Arsenic biogeochemistry from paddy soil to rice

F.-J. Zhao

College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing, P.R. China

ABSTRACT: Rice is a major dietary source of inorganic arsenic for the population who consumes rice as the staple food. Paddy rice accumulates much more arsenic than other cereal crops because the anaerobic conditions in submerged paddy soil is conducive to the mobilization of arsenite, and arsenite hitchhikes on the silicon uptake pathway which is highly expressed in rice roots. Although arsenite is the predominant arsenic species in submerged paddy soil, arsenate can still account for a significant portion of the soluble arsenic species. A number of denitrifying bacteria from paddy soils are able to mediate anaerobic arsenite oxidation by coupling with denitrification. Additions of nitrate enhanced anaerobic arsenite oxidation and decreased arsenic mobility in paddy soil. Anaerobic conditions also enhance arsenic methylation, whereas methylated arsenic species can be demethylated by some microbial populations. The dynamics of arsenic methylation and demethylation control the accumulation of dimethylarsenate, which is highly phytotoxic. Different arsenic species are taken up by rice via different transporters. Recent studies have identified a new class of enzymes that can reduce arsenate to arsenite, allowing arsenite to be extruded from rice roots to the external medium for detoxification.

1 INTRODUCTION

Rice is the staple food for about half of the world population and is also a major dietary source of inorganic arsenic (As), a class-one carcinogen for humans. Rice accumulates As much more efficiently than other cereal crops. This results from a combination of an elevated As bioavailability in anaerobic paddy soil and efficient uptake of As by rice roots (Zhao *et al.*, 2010). Paddy soils in many areas in Asia are contaminated with As due to mining activities and irrigation of As-laden groundwater, leading to phytotoxicity in rice crop and substantial yield losses (Panaullah *et al.*, 2009). The straight-head disease, a physiological disorder in rice prevalent in the USA and China, is thought to be related to As. Understanding the As biogeochemistry in paddy environments and the mechanisms of As uptake and transport in rice plants is important for both food security and safety.

2 RESULTS AND DISCUSSION

2.1 *Arsenic biogeochemistry in paddy environments*

Arsenic is a redox sensitive metalloid. Arsenate [As(V)] is the predominant As species under aerobic conditions. In flooded paddy soil, As(V) is readily reduced to arsenite [As(III)], which is less strongly adsorbed by iron oxyhydroxides and therefore more mobile than As(V). Arsenic bioavailability in paddy soils is greatly enhanced under anaerobic conditions.

As(V) reduction is mediated by soil microbes via either the detoxification mechanism, in which As(V) is reduced to As(III) by microbial As(V) reductases (e.g. ArsC) and extruded out of the cell, or the dissimilatory pathway, in which As(V) serves as the terminal electron acceptor for microbial respiration. Paradoxically, As(V) can still account for considerable proportions (10–30%) of the As in the solution of anaerobic paddy soils, even though thermodynamic calculations predict negligible presence of As(V). Our recent studies have shown that some denitrifiers in paddy soils are able to couple denitrification with anaerobic As(III) oxidation (Zhang *et al.*, 2015; Zhang *et al.*, 2017). Additions of nitrate to anaerobic paddy soils enhanced the population of denitrifiers, the abundance of the genes encoding As(III) oxidases and the oxidation of As(III) to As(V). These effects attenuated As bioavailability in flooded paddy soil.

Arsenic can be methylated into mono-, di- and tri-methylated As species by soil microbes. Some of the methylated As species, methylarsines, are volatile. Arsenic methylation and volatilization are enhanced under anaerobic conditions in paddy soils. Arsenic methylation in anaerobic paddy soils appears to be driven primarily by sulphate reducing bacteria. In contrast, dimethylarsenate (DMA) can be demethylated by methanogens. Arsenic methylation is catalyzed by arsenite S-adenosylmethionine methyltransferase (ArsM), which is present in some soil microbes (Huang *et al.*, 2016; Qin *et al.*, 2006). Higher plants do not appear to possess the ability to methylate As, but are able to take up methylated As species from the soil (Lomax *et al.*, 2012). Transgenic rice expressing

microbial ArsM was able to convert most inorganic As into DMA and TMAO, which caused phytotoxicity similar to the straight-head disease in rice.

2.2 Arsenic uptake and detoxification in rice

Arsenite is taken up mainly by the silicon transporters in rice (Ma *et al.*, 2008), whilst As(V) is taken up by phosphate transporters (e.g. OsPT8) (Wang *et al.*, 2016). As(V) reduction followed by As(III) efflux is a major mechanism of As detoxification in microorganisms. This has been found to be true in plants as well. Recent studies have identified a new class of As(V) reductases, named HAC, in *Arabidopsis thaliana* (Chao *et al.*, 2014). Our recent studies have identified OsHAC1;1, OsHAC1;2 and OsHAC4 as new As(V) reductases in rice that play a key role in As(V) tolerance and As accumulation in rice plants (Shi *et al.*, 2016; Xu *et al.*, 2017). These enzymes reduce As(V) to As(III); the latter is then effluxed to the external medium to avoid excessive build-up of As in the cells. Mutation in the OsHAC genes resulted in greatly increased accumulation of As in the above-ground tissues of rice, whereas overexpression of OsHAC genes decreased As accumulation.

DMA is taken up by rice roots partly via the silicon transporter Lsi1 (Li *et al.*, 2009) and transported to rice grain via the peptide transporter OsPTR7 (Tang *et al.*, 2017). DMA is more toxic to plants than inorganic As (Tang *et al.*, 2016). This is because DMA cannot be detoxified by complexation with phytochelatins and, as a result, is highly mobile during the long-distance translocation in rice plants. The high mobility and high toxicity of DMA explains its high potency in causing spikelet infertility in rice panicle, the key symptom of the straight-head disease.

ACKNOWLEDGEMENTS

The study was supported by the National Natural Science Foundation of China (grant No. 41330853 and 21661132001).

REFERENCES

Chao, D.Y., Chen, Y., Chen, J.G., Shi, S.L., Chen, Z.R., Wang, C.C., Danku, J.M. Zhao, F.J. & Salt, D.E. 2014. Genome-wide association mapping identifies a new arsenate reductase enzyme critical for limiting arsenic accumulation in plants. *PLoS Biol.* 12(2): e1002009.
Huang, K., Chen, C., Zhang, J., Tang, Z., Shen, Q., Rosen, B.P. & Zhao, F.J. 2016. Efficient arsenic methylation and

volatilization mediated by a novel bacterium from an arsenic-contaminated paddy soil. *Environ. Sci. Technol.* 50(12): 6389–6396.
Li, R.Y., Ago, Y., Liu, W.J., Mitani, N., Feldmann, J., McGrath, S.P., Ma, J.F. & Zhao, F.J. 2009. The rice aquaporin Lsi1 mediates uptake of methylated arsenic species. *Plant Physiol.* 150(4): 2071–2080.
Lomax, C., Liu, W.J., Wu, L., Xue, K., Xiong, J., Zhou, J., McGrath, S.P., Meharg, A.A., Miller, A.J. & Zhao, F.J. 2012. Methylated arsenic species in plants originate from soil microorganisms. *New Phytol.* 193(3): 665–672.
Ma, J.F., Yamaji, N., Mitani, N., Xu, X.Y., Su, Y.H., McGrath, S.P. & Zhao, F.J. 2008. Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. *Proc. Nat. Acad. Sci. U.S.A.* 105(29): 9931–9935.
Panaullah, G.M., Alam, T., Hossain, M.B., Loeppert, R.H., Lauren, J.G., Meisner, C.A., Ahmed, Z.U. & Duxbury, J.M. 2009. Arsenic toxicity to rice (*Oryza sativa* L.) in Bangladesh. *Plant Soil* 317(1–2): 31–39.
Qin, J., Rosen, B.P., Zhang, Y., Wang, G.J., Franke, S. & Rensing, C. 2006. Arsenic detoxification and evolution of trimethylarsine gas by a microbial arsenite S-adenosylmethionine methyltransferase. *Proc. Nat. Acad. Sci. U.S.A.* 103(7): 2075–2080.
Shi, S., Wang, T., Chen, Z., Tang, Z., Wu, Z.C., Salt, D.E., Chao, D.Y. & Zhao, F.J. 2016. OsHAC1;1 and OsHAC1;2 function as arsenate reductases and regulate arsenic accumulation. *Plant Physiol.* 172: 1708–1719.
Tang, Z., Kang, Y.Y., Wang, P.T. & Zhao, F.J. 2016. Phytotoxicity and detoxification mechanism differ among inorganic and methylated arsenic species in *Arabidopsis thaliana*. *Plant Soil* 401(1–2): 243–257.
Tang, Z., Chen, Y., Chen, F., Ji, Y.C. & Zhao, F.J. 2017. OsPTR7 (OsNPF8.1), a putative peptide transporter in rice, is involved in dimethylarsenate accumulation in rice grain. *Plant Cell Physiol.* 58(5): 904–913.
Wang, P.T., Zhang, W.W., Mao, C.Z., Xu, G.H. & Zhao, F.J. 2016. The role of OsPT8 in arsenate uptake and varietal difference in arsenate tolerance in rice. *J. Exp. Bot.* 67(21): 6051–6059.
Xu, J.M., Shi, S.L., Wang, L., Tang, Z., Lv, T.T., Zhu, X.L., Ding, X.M., Wang, Y.F., Zhao, F.J. & Wu, Z.C. 2017. OsHAC4 is critical for arsenate tolerance and regulates arsenic accumulation in rice. *New Phytol.* 215(3): 1090–1101.
Zhang, J., Zhou, W., Liu, B., He, J., Shen, Q. & Zhao, F.-J. 2015. Anaerobic arsenite oxidation by an autotrophic arsenite-oxidizing bacterium from an arsenic-contaminated paddy soil. *Environ. Sci. Technol.* 49(10): 5956–5964.
Zhang, J., Zhao, S.C., Xu, Y., Zhou, W.X., Huang, K., Tang, Z. & Zhao, F.-J. 2017. Nitrate stimulates anaerobic microbial arsenite oxidation in paddy soils. *Environ. Sci. Technol.* 51(8): 4377–4386.
Zhao, F.J., McGrath, S.P. & Meharg, A.A. 2010. Arsenic as a food-chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. *Ann. Rev. Plant Biol.* 61: 535–559.