Summary

Knowledge regarding dynamics of As-species and their interactions under gradient redox conditions in the rhizosphere of treatment wetlands is still insufficient. Therefore, it is necessary to understand the fundamental processes and mechanisms operative in treatment wetlands to realize long-term stability and high As-removal efficiencies, both in the presence and absence of wetland plants. In the past, little attention has been paid to the biotransformation processes and metabolism of As in constructed wetlands. Hence, the aim of this investigation was to gain more information on the biotransformation of As and the dynamics of As- species in predominantly multi-gradient (both micro- and macro-) horizontal subsurface-flow constructed wetlands. Experiments were carried out in laboratory-scale wetland systems, two planted with *Juncus effusus* and one unplanted, using an artificial wastewater containing As (0.2 mg l^{-1}) under defined conditions of organic C- and SO_4^{2-}-loading.

Immobilization of As was found in all systems (both planted and unplanted) under conditions of limited C, obviously due to adsorption and/or co-precipitation. Removal efficiencies were substantially higher in the planted systems (60-70%) as compared to the unplanted system (37% on average). Immobilization under such conditions appeared to decrease over time in all systems.

At the beginning, the dosage of organic carbon (COD~340 mg l^{-1}; SO_4^{2-}~75 mg l^{-1}) immediately caused intensive microbial dissimilatory sulphate reduction in all systems (in the range of 85-95%) and highly efficient removal of total arsenic (81-96% on average), most likely as As_2S_3 precipitation. A significant amount of reduced As [As(III)] was found in the effluent of the planted systems (>75% of total As) during this period of efficient microbial sulphate reduction, compared to the unplanted system (>25% of total As). Later on in this operation period, the intensity of sulphate reduction and simultaneous removal of As decreased, particularly in the planted wetlands (ranging from 30-46%). One reason could be the re-oxidation of reduced compounds due to oxygenation of the rhizosphere by the emergent water plants (helophytes). Only traces (2-3 µg As l^{-1}) of DMA were found in the temporal dynamics of the planted wetlands under these conditions.

The immobilization of arsenic was found to be more stable in the planted beds than in the unplanted bed in a more oxidized environment with and restricted microbial sulphate

reduction (stopping of inflow C-dosage; SO_4^{2-}~ 0.2 mg l^{-1}).

In principle, both systems (planted and unplanted) were suitable to treat wastewater containing As, particularly under sulphate reducing conditions. The unplanted system seemed to be more efficient regarding the immobilization of As, but planted systems showed a better stability of immobilized As.

Total As-mass retention in planted wetlands was substantially higher (nearly 60% of the inflow) than in the unplanted bed (only 43%). In general, a higher level of As was found in the roots than in the shoots in the planted beds. Only 1% of the inflow As-mass was retained in the shoots while more than 55% was sequestered in and/or on the roots and sediments. However, the retention of As varied widely between each segment along the flow path of the planted wetlands. It was shown that there was a substantial increase in the As-accumulation level in the inflow regions (first half of the bed) and the declination of the As-concentration level was more pronounced along the flow path and in the outflow regions.

In the frame of investigating As-species dynamics within the horizontal subsurface-flow planted soil beds of treatment wetlands, redox dynamics of As-species particularly in the root-near environment of the rhizosphere were also investigated. Therefore, long-term experiments were carried out using a specially designed macro-gradient-free rooted gravel bed reactor, planted with *Juncus effusus* to treat an artificial wastewater containing As (0.2 mg l^{-1}). The exceptional quality of the biofilm processes at the root-surface of helophytes in treatment wetlands were of special importance in this investigation.

The experimental results showed that under carbon surplus and strict microbial dissimilatory sulphate reducing conditions (COD~340 mg l^{-1}; SO_4^{2-}~75 mg l^{-1}), a higher As-removal efficiency (up to 82%) was attained, probably due to idealized flow conditions within the rhizosphere (macro-gradient-free rooted gravel bed reactor) compared to the whole multi-gradient prevailed horizontal subsurface-flow planted wetlands (44-47%). Under such carbon surplus conditions (COD~340 mg l^{-1}), it was also observed in this specially designed rooted gravel bed reactor that there was a better As deposition and accumulation under a high SO_4^{2-} (75 mg l^{-1}) load compared to a low SO_4^{2-} (0.2 mg l^{-1}) inflow concentration. Therefore, it can be concluded from this investigation that SO_4^{2-} loading under carbon surplus conditions is a promising strategy to improve the retention of As in the rhizosphere of constructed wetlands. However, the plants exhibited apparent toxic symptoms, probably due to toxic sulphide formation along with reduced As-species, arsenite [As(III)].

As mentioned earlier, a potentially higher stability of immobilized As was observed in the horizontal subsurface-flow planted wetlands under more oxidized environment with restricted microbial sulphate reduction (stopping of inflow C-dosage; SO_4^{2-}~ 0.2 mg l^{-1}). However, in the root-near environment of the rhizosphere (macro-gradient-free rooted gravel bed reactor), immobilized As showed greater instability, releasing up to 85% total As effluent predominantly as As(V) under such conditions. The findings of this study highlighted the importance of the plants in multi-redox gradient prevailed horizontal subsurface-flow planted soil beds in treatment wetlands.

Based on As mass-balance analysis, the rooted gravel bed reactor with high SO_4^{2-} loading along with wetland vegetation (*Juncus effusus*) was found to retain more than 76% of the total As input, while the 9% unaccounted values were postulated to be due to some other microbial reactions, adsorption and even volatilizations. Similar to the multi-gradient prevailed horizontal subsurface-flow planted wetlands, both plant biomass (specifically roots) and sediments comprise the ultimate sink for As in the rhizosphere (macro-gradient-free rooted gravel bed reactor). A substantially higher mass of arsenic is retained in the roots and sediment (>60% altogether) as compared to shoots (<1%) in the rooted gravel bed reactor system.

In conclusion, the obtained results demonstrated that horizontal subsurface-flow constructed wetlands seem to be viable alternatives for effective elimination of elevated As concentration from secondary domestic wastewater effluents prior to disposal to the receiving water bodies (rivers, lakes etc.) or application for agricultural field irrigation purposes. Long-term accumulation of As in the wetland vegetation (mostly in the below-ground biomass) and soil sediments may reduce widespread distribution of As in the environment.