Journal of Hazardous Materials 189 (2011) 640–646

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Hazardous concentrations of selenium in soil and groundwater in North-West India

Mini Bajaj [a], Elisabeth Eiche [b], Thomas Neumann [b], Josef Winter [a,*], Claudia Gallert [a]

[a] Institute of Biology for Engineers and Biotechnology of Wastewater, Am Fasanengarten, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany
[b] Institute of Mineralogy and Geochemistry, Forschungszentrum Umwelt (FZU), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 29 September 2010
Received in revised form 20 January 2011
Accepted 21 January 2011
Available online 28 January 2011

Keywords:
Selenium
Agricultural soil
Irrigation water
Elemental analyses
Mineralogical analyses
Selenate reduction

ABSTRACT

Soil and groundwater samples were collected for bulk elemental analyses in particular for selenium (Se) concentrations from six agricultural sites located in states of Punjab and Haryana in North-West India. Toxic concentrations of Se (45–341 $\mu g\,L^{-1}$) were present in groundwater (76 m deep) of Jainpur and Barwa villages in Punjab. Selenium enrichments were also found in top soil layers (0–15 cm) of Jainpur (2.3–11.6 $mg\,kg^{-1}$) and Barwa (3.1 $mg\,kg^{-1}$). Mineralogical analyses confirmed silicates and phyllosilicates as main components of these soils, also reflected by the high content of SiO_2 (40–62 wt.%), Al_2O_3 (9–21 wt.%) and K_2O (2.2–3.2 wt.%). Prevailing intensive irrigation practices in Punjab with Se enriched groundwater may be the cause of Se accumulation in soils. Sequential extraction revealed >50% Se bioavailability in Jainpur soils. Appearance of selenite was observed in some of the batch assays with soil slurries under reducing conditions. Although safe Se concentrations were found in Hisar, Haryana, yet high levels of As, Mo and U present in groundwater indicated its unsuitability for drinking purposes. Detailed biogeochemical studies of Se in sediments or groundwater of Punjab are not available so far; intensive investigations should be started for better understanding of the problem of Se toxicity.

1. Introduction

Selenium (Se) is required as micronutrient for several physiological and biochemical processes mainly as a component of selenoproteins or of amino-acids such as selenomethionine and selenocysteine. The recommended daily dietary allowance for selenium is 55 $\mu g\,d^{-1}$ for persons above 14 years and the tolerable upper intake level (TUL) is 400 $\mu g\,d^{-1}$. Exceeding TUL can lead to chronic or acute selenosis [1,2]. Selenium enters the food chain mainly through the soil–plant-system. Although it is still unclear if Se is essential for plant growth the high Se level in some food and forage plants are toxic for animals and humans [3–5].

In natural environments, four inorganic Se species are known. These are selenate ($SeO_4{}^{2-}$), selenite ($SeO_3{}^{2-}$), elemental Se (Se^0) and selenide (Se^{2-}). The Se oxy-anions are among the trace elements common in soils. The oxy-anions are soluble in water and especially the $SeO_4{}^{2-}$ is leaching into the aqueous phase [6]. Generally, Se (IV) (selenite) has a much higher affinity to adsorb onto soil particles compared to Se (VI) (selenate) [7]. As a consequence, Se (VI) is more mobile and easily available to plants especially under oxidizing, neutral to alkaline conditions, where it is the dominant species [6]. Se^0 mainly occurs under reducing conditions, is insoluble and exhibits no or very little toxicity. Se^{2-} is a highly toxic gas; however it is rapidly oxidized to non-toxic elemental Se in the presence of air [8,9]. Considerable enrichments of Se can be found in carbon shales (≥600 $mg\,kg^{-1}$, phosphatic rocks (≤300 $mg\,kg^{-1}$) or coal (≤6500 $mg\,kg^{-1}$) [4,9–11]. Selenium concentrations in soils are generally low with 0.01–2 $mg\,kg^{-1}$ (average: 0.4 $mg\,kg^{-1}$) but soils with highly elevated Se concentrations (>2–5000 $mg\,kg^{-1}$), called seleniferous soils, are widely distributed throughout the world (USA: up to 28 $mg\,kg^{-1}$; Ireland: up to 1200 $mg\,kg^{-1}$, China: up to 59 $mg\,kg^{-1}$ [3,6,9,11]. The Se concentration in soils is mainly determined by the Se content of the parent rock, the topography and the climate, but introduction of seleniferous erosion material, poor drainage of soils, irrigation with Se containing water, usage of phosphate fertilizer, influence of mining operations or volcanic eruptions and combustion of coal and petroleum can considerably enhance the soil Se content [6,9,12,13]. The mobility and bioavailability of Se depends on processes such as adsorption, precipitation and transformation which are heavily influenced by the pH-value, redox conditions, amount of competing ions, Se-speciation, soil mineralogy, organic matter content, microbiology, plant species, etc. [3,6,9,14]. Therefore, knowledge of total Se concentrations in soil is not sufficient in order to predict possible health threats

* Corresponding author. Tel.: +49 721 608 42297; fax: +49 721 608 47704.
E-mail addresses: mini.bajaj@kit.edu (M. Bajaj), elisabeth.eiche@kit.edu (E. Eiche), neumann@kit.edu (T. Neumann), josef.winter@kit.edu (J. Winter), claudia.gallert@kit.edu (C. Gallert).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.01.086

related to food and forage grown on seleniferous soils. An easy and frequently used way to assess bioavailability of Se in soils is to determine the water-soluble content e.g., by several sequential extractions schemes developed and adopted over the years [10,15,16]. Several regions throughout the world are known to suffer from Se intoxication due to consumption of food and forage grown on seleniferous soils, e.g., in Australia, China, India and the USA [10,17,18]. In India both, Se deficient (0.025–0.71 mg kg^{-1}) and seleniferous soils (1–20 mg kg^{-1}) have been recognized [9]. Selenium came into the scientific focus in India in the mid seventies after an animal disease locally called 'Degnala' was found to be associated with high intake of Se in fodder grown on alkali soils of Haryana [19]. But since the last two decades the presence of high concentration of selenium and it's toxicity to farm animals has been mainly reported for the Northeastern parts of Punjab, namely in Nawanshahr (renamed as Shahid Bhagat Singh (SBS) nagar) and Hoshiarpur districts [18,20–23]. Acceptable limits for Se in forage plants by the EPA of USA are 2–5 mg kg^{-1}. An acute long-term toxic effect of Se for animals is likely to occur when the Se concentration is above 5 mg kg^{-1} in forage. The presence of up to 69.5 μg L^{-1} Se in groundwater, 6.5 mg kg^{-1} Se in soil and 3–670 mg kg^{-1} Se in plants in locations at or near to present study area had been reported previously [18,23–25]. A study conducted two decades ago, reported that Se toxic sites ranging from 4 to 6 ha were spread over an area occupying >1000 ha in North-Eastern Punjab [18,24].

In the present study, the elemental composition of soil and groundwater as well as the speciation of Se in the topsoil was determined in samples collected from North-Eastern Punjab and Haryana. Apart from some reports [18,24], data on ground water quality of the selected study area is very scarce, although the region is well known for high levels of Se in soils and crops. The aim of the present study was to assess the influence of long-term irrigation with Se-burdened groundwater on the total concentration and speciation of Se in the top soil profile. Another aim was to estimate the potential microbial reduction of Se (VI) in the soils, which is thought to occur primarily via bacterial dissimilatory reduction [26–28] and alters the speciation/mobility of Se. Understanding the influence of long-term irrigation as well as speciation control mechanisms on the Se cycling will help to assess the fate of additional Se from irrigation water within the soil profile and to predict a possible health threat in the area.

2. Study area

The study area is located in the North-West of India. Out of six sampling sites, four sites were situated in the state of Punjab, one in the state of Haryana and one in Chandigarh, the capital of both states. In Punjab, samples were taken in Jainpur and Barwa villages in the SBS Nagar district (formerly known as Nawanshahr, 33.12°N, 76.13°E) and in the village of Simbli which is part of the Hoshiarpur district (31.12°N, 76.13°E) and situated approximately 3 km away from the other two villages. Both districts are situated in the North-Eastern part of Punjab. The map of study area in Punjab can be found in a report by Dhillon and Dhillon [18]. Total rainfall in that area varies from 631 to 1325 mm a^{-1} and about 80% of the yearly rainfall of approximately 1000 mm occurs in the rainy season, mainly from July to September [24,29]. The soils of the area are mostly loamy and alkaline in reaction and are considered to be formed from the alluvium deposited by Indus rivers system [18].

All sampling sites were fertile fields growing two seasonal crops (rice or maize and wheat) per year. There are some seasonal rivulet formations but farmers at the sampling sites depend mainly upon groundwater for irrigation purposes.

The sampling sites in Punjab were selected based on the known distribution of seleniferous soils and on related health problems that have been reported in previous studies [18,20,30] or on current complaints about selenosis from farmers, especially in Jainpur village. Feeding of forage grown on these seleniferous soils, which often show white chlorosis (Fig. 1), has evoked characteristic signs of selenosis in livestock, such as cracks in the hoofs, peeling-off of horns and loss of hair, premature abortions and even occasional death ([18,20]; personal communication with farmers). Meanwhile the local population has also been affected after regular consumption of cereals grown in the area, showing visible symptoms like cracked and discoloured nails (Fig. 2). This happened, although state authorities recommended to food grain procurement agencies in 2003/2004, to collect the grains from seleniferous soil separately and mix them with grains that were harvested from non-seleniferous fields to bring Se level within health safe limits before marketing.

Fig. 1. A strong white patch (outlined as rectangle) in between a wheat field at Jainpur village (site 1).

Apart from three seleniferous sites (Jainpur 1, Barwa, Simbli), one field thought to be free of contamination (based on non visible symptoms of Se toxicity) by local farmers (Jainpur 2) was chosen in Punjab. However, this non-seleniferous site has been irrigated with Se burdened groundwater for some time. One sample was taken in the district of Hisar (29.5°N; 75.45°E), Haryana, from grounds of Guru Jambeshwar University of Science and Technology, Hisar. An earlier study by Sharma [19] has also reported increased Se concentrations in soils from Hisar (up to 6 mg kg^{-1}). The area is semi-arid and is located just 30 km North-East of the Thar Desert. The annual average rainfall is only 450 mm and agriculture is supported mainly by canals and irrigation with groundwater. A further sample was collected from the outskirts of Chandigarh (30.75°N; 76.78°E), which is a union territory of India as well as the capital city of both Punjab and Haryana. The average rainfall there is 1101 mm [31]. Chandigarh is located near the foothills of the Shivalik mountain range of the Himalaya but no seleniferous soils or Se toxicity symptoms have been reported from this area. Therefore, it was considered as control site.

3. Material and methods

3.1. Sampling

Soil samples were taken in January 2010 from different depths by manual drilling with a soil auger and stored in plastic bags at 4 °C till further analysis to minimise the effect of bio-geochemical activities and of evaporation on initial elemental composition. Groundwater was sampled from existing tube wells which were