【Workshop 1】Development of phyto-technology for decreasing heavy metal in food

**Determination of aromatic arsenicals related to chemical warfare agents in rice and soil**

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Recently, at Kizaki area in Kamisu-town, Japan, prominent cerebellar symptoms were observed in the residents, presumably due to the presence of diphenylarsinic acid (DPAA). The maximum level of DPAA in the contaminated drinking well water in the area was 15 mg of As kg$^{-1}$. Phenylarsonic acid (PAA) was also detected in a much lower range. There were facilities of the former Japanese Army at Kizaki area, but the relation between DPAA and the military facilities are yet uncertain. According to records of those days, DPAA might have been used as a material for synthesizing CLARK. Other AAs, such as methylphenylarsinic acid (MPAA), dimethylphenylarsine oxide (DMPAO), and methyldiphenylarsine oxide (MDPAO), were detected in some underground water in this area. These methylated species will be produced by microorganisms. In addition, the Japanese Ministry of the Environment reported that MPAA was detected in brown rice cultivated in paddy fields irrigated with the contaminated underground water. Analyses of DPAA and PAA in soil and well water were recently reported. However, quantitative methods of AAs, especially MPAA, DMPAO, and MDPAO, in high matrix samples such as soil and plants must be established. The aim of our study is to develop a determination method for AAs in rice (grain and straw) and soil.

AAs and inorganic As were separated by reversed-phase chromatography, and quantified by ICP–MS with a membrane desolvating system. For the extraction of arsenicals from rice grain and straw, 68% HNO$_3$ provided better extraction efficiency than water, 50% methanol (CH$_3$OH), or 2.0 mol L$^{-1}$ trifluoroacetic acid (TFA). For the extraction from soil, 68% HNO$_3$ provided better extraction efficiency than H$_2$O, 1 mol L$^{-1}$ H$_3$PO$_4$, or 1 mol L$^{-1}$ NaOH. The contaminated soil contained all five AAs along with inorganic arsenicals as main species (5.86 ± 0.19 mg of As kg$^{-1}$: 60.8 ± 2.0% of total extracted As). After pot experiments, rice straw contained mainly DMPAO (7.71 ± 0.48 mg of As kg$^{-1}$: 60.5 ± 3.7%), MDPAO (0.91 ± 0.07 mg of As kg$^{-1}$: 7.2 ± 0.5%), and inorganic As (2.85 ± 0.20 mg of As kg$^{-1}$: 22.3 ± 1.6%). On the other hand, rice grain contained mainly MPAA (1.17 ± 0.04 mg of As kg$^{-1}$: 86.7 ± 2.7%). The root uptake of each species from the soil and transport from straw to grains were significantly related to the calculated log $K_{ow}$ values.