

Extended abstracts of the scientific seminar:

# Coupled biogeochemical cycles and ecosystem services

Jouni Lehtoranta, Petri Ekholm, Petteri Vihervaara,  
Pirkko Kortelainen (editors)





REPORTS OF THE FINNISH ENVIRONMENT  
INSTITUTE 21 | 2014

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Helsinki 2014

FINNISH ENVIRONMENT INSTITUTE



S Y K E

Reports of the Finnish Environment  
Institute 21 | 2014  
Finnish Environment Institute  
Marine Research Centre

Layout: Seija Aspola

The publication is available in the internet: [www.syke.fi/publications](http://www.syke.fi/publications)  
| [helda.helsinki.fi/syke](http://helda.helsinki.fi/syke)

ISBN 978-952-11-4349-6 (PDF)  
ISSN 1796-1726 (verkkoj.)

## PREFACE

The publication at hand includes the extended abstracts of the presentations given in a seminar “Coupled biogeochemical cycles and links to ecosystem services” held at the Finnish Environment Institute in November 2013. The idea to organize a seminar on the topic originated from the limited knowledge available about the coupled biogeochemical cycles in various ecosystems, despite their apparently large role in ecosystems. We believe that understanding and acknowledging the coupled biogeochemical processes could improve the planning of measures aimed at improving environment quality.

The organizers are impressed that as much as 110 participants registered in the seminar. The large interest may be due the seminar offering a screening point on the subject from both terrestrial and aquatic sides. The seminar revealed unexplored areas in biogeochemistry that have a clear policy implication e.g. in relation to abating eutrophication and climate change.

Involving coupled biogeochemical cycles in their research agenda can give Finnish researchers a possibility to stand in the front line of an emerging research topic. Hopefully, the seminar will spawn national and international cooperation, finally to be realized as multidisciplinary joint projects on the topic.

Finnish researchers have an outstanding asset for this specific topic: today we have a free access to one of the world’s largest national environmental databases covering both terrestrial and aquatic systems. Exploiting these data gives us a possibility to extrapolate the outcome of process studies on larger scales and test new hypotheses based on monitoring results. If investigators of biogeochemistry and ecosystem science also combine their experience with economy and policy research, we have a realistic opportunity to improve the state of the environment by implementing science-based and socially feasible mitigation measures.

The seminar was part of TEA-SERVICES, an internal seed-money project funded by the Finnish Environment Institute and TEAQUILA project (decision number 263476) in the Research Programme on Sustainable Governance of Aquatic Resources (AKVA) funded by the Academy of Finland.



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Photo Aarno Torvinen

## 1. Introduction

### Linking coupled biogeochemical cycles to ecosystem services

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#### Environmental problems from the ecosystem services viewpoint

Humans modify the biogeochemical cycles of carbon, nitrogen and phosphorus, which has resulted in limited ecosystem services both in terrestrial and aquatic systems. Increasing awareness of our dependence on ecosystem services is noted in EU policies such as the Blueprint to Safeguard Europe's Waters, Biodiversity 2020 Strategy, and agricultural policy. Research on ecosystem services has concentrated on provisioning and cultural services. However, environmental degradation impacts the regulating and maintenance services (also called supporting services), which then cascades to provisioning and cultural services, as the system's ability to cope with pressures is weakened.

Many of the regulating and maintenance services, such as nutrient removal, are linked to biogeochemical cycles driven by microorganisms, but these have mainly been omitted from ecosystem service studies (MA 2005; TEEB 2010). To acknowledge the gap, there is a need to develop indicators for ecosystem services that would enable the linking of ecosystem structure, processes and functions with ecosystem services and that would also allow quantification and valuation for economic analyses. Here, basic

research is not seeking to identify proxies of ecosystem services to be monetarized, but rather include the processes that regulate element cycling in terrestrial and aquatic environments in to the framework of ecosystem services.

Omission of biogeochemical cycles from the ecosystem service suite may be due to their usually slow response to pressures, which are difficult to detect without specific measurements. Furthermore, when occurring deep in the soil, ground water or sediment, they may not be immediately visible. Yet, the term of ecosystem services helps to define and describe the significance of the biogeochemical processes for the researchers and experts from other disciplines.

### **Coupling of biogeochemical cycles in aquatic ecosystems and eutrophication abatement**

The lack of knowledge on the processes coupling the element cycles in ecosystems may partly explain failures in combating environmental problems. For example, eutrophication is described to be dependent on external nutrient loading and abatement measures have targeted at decreasing the loading of nutrients, especially those considered to boost production. A number of political programmes and targets have been issued setting levels for nutrient loading (e.g., the Decision-in-principle by the Finnish Government of the Policy Outlines and HELCOM's Baltic Sea Action Plan). EU's Water Framework Directive does not include limits for nutrient loading as such, but it is translated to nutrient reduction measures in the River Basin Management Plans. The same applies for the implementation of the Marine Strategy Framework Directive.

The coupling of biogeochemical cycles presented in this publication suggests that the status of the ecosystem is not reliant only on nutrient loading but also on fluxes of other substances. Given the fact that a multitude of microbial processes modify cycling of elements a question emerges: which substances the decision maker should prefer/avoid to promote supporting ecosystem services. The question is not a theoretical one, since human actions, including environmental protection measures, influence not only the fluxes of nutrients, but also many other substances. It is evident that a comprehensive control of supporting and regulating ecosystem services can be achieved only through management of a large and representative set of substances.

### **Holistic system approach needed**

The elements having the major importance in the environment are carbon, nitrogen, phosphorus, manganese, iron and sulphur. Regarding coupled biogeochemical cycles we should be able to define the micro-scale processes and couplings generated by the biota which, indeed, produce much of the macro-scale responses in the ecosystems. Now, the efforts put to monetarize provisioning (e.g. bias in fish community) and cultural services (e.g. decreased recreational values) may not be able to take into account the origin of the problem. So, from the viewpoint of ecosystem services we should control the supporting ecosystem processes to generate regulating ecosystem services, which are reflected in provisioning and cultural services. Here, we should be able to define the main environmental drivers and detect the spatial-temporal occurrence of the processes. Although one may find this unfeasible or unrealistic, it would give a possibility for a holistic control and sound management of the system.

## Further research:

### **The process and flux studies have to include coupling of elements**

The human activity tends to cause a cocktail of fluxes with abnormal stoichiometric ratios causing problems in recipient systems. Research tradition restricted on only one element should be widened to include coupled cycling and studying only a single element may lead to suboptimal and even harmful decisions.

### **Coverage of fluxes**

Research is often focused on either vertical or lateral fluxes although both directions should be covered. Thus, we should compare fluxes between the sub-compartments inside and among the ecosystems. The transport of substances and their forms (gaseous, dissolved and solid) at interfaces, for example, between soil and atmosphere, ground-water and soil, and sediment and water.

### **Acknowledging the various ecosystems**

More focus on the comparison of the ecosystem types, which would illustrate patterns in the relative ranges of fluxes and functions to reveal drivers of processes masked by separate consideration of ecosystems.

### **Recognizing the functionality of biota**

More concentration on interactions between animals, plants and fungi, and bacteria because their connections affect element fluxes and biogeochemical cycles.

### **Computing power and amount of environmental data**

Accumulating amount of environmental data and the free access on large databases maintained by the governmental research institutes including atmospheric, terrestrial and aquatic systems are now open for researchers. This gives an opportunity for researchers to combine the data sets covering the elements responsible for biogeochemical cycles.

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## 2. Extended abstracts

### Concepts of ecosystem services, coupled biogeochemical cycles and biodiversity from the viewpoint of land use

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Ecosystem services are underpinned by biodiversity adapted to physical and biogeochemical conditions in the environment. The invariably expanding land use, however, influences biogeochemical cycles which reflects to many supporting services provided by microbiota and other biological communities such as vegetation. This oversimplified explanation sounds reasonable, but there are only few studies available looking comprehensively at the wide continuum of coupled socio-ecological processes. The inter-connected parts of ecosystem functioning can be approached by formulating e.g. the following questions: 1) What kind of impacts can different land use practices have on coupled biogeochemical cycles, 2) How changes in coupled element cycling affect different aspects of biodiversity, 3) How the changes in biodiversity, e.g. species assemblages or functional traits, resonate human well-being, i.e. multiple ecosystem services?

Ecosystem services are often divided into provisioning, cultural and regulating and maintenance (also called supporting) services (CICES; MA 2005). Provisioning services,

such as food and drinking water are results of complex ecological interactions, largely provided by microbial functions. Similarly, many cultural services, say, recreation at the Baltic Sea free of algal blooms, also depend on micro-scale processes taking place in the catchment and the body of water. Many of these fundamental functions are placed into a category of regulating and maintenance services and they are seldom translated to direct human benefits. Yet, a decrease in regulating and maintenance services may result to diminishing provisioning and cultural services. Examples from the processes that are considered in regulating and maintenance services include nutrient uptake, mineralization and the overall biological control. Those processes can reduce nutrient losses, and thus improve water quality. Positive effects can also be seen in control of soil erosion and reduced greenhouse gas emissions from the soils. Value for the processes and their outcome can be measured either in economic terms, such as avoided costs, monetarized benefits of improved quality or stated preferences, or by social or health benefits.

Human population alters land cover and terrestrial and aquatic habitats with accelerating speed. Global economy forms the driving force for socio-economic activities realized in the forms of forestry, agriculture, mining and urban sprawl. Managing the utilization of natural resources can be realized in many ways. Theoretically, human exploitation of ecosystem functions shrinks the space for the natural processes evolved via slow evolutionary pathways, one potential outcome being a decrease in the resilience of ecosystems, i.e. their ability to recover from a disturbance may be weakened. Modern society is capable to produce rapid changes in which spatio-temporal ecological functions are seldom adapted. Here, the direct impacts of land-cover change on biodiversity are rather easy to monitor compared to the indirect ones e.g. caused by the shifted loads of elements. The loads of C, N, P, Mn, Fe and S affect the abiotic environmental conditions, but their sources and consequences may be difficult to trace back.

Forest management practices such as clear cutting, site preparation, fertilization and ditching increase nutrient losses to waters (Finer *et al.* 2010). Most of the previous studies have, however, been focusing either on N or P, but not on other elements and their couplings. There is a lack of studies in which element losses of forestry practices would be compared in various environmental conditions, such as from different soil types, and then linked to the cumulative biodiversity impacts in the end points. On the other hand, it has been stated that peatlands, often surrounding forestry areas in Finland, can effectively sequester elements leached from forest soils (Sallantausta, T., unpublished). The land use along the catchment may have both negative and positive impacts on water quality depending on the spatial hierarchy of land cover classes and flow paths of water. Similar functions of biodiversity can be found in urban settings where drainage waters are directed through more natural state and disturbed systems resulting in differences in nutrient uptake and other ecosystem services (see Setälä, this publication).

Agriculture is a well-known source of nutrients causing eutrophication. However, the quantity and quality of elements like Mn and Fe transported from Finnish agricultural landscapes is largely unknown. In fact, the present monitoring programme of small agricultural catchments does not even cover these substances. Some relationships have been found between land use and biodiversity of adjacent freshwaters, for instance in the abundance of macrophytes (Alahuhta 2012). Here, as in many similar studies the information on biogeochemistry is not well established and is seldom comprehensive. Recently the impacts of mining into ecosystem services have emerged into discussion via the Talvivaara case in Sotkamo, Finland. Talvivaara mine has caused serious losses of multitude of metals, sulphate and sodium to downstream waters (Kauppi *et al.* 2013). Salinity has increased and created a permanent stratification in the nearest lakes. The sediment studies have revealed shifts in biogeochemical processes, i.e. in

supporting services that may lead to negative impacts in human-wellbeing at many levels.

The examples of the interactions between land-use, coupled biogeochemical cycles and ecosystem services need yet a fourth part when solving the puzzle of sustainable management of socio-ecological system. That is the biodiversity in all forms and its ability to transfer substances among biota. Microbial diversity might play an important role in biogeochemical cycles thus contributing to the overall redox-state on earth. However, the multi-cellular organisms such as vascular plants and annelids – just to mention a couple of taxa – are also important engineers of the environmental conditions, and affected by the changes in ecosystem state. Today functional diversity and traits in particular are under research, because they may provide a shortcut to get a grip of the overwhelming taxonomic diversity and complexity of the functions in ecosystems. This approach may turn out to be useful from the management viewpoint. However, functional diversity is not the only set of biodiversity variables to be taken into account for land use management. Genetic diversity between the populations, rare species without special functional properties, and overall ecosystem diversity are also important aspects to be conserved. Finding out what is their dependence and influence on coupled biogeochemical cycles belong still in the future research duties.

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## Ecosystem functioning in natural and human-dominated settings

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## Introduction

Due to the scarcity of nutrients, biota in various ecosystems has evolved the ability to immobilise nutrients effectively into their biomass, thereby retaining growth-limiting nutrients within the ecosystem. Such “conservatism” in nutrient dynamics is typical to, e.g. boreal ecosystems with soils rich in organic matter and clear seasonal pattern in productivity. However, when such systems are disturbed, the reduced biomass and structural complexity of the biota result in a less conservative state with an increase in the leaching of nutrients and other elements from the system. In such “leaky” systems the role of water as a passive carrier of elements increases, which

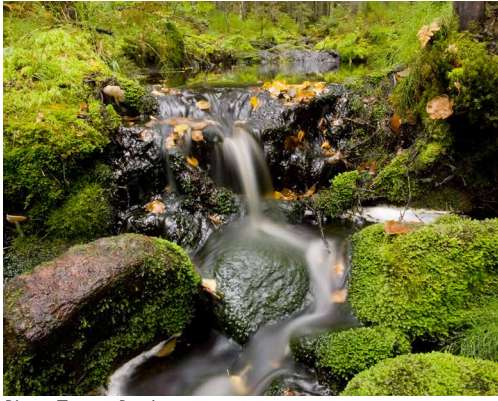


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Photo Riku Lumiaro

may potentially enhance the interconnectedness of biogeochemical cycles between adjacent ecosystems.

Here the following hypotheses are tested: 1) biomass and diversity of the soil decomposer biota associates with the ability of a system to retain nutrients within it, and 2) a strong linkage in biogeochemical cycles between two ecosystems is unnatural in northern latitudes and can be taken as a sign of abnormal ecosystem-level behavior of at least one of the systems. These hypotheses were tested using three ecosystems with divergent disturbance status: boreal forest, agricultural field, and the urban milieu.

## Results and Discussion

### Forested systems

Boreal forests represent relatively undisturbed systems when the rich layer of organic matter remains intact. Furthermore, such systems are likely to be resistant to disturbances, which should lead to a tight coupling between the (soil) biota and biogeochemical cycles. Empirical and observational evidence support this statement. First, controlled mini-ecosystem studies have repeatedly shown that nutrient dynamics and plant growth in coniferous forest soils are strongly controlled by the structural composition and activity of soil food webs (e.g. Setälä and Huhta 1991, Laakso and Setälä 1999). This should lead to tightly coupled nutrient dynamics between the below- and above ground systems and little potential for nutrients to leach out of the system. Second, there is consensus among forest scientists that, unlike in heavily managed forest systems prone to soil erosion, the thick top soil layer in boreal forests is effective in preventing nutrient washout – even after clear cutting (Finer *et al.* 2010). As a consequence, there is little evidence suggesting that nutrient dynamics in forests and, e.g. aquatic systems are clearly inter-connected. The situation can, however, differ at sites with steep slopes and soil preparation (e.g. harrowing) as was shown in the famous catchment manipulation study in Hubbard Brook, New Hampshire, USA (Likens and Borman 1975).

### Agricultural systems:

In contrast to forested ecosystems, agricultural systems, especially their soils, are often substantially disturbed by structural destruction of the surface soil, fertilization and other practices to improve yield. This results in soil erosion and concomitant losses of nutrients (880 kg/km<sup>2</sup>/y of N) and solid material (up to 2000 kg/ha/y) to adjacent water bodies (Uusitalo *et al.* 2007). It is not well known whether these losses are solely due to the physical-chemical alterations of the highly managed soils, or whether obvious changes in the soil biota inhabiting the organic matter poor arable soils also play a role.

This issue was tackled in an EU 7<sup>th</sup> framework project “SOILSERVICE” and the following question was presented: “Can strongly disturbed, organic matter deficient agricultural soils and their biota be managed so as to retain nutrients better in the system?” Ecological theory suggests that soils deficient in organic matter promote the growth of bacteria (inefficient in immobilising nutrients) relative to fungi (effective nutrient immobilisation), which should result in stimulated nutrient leakage from the soils (Moore and Hunt 1988). Supporting this hypothesis, strongly manipulated agricultural soils within four non-adjacent geographical regions in Europe promoted the establishment of bacterial-based soil food webs with concomitant losses of N, P and C from the soils. Soils having higher percentage of organic matter and relatively higher fungal biomass were commonly associated with a much better retention of N, P and C in the soils (de Vries 2013). These results indicate a high inter-connection between strongly managed agricultural systems and ecosystems adjacent to them, but also suggest that retention of elements can, at least partially, be improved by improving conditions for the soil biota, particularly for soil fungi.

### **Urban systems**

Urban systems are likely to have the most disturbed soils within a “soil management gradient”. Soils that are sealed with impervious structures and/or experience constant disturbance in the form of heavy contamination and structural changes are often devoid of organic matter and are thus unsupportive to biological life. This should, in theory, lead to low nutrient retention capacity of urban soils and thus a strong interconnectedness of urban systems and aquatic ecosystems (Setälä *et al.* VACCIA). This hypothesis was tested in six urban catchments with varying proportions – from ca. 20 to 80% – of permeable, natural/semi-natural soil in the cities of Lahti and Helsinki, Finland. Urban run-off water (stormwater) was used as an indicator of how natural the hydrological cycle in a given catchments was. Our results clearly showed that the more permeable the soil, the more of the incoming rain water stayed in the catchment and the better its quality (Valtanen *et al.* 2014). It can be concluded that the low proportion of “living” soils at the most urbanized catchments makes them extremely leaky for nutrients and other contaminants, suggesting (i) an utmost loose coupling between the soil biota and biochemical cycles and (ii) a strong linkage of biogeochemical cycles between urban and aquatic ecosystems.

### **Ecosystem services and the need for further studies**

These abovementioned examples of the biogeochemical cycles at three diverging ecosystems (forest, agricultural, urban) relate explicitly to life-supporting functions – or ecosystem services – which these ecosystems provide to society. In each ecosystem, the ability of the system to retain nutrients and other contaminants within the catchment area can be considered of high importance. This service is unlikely to work properly unless the soils in a given catchment harbor an active soil biota which, in turn, ensures continuous build-up of soil organic matter. Substantial decoupling of biogeochemical cycles within an ecosystem, and clear coupling of elemental dynamics between ecosystems due to, e.g. losses of nutrients or other elements from terrestrial to aquatic ecosystems can be taken as a first symptom of a mal-behaving ecosystem service apparatus. However, distorted ecosystem services and thus the well-being of, e.g. aquatic ecosystems can be restored by acknowledging the pivotal importance of the “living soil” in catchments. What is not known, however, is whether the type of vegetation and thus type/quality of the soil in the plant rhizosphere affects the ability of the plant-soil system to retain water, nutrients and other elements within a catchment. Scattered evidence suggests that vegetation type can control some hydrological processes at a small-scale in, e.g. urban catchments (Vauramo and



Setälä 2010), but the role of, e.g. urban parks, lawns and home yards in regulating biogeochemical cycles is not known.

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## The link between plant photosynthesis and soil carbon and nitrogen dynamics

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## Background

Climate change scenarios for northern boreal forest area predict that the air and soil temperatures will rise and the atmospheric CO<sub>2</sub> level increase in the future (IPCC, 2007). Elevated atmospheric CO<sub>2</sub> increase plant photosynthesis which increases belowground carbon (C) flux. However, how the climate change in the long run affects C balance of forest ecosystems is under debate. As boreal forest soils are globally a significant C pool, even small changes in the soil C storage pool may drastically affect the atmospheric CO<sub>2</sub> concentration (Kirschbaum *et al.* 2000).

In boreal forest soil, most of the soil nitrogen (N) is in organic form (SON) and only minor proportion is in easily accessible inorganic ammonium (NH<sub>4</sub>) or nitrate (NO<sub>3</sub>) forms. At Hyytiälä research forest (SMEAR II) in southern Finland around 0.08% of the N pool (approx. 2 kgs per ha) is in inorganic form, approx. 2% in microbial biomass, 35% in proteins and the rest in humic compounds. The amino acid pool is not known for this site. The N uptake of plants at the site is around 25 kg/ha, i.e. 1% of the size of the N pool. The N deposition is relatively low in northern boreal forests (in SMEAR II around 15 kgs i.e. 0.6%/pool/yr, including throughfall) (Korhonen *et al.* 2013) and it has been estimated not to increase, as is predicted to happen in other parts of Europe (Syri *et al.* 2004).

The C that is recently fixed by the plant and allocated into the soil is much more readily utilizable by soil microbes than older soil organic matter (SOM). Recent work

shows that the old SOM is decomposed more rapidly if easily utilizable C is available (e.g. Fontaine *et al.* 2007), a phenomena called priming effect (Kuzyakov, 2010). In addition to the role of sugars as a driving force in SOM decomposition, the key role of nitrogen (N) for decomposition, especially in N poor boreal forest soils, has recently been recognized. Drake *et al.* (2011) showed in a field study that increase in C flow belowground increases N uptake by plants, which has a positive feedback on ecosystem net primary production (NPP), thus CO<sub>2</sub> fixation. Phillips *et al.* (2011) and Brzostek and Finzi (2011) reported also the coupling of below ground C allocation and N uptake. They also showed that the increase in below ground C was shown to correlate with increased release of extracellular enzymes involved in the breakdown of organic N compounds in the soil and that this is associated with ectomycorrhizal (ECM) fungi. Brzostek and Finzi (2011) concluded that the abundance and activity of proteolytic enzymes is a principal driver of the within-system cycle of soil N, and that protein bioavailability is restricted due to binding to SOM compounds that need to be broken down by chitinolytic and ligninolytic enzymes. In accordance with Drake *et al.* (2011) and Phillips *et al.* (2011), they conclude that ECM roots control the proteolytic, ligninolytic and chitinolytic enzyme activities and therefore promote SOM decomposition.

Ericoid mycorrhizal (ERM) plants that are mostly studied in heathland ecosystems, are also dominating the ground vegetation in boreal Scots pine forests. For instance, in SMEAR II site in Hyytiälä, lingonberry (*Vaccinium vitis-idaea*) and blueberry (*V. myrtillus*) are the most common vascular plants of the ground vegetation (Ilvesniemi *et al.* 2009) and both of them form ericoid mycorrhizal symbiosis (Smith and Read, 2008). ERM plants have been shown to be able to utilize a wide range of peptides (Bajwa and Read, 1985) and proteins as sole N and C sources (Bajwa *et al.* 1985) while non-mycorrhizal controls were unable to use those substrates. ERM fungi produce acid protease with pH optima between 2 and 5 (Leake and Read, 1989). One of the most common organic N source in soils, chitin, can also be used as a sole N source by ericoid fungi, while ECM fungi could use chitin only in low amounts (Leake and Read, 1990). ERM fungi are also efficient as saprotrophs (Bajwa *et al.* 1985). Villarreal-Ruiz *et al.* (2004) showed that the same fungal isolate formed simultaneously ECM with *P. sylvestris* and ERM with *V. myrtillus*. The fungal isolate belonged to *Hymenoscyphus ericae* aggregate, species of which were also found to be some of the most common in Scots pine roots in Hyytiälä (Heinonsalo *et al.* 2007).

## Aims

The aims of Academy Research Fellow projects FASTCARBON and NITROFUNGI (2009-2017) are to verify the effect and quantity of plant-derived easily available C compounds on decomposition of recalcitrant SOM; and to clarify the interactions between trees, ground vegetation and organic N transformation that have potentially large impact of forest productivity in changing climate.

## Conclusions

Our Academy Research Fellow projects have so far clearly indicated that plants have a key role on soil C and N transformation processes. We have shown that increased plant photosynthesis by warming not only increase plant biomass accumulation but even more importantly, accelerate soil biological processes. In our study it was shown that easily-accessible carbohydrates increase decomposition of older C in soil, meaning that the effect of increased photosynthesis by plants on soil in changing climate is controversial. Currently we have investigations going on where we aim to estimate the significance of soil fungal communities and in particular,

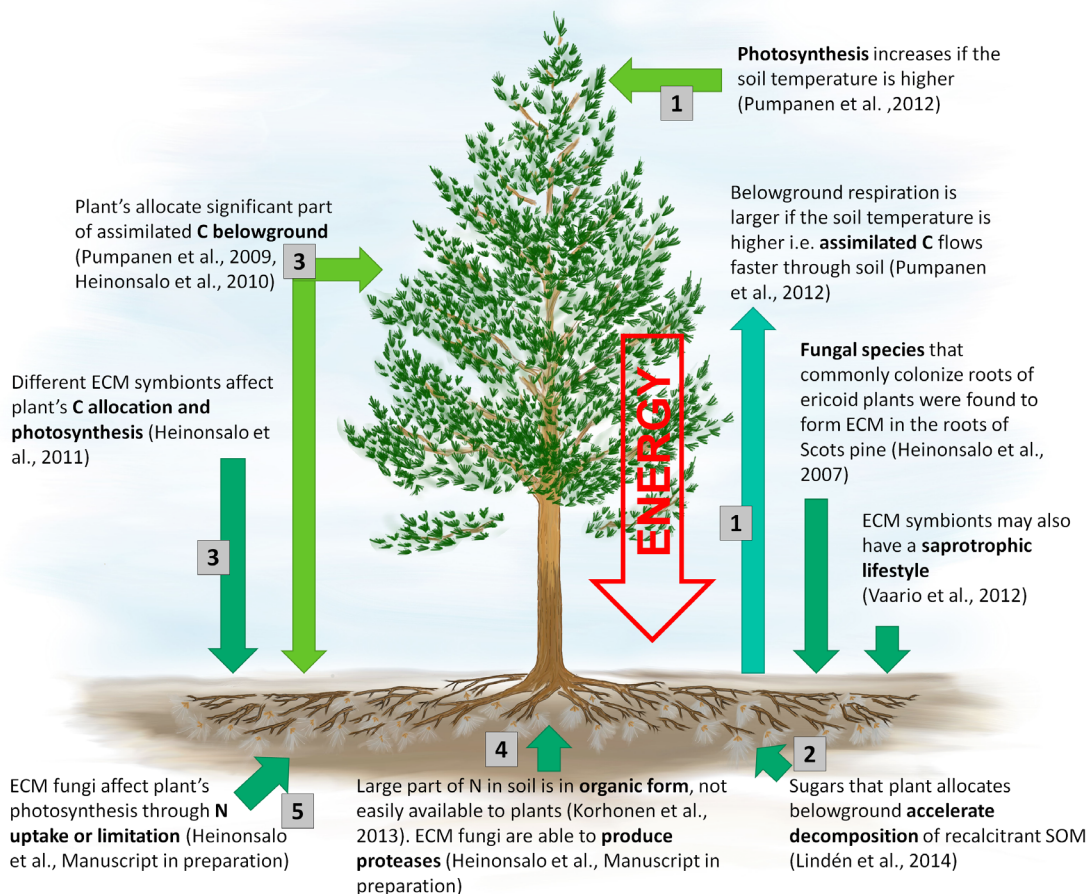


Figure 1. Increased soil temperature increase plant photosynthesis but also soil respiration resulting in faster plant-derived C turnover in soil (1). Plant-allocated sugars accelerate decomposition of recalcitrant SOM (2). Plants allocate significant part of their photosynthesis products belowground and different ectomycorrhizal fungi may alter plants C allocation patterns (3). Large part of nitrogen (N) in forest soil is in organic form and ECM fungi are able to produce enzymes increasing organic N uptake (4). As a feedback mechanism, ECM fungi affect plant photosynthesis through N and water uptake (5). (Background image: Antti-Jussi Kieloaho)

the role of ericoid plants and their symbiotic fungal associates in mobilization of recalcitrant soil organic N pool. This large N pool has been shown to be a driver for SOM decomposition in N limited forest environments.

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## Microbial processes linked to methane production and release in mires

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Mires are nutrient-poor, acidic and largely anoxic environments, where low rate of decomposition leads to accumulation of partially degraded organic matter as peat. As a consequence, mires store one third of soil carbon globally and are a large source of the greenhouse gas methane (CH<sub>4</sub>). Methane production by methanogenic archaea is a terminal step of decomposition in anoxic peat. Aerobic peat above water table level harbours methanotrophic bacteria, which oxidize CH<sub>4</sub> into carbon dioxide (CO<sub>2</sub>). Methanotrophic bacteria also reside inside *Sphagnum* mosses, making the moss layer a filter potentially reducing the CH<sub>4</sub> emission.

Methane emission into the atmosphere is regulated by the activity of CH<sub>4</sub> producers and oxidizers, controlled in turn by environmental conditions, such as water level, but also by interactions with other processes. As the last step in anaerobic decomposition, CH<sub>4</sub> production depends on the products of the earlier fermentation steps, and CH<sub>4</sub> producers compete for these products with other anaerobic microbes. Methane production has been considered to be the main terminal process in peat, because mires as nutrient-poor environments have low levels of electron acceptors for the competing processes such as nitrate and sulfate reduction. With CH<sub>4</sub> production as the terminal process, anaerobic decomposition should theoretically produce equal amounts of CH<sub>4</sub> and CO<sub>2</sub>. However, increasing evidence shows that the gas yield does not follow the 1:1 ratio but instead produces a large unaccounted excess of CO<sub>2</sub> (Ye et al. 2012, Kane et al. 2013). This was also the case in recent measurements in several Finnish mires, where ratios of CH<sub>4</sub> and CO<sub>2</sub> production ranged from 1:4 to 1:264. The unaccounted anaerobic CO<sub>2</sub> suggests the presence of unidentified processes releasing carbon from anoxic peat and affecting the balance of greenhouse gas emission.

A possible source for the excess CO<sub>2</sub> is another terminal process occurring at a high rate despite low levels of measured electron acceptors. Sulfate reduction has largely been ignored in peat because of low sulfate concentrations. However, recent measurements have revealed rates similar to marine sediments, where sulfate reduction is a major part of anaerobic carbon cycling and a competing process to CH<sub>4</sub> production (Pester et al. 2012). The measured sulfate reduction rates could account for up to 36-50% of carbon release from anoxic peat (Pester et al. 2012). Sulfate reducers have been detected in considerable numbers in pristine, drained and restored Finnish mires (Putkinen et al., in preparation).

Another process occurring in sulfate- or nitrate-containing sediments but long thought to be absent in peat is anaerobic CH<sub>4</sub> oxidation. This process converts CH<sub>4</sub> into CO<sub>2</sub> in anoxic environments and is linked to sulfate, nitrate, iron or manganese

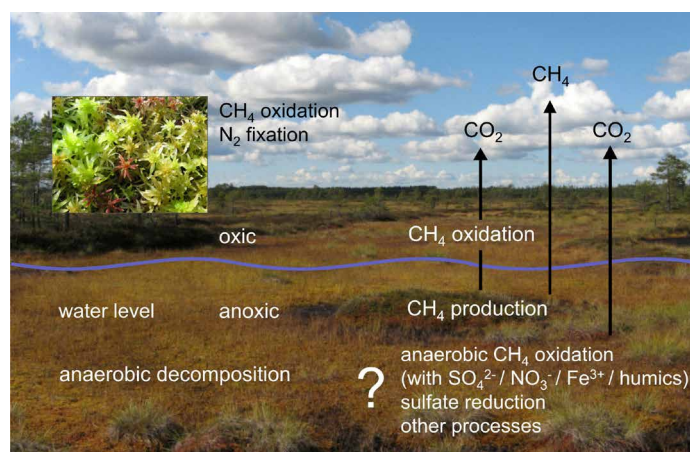


Figure 1. Coupling of oxidation of methane on terminal electron acceptors and humics.

reduction. The importance of anaerobic  $\text{CH}_4$  oxidation in mires is currently unclear, with estimates ranging from 0.3-0.8% and  $21 \pm 16\%$  of  $\text{CH}_4$  produced being oxidized anaerobically (Blazewicz et al. 2012, Gupta et al. 2013). Moreover, the electron acceptor facilitating the process in peat has not been identified and does not appear to be sulfate, nitrate or iron. Organic compounds such as humic substances have been suggested as an alternative but their role remains unverified.

Aerobic and anaerobic  $\text{CH}_4$  oxidizers have an important role in reducing the amount of  $\text{CH}_4$  emitted into the atmosphere. In addition, recent work has revealed how  $\text{CH}_4$  oxidizers in Sphagnum mosses are connected to nitrogen cycling with implications on the nitrogen budget of mires. Sphagnum methanotrophs not only provide carbon to the moss, but they were shown to be associated with nitrogen fixation (Larmola et al. 2014). Over one third of moss-associated nitrogen fixation was observed to be induced by  $\text{CH}_4$  oxidation in young mires. Methanotrophic nitrogen fixation can explain a discrepancy between atmospheric nitrogen deposition and long-term nitrogen accumulation in peat (Larmola et al. 2014).

Methane emission from peat is the result of anaerobic and aerobic microbial processes, which are further linked to other contributing or competing processes. Recent literature and observations suggest that there are unknown or unrecognized processes releasing carbon from anoxic peat. These processes and the microbes participating in them control the strength of mires as greenhouse gas sources. Better understanding of the role of fermentation processes, sulfate reduction and anaerobic  $\text{CH}_4$  oxidation in anoxic peat and the role of methanotrophs in Sphagnum mosses will help to evaluate how environmental changes and management including drainage and restoration will affect carbon storage and greenhouse gas production of mires.

#### Acknowledgements:

I thank Anuliina Putkinen and Hannu Fritze for data on sulfate reducers and Tuula Larmola for information on methanotrophic nitrogen fixation.

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Riku Lumiaro

## Coupled processes affecting fluxes of greenhouse gases in agricultural soil

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### The ecosystem services by greenhouse gas producing processes

Greenhouse gases (GHGs) include carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ) and dinitrogen oxide ( $\text{N}_2\text{O}$ ) and other multi-atomic gases that absorb IR radiation by molecular vibrations and cause warming of the atmosphere. Water vapour ( $\text{H}_2\text{O}$ ) is by far the most important greenhouse gas with a warming impact of  $+33^\circ\text{C}$ , but with rapid circulation, it is of minor environmental concern and less impacted by human activities in contrast to the emissions of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  that correspond to 57%, 16% and 6%, respectively, of the radiative forcing change since 1750 (Blasing 2013). As the production of  $\text{CO}_2$  in oxic and anoxic soils is broadly compensated by the plant synthesized C, and  $\text{CH}_4$  is produced in anoxic natural peat soils and consumed in the oxic conditions of drained cultivated soils,  $\text{N}_2\text{O}$  remains the most important GHG emitted from agricultural soils. The emissions of  $\text{N}_2\text{O}$  correspond to 60% of GHG emissions of agricultural sector in Finland and are the main focus here.

The ecosystem services by GHGs are not merely restricted to their contributions to climate warming but they have a larger role as part of the universal cycles of carbon and nitrogen. The processes producing and consuming GHGs are coupled to the decomposition and mineralization of organic matter, nitrification and denitrification by microbes in soil. These processes transform nutrients from organic to plant-available mineral forms and recycle C and N from soil back to the atmosphere, which ultimately make possible the biological production for food, feed, fiber, and other purposes.

### Coupled processes affecting GHG production in soil

Greenhouse gases, such as  $\text{N}_2\text{O}$ , are by-products of coupled processes of mineralization of organic matter, denitrification and nitrification in soil. The term “coupled process” implies that additional factors besides the components of process are involved and

something else occurs concurrently with a given process. If two processes are coupled, neither process is the same without the other. In soil, coupling often includes multiple concurrent processes with total or partial interactions. The processes of GHG production in soils are coupled at several levels, including the coupling by 1) interdisciplinary phenomena, e.g. biophysical phenomena such as gas fluxes and biochemical phenomena such as enzyme activities, 2) chemical reaction (reduction, oxidation), 3) reaction chains: sharing partly the same reactants, 4) transport of substances (temporal and spatial coupling), 5) the hierarchy of regulation (proximal and distal), and 6) the multiple impacts by the same factors.

Oxidation of organic matter, denitrification and nitrification are redox reactions, where the oxidation (electron loss) of one substance is coupled to the reduction (electron access) of another. In cellular respiration, the reduced organic compounds are oxidised back into inorganic forms and the electrons released are transferred by a respiratory chain to available terminal electron acceptors (TEA). For energetic reasons, microbes generally prefer molecular  $O_2$  over other TEAs, but in lack of oxygen, facultative and anoxic microbes can use other redox-sensitive molecules, such as  $NO_3^-$ , Mn(IV), Fe(III),  $SO_4^{2-}$ , and in extremely reduced conditions even  $CO_2$ , for the purpose.

Nitrification is a strictly oxic process that oxidizes ammonium to nitrite, and nitrite to nitrate. In soil, chemoautotrophic bacteria and Archaea assimilate  $CO_2$  by means of nitrification. At a slight oxygen deficiency nitrification produces  $N_2O$  as a by-product. Respiratory denitrification is not the opposite of nitrification, as it does not convert nitrate to ammonium. Instead, it is an important microbial process for the oxidation of organic matter in oxygen deficient soils. The respiration chain transfers the electrons in a stepwise manner to nitrate and other oxides of nitrogen, and eventually produces  $N_2O$  and  $N_2$  gases as end products. The so-called "co-denitrification" is still another process sharing common intermediates with nitrification and denitrification by which amino acids or other nitrogen containing molecules react with  $NO_2^-$  or  $NO$  by N-nitrosation (Spott *et al.* 2011). It produces  $N_2O$  and/or  $N_2$  depending on the substrates and immobilizes nitrite and nitrate into organic matter at conditions ranging from oxic to anoxic. The contribution of co-denitrification can explain why the total denitrification is at times larger than the amount of nitrate applied. The co-substrate utilization in denitrification has received renewed attention recently (Baggs 2011). The scarce data available indicate co-denitrification probably mobilizes mainly  $N_2$  rather than  $N_2O$  in soil (Spott *et al.* 2011).

In soil, mineralization, nitrification and denitrification are coupled as a reaction chain: mineralization releases ammonium that is oxidized by nitrification to nitrate that may be in turn be denitrified (Figure 1). In addition, sharing of reaction intermediates, such as  $NO_2^-$  and  $N_2O$ , and co-denitrification may cause additional coupling between the processes.

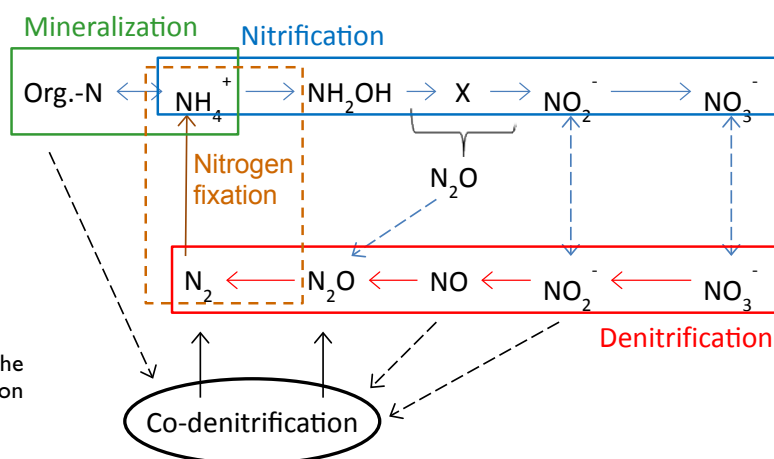


Figure 1. Interrelations between the processes affecting  $N_2O$  production in soil (modified from Schmidt 1982).

## Processes affecting N<sub>2</sub>O emissions from soil

The N<sub>2</sub>O emissions from soil are affected by its production and transport processes. The coupling of involved processes can be described by the leaky pipe model (Figure 2), where the N<sub>2</sub>O emissions are determined by the rate of N flow through the pipes and the release of N<sub>2</sub>O from each process (holes in the pipe). N<sub>2</sub>O emissions are thus increased by factors that increase the microbial activity in soil (mineralization, nitrification, denitrification), such as increased water content, organic residue incorporation, fertilization, temperature and pH. On the other hand, the plant uptake of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> reduces the emissions.

Mineralization, nitrification and denitrification are often temporally and spatially coupled by the transport of substances between oxic and anoxic soil parts even in apparently well aerated soil. The key concept is the development of anoxic microsites, e.g. when the O<sub>2</sub> diffusion from air-filled macropores is not rapid enough to supply the demands of the actively respiring microbes within the water-saturated aggregates (Figure 3). Oxic conditions at the aggregate surface facilitate rapid mineralization and nitrification that produce nitrate ions that may enter anoxic microsites by diffusion and become denitrified to N<sub>2</sub>O and N<sub>2</sub> gases.

Nitrification and denitrification are much dependent on the soil structure and water content that determine the water-filled habitat for microbes and the rate of gaseous diffusion in soil. In dry soil, N<sub>2</sub>O production is minimal. In well-aerated moist soil, N<sub>2</sub>O production increases but remains often small and dominated by nitrification. In wetter soil, especially at >60% of pores filled with water, denitrification increases rapidly and dominates the N<sub>2</sub>O production. Near saturation, denitrification produces increasingly more N<sub>2</sub> relative to N<sub>2</sub>O, which may reduce the production of N<sub>2</sub>O despite large denitrification, because anoxic microsites and the slow rate of gas diffusion increases the likelihood of N<sub>2</sub>O being reduced to N<sub>2</sub> before escaping from the soil. The volume of anoxic microsites increases rapidly with increasing temperature, because the rate of respiration increases more rapidly with temperature than diffusion of O<sub>2</sub>. The respiration of roots and microbes generally decreases with decreasing pH. However, the enzymes involved in the production of N<sub>2</sub>O differ in their sensitivity to acidity. Low pH favours the production of N<sub>2</sub>O over N<sub>2</sub>.

The different microbial species participating in the production of GHGs are not isolated from each other but live as microbial communities in soil. The production of GHGs is thus not only coupled to the immediate “proximal controls” (availability of organic substrates and mineral N forms, O<sub>2</sub>, temperature, pH) of the processes involved, but also to more “distal controls” (related to climate, land use, cropping techniques and soil management) that determine the composition of microbial communities. Čuhel & Šimek (2011) showed that the denitrifying enzyme activity (the denitrifying microbial community) is mainly under distal control, but as the lowering of pH increases the end product ratio of N<sub>2</sub>O/(N<sub>2</sub>O+N<sub>2</sub>), it is clearly under proximal pH control.

A given factor may have counteracting impacts on the GHG in production due to coupling of multiple processes. For instance, the impact of water depends on the water content. Mechanical soil tillage is often effective in loosening and enhancing soil aeration in topsoil only at the expense of compacting and impairing the aeration of underlying soil. The formation of large pores by burrowing earthworms is a well-known process of natural soil structure development that enhances the drainage and aeration of soil and facilitates easier rooting for plants. At the same time, the earthworm gut is recognized as an anoxic microsite and a habitat for denitrifying microbes causing positive correlations of earthworm numbers and N<sub>2</sub>O emissions in manipulated experiments (Drake & Horn 2007). The relative importance of the enhanced aeration by improved soil structure and the increased N<sub>2</sub>O emissions from earthworm guts in natural settings require future research.



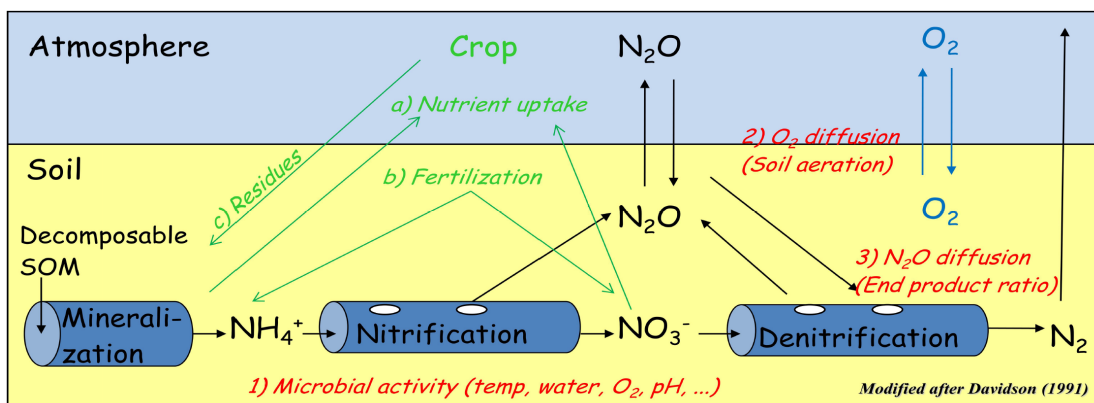


Figure 2. The leaky pipe model of processes affecting  $N_2O$  emissions from soil.

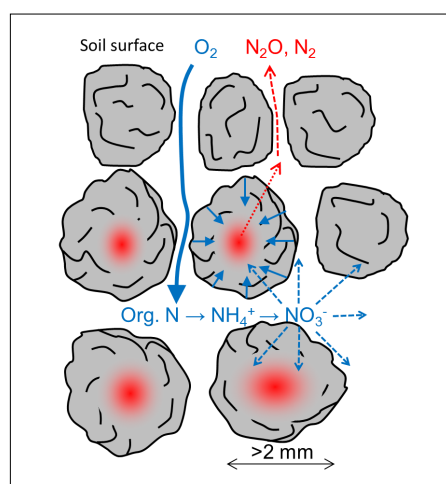


Figure 3. Coupling of mineralization, nitrification and denitrification for the production of  $N_2O$  at the anoxic microsites within soil aggregates (after Ball 2013).

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## Food webs and biogeochemistry in freshwater systems

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### Introduction

Early views of lakes as self-contained ecosystems have changed radically. Lakes (and rivers) are now viewed as integral components of a wider catchment-scale system. Delivery of nutrients, especially phosphorus (P), from catchments is well-established as a key process determining lake productivity and water quality. More recently, evidence has been accumulating that in more lakes than previously suspected productivity can be regulated by nitrogen (N) availability. However, it is important to recognise that the biogeochemical cycles of many of the key nutrients in lakes are closely coupled. For example, Finlay *et al.* (2013) showed how increased P inputs from human activities have stimulated N removal processes in many lakes. The corollary of this is that efforts to improve lake water quality by P removal will promote accumulation of N in the water column of lakes and its subsequent export. Hence alteration of one biogeochemical cycle can be expected to have ramifications in other, coupled cycles. Freshwaters are also now recognised to be strongly implicated in the global carbon (C) cycle, with one recent estimate of the global C emission from inland waters put at 2.1 PgCyr<sup>-1</sup>, or greater than the transport of C from the continents to the oceans (Raymond *et al.* 2013). This emitted carbon derives both from degassing of CO<sub>2</sub> from supersaturated catchment drainage water entering lakes (e.g. Maberly *et al.* 2012) and from CO<sub>2</sub> produced by processing of organic carbon of terrestrial origin transported into lakes, but the balance between these mechanisms is still poorly understood. My focus here is on how loading of terrestrial organic matter to lakes can affect lake carbon fluxes through its impact on food webs, coupling terrestrial and aquatic carbon biogeochemical cycles.

### A changing view of lake carbon fluxes

Accumulating evidence, especially from stable isotope studies, is showing how allochthonous (terrestrial) organic carbon can enter lake food webs, mainly via a microbial link between dissolved organic matter (DOM) and zooplankton (Figure 1). Grey *et al.* (2001) used natural abundance stable isotope analysis to show that around 40% of zooplankton carbon in Loch Ness could be traced to allochthonous carbon. To circumvent the frequent overlap of <sup>13</sup>C signatures of autochthonous and allochthonous end members in lakes, some studies have used whole-lake tracer additions of <sup>13</sup>C-labelled bicarbonate to label the phytoplankton. Such studies have generally also shown an important contribution of allochthonous C to zooplankton consumers (e.g. Taipale *et al.* 2008), at least in moderately brownwater lakes. A whole-lake addition of cane sugar (from a C<sub>4</sub> plant) to a small humic lake in southern Finland allowed the distinct <sup>13</sup>C signature of the sugar-C to be traced into zooplankton and littoral zoobenthos, and thence to fish, and suggested that around 20-30% of fish carbon in the lake could be derived from allochthonous C. However, the sugar addition produced a less than expected change in emissions of CO<sub>2</sub> from the lake (Peura *et al.* 2014), probably due to P and N availability constraining processing of DOM. This illustrates why efforts to understand likely impacts on lakes of increased transport of C from catchments as a predicted consequence of climate change will need to take into account the tight coupling between C, N and P cycles. Biogenic methane produced in the anaerobic sediments and hypolimnetic waters of lakes has also been identified

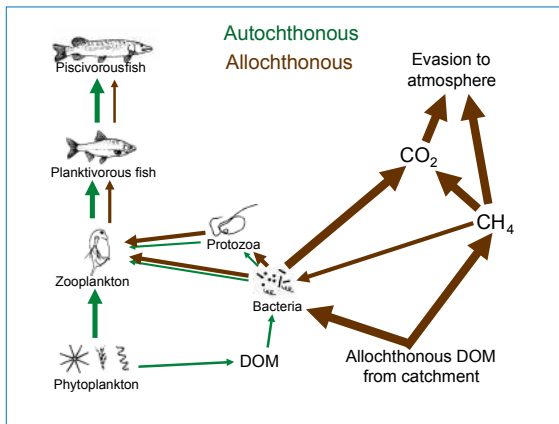


Figure 1. How allochthonous organic matter can contribute to lake food webs in parallel with autochthonous production. The magnitude of the contribution in different lake types is still contentious.

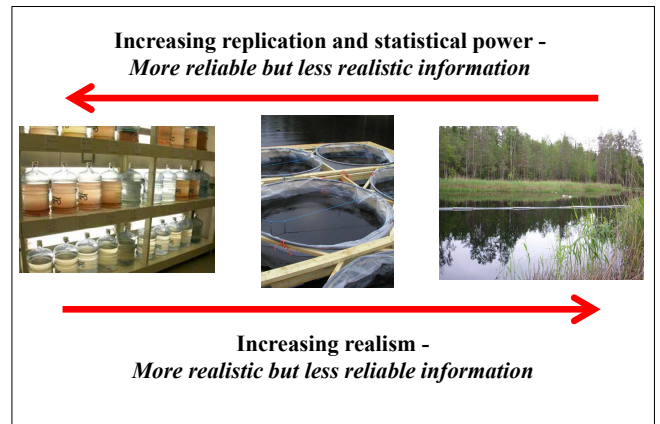


Figure 2. The balance between reliability and realism in experiments at different ecological scales

as contributing widely to lake food webs (Jones & Grey 2011). Around 20% of ruffe carbon biomass in Lake Jyväsjärvi was traceable to biogenic methane (Ravinet *et al.* 2010). In some lakes, especially in the boreal zone, this biogenic methane may derive largely from allochthonous organic matter originating in the lake catchment.

### Future studies

Ecological mechanisms can only properly be revealed and confirmed by experimentation. Ecological experiments have been conducted at various scales, offering a different balance between reliability and realism of the information produced (Figure 2). Realistic and meaningful information regarding coupled biogeochemical cycles can probably only be obtained from experiments at the whole-ecosystem scale, but such experiments have been rare and the information obtained has generally been of low reliability, because of the very high costs of large-scale experiments and the difficulty of incorporating any true replication. Therefore researchers and funding agencies need to think big for the future. Well-designed whole-lake-catchment manipulation studies of coupled biogeochemical cycles that will yield reliable information are badly needed, but will require innovative approaches to funding if they are to receive the levels of resources necessary to underpin them properly.

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## Multitude of microbial processes are coupled to cycling of nitrogen in aquatic systems

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The natural nitrogen cycle is an essential ecosystem service that includes processes that support growth of all life on planet Earth, nitrogen being a fundamental building block of biological macromolecules such as DNA and proteins. All nitrogen originates from the huge storage in the atmosphere, of which dinitrogen comprises about 80%. Bound in various organic and inorganic compounds, it flows through different reduction-oxidation (redox) processes to return back to the atmosphere. Since 1950s the increased use of artificial fertilizers has led to eutrophication. Too much nutrients enter the aquatic systems from drainage basin, either directly from e.g. waste water treatment plants (WWTPs), or indirectly, diffusing from the surrounding areas. Eutrophication increases the productivity of the water ecosystems, resulting in oxygen problems when increased algal biomass is mineralized. Oxygen deficiency is not only harmful to fish and benthic fauna, but affects nutrient cycling as well.

Nitrogen processes in aquatic systems are mainly run by microbes. Mineralization produces ammonium, which is oxidized to nitrite and nitrate in a nitrification process that needs oxygen. The nitrite and nitrate formed diffuse to bottom sediments that are usually anoxic just millimeters below sediment surface. In the sediments, nitrite and nitrate are reduced back to dinitrogen gas in denitrification and anammox processes that can only take place in anoxic conditions. Dinitrogen gas then diffuses out of the water ecosystem and returns to the atmosphere. This dinitrogen gas production is an efficient way to remove nitrogen from water ecosystems. For example, naturally occurring denitrification and anammox remove about 30% of nitrogen entering the Gulf of Finland annually (Hietanen & Kuparinen 2008, Jäntti *et al.* 2011). Both of these

microbial processes are also exploited commercially in nitrogen removal in WWTPs, such as the modern WWTP in Viikinmäki that reaches about 90% removal efficiency using the denitrification process. Removing nitrogen in such a plant is costly, though, highlighting the importance of keeping the conditions favorable for natural nitrogen removal in water ecosystems. For example, the city of Jyväskylä in central Finland does not need to invest in expensive nitrogen removal facility in the WWTP, because the high-nitrogen water discharged from the plant flows through a chain of lakes and rivers, each effectively removing nitrogen, before entering the nitrogen-limited Baltic Sea.

Because the processes are run by microbes, the nitrogen cycle is connected to the cycles of many other elements, and changes in these affect nitrogen cycle as well. Eutrophication induces imbalance in oxygen demand and supply, resulting in hypoxia (oxygen concentration below 2 mg per liter) and even anoxia in water ecosystems. When hypoxia is frequent or repeated, nitrogen removal can be replaced by another nitrate consuming process, dissimilatory nitrate reduction to ammonium (DNRA). In this process, nitrate formed in nitrification is reduced to ammonium instead of nitrogen gas, and no nitrogen removal takes place. Ammonium formed may then be nitrified again to nitrite and nitrate. If oxygen concentration drops further, nitrification ceases, no nitrite and nitrate is formed, nitrogen removal cannot proceed, and ammonium accumulates in the water. This situation is similar to the internal loading of phosphorus in which oxygen deficiency launches release of phosphorus from the sediments. Keeping the oxygen conditions well above hypoxia is therefore beneficial for both nitrogen and phosphorus cycles.

Phosphorus affects nitrogen removal in two different ways. Firstly, microbes need phosphorus for their growth and function, but it seldom is in short supply in sediments. Secondly, in order to be mineralized and, in the end, removed, the nitrogen entering water ecosystem has to reach the sediment. In freshwater ecosystems, decreasing phosphorus loading has led to decreased nitrogen removal, as less algae are produced, leading to less sedimentation and thereby less mineralization (Finlay *et al.* 2013). While decreasing phosphorus loading is good in terms of counteracting eutrophication, it may thus lead to increased transport of nitrogen to the sea.

Especially in marine ecosystems sulphur, mainly in the form of hydrogen sulphide, may either enhance or disrupt nitrogen cycle, depending on the microbes that run the nitrogen processes. Hydrogen sulphide is a compound toxic to most organisms, but some specialized microbes gain energy from oxidizing it. For example, in the Baltic Sea water column, intensive nitrogen removal is powered by hydrogen sulphide diffusing from the anoxic depths (Hietanen *et al.* 2012, Dalsgaard *et al.* 2013), whereas no nitrogen removal occurs in the sulphidic sediments of the Gulf of Finland (Jäntti & Hietanen 2012). In Pacific continental margin specialized microbes fuelled by sulphide co-operate with anammox bacteria that remove nitrogen (Prokopenko *et al.* 2013). New information about the role of sulphur in the nitrogen cycle is accumulating constantly.

Similar to sulphur, the effect of carbon depends on the community present. In sediments, denitrification gains energy from oxidizing organic carbon that enters the sediment for example as algal particles. Anammox bacteria, however, do not use organic carbon for energy but still need ammonium and nitrate produced in mineralization of organic material. Similarly, nitrification uses ammonium from mineralization, and therefore these processes depend on the availability of the organic material as well. Decreasing nutrient loading may lead to decreased organic matter availability, decreasing nitrogen removal, but on the other hand, too high availability leads to oxygen concentration decrease and again to disturbances in nitrogen removal. Nitrogen cycle is connected to the carbon cycle also via climate gas methane. Recent studies have shown that specialized bacteria, archaea and consortiums of these can

oxidize methane as well as ammonium in coupled ammonium-methane-oxidation processes, mitigating both eutrophication (by nitrogen removal) and climate change (by oxidizing methane to carbon dioxide) at the same time.

In addition to these major elements, nitrogen cycle connects with many trace element cycles. For example manganese has long been suspected to play a role in redox processes coupled to nitrogen, but no credible evidence exists to date. Some microbes normally reducing iron for energy can switch to nitrate reduction, and others oxidize reduced iron with nitrate. Recently, two microbes were proven capable of oxidizing iron and reducing nitrate to dinitrogen gas at the same time, although very slowly and only when there was plenty of both iron and nitrate available (Oshiki *et al.* 2013).

Nitrogen cycle research was long hampered by a lack of tools to study such microbial interactions. Recent leaps in technology and methods have challenged many old views, and more surprises are sure to follow.

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## Iron provides ecosystem services through coupled biogeochemical cycles

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## Human actions enhance the sensitivity of phosphorus towards microbial redox-reactions

There has been a world-wide increase in the exploitation of calcium phosphorus reserves (mainly apatite, Figure 1) after World War II. These reserves have remained

out of reach of biota but are now spread on fields to support agricultural production. It is likely that phosphorus in our bodies originates mainly from the mined rock. However, only about 20% of the mined phosphorus reaches human consumption, while the remaining phosphorus is building up in the soil or is transported to the water bodies. In agricultural soils phosphorus is bound to iron and aluminum oxides or converted to an organic form. Also the phosphorus coming from municipalities and industry is largely captured by iron in sewage treatment plants.

Thus, there is a world-wide shift underway from the pH sensitive calcium bound phosphorus to redox-sensitive iron and organically bound phosphorus. This anthropogenic phosphorus is now dispersed in the freshwater, estuarine and coastal systems. Despite the vast number of phosphorus studies, there is still lack in understanding of the ultimate fate of anthropogenic phosphorus. For example, we do not know well the behavior of organic phosphorus or that of soil- and humic-bound iron carrying P into aquatic systems (Figure 2).

### Eutrophication and mineralization processes

Loading of nutrients increases the amount of organic matter and causes pressure on mineralization. When oxygen – the most important oxidant of organic matter – is depleted, anaerobic mineralization processes begin to use nitrate, manganese and iron oxides and sulphate. These substances are called terminal electron acceptors (TEAs) and they gain electrons bound to organic matter in the redox-process.

It is not insignificant which TEA is used in mineralization, because mineralization processes may lead to further redox-reactions. Oxidic respiration producing carbon dioxide and water and denitrification producing nitrogen gas do not result in subsequent redox-reactions. However, the reduction of manganese, iron, sulphate, and production of methane may trigger secondary redox-reactions, which couple biogeochemical cycles. It is well known that the phosphorus bound to redox-sensitive iron oxides explains the release of phosphorus after the depletion of oxygen. However, the linkage between oxygen and phosphorus release is not that simple and here we describe how primary and secondary redox-reactions couple carbon, iron and sulphur to each other and link non-redox sensitive phosphorus to their cycles.



Figure 1. Opencast apatite mine in Siilinjärvi.



Figure 2. Anoxic groundwater surfacing in a stream resulting in the precipitation of iron oxides (wasteland in Helsinki, southern Finland)

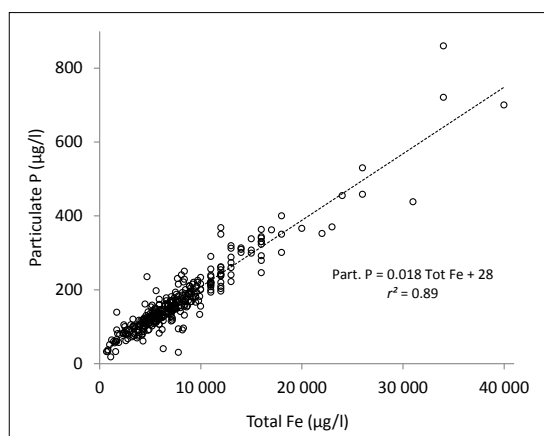


Figure 3. Relationship between total iron and particulate phosphorus in the agriculturally loaded river Paimionjoki.

### Coupling of carbon, iron and sulphur controls the phosphorus retention in aquatic systems

Low pH and the abundance of iron favor the binding of phosphorus to iron oxides in Finnish soils. As a result, the concentrations of iron and phosphorus correlate strongly in river water of the agriculturally dominated catchments (Figure 3). With regard to ecological impact of iron-bound phosphorus, it is relevant to examine which kind of system phosphorus enters, is settled, processed and eventually buried. Let's consider sulphate-poor and rich systems where the reduction of iron is mainly controlled by two contrasting microbial processes. In the first process, microbes use iron oxides as electron acceptors (dissimilatory iron reduction) and they grow just by using iron for their respiration. In the second process, sulphate reducing microbes (dissimilatory sulphate reduction) produce sulphides ( $H_2S$ ,  $HS^-$ ) which reduce iron oxides or form sulphides with reduced iron.

In oxic conditions, the sulphate poor and rich systems should have a similar ability to retain phosphorus. The difference between the systems emerges under anoxia. In sulphate poor systems iron oxides are reduced by iron reducers maintaining the concomitant release of iron and phosphorus to water (Figure 4). The excess of reduced iron guarantees the invariable potential of iron to bind phosphorus when re-oxidation occurs and a "ferrous wheel" is going on reducing and oxidizing iron, liberating and capturing phosphorus. On the contrary, in eutrophic sulphate-rich systems the cycling of iron is blocked by the formation of solid iron sulphides, the ferrous wheel is stopped, and sediments release only phosphorus without release of iron into bottom water. In this way, the reduction pathways couple the cycles of iron and sulphur and produce different consequences for iron and thereafter phosphorus availability.

Although severe symptoms of eutrophication are found in sulphate poor and rich systems, the coupled iron and phosphorus cycle is more sensitive to be deteriorated in sulphate rich systems. However, considerable amount of labile organic carbon is needed to generate sulphate reduction, so sulphate alone cannot support iron sulphide formation in surface sediments. When there is enough organic carbon, sulphate reduction may block the iron cycling giving way to accumulation of phosphorus in water (see Lehtoranta et al. 2009).



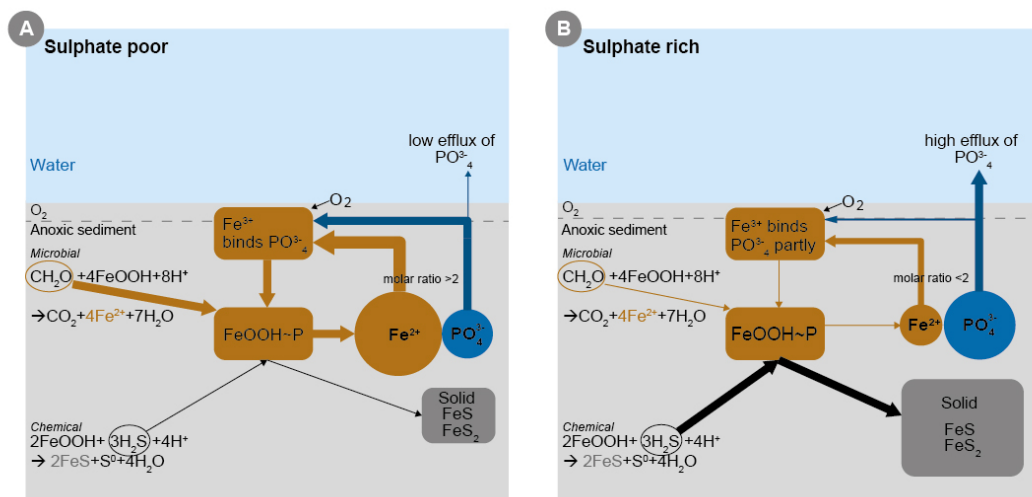


Figure 4. Cycling of iron, sulphur and phosphorus in sulphate-poor and sulphate-rich aquatic systems. A) In sulphate-poor systems, iron oxides are reduced by microbes to dissolved Fe<sup>2+</sup>. There is plenty of Fe<sup>2+</sup> to form new iron oxides, which capture phosphorus when the reduced iron meets the oxic zone. Cycling of iron and phosphorus is controlled by the microbial iron reduction and re-oxidation of iron. In these systems phosphorus release from sediment to water is small. B) In eutrophic sulphate-rich systems, sulphate reduction produces sulphides, which reduce iron oxides chemically and form solid iron sulphides. In these conditions Fe<sup>2+</sup> is in too short a supply to form enough iron oxides to bind phosphorus. Iron is buried as solid iron sulphides, whereas phosphorus is released to the water column. Modified from Lehtoranta and Ekholm (2012).

### Acknowledging regulating services provided by coupled biogeochemical cycles

Large part of the anthropogenic phosphorus is bound to iron. We acknowledge that the ability of iron to bind phosphorus is a dis-service, e.g. in cultivation of iron-rich soils, but in aquatic systems iron produce regulating ecosystem services by enhancing the system's ability to retain phosphorus out of reach of biota. In contrast, plentiful sulphate with increasing eutrophy may create dis-services by preventing the irons ability to bind phosphorus. Thus the loading of nutrients producing organic matter causes a greater threat for availability of phosphorus in sulphate-rich systems. More specifically, sulphate-rich systems may decouple the cycling of iron and phosphorus due to eutrophication and hence fail to maintain the regulation services for phosphorus. Iron and sulphate may also affect provisioning (e.g. bias in fish community) and cultural services (decreased recreational values) by influencing supporting ecosystem services. Such a change in services occurred in the Netherlands where an increase in the flux of electron acceptor alone (i.e. sulphate) triggered the release of phosphorus from sediment and deteriorated the water quality up to a point of a regime shift (Smolders and Roelofs 1993).

The present abatement measures to reduce nutrient loading from diffuse sources do not acknowledge that measures also affect electron acceptors such as iron oxides and sulphate. We state that the coupled biogeochemical cycles driven by the microbes and electron acceptors have to be taken into account when the water protection measures are planned to maintain the ecosystem services.

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## Coupling elements and disciplines

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The seminar “Coupled biogeochemical cycles and ecosystem services” examined the physics, chemistry and (micro)biology of terrestrial and aquatic systems and made an effort to relate these to human well-being through the concept of ecosystem services, the regulating and maintenance services in particular. Linking biogeochemistry and ecosystem services appears to be a novel approach. The Web of Science recognized 7753 articles on the topic “ecosystem service\*”, the number of citations to articles increasing exponentially from 1997 to 2013. The topic “coupled biogeochemical cycle\*” was examined only in 23 articles, of which the two articles on coupling only C and N received 42% of the citations. Although there are numerous papers where a multitude of substances have been determined simultaneously e.g. for monitoring purposes, only a few of them have linked the elements cycles together. Not surprising, a search with both “coupled biogeochemical cycle\*” and “ecosystem service\*” as topics found no hits.

The seminar also revealed that there exist unexplored territories even in excessively studied element cycles and highlighted the need for a broad perspective. Sound understanding of the functioning of the field, forest, peatland, freshwater and marine ecosystems is a key prerequisite for planning cost-efficient management strategies for each of them. Comparison of the biogeochemical processes and their drivers between the systems reveals the differences and shows that they must be managed accordingly.

One of the main shortages in our knowledge on coupling of processes is that we do not know to which direction the primary process continues under the invariably changing environmental conditions. For example, a primary process, oxidation of

ammonium to nitrate, may continue so that nitrate is used to oxidize reduced iron, sulphides or methane or it can be assimilated by biota. The question that arises is how to restore the system's ability to provide favourable processes and prevent the harmful ones and describe both processes from a point of view of ecosystem services? Perhaps the concept of ecosystem services can be used to define the realm of multidisciplinary environmental research: to study the impacts of human actions on the environment and find ways to manage these actions so that the consequences are tolerable.

Although the term multidisciplinary may be seen as yet another buzzword, shedding only one light on a multifaceted environmental problem poses a risk that the diagnosis is wanting and the cure inefficient. Often a genuinely multidisciplinary approach is really needed to understand the complex linkage between human actions and environmental problems. We acknowledge that it is challenging to combine novel hypotheses of natural science to innovative socio-economic or policy research, especially in one and only project. Sometimes the outcome has been that most of the project period is spent in testing the hypothesis set for natural science, which should have formed the starting point for socio-economic work package. Still, according to our experience, co-operation between ecological, socio-economic and policy research can be beneficial for all the disciplines, if sufficient time is left for "cross-fertilization", i.e. fruitful discussions of discipline-specific research questions, terms and approaches. As in dialects, a term may have different meaning among academic disciplines. Yet another problem is that the results of an interdisciplinary project may not be interesting from the standpoint of any of the participating disciplines alone, although they would greatly enhance our understanding of the socio-ecological system and its management. On the other hand, the mere fact that a paper is multidisciplinary should not earn publishing, but it should really reveal something new or corroborate tentative findings.

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## DOCUMENTATION PAGE

<i>Publisher</i>	Finnish Environment Institute			<i>Date</i> June 2014
<i>Author(s)</i>	Jouni Lehtoranta, Petri Ekholm, Petteri Vihervaara, Pirkko Kortelainen			
<i>Title of publication</i>	<b>Coupled biogeochemical cycles and ecosystem services</b>			
<i>Publication series and number</i>	<i>Reports of the Finnish Environment Institute</i> 21 / 2014			
<i>Theme of publication</i>				
<i>Parts of publication/ other project publications</i>	The publication is available in the internet: <a href="http://www.syke.fi/publications">www.syke.fi/publications</a>   <a href="http://helda.helsinki.fi/syke">helda.helsinki.fi/syke</a>			
<i>Abstract</i>	<p>Human activities disturb the biogeochemical cycles often resulting in limited eco-system services. The cycles of biologically active elements are also coupled to each other which is rarely acknowledged in ecosystem studies. Many of the regulating and maintenance services are linked to element cycles driven by micro-organisms, but these have often been omitted in ecosystem service studies. In the present publication the terminology of ecosystem services are used to help to define and describe the coupled biogeochemical processes and to highlight their importance in both terrestrial and aquatic ecosystems. The extended abstracts offer fresh viewpoints on biogeochemical cycles and on the management of their fluxes. The abstracts may also function as basis for new themes for research.</p>			
<i>Keywords</i>	regulating ecosystem services, biogeochemical cycles, ecosystem, mineralization,			
<i>Financier/ commissioner</i>				
	ISBN (pbk.) -	ISBN (PDF) 978-952-11-4349-6	ISSN (print) -	ISSN (online) 1796-1726
	<i>No. of pages</i> 39	<i>Language</i> English	<i>Restrictions</i> public	<i>Price (incl. tax 8 %)</i> -
<i>For sale at/ distributor</i>	Finnish Environment Institute (SYKE), neuvonta P.O. Box 140, FI-00251 Helsinki, Finland Email: <a href="mailto:neuvonta.syke@ymparisto.fi">neuvonta.syke@ymparisto.fi</a>			
<i>Financier of publication</i>	Finnish Environment Institute (SYKE), P.O. Box 140, FI-00251 Helsinki, Finland Phone +358 20 610 123 (from 30.10.2013 number is 0295 251 000)			
<i>Printing place and year</i>				

## KUVAILULEHTI

Julkaisija	Suomen ympäristökeskus SYKE			Julkaisu-aika Kesäkuu 2014
Tekijä(t)				
Julkaisun nimi	<b>Coupled biogeochemical cycles and ecosystem services</b> (Toisiinsa kytkeytyneet ainekierrot ja ekosysteemipalvelut)			
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen raportteja 21 / 2014			
Julkaisun teema				
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana vain internetistä: <a href="http://www.syke.fi/julkaisut">www.syke.fi/julkaisut</a>   <a href="http://helda.helsinki.fi/syke">helda.helsinki.fi/syke</a>			
Tiivistelmä	<p>Ihmisen toiminta muokkaa ainekiertoja, mikä rajoittaa luonnon kykyä tuottaa ekosysteemipalveluja. Biologisesti aktiivisten aineiden kierrot ovat myös kytkeytyneet toisiinsa, mikä huomioidaan harvoin tarkasteltaessa aineiden kulkeutumista ekosysteemeissä. Mikrobiologiset prosessit ohjaavat sääteleviä ja ylläpitäviä palveluja, mutta niitä ei juurikaan huomioida ekosysteemipalveluihin liittyvässä tutkimuksessa. Tässä julkaisussa määritellään ja kuvataan kytkeytyneisiin ainekiertoihin liittyviä prosesseja, joilla havainnollistetaan sääteleviä ja ylläpitäviä ekosysteemi-palveluja sekä maa- että vesiekosysteemeissä. Laajennetut tutkimustiivistelmät tarjoavat tuoreita näkökulmia ainekiertoihin ja kuormituksen hallintaan ja voivat toimia uusien tutkimusaiheiden pohjana.</p>			
Asiasanat	ekosysteemipalvelut, ainekierrot, ekosysteemi, mineralisaatio,			
Rahoittaja/ toimeksiantaja				
	ISBN (nid.)	ISBN (PDF) 978-952-11-4349-6	ISSN (pain.)	ISSN (verkkoj.) 1796-1726
	Sivuja 39	Kieli Englanti	Luottamuksellisuus julkinen	Hinta (sis.alv 8 %)
Julkaisun myynti/ jakaja	Suomen ympäristökeskus (SYKE), neuvonta PL 140, 00251, Helsinki Sähköposti: <a href="mailto:neuvonta.syke@ymparisto.fi">neuvonta.syke@ymparisto.fi</a>			
Julkaisun kustantaja	Suomen ympäristökeskus (SYKE), syke.fi PL 140, 00251, Helsinki, puh. 0295 251 000			
Painopaikka ja -aika				



## PRESENTATIONSBLAD

Utgivare	Finlands miljöcentral SYKE			Datum Juni
Författare	Jouni Lehtoranta, Petri Ekholm, Petteri Vihervaara, Pirkko Kortelainen			
Publikationens titel	<b>Coupled biogeochemical cycles and ecosystem services</b> (Kopplade biogeokemiska kretslopp och ekosystemtjänster)			
Publikationsserie och nummer	Finlands miljöcentrals rapporter 21 / 2014			
Publikationens tema				
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig på internet: <a href="http://www.syke.fi/publikationer">www.syke.fi/publikationer</a>   <a href="http://helda.helsinki.fi/syke">helda.helsinki.fi/syke</a>			
Sammandrag	<p>Mänsklig verksamhet stör de biogeokemiska kretsloppen, vilket ofta leder till begränsade ekosystemtjänster. De biologiskt aktiva ämnens kretslopp är också kopplade till varandra, vilket sällan beaktas i ekosystemstudier. Många reglerande och upprätthållande funktioner är kopplade till grundämneskretslopp styrda av mikroorganismer, men dessa har ofta ignorerats i forskning berörande ekosystemtjänster. I den föreliggande publikationen används terminologi från området ekosystemtjänster för att underlätta definiering och beskrivning av de kopplade biogeokemiska processerna och för att betona deras betydelse för både terrestra och akvatiska ekosystem. Sammanfattningarna erbjuder färsk synvinklar på biogeokemiska kretslopp och på styrningen av kretsloppens ämnesflöden. Dessa sammanfattningar kan även bilda en grund för nya forskningstemat.</p>			
Nyckelord	ekosystem, ekosystem tjänster, kretslopp, mineralisering			
Finansiär/ uppdragsgivare				
	ISBN (hft.)	ISBN (PDF) 978-952-11-4349-6	ISSN (print)	ISSN (online) 1796-1726
	Sidantal 39	Språk Engelska	Offentlighet offentlig	Pris (inneh. moms 8 %)
Beställningar/ distribution	Finlands miljöcentral (SYKE), PB 140, 00251 Helsingfors Epost: <a href="mailto:neuvonta.syke@ymparisto.fi">neuvonta.syke@ymparisto.fi</a>			
Förläggare	Finlands miljöcentral (SYKE), PB 140, 00251 Helsingfors, Tel. 0295 251 000 Epost: <a href="mailto:neuvonta.syke@ymparisto.fi">neuvonta.syke@ymparisto.fi</a>			
Tryckeri/tryckningsort och -år				

This report aims to improve our ability to discover the coupled biogeochemical cycles of elements in the terrestrial and aquatic ecosystems. The seminar abstracts distribute fresh viewpoints on the importance of coupled element cycles and processes and on their possible position in the control of ecosystem functions. The concepts of ecosystem services help to define and describe the chemical and microbial processes involved and to highlight their importance when pursuing towards better environmental management.



ISBN 978-952-11-4349-6 (PDF)

ISSN 1796-1726 (verkkoj.)