Characterizing vadose zone hydrocarbon biodegradation using CO$_2$ effluxes, isotopes, and reactive transport modeling

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Introduction

Biodegradation in the vadose zone may result in substantial mass removal at hydrocarbon spill sites. At these sites, estimates of contaminant loss rates are needed to evaluate source zone longevity and long-term impact on the environment. Recently, Sihota et al. [1] showed that the measurement of CO$_2$ effluxes at the ground surface is a suitable method to derive depth-integrated rates of contaminant degradation. However, the accuracy of loss rate estimates obtained from CO$_2$ effluxes is limited by the ability to quantitatively separate CO$_2$ effluxes from contaminant destruction and naturally occuring soil respiration. To address this gap, measured CO$_2$ effluxes were complemented with detailed analysis of vadose zone gas composition, including stable and radioisotope analysis in CO$_2$. Results of field measurements were integrated using the reactive transport code MIN3P-DUSTY [2], which accounts for advective and multicomponent diffusive gas transport.

Results and Conclusions

Comparison of measured pore gas distributions to previous observations at the Bemijdi site [3] show biodegradation has approached a quasi steady state within the vadose zone. Radiocarbon results prove that, in the source zone, the majority of CO$_2$ is produced from contaminant destruction and indicate that the CO$_2$ efflux method provides an adequate estimate of contaminant mass loss rates.
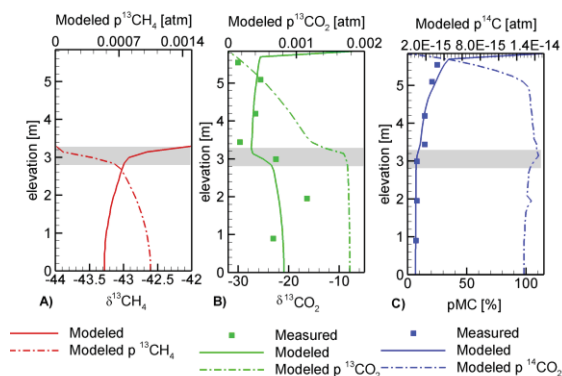
Figure 1: Comparison of measured and simulated isotopic values for a 1D vertical profile in the vadose zone at the Bemidji site.

Highly constrained simulations for a 1D vertical profile in the source zone are able to closely reproduce historical saturations, field observed fluxes, concentration profiles, and isotopic signatures. Simulation results also showcase that gas transport is diffusion-dominated and strongly affects measured isotopic signatures, in addition to effects caused by biogeochemical reactions.

[1] Sihota, Singurindy & Mayer (2011) *Environ. Sci. Tech.* **45**, 482-488. [2] Molins & Mayer (2007) *Water Resour. Res.* **43**, W05435. [6] Molins *et al.* (2010) *J. Contam. Hydrol.* **112**, 15-29.

Hand-held XRF in exploration for REE–bearing phosphate deposits.

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Sedimentary phosphate deposits consist of francolite [(Ca$_5$(PO$_4$)$_3$(OH,F,Cl)] and gangue minerals. They supply most of the phosphate raw materials used by the phosphate fertilizer industry and they are also considered as potential sources of F, REE, and/or U. Samples of phosphate rocks from the Fernie Formation (British Columbia) were analysed using a hand-held XRF analyser (HhXRF) and by lithium metaborate fusion–inductively coupled plasma (LMB-ICPMS) method. The results from both methods were compared; and correction factors for the HhXRF analyser were developed. HhXRFs can be used in exploration for phosphate deposits by analyzing samples directly for phosphorus (P) and if correction factors are applied for vectoring towards REE-rich zones, and/or delineating zones with high levels of deleterious elements such as U, Th, Cr, As, Hg, Cd and Se. Figures 1 illustrates two examples of relationships between hhXRF and LMB-ICPMS methods. Following a successful orientation survey, HhXRF does become fast and reliable vectoring tool that is easily incorporated into integrated exploration programs.
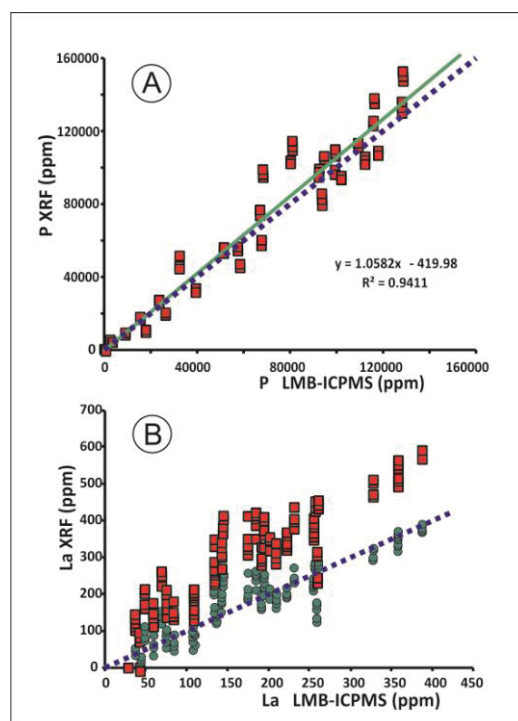
Figures 1: Comparison of the HhXRF and LMB-ICPMS for P (A) and La (B). Raw data as red squares. Corrected values as green circles. No correction was required for P.