

## Methane transport and release to the atmosphere in permafrost areas via subterranean groundwater discharge

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Methane release to the atmosphere in permafrost regions of the Arctic is exacerbated by global warming. This may result in a positive feedback effect, as methane is a powerful greenhouse gas. Accordingly, it is important to gain a good understanding of the processes that contribute methane to the atmosphere, particularly in this region. Large quantities of methane are stored in the Arctic in natural gas deposits, permafrost, and as submarine clathrates. Releases from these sources arising from warming have been reported, however, there are still considerable gaps in our understanding of the methane cycle at present and particularly how predicted climate changes will impact the methane cycle.

Subterranean groundwater discharge (SGD) has been recognized as an important conduit for transport of nutrients, metals, methane and other pollutants from land to receiving water bodies throughout the world, and could be a potential important, yet not quantified, source of methane in the Arctic. SGD can be quantified using geochemical tracers such as Ra and Rn and when combined with methane measurements can elucidate the role SGD has in transporting methane from groundwater to surface water bodies such as Arctic lakes and the coastal ocean, from which this methane will be released to the atmosphere.

We have used Ra and Rn along with analytical calculations and methane concentration and isotope analyses in order to determine the contribution of SGD to the methane budget in areas of different hydrological and permafrost conditions in Alaska. Our results indicate that SGD is a major conduit for methane release contributing significant amounts of methane to surface waters particularly in areas where permafrost is abundant and impacted by seasonal temperature changes.

## Bioessential metal sorption at ferrihydrite-bacteria interfaces

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The association of organic matter with mineral surfaces can exert a profound effect on the behaviour of both the mineral and organic phases. It is becoming apparent that a direct relationship exists between minerals and organics whereby organic matter acts to significantly modify mineral surface physiochemistry and may help preserve mineral reactivity during diagenesis, while minerals similarly help preserve organic carbon leading to burial and long-term carbon storage [e.g., 1]. This relationship is particularly apparent for organics associated with iron (hydr)oxides like ferrihydrite. In these composites the unique surface physiochemistry also produces a complex sorbent with metal sorption properties very distinct from pure iron (hydr)oxides [e.g., 2]. Despite the wide occurrence of iron (hydr)oxide – organic composites, and the major control on metal cycling exerted by the pure end-member components, metal sorption at the composite-water interface is poorly understood.

Here we present the results of on-going research to determine the molecular-level sorption behaviour of bioessential metals with ferrihydrite-bacteria composites. We will show directly for the first time that Cu binds to each of the composite fractions, via the same molecular mechanisms as to the end-member components; namely, a bidentate edge-sharing complex on the ferrihydrite fraction and a monodentate complex to carboxyl functional groups on the bacterial fraction [3]. The presence of the carboxyl groups significantly modifies Cu sorption behaviour on the composites compared to pure ferrihydrite [3,4]. We find that for composites composed predominantly of ferrihydrite this modified behaviour can be modelled in a thermodynamic surface complexation framework by adopting a linear additivity approach, where sorption on the composites is the sum of the pure end-member Cu sorptivities [4]. However, composites composed mainly of bacteria behave in a non-additive manner, which we can explain as a result of their unique surface charge [4]. Modelling and thus predicting metal sorption on these composites is a new challenge.

[1] Lalonde *et al* (2012) *Nature* **483**, 198. [2] Small *et al* (1999) *ES&T* **33**, 4465. [3] Moon and Peacock (2012) *GCA* **92**, 203. [4] Moon and Peacock (2013) *GCA* **104**, 148.