Discovery and characterization of contrasting siderophores produced by related nitrogen fixing bacteria using high resolution LC-MS

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Azotobacter vinelandii (AV) and *Azotobacter chroococcum* (AC) are closely related N_2 fixing bacteria. Whereas the structures and physiological functions of siderophores produced by AV have been much studied, those of AC remain unidentified beyond a general chemical characterization. Here we have exploited the characteristic iron isotopic fingerprint to identify known and unknown siderophores and characterize them structurally using ultra-sensitive high-resolution nano-flow UPLC-MS on an LTQ-Orbitrap XL platform.

Interrogation of preliminary data for AV revealed many putative Fe-chelators with high abundances, including those previously identified and other, yet unreported compounds.

Siderophores produced by AC were unrelated to those of AV. Many AC siderophores possess aliphatic side chains of variable length with corresponding changes in hydrophobicity. Current work investigates how these chemical differences in siderophore production relate to different metal acquisition strategies and occupation of different ecological niches.

Using isotopic analysis of copper to assess copper transport and partitioning in wetland systems

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Copper isotopes ($^{65}Cu/^{63}Cu$) are potentially powerful new geochemical proxies for transport and oxidation–reduction processes in hydromorphic soils, rivers and lake sediments. However, the integrative signal of $\delta^{65}Cu$ has not been used so far to investigate the transport and partitioning of copper in wetland systems with respect to both hydrological and biogeochemical conditions. Here we used copper isotopes to investigate the copper cycling in a stormwater wetland (as a 'natural laboratory') that regularly received copper-contaminated runoff from a 42 ha vineyard catchment (Rouffach, Alsace, France). Runoff water, suspended solids, sediments and plants were regularly collected throughout the period of copper-based fungicides application (May to July 2011) to establish the copper mass balance and study isotopic fractionations.

60 to 93% of copper in runoff was associated with suspended solids, which were efficiently retained by the wetland (93 to 96%). Copper bound to suspended solids had negative isotope signatures (-0.33 to -0.1 ± 0.1‰), whereas dissolved copper was enriched in ^{65}Cu (0.23 to 1.35 ± 0.06‰). Dissolved copper retention largely varied (68 to 95%) and became depleted in ^{65}Cu when passing through the wetland ($\delta^{65}Cu_{inlet}$-$\delta^{65}Cu_{outlet}$: 0.03 to 0.77 ± 0.08‰). This isotopic shift suggests that copper rapidely sorbed to organic matter or mineral phases of the wetland sediments. Under high-flow conditions, copper was less retained by the wetland and was likely mobilised from the wetland sediments. This was attested by a lower $\delta^{65}Cu$ value of the outflowing dissolved copper, thereby reflecting the contribution of sediment-bound copper (0.02 ± 0.1‰). Copper uptake by the vegetation (*Phragmites australis*, Cav.) was not a significant retention process in the wetland, and accounted for less than 1.5% of the total copper amount in the wetland.

We anticipate our results to be a starting point for using copper isotopes in a comprehensive approach to evaluate processes affecting copper cycling in hydro-biogeochemically dynamic systems, such as wetlands or hyporheic zones.

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