

Challenges to predicting the fate of emerging classes of organic micropollutants in subsurface environments

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Widespread detection of emerging micropollutants (e.g. antibiotics, hormones, personal care products) in soil and aquatic environments has raised serious concerns that necessitate improved understanding of processes controlling their environmental fate. However, existing models and reaction mechanisms are inadequate for predicting the fate of micropollutants that possess complex structures and functional groups not usually present in more commonly studied contaminants. Here, we describe recent efforts to characterize processes and mechanisms contributing to the fate of two widely detected classes of antibiotic micropollutants (sulfonamides, fluoroquinolones). First, we describe a novel microbially mediated-abiotic transformation mechanism for the antibiotic sulfamethoxazole (SMX) in subsurface environments. Rapid dissipation of SMX is observed in iron-reducing soil microcosms, and mechanistic studies demonstrate that SMX transformation occurs via abiotic reactions of sorbed Fe(II) with an isoxazole group in the SMX structure, a moiety not previously reported to be amenable to reductive transformation in soil environments.

The complex poly-ionogenic structures of some micropollutants have complicated efforts to predict sorption and speciation in subsurface environments. For example, the unique characteristics of zwitterionic fluoroquinolone (FQ) structures (presence of both positively and negatively charged groups) lead to complex electrostatic interactions with charged surfaces that cannot be accounted for by isotherm or point-charge surface complexation models. Here, we describe the application of a charge-distribution (CD) surface complexation model for zwitterionic species sorbing to variably charged oxide minerals. Model formulation includes functional group-specific inner- and outer-sphere bonding interactions with mineral surfaces, in accordance ATR-FTIR spectroscopic observations. CD model predictions agree closely with measurements of FQ sorption to three oxide soil minerals (TiO₂, α-FeOOH, and γ-AlOOH) collected over a wide range of pH, ionic strength and FQ concentrations.

Multiple sulfur isotopic evidence for multiple origins of late Archean and early Proterozoic sediment-hosted pyrite, Quadrilátero Ferrífero of Minas Gerais

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Multiple sulfur isotopes were measured in different types of pyrite (detrital, framboidal, euhedral, finely disseminated) from a late Archean to early Proterozoic metasedimentary succession in the Quadrilátero Ferrífero of Minas Gerais, southern São Francisco craton, Brazil. Samples derive from the Moeda Formation, a coarse clastic, metaconglomeratic unit, and carbonaceous phyllite of the Batatal Formation. The Moeda Formation rests unconformably on Archean greenstone rocks and is conformably overlain by the Batatal Formation. The depositional age for both sedimentary units is bracketed between 2580 and 2420 Ma [1].

Multiple sulfur isotope results display distinct differences between the type of pyrite and the stratigraphic position of the host metasedimentary rocks. This offers the potential for resolving pyrite provenance and formation, for distinguishing prevailing metabolic pathways, and identifying the overall oxidation state of Earth's atmosphere.

All pyrite samples show clear mass-independently fractionated sulfur isotopes, defining a slope of -1 in a $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ plot. This confirms previously published data and underlines the interpretation of a low atmospheric oxygen abundance [2]. Combining $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$, detrital and euhedral pyrite from the Moeda metaconglomerate exhibit largely positive values of $\Delta^{33}\text{S}$ (up to +8‰). In contrast, framboidal pyrite from the Moeda Formation has negative multiple sulfur isotope values. Pyrite from the overlying Batatal Formation displays also mostly negative $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values. These results indicate at least two different metabolic pathways archived: microbial turnover of elemental sulfur and sulfate reduction.

[1] Hartmann *et al.* (2006) *J. South Amer. Earth Sci.* **20**, 273–285. [2] Johnston (2011) *Earth Sci. Rev.* **106**, 161–183.