Thioarsenates - so far unrecognized arsenic species in paddy soils

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Thioarsenates ($HAs^{V}S^{-II}_{n}O_{4-n}^{2-}$, n=1-4) are structural analogues to arsenate and have been reported to form from arsenite under sulfate-reducing conditions in a variety of environments. Paddy soils, where rice is grown for several months flooded, are environments prone to establishing strongly reducing conditions with production of methane (< -120 mV) and sulfide (< -50 mV). Free sulfide concentrations in solution are often limited by precipitation with iron. Arsenic is a well-known contaminant in rice. It is generally assumed that its accumulation in rice is due to a dominance of dissolved arsenite ($H_3As^{III}O_3$) under reducing conditions, but also arsenate ($H_3As^{V}O_4$) and methylated arsenates, produced by rhizosphere bacteria, may occur. Methylated arsenates are considered less toxic and exempt from the recently introduced As limits in rice. In an effort to reduce As accumulation in rice, major advances have recently been made in understanding the uptake, translocation, and detoxification pathways of the oxyanions. The uptake of arsenite is known to be promoted by silicon transporters while arsenate is taken up by phosphate transporters.

In contrast to the oxyanions arsenite and arsenate and the methylated species, thioarsenates have never been studied in paddy soils before. For paddy soils in Italy and France, we have been able to prove natural occurrence of mono- and dithioarsenate for the first time. Thioarsenates contributed up to 10% to total As which is comparable to concentrations measured for mono- and dimethylarsenate - species typically considered when studying As in rice and paddy soil. We furthermore detected up to 3% mixed methylthiolated arsenates. Laboratory incubation experiments with different types of soil showed that acetate addition and high sulfate concentrations promoted thioarsenate formation. In low iron (~3 $g \cdot kg^{-1}$) soils, we even detected trithioarsenate and the sum of thioarsenates reached up to 60% of total As. On a temporal scale, As thiolation preceded As methylation.

With the now proven occurrence of thioarsenates in paddy soils, their uptake, transformation, translocation, and accumulation in rice urgently need to be addressed.