

Figure 1. Bioavailability of Arsenic in paddy soil samples before and after anaerobic simulation

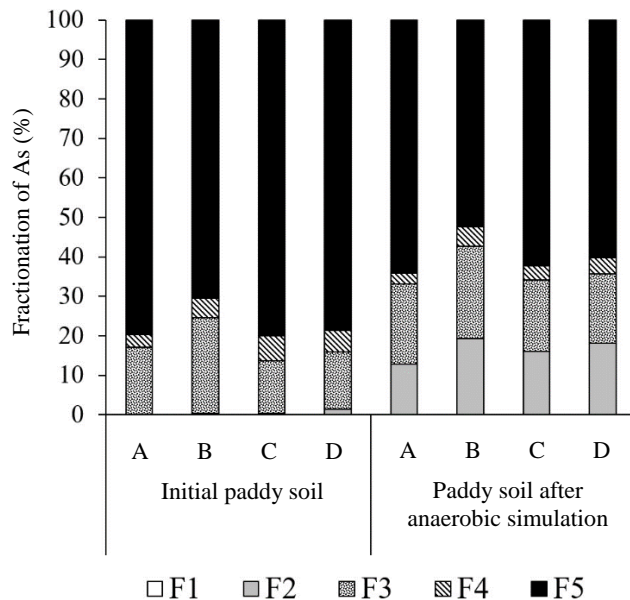


Figure 2. Fractionation of Arsenic in paddy soil samples before and after anaerobic simulation

Concentrations of As and Fe in the soil before and after the simulation were similar, while As in the supernatant was not measurable (<0.005 mg/L). Bioavailable As of the anaerobic paddy soil samples increased markedly from 0.66-0.79 mg/kg to 9.9-11.8 mg/kg (23-32% of total As) (Figure 1). The F2 and F5 values of As in paddy soil altered remarkably, while F1, F3, and F4 did not change significantly ($p>0.05$). The As content in F5 decreased from $77\pm 5\%$ to $60\pm 5\%$, whereas As in F2 increased from $0.56\pm 0.62\%$ to $17\pm 3\%$ (Figure 2).

4. DISCUSSION

In the soil samples, As was mainly distributed in F5, indicating the geogenic origin of As in this area (Fu et al., 2011; Wang et al., 2015), which was considered stable. Due to the As in mobile forms, As bound to amorphous oxides and bound to organic matters were eliminated during the 1st to 4th extraction step. The As content in F5 of Tessier's fractionation likely comprised of As-sulfide minerals and well-crystallized forms of Fe and As. Drahota and Filippi (2009) and Kim et al. (2014) found that the major As-sulfide minerals in the mining area were arsenopyrite, orpiment and arsenic-bearing pyrite, while their main weathered minerals were well-crystallized Fe arsenates (scorodite) and As associated with well-crystallized Fe oxides generally found in naturally As-rich soil. In this study, based on the soil sample characteristics, we presumed that As in F5 was likely predominated by well-crystallized weathered minerals.

Similar to other studies, despite the stable form of As in the soil, As bound to amorphous ferric oxide formed the major fraction of As (Baig et al., 2009; Farooq et al., 2010; Devesa-Rey et al., 2008; Hsu et al., 2012; Kim et al., 2014; Wang et al., 2015). Natural soil generally contains high amounts of ferric oxide that can adsorb various trace elements by various mechanisms (Hooda, 2010). The distribution of As in our paddy soil samples conformed to trends that As in F3 was the second major fraction.

The As in F4 was released from oxidizable components in the soil as organic compounds and some sulfide compounds. However, the AVS in this soil sample was not detectable. As content in F4 was believed to be bound to organic compounds. Similar to other studies, the As content in F4 was a minor fraction (Baig et al., 2009; Farooq et al., 2010; Fu et al., 2011). The As in F1 was the exchangeable fraction, while F2 contained As that was readily releasable by mild acid conditions, such as As bound to carbonate compounds or fresh precipitates. Both these fractions contributed less than 1% of the total As in the soil samples.

After one month of anaerobic induction by microbial activity, only As in F5 (stable fraction) and F2 (mild acid-soluble fraction) changed. A 17% decrease of As in F5 was observed, responding to a 16% increase of As in F2. This change of As fractionation indicated the release and resorption of As among the soil materials. However, we did not anticipate any change of As in F5 but expected F3

(bound to amorphous Fe oxide) to decrease via the iron reduction process.

Some toxic heavy metals become non-mobile under anaerobic environmental conditions via sulfidation (Hartley and Dickinson, 2010), but As can be altered to mobile forms (Kumarathilaka et al., 2018) or released to an aqueous solution (Hartley and Dickinson, 2010; Xue et al., 2020; Zhang et al., 2019). The released As content correlated well with released iron as ferrous (Xue et al., 2020). The iron redox cycle is governed by wet/dry cycles in paddy fields. The general explanation is that the source of released As is associated with ferric hydrous oxides in the soil (Hashimoto and Kanke, 2018; Rinklebe et al., 2016; Xue et al., 2020; Yamaguchi et al., 2011). Amorphous ferric hydrous oxide plays a much larger role in this dynamic environment than well-crystallized forms, with greater sensitivity toward released/resorbed ions in soil-water systems due to greater surface area and surface activity (Yang et al., 2020). It is reductively dissolute during wet periods and oxidatively reformed to be the amorphous ferric hydrous oxide state during dry periods (Winkler et al., 2018). Well-crystallized forms of ferric hydrous oxide are less sensitive to both redox reactions and release/resorption. Once dissolute, it cannot easily reform under general paddy conditions (Yang et al., 2020). Therefore, major As contents released and resorbed normally relate to amorphous ferric hydrous oxides. Nevertheless, only a small fraction of ferric hydrous oxide in the soil (e.g., surface of materials) contributes to this redox cycle, while most remains to resorb released ions. Fractionation of metals (and metalloids) associated with ferric hydrous oxide decreases, remains unchanged or increases when immersed in anaerobic conditions, depending on complex interactions between the many ions in the soil (Damrongsiri, 2018). This might explain why the F3 As content did not change significantly.

The stable form of As is less sensitive to environmental degradation. A recent study on the effects of farming on As-contaminated land by Yang et al. (2020) pointed out that scorodite can be reductively dissolved in the paddy environment. Arsenopyrites, which are stable, were can be significantly reduced and dissolved under anaerobic conditions (Kawa et al., 2019). Therefore, we presumed that both well-crystallized forms of As and Fe and arsenic sulfide minerals could be reductively dissolved, possibly explaining why the As content in F5 decreased during anaerobic incubation.

Once released, As is available for further reaction in anaerobic soil-water systems and re-associates with other soil materials. These resorbed materials and co-precipitates of As in soil initially appear as an early fraction, having loosely bound (Lu et al., 2019; Zhang et al., 2019). In our Eh-pH anaerobic system, dissolved As was near the theoretical transition line of H_2AsO_4^- , HAsO_4^{2-} , As_2O_3 , and As_2S_3 in As-S-O-H systems (Brookins, 1988) and trending to become HAsO_4^{2-} (As(V)); however, the speciation of As in soil is far more complex. In soil under anaerobic conditions, As(V) is released when As-bearing ferric hydrous oxide is dissolute. Some released As(V) is reduced to As(III) by microorganisms that can reduce both ferric materials and As(V) (Yu et al., 2016). Therefore, in an anaerobic paddy soil system, a large amount of As is in form of As(III) (Yamaguchi et al., 2011; Xu et al., 2016).

Under an anaerobic water-soil system, As(V) precipitates as ferric arsenate and ferrous arsenate (Fan et al., 2014). Beside, both As(V) and As(III) sorb to remaining ferric hydrous oxide and many freshly formed solids (Coker et al., 2006; Fan et al., 2014; Khalid et al., 2017). As could adsorbed to siderite (ferrous carbonate, FeCO_3) (Guo et al., 2013), troilite (ferrous sulfide, FeS) and pyrite (ferrous disulfide, FeS_2) (Bostick and Fendorf, 2003). In our anaerobic induction experiment, released As was reformed into F2 that was likely combination of these reviewed forms.

The very low bioavailability of As in our collected soil samples may relate to the very low distribution of As in F1 and F2. After one month of anaerobic induction, only As in F2 increased, responding directly to the increased bioavailability of As in the soil. In general, the bioavailability of elements relates to their mobile fraction (e.g., F1 and F2 of Tessier's fractionation). Liu et al. (2015) investigated the relationship between As in rice and the fractionation of As in soil. They found a positive correlation between As in rice and F1 and F2 of Wenzel's fractionation (non-specifically sorbed fraction and specifically sorbed fraction) of As in soil but a negative correlation with As bound to amorphous and crystallized iron oxide fraction and stable fraction. A similar result was shown by Wang et al. (2015). They used NaHCO_3 extractable As to indicate As bioavailability and investigated its relationship with the fractionation of As in soil, while Yu et al. (2017) demonstrated that the application of iron compounds in soil significantly decreased As accumulation in rice. These studies confirmed that, under anaerobic

condition, bioavailable As in soil was freshly precipitated As compounds, As re-adsorbed onto soil materials and As associated with freshly formed solids.

5. CONCLUSION

Samples of As-contaminated soil were collected and used in a simulation experiment. The soil samples exhibited aerobic conditions with 35-49 mg/kg As. The As was mainly distributed as a stable fraction, with a limited mobile fraction (<1%). The bioavailability of As was also very low (<2%). After one month of anaerobic incubation, the stable fraction of As (F5) in soil decreased significantly and reformed as As in the mobile fraction (F2), corresponding to an increase in bioavailability. Results indicated that the stable form of As in soil was released under an anaerobic environment. The released As then precipitated, bounded to soil materials or bounded to freshly-precipitated compounds. Results indicated that the bioavailability of As in paddy soil increased when the soil was subjected to anaerobic conditions for a long period. Therefore, agricultural activity that causes anaerobic induction in As-contaminated soil should be avoided. Cultivation of other crops without a waterlogging period or non-food plants should be considered.

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