Cryptic sulfur cycling in paddy soils leads to formation of novel arsenic species important for rice research

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Rice paddy fields are known methane emitters. Sulfate reduction, though thermodynamically favored relative to methanogenesis, is often considered insignificant because pool sizes of sulfate are low and dissolved sulfide is supposed to be limited by FeS precipitation. There is, however, evidence for a "hidden" sulfur-cycle where reduced sulfur is reoxidized to zero-valent sulfur, thiosulfate, and sulfate coupled to Fe(III), nitrate or oxygen reduction. Such a sulfur-cycle sustains high sulfate reduction rates in the bulk soil and especially in the rhizosphere. We postulated that continuous production of low amounts of sulfide and zero-valent sulfur could promote formation of thioarsenates (pentavalent Arsenic (As) species in which sulfur replaces oxygen) instead of scavenging of the known oxyarsenic species on FeS phases at excess sulfide. To date, behavior of inorganic and methylated oxyarsenates in paddy soil pore water is in the focus of rice research due to the fact that arsenic, as a class I carcinogen, is readily taken up by rice plants and accumulating in the grains. Thioarsenates have not been considered so far, likely because the importance of sulfur cycling in paddy soils is currently still underestimated.

Here, we show combining results from field, mesocosm, and soil incubation studies that soil pH, original soil zero-valent sulfur concentrations, sulfate additions e.g. by fertilization, and As methylation potential (which is probably also determined by sulfate-reducing bacteria) are the main factors determining As thiolation. Thioarsenates thereby form in a large diversity of soils and even persist through alternate wet-drying cycles. Our results highlight the global relevance of thioarsenates in paddy soil pore waters. Whether thiolation is a chance or challenge for safe production of rice remains to be investigated.