environments where biogeochemical decoupling has taken place.

Thingstad *et al.* (2013) and for N by Dijkstra *et al.* (2012), but this cannot be included as true biogeochemical decoupling since such a process must imply at least two chemical elements.

So far, the biogeochemical processes reported to be involved in decoupling are stream benthic photosynthesis, respiration and P adsorption and uptake (Oviedo-Vargas et al. 2013), soil respiration and denitrification (Evans and Burke 2013), sedimentation and denitrification (Ebise and Inoue 1991), stream benthic photosynthesis, respiration and N uptake (Johnson et al. 2012), water- (Tanaka and Mackenzie 2005) and wind-driven transport (Asner et al. 1997; Herut et al. 2002; Morales-Baquero et al. 2006).

Water transports chemical elements between Earth compartments. Coupling/decoupling across scales arising from linking hydrology and biogeochemistry, however, remain poorly understood and represent an important challenge to researchers (Lohse et al. 2009). In lakes impacted by high inputs of a given element (*e.g.* N or P), element decoupling can be offset or enhanced by *in situ* processes (*e.g.* denitrification, CO_2 degassing, sedimentation and nutrient uptake) and this is related to water renewal (Harris 1999). Biogeochemical decoupling (either increasing or decreasing) will likely be higher as water retention increases and biotic processes play a more important role in biogeochemical cycles. Compensation of primary production among habitats (pelagic *vs* benthic) has been reported in lakes subject to nutrient enrichment (Vadeboncoeur et al. 2000), thus providing a means to cope with enrichment and hence to reverse element decoupling. As our own results suggest (Álvarez-Cobelas and Sánchez-Carrillo 2016), stream and groundwater transport of increased chemical elements as a result of pollution will likely show decoupling in urban-dominated and crop-dominated catchments (high P relative to N in the former and the opposite in the latter).

Another important process that may promote decoupling is element chelation (Schlesinger et al. 2011). Research has mostly dealt with balanced mineral nutrition of plants growing on soils. Organic C often forms chemical complexes with metals (mostly Fe and Al), often withdrawing them from the soil matrix and impairing balanced growth of plants (Schlesinger 1997). In the ocean, the recent discovery of frequent aggregation of DOC substances to produce porous microscopic gels of POC (Verdugo and Santschi 2010) adds unexpected complexity to the Fe-DOC chelation process, which certainly occurs in the water column. Fe is an important limiting factor in many areas of the ocean (Boyd and Doney 2003) and there chelation with organic matter certainly results in biogeochemical element decoupling (Benner 2011), but this topic has hardly been explored yet.

So far biogeochemical decoupling has been observed in many environments (soil (Evans and Burke 2013), freshwater (Oviedo-Vargas et al. 2013), ocean (Tanaka and Mackenzie 2005)). It appears to be a widespread process, taking place at many spatial scales, from the very local (*e.g.* stream reach (Johnson et al. 2012) to the planetary (Mackenzie and Lerman 2006) scale. One may wonder if decoupling hot spots occur; they are not unlikely because, for example, they occur for denitrification (Groffman et al. 2009) and therefore this local depletion of nitrogen might result in decoupling to carbon, since benthic photosynthesis can be N limited in areas of P excess, such as those occurring in eutrophicated sites.

For element decoupling to occur, the time scales involved also range from days (Oviedo-Vargas et al. 2013), seasons (Augustine and McNaughton 2004) to long-term (several years; Asner et al. 1997; Mackenzie and Lerman 2006; Evans and Burke 2013). However, it is unclear how long it persists, and if it can become permanent or not. Some authors suggest that element decoupling can be reversed in the short-term (Evans and Burke 2013). Thus, it is legitimate to ask ourselves if resiliency (Gunderson 2000) of element coupling exists. If so, when, where and at what rates? When is biogeochemical decoupling irreversible? Furthermore, can short-term decoupling be considered as a transient state towards resilient behavior of coupled element cycles?

When do some elements decouple? How much does this affect the ecosystem?

Biogeochemical decoupling results in unbalanced ecosystem functions because it usually reduces the supply of elements needed to drive some biogeochemical processes. Element supply and export, along with their use and transformations by organisms within the system, are to be considered when addressing implications of element decoupling for ecosystems and the services they provide.

Ecosystems can be stoichiometrically balanced or unbalanced (Sterner and Elser 2002), namely chemical elements can be coupled or decoupled therein. In the former case, autotrophs roughly respond to Redfield ratios of nutrients, which do not occur in the latter case. Trophic cascades are enhanced in balanced ecosystems as opposed to what occurs in environments experiencing element decoupling (Sterner and Elser 2002). Energy will preferentially circulate through the herbivore food web in balanced ecosystems and through detritivore pathways in the elementally-imbalanced environments. The limiting factors of autotrophs are light and nutrients, while they are C or energy and nutrients for herbivores in balanced and unbalanced ecosystems, respectively. Since microbes are not nutrient limited in stoichiometrically balanced ecosystems, decomposition rates will be faster in these ecosystems than in unbalanced environments; as a result, there will be lower C burial levels in the sediments in the former and higher levels in the latter (Sterner and Elser 2002). To further complicate this scenario, a recent study in a boreal estuary (Bradshaw et al. 2012) reports that autotrophs do not show weak stoichiometric homeostasis during the spring algal bloom and homeostasis strength by consumers depends upon the type of element (macro- *vs* trace element), contrary to earlier suggestions (Sterner and Elser 2002); then autotrophs and consumers should be able to withstand decoupling of some elements more than previously envisaged, but is this so everywhere?

Also, some questions concerning the relationship between organisms (other than Man) and biogeochemical coupling have yet to be solved. For instance, how and when do they cope with element decoupling? Examples such as the release of saccharides by oceanic phytoplankton to chelate Fe in a bioavailable form (Hassler et al. 2011) must be frequent in Nature, but there are no other reports on this subject. Can organisms alter element ratios for a long time in a given ecosystem? Strong homeostasis of stoichiometry has been reported for submerged macrophytes (Li et al. 2013) and soil microbial communities (Mooshammer et al. 2014), but how strong can homeostasis of organismal stoichiometry be (Hessen et al. 2013)? How important and widespread is stoichiometric plasticity (Arbačiauskas et al. 2013) of organisms to cope with element decoupling? Besides homeostasis, are organisms able to reverse biogeochemical decoupling? There is a report of primary production compensation in different habitats in the same ecosystem (Vadeboncoeur et al. 2000) but other mechanisms have yet to be disclosed.

At the Biosphere level, humans are the most important force influencing element decoupling

Box 3. Further studies.

The studies outlined in this opinion paper suggest that biogeochemical decoupling must be a very frequent process in many ecosystems. However, the evidence available is still scarce. Then there is a huge field of study to be tackled. Some topics that deserve closer scrutiny are the following:

-A more thorough survey of element decoupling in ecosystems of different latitudes and biomes, paying special attention to hotspots and hot moments

-Observations of decoupling in different habitats of the same ecosystem (for example, the forest canopy vs soil or plankton vs benthos)

-An assessment of variance partitioning between the effects of biotic and abiotic processes on biogeochemical decoupling

-The amelioration of decoupling (i.e. diminishing changes in element ratios) as a result of organismal activity or transportation of unbalanced elements by water or wind

-The element recoupling process, emphasizing resilience and temporal scales of element resynchronization

-Quantitative assessments of the effects of element decoupling on the dynamics of populations, communities and ecosystems

-Chelation effects on element decoupling are presumed but up to date very few have been reported

-The role of biological assemblages, key-stone species and foodwebs on the resilience of element coupling. More specifically, the role of organismal homeostatic flexibility on biogeochemical recoupling should be addressed.

-The effects of global warming (and hence C outgassing from Biosphere) on C decoupling from other elements. There are some recent reports on alterations of stoichiometry of grasslands (Gao et al. 2013) and wetland sediment microbes (Wang et al. 2014) by global warming, and this might occur through element decoupling, but it has not been ascertained as yet.

given our escalating use of elements, be they synthesized (ammonia) or extracted from buried areas (oil, P mining), which are released into the Biosphere pathways and result in biogeochemical decoupling. Humans are accelerating global cycles of N and P at disproportionate rates compared to C (Falkowski et al. 2000). Changed balances of elements at larger scales may have a major impact on the distribution of organisms at smaller scales (Mooshammer et al. 2014), but this is a very poorly explored topic to date.

In environmental management it seems advisable to enhance reversal actions for biogeochemical decoupling when the cause is anthropogenic. Since the main sources of element decoupling are through man-made actions, humans must act to reduce this unbalanced behavior and, if possible, mitigate its effects (Dijkstra et al. 2012). Diverting P effluents, reducing N fertilizers, diminishing N emissions, reducing C emissions, all these man-made actions will likely reduce the ongoing (and steadily increasing) element decoupling, both at the ecosystem and the Biosphere level.

In summary, this short opinion paper has emphasized that 1st) biogeochemical decoupling may occur in most ecosystems, 2nd) it has many ecological implications, 3rd) it is important from local to global scales, 4th) there are only a few examples of specific cases reported to date, and 5th) many research topics have yet to be tackled. In our view, all these topics must be studied to fully understand biogeochemical decoupling and its short- and long-term implications in the light of the global changes Mankind is now facing (Box 3). These suggested studies must be jointly carried out by biogeochemists and ecologists to be fruitful.

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