



A biogeochemical-hydrological framework for the role of redox-active compounds in aquatic systems

S. Peiffer¹✉, A. Kappler², S. B. Haderlein³, C. Schmidt², J. M. Byrne², S. Kleindienst⁴, C. Vogt⁵, H. H. Richnow⁵, M. Obst⁶, L. T. Angenent⁷, C. Bryce², C. McCammon⁸ and B. Planer-Friedrich⁹

Redox-driven biogeochemical element cycles play a central role in converting organic matter in aquatic ecosystems. They also perform key functions such as removing nitrate, mitigating the formation of greenhouse gases and weakening the effects of contaminants. Recent research has revealed the presence of redox-active compounds in these ecosystems with hitherto unknown redox properties. These substances are metastable (that is, non-equilibrium solid phases), which can both donate and accept electrons. They are highly redox reactive and recyclable and may act as biogebatteries by temporarily storing electrons. Their lifetime, however, is limited, and with time they become more crystalline and less reactive. In this Review, we argue that these redox-active metastable phases require activation by fluctuating redox conditions to maintain their high reactivity. In aquatic ecosystems, switching between oxidizing and reducing conditions can be achieved only through hydrological perturbations at hydrological interfaces (for example, water level fluctuations). We present a novel framework that links microscale biogeochemical processes to large-scale hydrological processes, and discuss implications and future research directions for biogeochemical element cycles in aquatic systems exposed to frequent hydrological disturbances.

Mitigation of greenhouse gas formation (for example, CO₂, CH₄ and NO_x), storage of carbon, removal of environmental pollutants such as nitrate and maintenance of the supply of high-quality drinking water are all key services provided by ecosystems. However, their function is ultimately linked to biogeochemical element cycles^{1–3} that can be fundamentally altered by changing climate and land use conditions. For example, increased extreme precipitation and drought events⁴ will amplify hydrological fluctuations (for instance, fluctuations in water level and changes of groundwater flow direction) that will directly affect feedback and processing of major element cycles in aquatic ecosystems. So, how do hydrological fluctuations affect element cycling?

Answering this question is challenging because the cycling of elements is driven by a complex network of biogeochemical processes (in most cases, redox reactions) that in many environments are tightly coupled to the dynamics of hydrological processes^{5–8}. Based on research from the past 10–15 years, we can now disentangle how this coupling operates from a biogeochemical point of view. Numerous laboratory studies have shown that the properties (for example, redox potentials and catalytic effects) of redox-active substances are dynamic, not static, and they vary over both time and space. These redox-active metastable phases (RAMPs) develop along a series of reactions between solid and aqueous redox substances and are sensitive to redox cycling (Box 1). Hence, they can play a critical role in element cycling in aqueous ecosystems. Yet, our knowledge about the formation of RAMPs, the activation of

their redox properties and, in particular, their function in natural systems is still in its infancy.

Here, we introduce the concept of RAMPs and argue that the temporal dynamics of small-scale (nano- to micrometre) redox reactivity is triggered by large-scale (metre to hectometre) hydrological fluctuations occurring at aquatic interfaces such as riparian zones, wetlands, root zones, anoxic/oxic-sediment/water interfaces or rice paddies. In addition, these small-scale geochemical responses affect large-scale ecosystem responses (for example, gas fluxes). The RAMP concept provides a comprehensive model to explain the occurrence of hot spots and hot moments of carbon mineralization rates at aquatic interfaces shaped by a large diversity of biogeochemical pathways and has many implications for the overall mass balance of carbon and nitrogen turnover, soil function and water purification processes.

Metastable phases under non-equilibrium conditions

Redox reactions are central to biogeochemical processes in aquatic systems. The redox ladder concept has been used to describe the sequence of redox reactions that take place along redox gradients according to the free energy gain obtained from oxidation of reduced substances with terminal electron acceptors and their availability⁹. The redox ladder concept predicts that the terminal electron acceptor with the highest free energy gain will be consumed first. Once it becomes depleted, the next terminal electron acceptor in the series will be consumed and so on. Inherent in this concept are end

¹Department of Hydrology, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Bayreuth, Germany.

²Geomicrobiology, Center for Applied Geoscience, University of Tübingen, Tübingen, Germany. ³Environmental Mineralogy, Center for Applied Geoscience, University of Tübingen, Tübingen, Germany. ⁴Microbial Ecology, Center for Applied Geoscience, University of Tübingen, Tübingen, Germany. ⁵Department of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research (UFZ), Leipzig, Germany. ⁶Experimental Biogeochemistry, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Bayreuth, Germany. ⁷Environmental Biotechnology Group, Center for Applied Geoscience, University of Tübingen, Tübingen, Germany. ⁸Bayerisches Geoinstitut, University of Bayreuth, Bayreuth, Germany. ⁹Environmental Geochemistry, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Bayreuth, Germany. ✉e-mail: s.peiffer@uni-bayreuth.de

Box 1 | What are RAMPs?

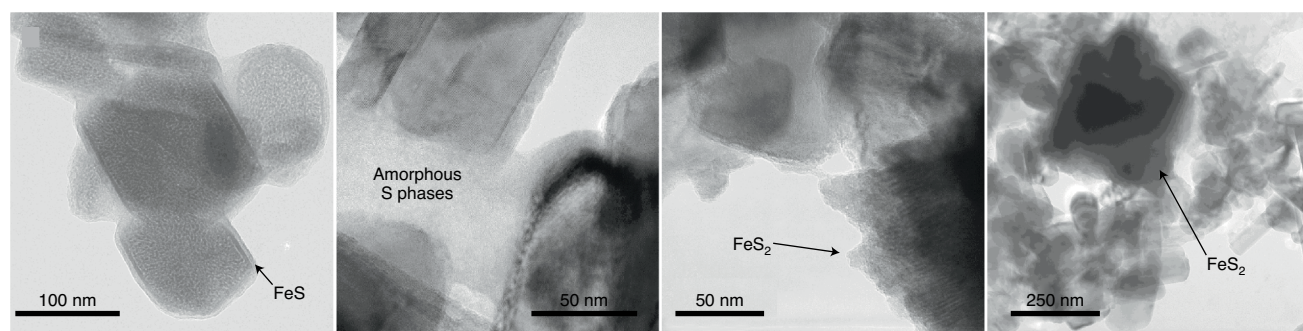
Metastability is a phenomenon commonly observed in low-temperature environments⁸⁹. Metastable phases do not match the Gibbs free energy minimum for a given atomic chemical composition and therefore reflect thermodynamic non-equilibrium states⁹⁰. Examples are the Fe(III) oxyhydroxide minerals ferrihydrite or goethite (which eventually transform to the Fe(III) oxide haematite (Fe₂O₃)⁹¹) or magnetite (Fe₃O₄) nanoparticles (which tend to develop towards more crystalline phases⁹²). The corresponding ripening process for humic materials involves dehydration and condensation processes upon their early diagenesis and, under non-ambient pressure and temperature conditions, the formation of kerogen, hydrocarbons and (eventually) coal compounds⁹³.

Metastable phases can participate in redox reactions as either electron donors or acceptors in which they are stoichiometrically reduced or oxidized along with formation of the reaction products. A classic example is dissimilatory reduction of ferric oxyhydroxides, which act as terminal electron acceptors for Fe(III)-reducing bacteria, with Fe(II) as a reaction product⁹⁴.

A number of such metastable phases to which we refer as RAMPs are, however, able to act as both electron donors and acceptors, thereby covering a broad range of redox potentials. RAMPs obtain their redox properties and enhanced reactivity upon interaction with redox-active constituents in solution.

For example, the adsorption of Fe(II) ions on the surface of ferric oxyhydroxides and subsequent internal electron transfer and atomic rearrangement⁹⁵ substantially decreases the redox potential of goethite^{96,97}, making it a powerful reductant for several oxidized contaminants⁹⁷. Redox reactions at mineral surfaces can also cause strong redox disequilibrium at the host mineral, which becomes dissipated with time (Fig. 1). In this example, the redox disequilibrium between the mineral surface (covered with FeS) and mineral core (lepidocrocite, γ -FeOOH) leads to a series of reactions that alter the redox properties of the surface, eventually forming pyrite. As a consequence, the redox potential of the surface changes from highly reduced (FeS coverage) to more oxidized upon ageing.

Some RAMPs, such as magnetite⁹⁸ or humic materials³⁶, may act as biogeobatteries. They are able to interact with the surrounding solution by accepting and storing electrons and reversibly transferring these electrons upon microbial mediation (see Box 2). Hence, the redox properties of biogeobatteries are intrinsic and derive from their structure, and they are recyclable. Unlike classic electron donors/acceptors or other RAMPs, biogeobatteries are thus able to build up charge capacity and change their redox potential with only a slight and/or reversible alteration of chemical structure upon electron transfer.



Dynamic processes involving the formation of RAMPs. Transmission electron microscopy images following the reaction between sulfide (10 mM) and lepidocrocite (40 mM). Transmission electron microscopy-amorphous phases were identified to be surface-bound polysulfides³⁰. The time steps from left to right are 2 h, 2–3 d, 1 week and 2 weeks²⁹. The images represent dynamic redox processes occurring at the surface of lepidocrocite following initial sulfidization, with formation of an FeS rim covering the lepidocrocite crystallite. Within several days, a large fraction (up to 50%) of initial sulfide that reacted with ferric oxyhydroxides develops as surface-bound, redox-active polysulfides^{29,30} that eventually react to form nanopyrite. Figure adapted with permission from ref. ²⁹, Elsevier.

members of redox reactions with well-defined thermodynamic, chemical and physical properties (redox potential, crystallinity and solubility) that are either fully oxidized (for example, sulfate or Fe(III) minerals) or fully reduced (for example, sulfide and Fe(II)).

The redox ladder concept has, however, been increasingly challenged by the discovery of redox reactions that cannot be explained by the standard framework. Using electrochemical methods, Aeschbacher et al.¹⁰ determined the redox potentials for a number of standard humic acids. The apparent standard reduction potentials at pH 7 ($E_h^\circ(w)$ values) were determined for fully oxidized and fully reduced states of the humic acid samples and typically ranged from +0.2 to -0.4 V. Thus, depending on its actual redox state, a given humic acid could serve either as a reductant or as an oxidant for traditional dissolved redox couples such as $\text{NO}_3^-/\text{NH}_4^+$ ($E_h^\circ(w) = +0.36$ V) or $\text{SO}_4^{2-}/\text{H}_2\text{S}$ ($E_h^\circ(w) = -0.23$ V)⁹.

Another example is magnetite, which has a standard redox potential of -314 mV¹¹. Based on this value, the microbial reduction

of magnetite by accepting electrons from oxidation of organic compounds such as acetate ($E_h^\circ = -290$ mV) or lactate ($E_h^\circ = -190$ mV for the oxidation to pyruvate) should be barely or not even possible. However, there are several examples in which microbially produced or chemically synthesized magnetite has been reduced by microorganisms^{12,13}, suggesting that the effective redox potential of the metastable mixed-valent iron mineral magnetite used in these experiments was less negative and thus more favourable for accepting electrons by microorganisms. Similarly, interaction of Fe(II) or Mn(II) with ferric iron appears to modify the redox potential of Fe(III) (for example, in clay minerals) to an extent that it allows for oxidation of contaminants such as As(III)^{14–16}.

Natural organic matter, such as humic substances, can both accept and donate electrons in microbial redox processes^{17–19}. Natural organic matter has a high affinity for both sulfide^{20,21} and Fe(II)²². During these redox reactions, humic substances form species involving hydroquinone, semiquinone, quinone and sulfur that

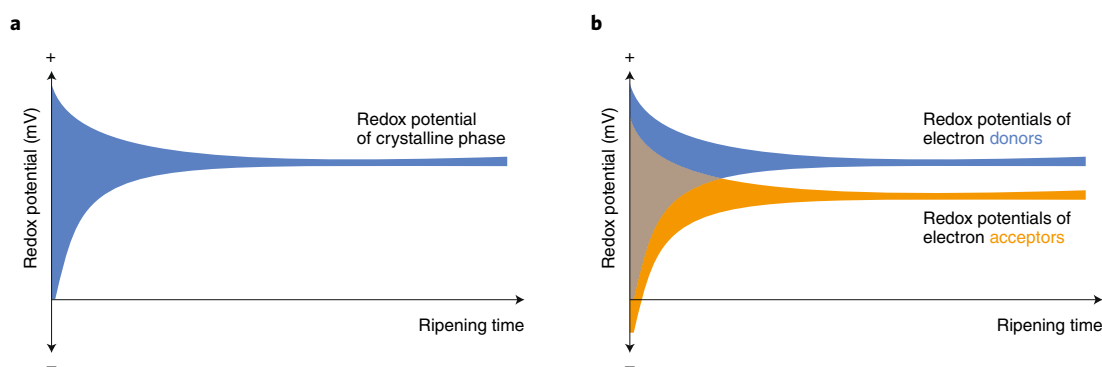


Fig. 1 | Schematic of RAMP ripening. **a**, The heterogeneity of reactive sites, and thus the wide range of redox potentials covered by a specific RAMP directly after its formation, converges towards a well-defined redox potential upon ageing. The wide range of redox potentials of the RAMP directly after formation offers a large diversity of potential interactions with other compounds and microorganisms. **b**, Overlapping ranges of redox potentials of RAMPs as electron donors and acceptors allow chemical interactions that would not be possible upon ripening (that is, after the RAMPs have reached a thermodynamically more stable state).

act as both electron acceptors and donors to microorganisms, and abiotically react with various Fe(III) species^{23,24}, molecular oxygen²³ and contaminants such as arsenic, uranium, chlorinated compounds and nitrobenzenes (for example, ref. 25). Similarly, clay minerals can also simultaneously have reducing and oxidative reactivity provided by Fe(II)–O–Fe(III) edge sites²⁶, where oxidation reactions by Fe(III) require activation by Fe(II).

The redox properties of such phases cannot be predicted a priori from standard free energies. Rather, the occurrence of these species is kinetically controlled. They are metastable products of a series of redox reactions that substantially shape and influence biogeochemical element cycles. As an example, dissolved sulfide is a reductant that rapidly reacts abiotically with lepidocrocite and poorly ordered ferric oxyhydroxides^{27,28}. Within several days, a large fraction (up to 50%) of sulfide that has reacted with ferric oxyhydroxides develops as surface-bound, mixed-valent, redox-active polysulfides^{29,30}. Box 1 illustrates the dynamic nature of the underlying process. The role of these hitherto unknown surface-bound sulfur species in the sulfur cycle and its coupling to the C and Fe cycles remains unknown. It is well established that dissolved polysulfides can act as electron acceptors³¹ or become disproportionated^{32,33}, which provides evidence for the potential of surface-bound reduced sulfur species to trigger distinct biogeochemical reactions. Features common to all such redox-active substances are that they are poorly ordered solid phases and/or minerals that form as metastable components under kinetically controlled conditions; we therefore refer to them as RAMPs (see Box 1).

Upon ripening, RAMPs achieve thermodynamically well-defined redox potentials. For example, microbial reductive dissolution of six-line ferrihydrite and subsequent adsorption of Fe(II) and transformation to the more thermodynamically stable Fe(III)-containing products magnetite and goethite substantially decrease the microbial ability to perform reductive reactions, as determined by mediated electrochemical reduction^{34,35}. These mineral transformation products have a higher crystallinity, as indicated by their X-ray diffraction patterns and larger particle sizes compared with ferrihydrite. In the initial stage, however, the range of redox potentials of RAMPs allows chemical interactions that would not be possible once RAMPs have reached a thermodynamically stable state (Fig. 1).

RAMPs can function as biogeochemical batteries that can reversibly transfer electrons to or from electron-storing compounds (Box 2). Such biogeochemical batteries include magnetite, which (unlike classical electron donors or acceptors) can accept or donate electrons, successively changing its redox potential with only moderate and/or reversible

alteration of its chemical structure. Humic material also functions as a reversible electron storage component³⁶ that may control the availability, storage and recycling of redox equivalents during oxidation and reduction cycles, thus affecting the extent of methanogenesis and the overall methane emission rates in peatlands^{37,38}. Further examples of biogeochemical batteries are clay Fe(II)–Fe(III) redox couples that play an important role in both abiotic³⁹ and microbial⁴⁰ redox reactions in environments with variable redox conditions. Iron in clays can be used by microbes not only as an electron acceptor for dissimilatory Fe(III)-reducing bacteria⁴¹, sulfate-reducing bacteria⁴² and methanogens^{43,44}, but also as an electron donor by iron-oxidizing bacteria⁴⁵. Numerous organic and inorganic chemicals can abiotically reduce or oxidize structural iron in clays⁴⁶ and thus actively influence the iron, sulfur and carbon cycles of the biosphere.

Altogether, RAMPs are redox-active substances with unique redox properties. Their redox reactivity is recyclable and persists for multiple oxidation–reduction cycles. Based on this concept of RAMP formation during abiotic and microbial redox reactions, low-temperature aqueous systems are expected to host a multitude of metastable phases, such as mixed-valence iron and manganese phases, sulfur-containing compounds or natural organic matter, that are part of biogeochemical redox cycles. The presence of RAMPs leads to new, unexpected and so-far-overlooked reaction kinetics and reaction pathways, because the reactivity of RAMPs is higher and they have different redox potentials compared with those usually considered for major redox species of the iron, nitrogen and sulfur cycles.

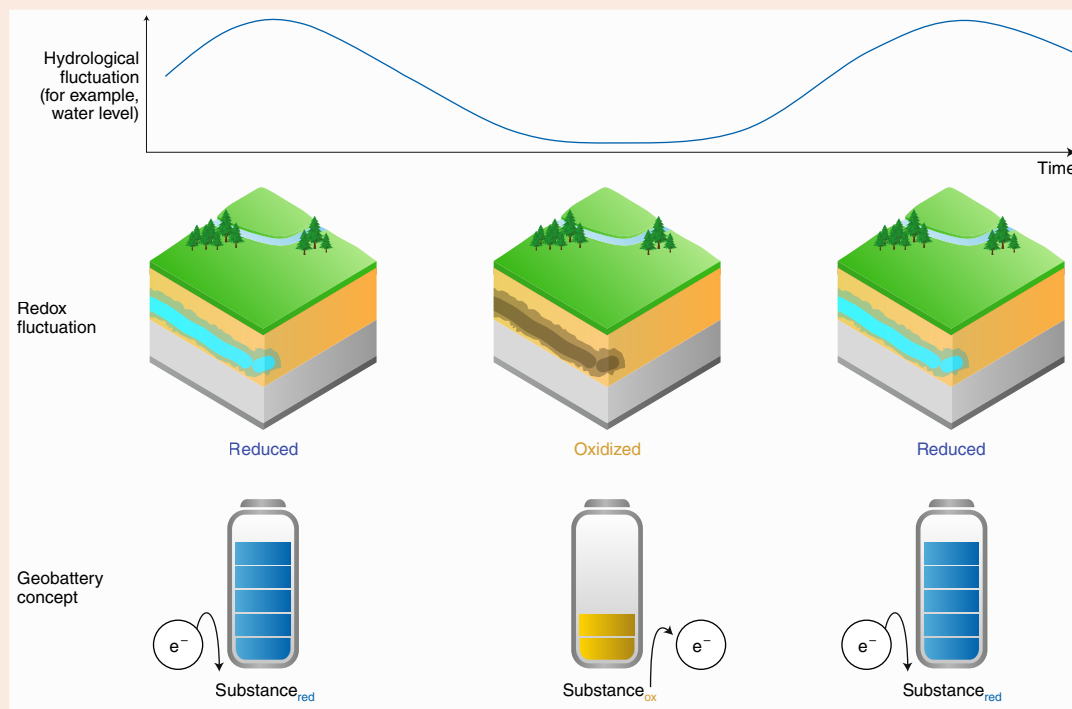
Importance of RAMPs in the biogeochemistry of element cycles

RAMPs play a prominent role in elemental cycles as a consequence of their redox reversibility and their capacity to be a powerful redox buffer. Based on field observations and isotopic data, Blodau et al.⁴⁷ showed clear evidence for anaerobic sulfur cycling in ombrotrophic bogs (that is, bogs that receive water from precipitation only) that maintain bacterial sulfate reduction and contribute to distinctly less methane production than would be expected for these environments. They proposed that electrons are stored in humic material under reducing conditions and are then transferred under oxic conditions to O₂. Up to 15% of global wetland methane emissions are estimated to be suppressed by sulfate reduction⁴⁸, with a large, yet unknown, fraction that is fuelled by anaerobic sulfur cycling⁴⁹. In another study³⁸, the electron-accepting capacity of organic matter in peatland samples channelled up to 50% of carbon flow into

Box 2 | Biogeobatteries in fluctuating redox systems

The discovery of biogeobatteries that can take up, store and reversibly release electrons has changed our thinking about redox processes in natural systems exposed to fluctuating redox conditions. Instead of being driven by the consumption and production of terminal electron acceptors or donors, redox reactions can be mediated by compounds that change their redox potential without changing their chemical structure, or with readily reversible changes only. For example, magnetite can be used as an electron donor by

phototrophic Fe(II)-oxidizing bacteria or as an electron acceptor by Fe(III)-reducing bacteria, in combination with the oxidation of organic compounds⁵⁷. In alternating redox cycles, these two metabolic groups of microorganisms use magnetite as both a sink and source of electrons for their metabolism. As a consequence, fluctuating redox conditions supplying electron donors (for example, Fe(II) or S(II)) or acceptors (for example, O₂) will charge or discharge biogeobatteries, which then serve as mediators for biogeochemical reactions.



Biogeobattery charging and discharging under fluctuating redox conditions. Water table fluctuations (for example, in a wetland) cycle conditions between oxidizing and reducing. Magnetite—a redox-active, mixed-valence iron mineral—can change its redox state⁹⁸. During the reducing phase, it takes up electrons and becomes charged. During the oxidizing phase, it discharges by releasing electrons and can then function as an electron acceptor again. Thus, it acts as a biogeobattery that is able to transfer electrons to either substances or microorganisms that use the biogeobattery as an electron donor or acceptor.

anaerobic respiration processes, and methanogenesis could only occur after exhaustion of their electron-accepting capacity.

RAMPs can also play an important role in cryptic element cycling (that is, the rapid production and consumption of short-lived reactive intermediates that are typically low in concentration)^{50,51}. Reoxidation of sulfide by ferric iron may drive a cryptic sulfur cycle through reoxidation of sulfide in the methane zone of marine⁵² and low-sulfate freshwater sediments⁵³. Mixed-valence, surface-bound polysulfides that form during the reaction between aqueous sulfide and ferric hydroxides³⁰ are top candidates to fuel a chain of microbial reactions to recycle sulfate⁵⁴. Cryptic iron cycling has been observed at the chemocline of a meromictic lake where oxidation of Fe(II) by photoferrotrophic and microaerophilic bacteria was immediately followed by heterotrophic reduction of highly reactive ferric oxyhydroxides⁵⁵ or phototrophic Fe(II)-oxidizing bacteria coupled to photoreduction of Fe(III)⁵⁶.

The redox ladder has long been used to predict microbial distribution patterns, assuming that distinct physiological groups follow geochemical gradients of electron acceptors and donors; however,

unexpected distribution patterns of microorganisms in environmental samples have been detected, particularly when focusing on active microorganisms. The redox ladder concept has been challenged following observations in which the usable energy did not govern microbial activity in long-term bioreactor experiments⁵⁷. The authors concluded that the distribution of microbial life cannot be understood in terms of thermodynamics alone but is controlled by both physiological and ecological factors.

We propose that RAMPs may play a role in some microbial electron-accepting and electron-donating processes. For example, active Fe(III)-reducing microorganisms unexpectedly appear in redox zones of sediments where no microbial Fe(III) reduction is predicted based on geochemical analyses (that is, the absence of Fe(II))⁵⁸, and microaerophilic or nitrate-reducing Fe(II)-oxidizing bacteria unexpectedly appear in sediment zones where no O₂ or nitrate has been detected⁵⁸. Both processes could be explained in terms of a metabolic utilization of other electron acceptors/donors. However, several studies have shown that, for example, humic materials acting as RAMPs may accept or donate electrons to

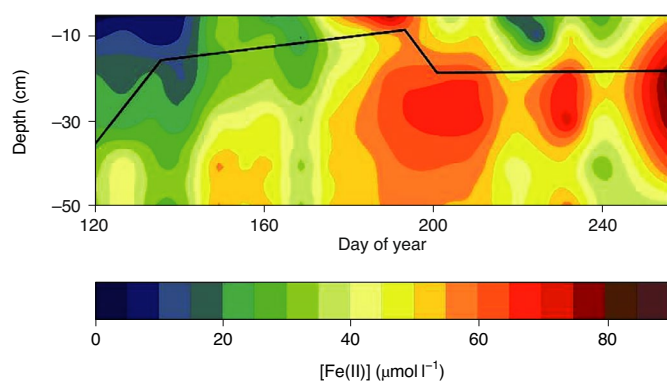


Fig. 2 | Hot spots of dissolved Fe(II) concentration in pore waters of a wetland following water level fluctuations and rainfall events. The black line denotes the approximate water table as a function of time and depth. Activation of RAMPs follows such hydrologically triggered redox dynamics and will be most prominent in the hot spot zones. Figure adapted with permission from ref. 5, Elsevier.

provoke unexpected processes^{18,23,36}. Overall, the impact of RAMPs on microbial diversity remains largely unknown. RAMPs may increase microbial diversity by adding to the complexity of available electron donors and acceptors and, in turn, a RAMP-induced shift in microbial distribution patterns and higher microbial diversity may substantially affect the biogeochemistry of element cycles.

Recycling of RAMPs and the role of hydrological processes

We have discussed the occurrence and properties of RAMPs based on observations made at the nano- or micrometre scale in laboratory experiments and their potential role in element cycling in aquatic ecosystems. However, RAMPs are intermediate substances (in terms of redox state, structure, crystallinity and so on) that tend to ripen towards products of higher stability, and eventually to thermodynamic end members⁵⁹, unless the ripening process is disturbed by external forces. These can be provided by hydrological dynamics in aqueous ecosystems at scales of tens to hundreds of metres.

At hydrological interfaces (hyporheic and riparian zones, wetlands, root zones, sediment–water interfaces, capillary fringes of groundwater bodies and plume fringes), the disturbance frequency follows the frequency of hydrological fluctuations, such as water table fluctuations or the change in streams in contact with groundwater. Typically, changes in redox state are caused by hydrological

fluctuations in zones with strong redox gradients where biogeochemical material processing is highest^{6,7,60}, thereby creating transient hot spots of enhanced concentration of oxidized or reduced substances in the pore water^{5,8} (Fig. 2).

Hot spot formation occurs along different subsurface flow-path lines and depends on dynamically changing hydrological conditions (such as hydraulic pressure gradients) that either facilitate or suppress biogeochemical reactions⁶¹. Even under conditions when oxygen-containing water is supplied, microsites exist that require diffusive exchange with the surrounding advectively transported water and may become reducing if perturbations are too short to allow for O₂ penetration⁶². Such microsites will host a diversity of RAMPs and contribute to the spatial redox heterogeneity typically observed in many aquatic systems^{63,64}.

Time-series analyses revealed that biogeochemical hot moments in a contaminated floodplain were transport driven and correlated with hydrological variations in snowfall and precipitation data in seasonal (month periodicity) hydrological interactions⁶⁵. In contrast, the groundwater residence time (32-month periodicity) is the governing control on temporal variability in seep zones where groundwater drains into the floodplain. Such dependence on hydrology appears to also affect the delivery of groundwater-borne solutes to streams during storm events that depend on interactions of vertical infiltration along preferential pathways and subsequent perturbations to groundwater geochemistry⁶⁶.

As a consequence of biogeochemical perturbations occurring at hydrological interfaces, the typical lifetimes of RAMPs at such interfaces are expected to be on the order of hours (storm events and diurnal cycles) to months (groundwater recharge), following the duration of a hydrological event. This lifetime range in turn implies a certain geochemical window for the occurrence of RAMPs:

- The exposure time of reactants to conditions suitable for the formation of RAMPs needs to be sufficiently long to allow RAMPs to develop.
- The ripening of RAMPs towards thermodynamic end members needs to be interrupted (for example, through redox oscillations) for RAMPs to regenerate or recharge.

Coupled with the change in stability, the reactivity also changes, where the highest reactivity is associated with very fresh phases. Hydrological disturbances therefore lead to a refreshing of reactivity (Fig. 3) and determine the degree of ripening, with short fluctuations interrupting the ripening process. Moreover, hydrological fluctuations are also the drivers for reactions that bring together reactants that would otherwise not encounter one another, thereby leading to spatial and temporal coupling of reactions.

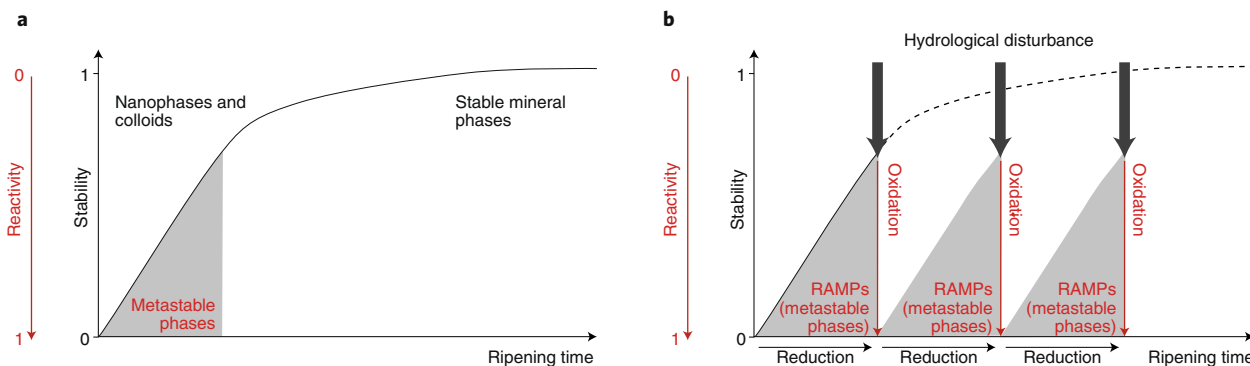
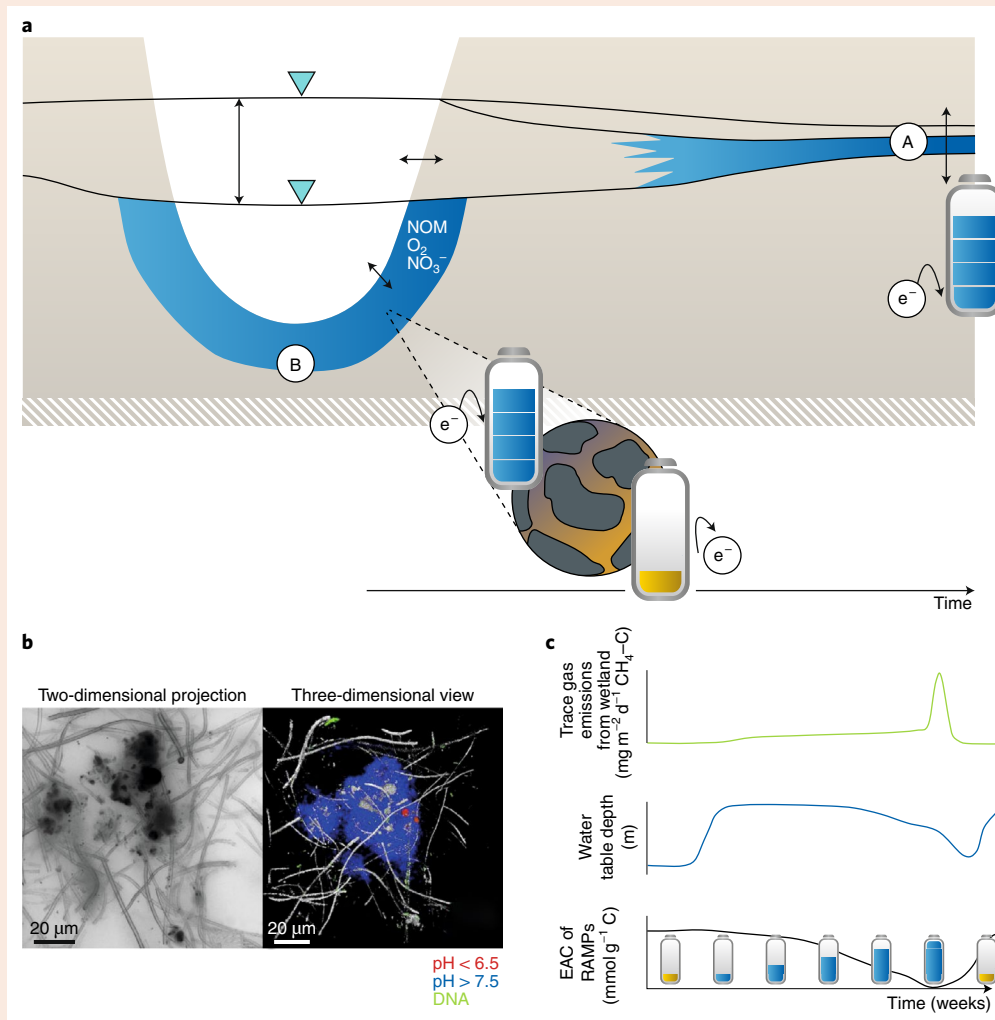


Fig. 3 | Influence of hydrological fluctuations on RAMPs. a, Ripening time enhances the stability of RAMPs and decreases their reactivity. **b**, Hydrological events with suitable recurrence frequencies interrupt the ripening process and lead to the regeneration of RAMP properties.

Box 3 | Link between hydrological fluctuations, RAMP response and ecosystems

Hydrological settings in wetlands cause redox fluctuations and associated transition zones where RAMP formation occurs (see figure below). Following water table fluctuations, electron donors (for example, dissolved organic carbon and Fe(II)) and acceptors (for example, O_2 , NO_3^- and SO_4^{2-}) become available as dissolved substances. RAMPs are largely associated with the matrix of the

porous medium, so that changing boundaries between reducing and oxidizing water bodies will pass over them, facilitating reactions by local disequilibria. Consequently, electron transfer reactions take place that lead to fluctuations between the uptake and release of electrons. The time scales at which hydrological and biogeochemical processes operate are nonlinearly interlinked.



Water table fluctuations in wetlands, and associated zones of RAMP formation. **a**, In scenario A, water table fluctuations in streams (as denoted by the triangles) propagate to adjacent wetlands, causing groundwater table fluctuations at some distance. The exposure to oxygen-rich soil gas leads to oxidation of RAMPs when the groundwater table is low, whereas anoxia can occur at high groundwater tables if sediments are rich in labile organic carbon. In scenario B, the flow direction at the stream-groundwater interface changes. At low stream water tables, reduced groundwater is discharged into the stream. In contrast, at high water tables, oxidized stream water is recharged from the stream to groundwater. In both scenarios, solute transport is triggered by hydrological processes on a regional scale (>1 m). Such solutes will interact with the RAMP-containing soil matrix and generate hot moments of redox reactivity. NOM, natural organic matter. **b**, Hydraulic mixing in the hyporheic zone of a pH-neutral creek appears to impede the development of homogeneous redox gradients in a Fe(II)-oxidizing biofilm covering the creek bed. The biofilm was analysed 1–2 h after sampling with a pH-sensitive fluorescence dye and confocal laser scanning microscopy, and consisted of agglomerates of microbial extracellular polymeric substances and mineral particles (left). Local regions of reduced pH (right) were identified that can be attributed to microbial Fe(II)-oxidizing activity embedded into Fe(III)-reducing conditions. The occurrence of micrometre pH and redox gradients suggests a response to external perturbations driving local charging and discharging of RAMPs. **c**, Ecosystem response as methane flux from a wetland on the hectometre scale follows changes in water table fluctuations on the metre scale that stimulate exhaustion of the electron-accepting capacity (EAC) in organic matter geobatteries on the nano- to micrometre scale. Substantial fluxes occur only when the electron-accepting capacity becomes depleted and allows substantial methanogenesis and subsequent methane emission to occur.

Changes in the redox state of an aqueous system will exert strong feedbacks on RAMP properties. For example, our current understanding suggests that oxidizing conditions will initially favour the formation of poorly crystalline Fe(III) minerals instead of well-ordered phases⁶⁷. Reducing conditions can thus lead to rapid abiotic and microbial dissolution of such metastable mineral phases. Consequently, ferrihydrite transformation to a phase with higher crystallinity (for example, goethite) was incomplete after multiple short redox cycles⁶⁸. Redox cycling also affects the rate of contaminant transformation by RAMPs. For example, the initial rate of Cr(vi) reduction by sedimentary solid-phase bound Fe(II) generally increased with each redox cycle⁶⁹, indicating enhancement of the reactivity of Fe(II)-bearing RAMPs by redox cycling.

Changes in redox state are provoked not only by intrusion of oxygen, but also by periodic input of dissolved organic carbon or sulfate. Input that drives redox processes may come from surface water into groundwater^{60,70}, or from saline and fresh water into reduced groundwater in intertidal aquifers⁷¹. Even periodic input of heat that increases the temperature may affect microbial pathways of activities and subsequently affect RAMP formation.

On the basis of these considerations, we conclude that the frequency and amplitudes of hydrological oscillations control exposure times to specific geochemical conditions and are therefore key factors for understanding the formation of RAMPs. Thus, the spatial and temporal distribution of RAMPs in natural systems depends on the time scales of both physical transport and geochemical kinetics of RAMP formation arising from the link between macroscopic (hydrological) and microscopic (biogeochemical) scales (Box 3). Further research is required to understand the formation of geochemically distinct microzones and, ultimately, the potentials, rates and locations of biogeochemical processes, as well as microbiological diversity and distribution patterns.

Role of microscale redox cycling in ecosystem-scale response

We have discussed how RAMP properties are affected by hydrological perturbations, but how do these interactions affect the response on an ecosystem scale? While the response of aquatic ecosystems to hydrological fluctuations such as gas emissions from wetlands is well documented (for example, N₂O and NO fluxes⁷² and CH₄ fluxes⁷³), the relationship between peatland CH₄ emissions and the water table appears to be complex. Peak CH₄ emissions did not occur when the water table was closest to the surface, but instead after some delay, only when it dropped to 40–55 cm below the surface⁷⁴. The authors interpreted this delay as a drop of redox potentials to values required for methanogenesis. Substantial delay of methane emission following an experimental drought was also observed in peat mesocosm studies performed with 16 samples distributed across Europe⁷⁵.

The RAMP concept provides an explanation for this delay. Before the onset of methanogenesis, the oxidation capacity of microscale RAMPs controlling the redox potential must become exhausted upon sufficient supply of reactants by macroscale hydrological processes (for example, dissolved organic carbon or Fe(II); panel c of the figure in Box 3). Such an explanation also implies a substantial influence of redox-active soil constituents on methane emissions, as demonstrated in a study on wetland CH₄ emissions⁷⁶. Annual CH₄ fluxes from an alluvium wetland were significantly lower than those from an adjacent peat site over multiple years, but these differences could not be explained by variations in dominant climate drivers or productivity across wetlands. Soil Fe concentrations were significantly higher in alluvium soils, and alluvium CH₄ fluxes were decoupled from plant processes compared with the peat site, as expected when Fe reduction inhibits CH₄ production in the rhizosphere. Soil carbon content and CO₂ uptake rates did not vary across wetlands and thus could also be ruled out as drivers of initial

CH₄ flux differences. The overall conclusion of the authors was that alluvium soil properties (probably Fe content) are capable of inhibiting ecosystem-scale wetland CH₄ fluxes, which we argue is due to activation of Fe RAMPs. Temporal fluctuations of temperature and water table depth also contributed significantly to subsurface CO₂ fluxes in flood plains upon activation of biogeochemical hot spots in the subsurface⁷⁷ in which RAMPs are potentially involved.

Implications and open questions

The coupled biogeochemical–hydrological framework presented here predicts emergent aquatic ecosystem behaviour from processes occurring at the nano- to microscale propagated to a larger-scale response upon hydrological mediation. This framework has substantial implications for our perception of how aquatic ecosystems function, particularly at hydrological interfaces where hydrological perturbations are common. Importantly, it is not simply the inventory of available redox-active compounds that dictates their relevance to element cycling and electron flow, but rather their capacity to function as RAMPs. In the absence of frequent cycling between oxidizing and reducing conditions, RAMPs will tend to lose their unique redox properties and ripen towards thermodynamic end members with low reactivity. In contrast, continuous redox cycling of RAMPs stimulates biogeochemical turnover.

The role of RAMPs in aquatic ecosystems needs to be understood from two sides. The hydrological perspective needs to define the time at which RAMPs are exposed to solutions containing reducing or oxidizing substances. To date, studies on this topic are scarce and research is only in its infancy^{65,78,79}. The biogeochemical perspective, which is the detection and quantitative assessment of redox dynamics under in situ conditions, remains a challenge. Appropriate field techniques are required that are able to determine the spatial distribution of electron transfer capacity, redox potential and their temporal changes. The scientific community generally agrees that E_h measurements using potentiometric approaches fail to determine the accurate redox potential of an aqueous system⁸⁰. Promising attempts to determine hot spots of redox activity in the subsurface using induced-polarization imaging have been made^{81,82}. Induced polarization is a non-invasive geophysical technique that uses an innovative approach to determine the redox properties of a porous material with both spatial and temporal resolution⁸³. However, our understanding of the causes of polarization of redox-active substances is still developing and research on the contribution of dissolved redox species to polarization is urgently required⁸⁴.

Overall, a broad body of evidence from research into biogeochemical processes supports the occurrence of RAMPs and their properties and inspired this Review. Future research at the ecosystem scale needs to combine innovative non-invasive techniques with ecosystem response measurements such as greenhouse gas emissions, as well as stable or labile isotope labelling⁸⁵. Many unknowns exist with regard to electron transfer mechanisms, electron storage capacities and the underlying kinetics. To date, no sound approach exists regarding how to implement RAMP properties into reactive transport models. Advances have been made in microbial reaction rate modelling and mineral kinetics^{89,86,87}, but these approaches fail to account for the wide range of RAMP complexities, including storage capacities, intermediate redox potentials and intermediate redox-active substances. Future RAMP research should include a parametrization of their reactivity. This should include quantitative models to account for temporary electron storage in biogeochemical batteries as well as the wide range of RAMP redox potentials. The role of RAMPs in geomicrobiology (for example, in cryptic element cycling) needs to be resolved. Moreover, the unique properties of RAMPs and their dependence on redox fluctuations warrants exploration of environmental engineering applications such as redox-driven transformation or mineralization of pollutants⁸⁸.

Overall, we consider the RAMP concept to be a key player in biogeochemical processes occurring at hydrological interfaces. RAMPs will provide a basic framework for future research into the functioning of aquatic ecosystems such as wetlands, riparian zones and the interface between groundwater and the vadose zone.

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Author contributions

All authors participated in generating the concept. S.P., C.S. and M.O. drafted the first versions of the figures. All authors contributed to writing and editing.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence should be addressed to S.P.

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