

## Daily geochemical monitoring of volcanic rivers: A tool for eruption prediction?

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The exsolution of volatiles and magma degassing can have a profound impact on the behaviour of volcanic systems and eruption style and frequency. Measuring volcanic degassing has traditionally focused on atmospheric emissions. However, volatiles can become dissolved in proximal water bodies en route to the surface, thus the monitoring of rivers draining active volcanoes can be integral to understanding the state of the volcano and potentially be used as a tool for predicting changes in activity or imminent eruptions. This method of monitoring is hampered by the dependence on spot-sampling due to financial and equipment constraints.

Recent advances in the design of osmotic samplers now allow for the continuous collection of water, providing a daily-averaged sample for weeks to months without the need of electricity or human supervision [1]. Deployment and testing of these osmotic samplers has been conducted in the rivers draining Mýrdalsjökull glacier and Katla volcano in southern Iceland. Preliminary results suggest that daily-averaged samples are able to track changes in volatile and metal concentrations over days to months. Results are used in conjunction with continuous monitoring of conductivity and temperature by the Icelandic Meteorological Office to highlight the differences in glacial, meteoric, volcanic and spring sources to the river chemistry from season to season. We envision that this form of sampling and monitoring can provide vital information on the behaviour and activity of volcanoes, and with further data become a potential method of eruption forecasting.

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[1] Gkrtzalis-Papadopoulous *et al.*. (2012) *Environ. Sci. Technol.* **46**, 7293-7300.

## Effects of sediment porosity and particulate organic carbon on Fe, S and U cycling in Naturally Reduced Zones (NRZs) of a contaminated aquifer

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Previous studies have illustrated the importance of Naturally Reduced Zones (NRZs) within saturated sediments as a source of reduced organic compounds and hydrogen, providing electron donor for subsurface microbial respiration. NRZ's are typically characterized by low permeability and elevated concentrations of organic carbon and trace metals. However, both the formation of NRZs and their importance to the overall aquifer carbon remineralization is not fully understood.

Within NRZs the hydrolysis of particulate organic carbon (POC) and subsequent fermentation of dissolved organic carbon (DOC) to form low molecular weight dissolved organic carbon (LMW-DOC) provides electron donors necessary for the respiration of Fe, S, and in the case of the Rifle aquifer, U. Rates of POC hydrolysis and subsequent fermentation have been poorly constrained and rates in excess and deficit to the rates of subsurface anaerobic respiratory processes have been suggested.

In this study, we simulate the development of NRZ sediments in diffusion-limited aggregates to investigate the physical and chemical conditions required for NRZ formation. Effects of sediment porosity and POC loading on Fe, S, and U cycling on molecular and nanoscale are investigated with synchrotron-based Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS). Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) and Fourier Transform Infrared spectroscopy (FTIR) are used to characterize the transformations in POC and DOC. Sediment aggregates are inoculated with the natural microbial biota from the Rifle aquifer and population dynamics are monitored by 16S RNA analysis.

Overall, establishment of low permeability NRZs within the aquifer stimulate microbial respiration beyond the diffusion-limited zones and can limit the transport of U through a contaminated aquifer. However, the long-term stability of NRZs and the collocated U is unknown and requires further study.