



Mobilization, release and speciation of arsenic in an As-contaminated gold mine spoil under varied soil redox conditions

Albert Kobina Mensah¹, Bernd Marschner¹, Jianxu Wang^{2,3}, Sabry M. Shaheen^{2,4,5}, and Jörg Rinklebe^{2,6}

¹Ruhr Universitaet Bochum, Geography, Soil Science/Soil Ecology, Germany (albert.mensah@rub.de; bernd.marschner@rub.de)

²University of Wuppertal, School of Architecture and Civil Engineering, Laboratory of Soil- and Groundwater-Management, Pauluskirchstraße 7, 42285 Wuppertal, Germany (rinklebe@uni-wuppertal.de)

³State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, P.R. China (wangjianxu@vip.gyig.ac.cn; fengxinbin@vip.skleg.cn)

⁴University of Kafrelsheikh, Faculty of Agriculture, Department of Soil and Water Sciences, 33516 Kafr El-Sheikh, Egypt (smshaheen@agr.kfs.edu.eg)

⁵King Abdulaziz University, Faculty of Meteorology, Environment, and Arid Land Agriculture, Department of Arid Land Agriculture, Jeddah 21589, Saudi Arabia

⁶University of Sejong, Department of Environment, Energy and Geoinformatics, 98 Gunja-Dong, Guangjin-Gu, Seoul, Republic of Korea.

Redox-induced release dynamics of arsenic (As) in an abandoned geogenic arsenic-contaminated gold mine spoil in Ghana has never been studied. Therefore, our aim was to investigate the effects of varied soil redox conditions on mobilisation and speciation of As from an abandoned highly contaminated gold mine spoil (with 4,283 mg As/kg soil) using an automated biogeochemical microcosm set-up. We also studied the impact of redox potential (E_H)-dependent changes of pH, Fe, Mn, Al, S, Cl⁻, SO₄²⁻, DOC, DIC, DC, DN and SUVA on the release dynamics of As. As mineralogical composition and speciation were further determined using a synchrotron-based X-ray absorption spectroscopy (XANES). Linear combination fits of XANES results indicated that scorodite (FeAsSO₄) and arsenopyrite (FeAsS) are the two major As-containing minerals in the studied mine spoil. Geochemical fractionation using sequential extraction procedure indicated greater proportions of the extracted As in the amorphous iron oxide fraction III (1390.13 mg kg⁻¹, 32.5% of the total As) and residual fraction V (2591.67 mg kg⁻¹, 60.5% of the total As). Concentrations of dissolved Fe and SUVA were higher during reducing conditions and decreased under oxidising conditions and both showed negative significant relationships with E_H (E_H and SUVA: $r = -0.76$, $P < 0.01$; E_H and Fe: $r = -0.75$). Mobilisation of As was greater under reducing conditions (dissolved As = 136.68 mg/L) than in oxidising environments (dissolved As = 8.06 mg/L). The release of As under low E_H can be explained by the associated reductive dissolution of Fe oxides, as demonstrated by the high positive significant relationship between Fe and As ($r = +0.97$, $P < 0.01$). Dissolved As release dynamics can also be linked to desorption of aromatic carbon compounds on the surfaces of dissolved organic carbon, as demonstrated by the high positive significant correlation between SUVA and As ($r = +0.573$, $P < 0.01$). Further, the release dynamics of dissolved As was also affected

by changes in pH ($r = -0.4$, $P < 0.05$), but were not affected by redox-induced dynamics of Mn, Al, S, Cl⁻, SO₄²⁻, DOC, DIC, DC, DN. We conclude that conditions such as flooding and high rainfall in this contaminated mine spoil could create reducing conditions, leading to reductive dissolution of the arsenopyrite As-bearing primary mineral and may lead to higher As release into the groundwater, translocation into the food chain with potential impacts on human health.

Keywords: Arsenopyrite, redox chemistry, arsenic mobilisation, gold mine spoil, reductive and oxidative dissolution.