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Review

Synthesizing redox biogeochemistry at aquatic interfaces

Maximilian Peter Lau^{a,*}, Robert Niederdorfer^b, Armando Sepulveda-Jauregui^c, Michael Hupfer^a^a Leibniz Institute of Freshwater Ecology and Inland Fisheries, Department of Chemical Analytics and Biogeochemistry, Mueggelseedamm 301, 12587 Berlin, Germany^b University of Vienna, Department of Limnology and Bio-Oceanography, Althanstrasse 14, 1090 Vienna, Austria^c University of Magallanes (UMAG), Institute of Patagonia, Av. Manuel Bulnes 01890, Punta Arenas, Chile

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ABSTRACT

The exchange of matter and energy between confined components of aquatic ecosystems requires the passage through their interfaces. This passage is characterized by rapid changes in physical, chemical and biological conditions and often triggers chemical transformations that involve the exchange of electrons: redox reactions.

Over the last decades, research in aquatic biogeochemistry has resulted in many new but conceptually isolated findings that, together, frame an emergent view on the overarching principles of aquatic redox processes. A thermodynamic assessment may reveal the maximum available energy from such redox reactions. However, this energy can rarely be released due to various morphological, ecological and kinetic constraints on the turnover reactions. As these constraints set the boundary conditions for aquatic ecosystem functioning, they deserve particular attention in freshwater research.

Here, we illustrate how physical and structural traits shape a complex redox environment and how this environment ultimately exercises control on the inhabiting microbial community and its metabolism. This aquatic microbiome is the key entity of material turnover. At the same time, the biome possesses the capability to feed back on its environment by shaping the local redox conditions and sustain niche existences. We discuss current and emerging ideas of how microorganisms engineer their environment, affecting aquatic redox reactions. In total, we examine this feed-back cycling between the physical environment and its colonizing biome to encourage the reader to take on the redox perspective when analyzing processes at aquatic interfaces. Understanding electron fluxes on both temporal and spatial scales is essential for the overall comprehension of matter and energy fluxes through freshwater environments. We pinpoint the methodological frontiers that will need to be challenged in future studies of aquatic redox processes. An improved mechanistic understanding will be instrumental in estimating sink and source properties of aquatic ecosystems.

1. Introduction

Biogeochemical cycling of inorganic and organic material in freshwater ecosystems involves the exchange of electrons between chemical species across the interfaces between system components. This exchange of electrons in redox reactions does not only control chemical speciation but also the mobility, bioavailability and toxicity of dissolved and particulate substances (Tratnyek et al., 2011). Any redox reaction is the sum of two half reactions, the oxidation of the reductant and the reduction of the oxidant that are inter-aligned by the transfer of electrons. A redox reaction is accompanied by a change in the system's free energy. The difference in Gibb's free energy (ΔG) of reactants to products indicates if the reaction is thermodynamically favorable

(Migonigal et al., 2003). If ΔG is negative (< 0) the reaction can run spontaneously (i.e., without the addition of energy). Microorganisms overcome the kinetic limitation of reactions between chemical species that are not in equilibrium. The chemical energy released by the redox reaction may also be utilized by heterotrophic organisms (Schlesinger, 2005). Heterotrophs are critical mediators for matter turnover in many ecosystems because they couple the oxidation of organic carbon to the reduction of extracellular, terminal electron acceptors (TEA) in their respiratory activity. They ultimately aim for the formation of adenosine triphosphate by substrate level phosphorylation and electron transport phosphorylation. The net energy microorganisms may acquire in this process is a combination of the energy freed in the electron donating half-reaction and the electron accepting half reaction (LaRowe and Van

Abbreviations: AOM, anaerobic oxidation of methane; AOM-SR, anaerobic oxidation of methane coupled to sulfate reduction; AOM-D, anaerobic oxidation of methane coupled to denitrification; AOM-O, anaerobic oxidation of methane coupled to OM reduction; DOM, dissolved organic matter; E_h , reduction potential; ΔG , difference in Gibb's free energy; OM, organic matter; TEA, terminal electron acceptor

* Corresponding author at: Université du Québec à Montréal, Pavillon des sciences biologiques, SB-2855, 2080 St-Urbain, Montréal, Québec H2X 3X8.

E-mail address: lau@igb-berlin.de (M.P. Lau).

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Cappellen, 2011). Competition within microbial communities prompts for efficient energy conversion, favoring the usage of the TEA with the highest reduction potential (E_h) available (Megonigal et al., 2003). However, natural reactions are confined to the E_h range from water's reduction- to oxidation endpoint-products, hydrogen and oxygen (Grundl et al., 2011). The decrease in standard E_h of the most common TEA species from O_2 via NO_3^- , $Mn^{(IV)}$ and $Fe^{(III)}$ minerals to SO_4^{2-} , is often reproduced in the temporal and/or spatial succession of microbial redox processes (Champ et al., 1979). That succession model is commonly referred to as the 'redox ladder' and key framework to understand the geomicrobiological processes in environments that are not in equilibrium.

Such thermodynamic dis-equilibria occur, for example, in depositional environments (e.g. freshwater and marine sediments) where the downward flux of organic carbon (previously fixed in primary production) constantly introduces energy to the system and fuels biogeochemical turnover. Many local to global biogeochemical cycles are dependent on this spatial decoupling of the zones that are either autotrophic (i.e., dominated by primary production) or heterotrophic (dominated by respiration). Interfaces between these (and other) compartments of aquatic environments are areas of steep physical, chemical or biological gradients. Matter and energy (in the form of e.g. light, temperature or electrons) that traverses aquatic interfaces set the boundary conditions for the functioning of aquatic ecosystem. Understanding electron transport dynamics across interfaces is thus of extraordinary relevance for freshwater sciences.

In this review we discuss what is currently known about respiration-induced redox processes at aquatic interfaces. We specifically address interfaces, as they are identified to be the critical sites for turnover and biodiversity. Many factors including the physical conditions, availability of nutrients and electron acceptors and community dynamics exercise control on the spatial and temporal activity-distribution of the redox reactions. Contributions to this subject have come from a wide range of disciplines. However, little synthesis between these contributions has been achieved.

We organized this multidisciplinary review around a conceptual framework that reflects the feedbacks between redox environments and associated microbial communities: We begin our discussion by examining what is known about the factors that define the redox environment at aquatic interfaces (Chapter 2). We follow this with a review of the active controls (Chapter 3) on, and the resulting structure of the microbial community at these interfaces (Chapter 4). Finally we discuss how that community, at the same time, shapes its own redox environment (Chapter 5) to sustain optimum conditions for growth. This feedback cycle gains momentum through the continuous supply of energy (mainly via allochthonous organic matter, OM), keeping the system in dis-equilibrium.

The subject of environmental redox processes has certainly been reviewed by others (e.g. Borch et al., 2010); here, however, we explicitly address process studies in the freshwater sciences. By examining how microbial process communities shape and are shaped by redox conditions of their surrounding habitat, we discuss the thermodynamic and kinetic constraints on microbial processes, as such constraints may give us insight in the organizing principles of aquatic ecosystems. Clearly, resource limitation directs the attention of researchers towards fields of particular global relevance (as e.g. greenhouse gas emissions). Lately, such efforts presented significant amendments to the current perception of redox processes at aquatic interfaces, some of which we discuss in greater detail. In this paper, we argue that rigorous application of the underlying, novel (redox) concepts allow for advances across much wider areas of the freshwater sciences, and wish to project some of the current frontiers that may thus be breached.

2. The benthic redox environment

The sediment surface that encloses the water body is potentially the

most important aquatic interface and a critical zone for microbial turnover in any aquatic environment. Volumetric bacterial abundance in the sediment exceeds that of the water column by up to three orders of magnitude (Schmidt et al., 1998). The benthic space hosts a disproportionate share of aquatic microorganisms, so that the physical characteristics of that space are of great importance for the major share of microorganisms at the sediment/water interface. Despite that importance, solid phases in sediments are structurally more diverse than generally acknowledged. Microorganisms cover only minor parts of the available surface area (fertile soils: about 1%, Young et al., 2008), so that microbial distribution patterns may be critically affected by the microtopography and redox properties of the solid phases. Therefore, this chapter deals with the emerging appreciation of the redox characteristics of solid phases in benthic environments.

Generally, the physical conditions that exercise control on the microbiome are, among others, pH, porosity, accessible surface area, salinity, abundance of nutrients and toxins and redox conditions (Horner-Devine et al., 2004). The redox conditions are commonly specified by E_h measurements. Despite the popularity across freshwater scientists, the significance of measured E_h values is constrained by two critical limitations. First and foremost, chemical species are rarely in equilibrium with each other so that the E_h only reflects a mixed potential of species that are in electrochemical contact with the electrode (Grundl et al., 2011). Additionally, such determinations underestimate the contribution of particulate species to the bulk E_h although it is established that particles in aquatic environments contain a range of redox-active material both in solid state or adsorbed to solid surfaces. These solid "geochemical" phases (Sander et al., 2015) typically contain particulate organic and mineral species as e.g. metal (oxy)-hydroxides and sulfides, calcite phases and clay minerals. Despite this structural and chemical complexity, benthic environments are regularly perceived as homogeneous and absent from participation in reactions between microorganisms and solutes. Therefore, we first discuss the emergent view of the microscopic properties of solid sedimentary phases and second, illustrate how they participate in redox reactions at aquatic interfaces. This will ultimately prepare the ground for discussing how redox conditions can then determine the active microbial community (Chapter 3).

2.1 Structure and topology of the sediment/water interface

Understanding the morphological features of surfaces at aquatic interfaces is fundamental to the determination of constraints on material transport and reactivity. While the benthic space in marine and freshwater environments is well characterized on a macroscopic level (e.g., Huettel et al., 2014), comparatively little is known about its structure on the sub-millimeter scale with its particular relevance for electron exchange reactions (Fig. 1).

The microtopographical features of soils and sediments that are deemed most relevant are small mesopores (2–10 nm); in particular because these pores are suggested to be preferential sorption sites for organic molecules (Kleber et al., 2015). For parts of the available organic matter, multisite attachment to such pores is reflected in greater adsorption and inhibited desorption when compared to a nonporous surface analogue (Mayer et al., 2004; Zimmerman et al., 2004). The role of the microtopography (cracks in minerals and pores in organics) in the formation of heterogeneous microenvironments as hotspots for specific turnover reactions is vividly discussed (Fenner et al., 2011; McClain et al., 2003; Pedersen et al., 2015). Controversies include e.g., whether or not the microbial respiration and turnover in confined soil aggregates exceeds that of bulk soil (Chenu and Cosentino, 2011; Ranjard and Richaume, 2001).

Not only does the microtopography influence surface reactivity but also the transport through the benthic space. The limitation of solute delivery clearly constrains microbial activity beyond the water/sediment interface. In sediments, dissolved electron acceptors are subject to

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