Sorption and transformation of methylated thioarsenates in the rice rhizosphere by iron (oxy)hydroxides

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Iron(oxy)hydroxides are known as important sorption sites for arsenic (As) in oxic soils. However, reductive dissolution of iron(oxy)hydroxides in anoxic environments (e.g. paddy fields) limits sorption sites for As sequestration. Root oxygen loss of rice roots creates micro-oxic zones where iron plaque (mainly ferrihydrite, goethite, lepidocrocite, and siderite) can be formed and sequester As before it is taken up by rice plants. Sorption of inorganic and methylated As to iron(oxy)hydroxides is well-studied, but no information about the behavior of methylated thioarsenates, a group of newly discovered As-species in paddy soils, is available. Methylated thioarsenates form via ligand exchange of OH-/SH- in mono- (MMA) or dimethylarsenate (DMA) molecules. Rice plants are able to take up methylated thioarsenates, which are highly toxic for humans, and transport them in the xylem.

The pH- and ionic strength-dependent sorption of mono- (MMMTA) and dimethylmonothioarsenate (DMMTA) on goethite was compared to MMA and DMA. All As-species showed decreasing sorption on goethite with increasing pH and ionic strength, following the order MMA > MMMTA > DMA > DMMTA. Most As was sorbed in kinetic sorption studies within the first 10 minutes. However, iron(oxy)hydroxides transformed methylated thioarsenates to MMA and DMA over time and thus, increased sorption over time, as sorption of MMA and DMA was higher than for their methylated-thiolated analogues.

The influence of iron plaque on the uptake of methylated thioarsenates in rice plants is currently unclear and investigated in further experiments. Low sorption affinity of MMMTA and DMMTA could favor their uptake compared to MMA and DMA. However, transformation of methylated thioarsenates to less toxic methylated oxyarsenates in presence of iron plaque could limit As uptake and toxicity.