Bull. Environ. Contam. Toxicol. (2004) 72:1115–1121

DOI: 10.1007/s00128-004-0359-3

Bulletin of Environmental Contamination and Toxicology

Arsenic Bioaccumulation by Beetles in an Arsenic-Rich Region

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Received: 1 November 2002/Accepted: 12 March 2004

Arsenic is one of the most toxic elements, particularly for soil-living animals (Ramade 1987; Eisler 1994; Yeates et al. 1995). Usually it occurs in the environment in rather low concentrations. Its amounts in uncontaminated soils range from 0.01 to 95 mg kg^{-1} (Walsh et al. 1977; Kabata-Pendias and Pendias 2001). The NOEC limit for soils is 2 mg kg^{-1}. At the same time, vegetation is known to concentrate it up to 62 mg kg^{-1} (Torres and Johnson 2001). Arsenic has very low accumulation rates in animals (Pascoe et al. 1994; Mandal and Suzuki 2002) and is poorly accumulated in food chains (Milton and Johnson 1999). Studies of its concentration in invertebrates from As-enriched habitats are important for understanding its migration through food-webs and forecasting permissible bioaccumulation caused by anthropogenic pollution.

The aim of the study was to estimate the uptake of As by beetles of different trophic groups inhabiting ecosystems with naturally high As concentrations and areas enriched in As by human activity. Saprophagous tenebrionids *Blaps rugosa* Gebl. and predatory carabids *Poecilus* spp. chosen for the study are surface-dwelling species, they usually inhabit an area not more than 200 m diameter, so they were inhabiting the sampling sites for most of their lives. Conversely, necrophagous *Nicrophorus investigator* Zett. is a good flier. We hypothesised that beetles of various trophic groups should have accumulated arsenic differently: in contrast with the heavy metals arsenic is a very toxic element itself, and even low concentrations of it in the bodies may kill animals.

MATERIALS AND METHODS

The investigation was carried out in the vicinity of the Priargunsky Mining-Chemical Production Company (PPGHO), in south-eastern Siberia, 18 km east from Krasnokamensk, Russia (50°05′ N, 118°15′ E). The area belongs to the geobotanical province of Dauria dry steppe on kastanozem soils. The relief is represented by low mountains with a maximum elevation of 800-1300 m above sea level. The climate is extremely continental, the difference between mean summer and winter temperatures is ca. 40°C. Only 5% of the annual precipitation rate of 400 mm falls in winter. Soils freeze up to 3 m deep (Nogina 1964).

Since 1968, PPGHO has been exploiting a U-Mo ore deposit of the Streltsovsky

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ore region. The annual uranium production is about 2500 tonnes (OECD 1999; Velichkin et al. 2000). Liquid and solid wastes of the hydro-metallurgic plant contained in the tailing ponds consist of pulp, which is made of fine-shattered rock, 96% composed of particles of less than 1 mm. It contains high concentrations of U (up to 260), Mo (500), As (7200), Mn (7570), Sr (3040 mg kg^{-1}) and other elements. In dry seasons, the pulp is easily spread in the surroundings by strong winds, which are quite usual in the area. Prevailing wind directions are north-westerly and westerly. This is the reason why the soils in the vicinity of PPGHO are enriched in the elements stored in the tailing ponds. Unpolluted soils contain large amounts of Th (12.0), U (3.0) and Mo (1.3 mg kg^{-1}) (Velichkin et al. 2000).

The area investigated was covered by steppe with grasses *Leymus chinensis* Trin., *Stipa baicalensis* Roshev., herbs *Bupleurum scorzonerifolium* Willd., *Adenophora gmelinii* Spreng. and a number of *Artemisia* species. Three study plots were chosen. Plot 1 (reference), 10 km north-east from the complex, was covered by unpolluted steppe. Plot 2 was situated about 100 m from the tailing pond of the sulphuric acid producing plant; plot 3 was situated 100 m from the hydro-metallurgic plant. Field sampling was carried out in August 2000 and 2001.

Physical and chemical parameters of the soil were obtained according to Arinushkina (1970) and Schinner et al. (1996). The samples were collected by using a corer of 9 cm diameter, the top 10 cm was taken into analysis over a sampling area of 0.4 m^2. For pH determination, 10 g of soil was put into a plastic container, 25 mL of 0.01 *M* solution of $CaCl_2$ was added and mixed. The container was closed hermetically and stored for 24 hrs at room temperature. The determination of pH was carried out using an electronic pH-meter *Consort* with ion-selective electrode and 0.01 pH precision.

Water holding capacity (WHC) was calculated as the proportion of water that can be held by an absolutely dry soil sample. Ten grams of soil was placed on filter paper with 0.3 nm pore size in a funnel and about 50 mL of distilled water was added twice in the time interval of 10-15 min. The funnel was placed into a glass so that its spout was dipped into the sand placed in the bottom of a glass. This allowed water to ooze through the soil slowly. After 3 hrs, soil from the funnel was put into a crucible, weighed and stored at a temperature of 105°C during 6 hr and weighed again after cooling. Soil carbon was measured by a method of wet combustion (Arinushkina 1970), for this 0.1 g of fine-shattered soil passed through 0.25 mm mesh was combined with 10 mL of oxidizing liquid. The latter consisted of 0.4 *N* $K_2Cr_2O_7$ and sulfuric acid mixture in a proportion 1:1. The mixture was boiled for 5 min at 140–180° C. The liquid obtained was titrated with 0.1 *N* Mohr's salt solution in the presence of phenylanthranylic acid as an indicator.

The soil and vegetation samples were analysed by an X-ray-fluorescence analyser in the Geological Institute of the Russian Academy of Sciences. From each plot, soil of the upper 10 cm layer was taken for analysis. Soil samples were air-dried (20-25°C). Soil aggregates were crushed to pass through 1 mm mesh and analyzed

for total As content. The vegetation was ashed by heating at 400°C in a muffle furnace for 6 hrs and was analyzed. Vegetation samples consisted of a mixture of dry *L. chinensis, Artemisia communis* L. and *B. scorzonerifolium* in equal proportions. Twenty specimens of each species were collected over a plot about 0.25 ha. Total As content in soil and in vegetation samples was obtained by using X-ray-fluorescence with an instrument detection limit 2 ppm for soil and 1 ppm for vegetation. To determine mobile forms, 10 g of soil was dissolved in 50 mL CH_3COONH_4 (pH = 4.8) and left for 18 hrs. The suspensions were filtered through filter paper with 0.3 nm pores and analyzed. HCl extractions of As were obtained by dissolving soil samples in 1*N* HCl. The procedure was identical to the previous one with soil to liquid mass ratio of 1:10. Arsenic mobile and HCl extractable forms in soil solutions were analyzed by X-ray fluorescence with an instrument detection limit of 0.003 mg L^{-1}. The difference between total and HCl extractable form concentrations was considered as the immobile share of As in soil. The value of weak mobile forms was determined by subtracting the concentration of mobile (CH_3COONH_4 extractable) forms from the concentration of HCl extractable As.

Beetle samples were studied by means of a neutron activation analyser in the Institute of Geology of Rare Elements. Four species collected at the three studied plots were analysed: *Poecilus fortipes* Chaud., *P. gebleri* Dej. (Carabidae), *Blaps rugosa* (Tenebrionidae) and *Nicrophorus investigator* (Silphidae). Adult beetles were kept alive 1-2 days to evacuate the digestive tract. Each sample (100 mg) for analysis was a mixture of 5 (*P. fortipes*) or 3 (other species) individuals to minimize individual variation within species. The instrument detection limit of the method was 0.1 mg kg^{-1} and the error of the analyzer was of 5-10%. Standards used in the analysis were IAEA-soil-7 for the soils and IAEA-336 (lichen) for vegetation and insects.

For each studied parameter, the mean value and standard error were calculated. An accumulation index for concentrations of chemical elements in beetle bodies was calculated as a ratio of an element concentration at contaminated plot vs. reference.

RESULTS AND DISCUSSION

In the soil of plot 1, almost no pebbles or stones were found. Soil acidity varied in a range from pH 5.9 to pH 6.4 (Table 1). The unpolluted plot was characterised by high water-holding capacity, organic matter content and naturally high concentrations of As (8.4-9.7 mg kg^{-1}) in the soil. The amount of its mobile forms did not exceed 1%. Arsenic was probably concentrated in crystals of primary minerals or in the inner layer of soil colloids, therefore it cannot be removed by acid water flows. As an anionogenic element, it becomes mobile only under alkaline conditions (Perelman and Kasimov 1999). Low rates of As mobile forms in soils caused its low concentrations in plants (Table 2). The pH value at plot 2 was higher than reference (7.0), the soil was impoverished in organic matter (1.2% C). The soil contained 2.98 times more As in comparison to the reference and 62 times more mobile As. Vegetation samples contained the largest amounts

Table 1. Soil physical parameters (mean ± SD).

Parameter	Plots		
	1	2	3
Litter mass (kg m^{-2})	2.31±0.15	1.19±0.16	0.75±0.05
Soil mass (%)	99.2±25.8	91.3±14.2	89.7±9.2
Stones (> 5.0 mm) mass (%)	0.4±0.2	1.4±0.6	1.3±0.7
Pebble (> 2.7 mm) mass (%)	0.4±0.4	7.0±1.8	9.0±2.5
pH	6.3±0.2	7.0±0.4	7.2±0.1
Total soil carbon (%)	2.06±0.07	1.19±0.35	0.92±0.28
Water holding capacity (%)	105±4.2	63.2±3.3	63.3±2.5

Plots: 1 – reference; 2 – close to the tailing pond of the sulphuric acid producing plant; 3 – close to the tailing pond of the hydro-metallurgic plant.

of As (27.7 mg kg^{-1}) among those investigated. At plot 3 the soil was impoverished in organic matter (0.9% C). The soil was slightly enriched in As (12.0 mg kg^{-1}). The weak mobile form content was approximately the same as in the reference. Soils of the contaminated plots in comparison to the reference contained significantly less organic matter and were more acid. This was possibly caused by mixing horizons during the arrangement of the tailing ponds. The plots close to the tailing ponds showed high As concentrations in the soils. The areas most polluted in As were those surrounding the sulphuric acid producing plant. Industrial impact turned out to be the most intensive because of large amounts of As coming out during the process of sulphuric acid production. Dry pulp dissipation, in turn, led to enrichment of the surrounding soils in As. Large amounts of this element occurred in easily consumable mobile form (Table 2), which was accumulated by vegetation at this area. This is also known from other areas (Bunzl et al. 2001; Francesconi et al. 2002).

Carabid beetles (*P. fortipes* and *P. gebleri*) from the reference area contained 0.2-0.6 mg kg^{-1} of As (Table 2). The other two beetle species contained larger amounts of As in their bodies (1.1-1.3 mg kg^{-1}). At the polluted plots, As concentrations in the beetles were higher (in necrophagous species *N. investigator* – 2.0-4.2 times, in predatory carabids 2.5-14.5, in saprophagous *B. rugosa* 10.0-26.3 times). The latter species contained the largest amount of As (29.0 mg kg^{-1}) among the studied beetles.

Arsenic concentrations in most of the beetles were about the average of the mean for the invertebrates (Zhulidov 1987; Beyer et al. 1990; Gongalsky 2000). At the same time they had a positive correlation with the total soil As. The strongest effect was observed for *B. rugosa.* Concentration of As depended on its concentration in food. Particularly, earthworms in a contaminated substrate over 104 days accumulated ca. 10^4 times As in comparison to controls (Fleckenstein and Graff 1982). Because of the high concentration of As in the food substrate (Table 1), the tenebrionid beetle had the highest accumulation ratio (polluted vs. reference plot concentration ratio) among the studied beetles. This fact can also be caused by the long life span (up to 3 years; Matyukhin, personal communication)

Table 2. Arsenic content (mg kg^{-1}) in soil, vegetation (mean ± SD) and beetles (mean of 3 measurements, analyzer error is 5-10%) in reference area and those polluted by PPGHO.

Substrate	Plots		
	1	2	3
Soil total, e.g.	8.4±1.8	25.0±3.0	12.0±1.4
Immobile	7.57±1.77	18.7±0.88	11.2±1.12
Weak mobile	0.82±0.12	5.71±0.67	0.72±0.08
Mobile	0.010±0.002	0.62±0.10	0.09±0.01
Vegetation	6.0±1.5	27.7±5.7	4.1±2.0
Beetle			
Poecilus gebleri	0.2	2.9	2.4
P. fortipes	0.6	2.7	1.5
Blaps rugosa	1.1	29.0	11.0
Nicrophorus investigator	1.3	2.6	5.5

Plots: 1 – reference; 2 – close to the tailing pond of the sulphuric acid producing plant; 3 – close to the tailing pond of the hydro-metallurgic plant.

of tenebrionid beetles. Being either predatory (such as the carabids) or necrophagous (such as silphids), other beetles were situated further in a hypothetical trophic chain from the soil and received less As in their food. Despite the fact that arsenic is a very toxic element, it accumulated in beetles' bodies. As accumulation may possibly depend on the proportion of mobile arsenic in the soil. On the one hand it was correlated with total As concentration; on the other hand, the proportion of mobile fraction at this site (2.48%) was higher than at the others (0.11-0.75%).

The chemical composition of macroinvertebrates is dependant on the chemical composition of the environment (Pokarzhevskii 1985). Many studies have shown that carabid beetles accumulated small amounts of pollutants, e.g. heavy metals (Heliövaara and Väisänen 1993). This fact was explained by their predatory life strategy. However, when a pollutant (arsenic in this case) occurs in the environment in an extremely high concentration, even poor accumulators (for example, carabid beetles) concentrate high amounts of it in their bodies. To see if the differences remain consistent, more types of beetles should be examined.

In conclusion, the beetles from polluted areas accumulated extremely high amounts of As in their bodies, although this element is known as poorly migratory through food webs.

Acknowledgments. We thank Dr. I.M. Miklyaeva (Moscow State University) who identified plants from the study area; F.A. Savin (MSU) who assisted in processing of the soil samples; Dr. S.M. Lyapunov (Geological Institute, Moscow) and E.P. Shevchenko (Institute of Geology of Rare Elements, Moscow), who carried out chemical analyses. The recommendations of Dr. A. Dhondt (Institute of Earth Sciences, Brussels), Dr. I. Boomer (University of Newcastle, UK) who kindly checked the manuscript, and two anonymous referees were very

useful. Financial support was received from Russian Foundation for Basic Research (grants 01-04-06227 and 03-05-64127) and PPGHO.

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