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Heavy Metal Accumulation in Some Plants in the Yesilirmak River Near the Antimony Mining Area Tokat, Northern Turkey

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The levels of Sb, Cd, Pb, Zn and Cu in *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.* in the Yesilirmak River near the antimony mining area from June 2004 to November 2004 were determined. Antimony, cadmium, lead, zinc and copper uptake are not efficient for these 5 species when the availability of the elements in the water or sedimet are low or intermediate. The present results suggest that *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.* can not use as a bioindicator for Sb, Pb, Cd, Cu and Zn accumulation. These 5 heavy metals level remained below at which toxic effect would be likely to occur in potential concern about macroinvertebrate and fish.

Key Words: *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia, Spirogyra sp.*, River Yesilirmak, Heavy metals.

INTRODUCTION

Antimony has been mined and utilized since *ca.* 4000 BC and has always been an element of medical, environmental and economic interest[1]. Antimony is a trace element with low content in the earth's crust about 0.2 ppm. Antimony is considered geochemically immobile[2]. Nevertheless, mobility and the biological role of antimony, its behaviour and transfer into food chain, are not well known[3].

The biological role of antimony and its compounds is not known. They are nearly as toxic as lead and have been listed as priority pollutants by the US Environmental Protection Agency[4]. However, antimony accumulation is not often studied for macrophytes[5]. Hence, there is an increasing interest in antimony concentrations in many kinds of environmental, biological and geochemical samples. Though less information is available on the effects of human activities on the global geochemical cycle of antimony[2].

In this study, the concentrations of Sb, Cd, Pb, Zn and Cu in 4 species of plants; *Phalaris arundinacea* (Gramineae), *Junculus inflexus* (Juncaceae), *Polygonum percicaria* (Polygonaceae) and *Carex riparia* (Cyperaceae) and 1 green alga genus; *Spirogyra sp.* (Chlorophyta) were examined in water and sediment near the active antimony mining area. The uses of these species as bioindicators of antimony and other heavy metals availability in water and sediment were also tested.

EXPERIMENTAL

The total basin of the Yesilirmak River is 2352.8 km^2 and 519 km length. The study area is located in the Turhal district which is a part of Tokat city (Northern Turkey). By the time, antimony production exceeded the Turkish domestic consumption. Hence, this mining area produced a significant proportion of the antimony which is exporting to other countries. Sampling sites were classified as reference site before the mining company (reference site = station 1-geographical coordinates 40° 24' 12.95" N) and mine-affected site just after the mining company (station 2 geographical coordinates 40° 25' 12.95" N). Plants samples were collected monthly from June 2004 to November 2004.

Sampling: Plant communities along the stream were sampled monthly from June 2004 to November 2004 at each of the 2 stations. The samples were taken from an area of nearly 100 m^2 in order to include all possible microhabitats at each station. Plant samples were separated and then transferred to ice box. The plants were sorted, identified to the lowest possible taxon and dried at the room in between sheets of newspaper.

Monthly sediment samples were dried for 3 h at 110 °C and ground to pass through 200 mesh sieves. After homogenization, 100 mg amount of sediment sample was digested with 10 mL of aqua regia at room temperature and then heated to 95 °C. After the NO_2 fumes ceased, the mixture was evaporated almost dry on a sand-bath and mixed with 10 mL of aqua regia. The mixture was again evaporated till dryness. 10 mL of distilled water was added to the residue. The suspension was filtered through a blue band filter paper (Whatmann No. 41) and the insoluble part was washed with distilled water. The final solution was diluted to 10 mL[6]. The same procedure was applied to the blank solution. The final solution was analyzed for the determination of total antimony and heavy metals by graphite furnace atomic absorption spectrophotometry (AAS, Perkin-Elmer Aanalyst 700).

Analyses of the water samples were performed monthly which was the size of the sample of 2.5 L for water. Water samples were filtered through a 0.45 µm millipore membrane and then acidified to pH = 2 using high purity HNO_3 immediately after sampling[7]. Then, the samples were kept in the refrigerator at 4 ºC until analysis. The same procedure was applied to the blank solution. The final solution was analyzed for the determination of total antimony and heavy metals by graphite furnace atomic absorption spectrophotometry (AAS, Perkin Elmer Aanalyst 700).

All the plants *viz.*, *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.* were weighed (1.0 g) and dissolved in 8 mL of the mixture of acids HNO_3:$HClO_4$:H_2O_2 (2:1:1). The samples were heated at 170 ºC for 3 h, cooled down and then 2 mL of H_2SO_4 and 8 mL of acid mixture were added. These solutions were centrifuged at 2500 rpm for 5 min. The solutions were filled[8] up to 25 mL with 1 M HNO_3. The total antimony and other heavy metals level was determined on the basis of dry weight of samples. A blank digest was carried out in the same way. The total antimony and heavy metals concentration in

the final solution was determined by graphite furnace atomic absorption spectrophotometry. Quality assurance measures included blanks, replicate analyses and matrix spikes. Recoveries from matrix spikes ranged about 90-112 %. Repeated analyses did not reveal differences higher than 10 %.

RESULTS AND DISCUSSION

In *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.* accumulation of total antimony not detected at both stations. Antimony only detected at mine-affected site in water and sediment (Table-1). Cadmium and lead level in these 5 plants, water and sediment were higher at refence site than at mine-affected site. However, zinc and copper levels in these plants species, water and sediment were higher at mine-affected site than at refence site (Table-1).

TABLE-1
AVERAGE CONCENTRATIONS OF HEAVY METALS IN SPECIES AND SEDIMENT (μg g^{-1} DRY WEIGHT) AND WATER (μg L^{-1}) FROM ACTIVE ANTIMONY MINE-IMPACTED (STATION 2) AND REFERENCE SITES (STATION 1) NEAR THE YESILIRMAK RIVER, IN THE TURHAL DISTRICT; ND = Not detected, S = Stations

Sample type	S	Sb	Cd	Pb	Zn	Cu
Phalaris arundinacea	S1	ND	0.0210±0.0600	0.037±0.010	17.100±0.96	16.195±0.82
	S2	ND	0.0297±0.0220	0.041±0.014	15.900±0.72	12.350±0.63
Juncus inflexus	S1	ND	0.0324±0.0520	ND	46.250±1.59	28.950±1.12
	S2	ND	0.0411±0.0630	ND	44.720±1.54	19.340±0.92
Polygonum persicaria	S1	ND	0.0176±0.0020	0.620±0.074	37.600±1.39	19.000±0.87
	S2	ND	0.0297±0.0025	0.880±0.010	32.940±1.22	16.950±0.88
Carex riparia	S1	ND	0.0315±0.0035	0.115±0.017	36.940±1.22	21.100±1.09
	S2	ND	0.0354±0.0043	3.698±0.190	28.140±1.19	18.640±0.79
Spirogyra sp.	S1	ND	0.0019±0.0010	ND	22.400±1.09	18.000±0.74
	S2	ND	0.0123±0.0010	0.952±0.140	19.400±0.92	12.394±0.48
Sedimen	S1	ND	0.0660±0.0920	19.063±1.060	37.400±1.39	56.250±1.89
	S2	0.500±0.002	0.0924±0.0370	28.613±1.180	32.220±1.22	31.520±1.20
Water	S1	ND	0.0250±0.0220	0.093±0.023	5.369±0.16	11.890±0.41
	S2	0.015±0.000	0.9670±0.2100	1.087±0.090	6.238±0.25	10.930±0.49

Cadmium, lead, zinc and copper concentrations in *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.*, water and sediment were not significantly different between at refence site and at mine-affected site (One-way ANOVA, $p > 0.05$). Also, antimony and heavy metals levels in *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.*, water and sediment were not significantly different among months and taxa (One-way ANOVA, $p > 0.05$). So, the average heavy metals concentrations for each species are used in this study.

Surprisingly, *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.* species considered Sb, Cd, Pb, Zn and Cu uptake are not efficient when the availability of the elements in the water or sedimet are

low or intermediate. Cadmium and lead concentrations in *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.*, sediment and water were relatively elevated at mine-affected site compared to at reference site. On the other hand, Zn and Cu levels in these plant species sediment and water were relatively decreased at the reference site compared to at mine-affected site. This may be due to the competition between H^+ and metal ions for binding sites on inorganic and organic ligands. Because of the relationship between pH and concentration of free metal ions, it has been assumed that metals are more likely to be toxic to biota in acidic medium than in neutral waters[9]. However, a research suggests that a decrease in pH can result in a decreased biological responce (*e.g.* toxicity) for some metals (Cd, Cu and Zn). Evidence to support the notion by Hare and Tessier[10] that H^+ ions compete with metal ions for binding sites was provided.

The concentration levels measured in this study are not higher than compared to other studies[3,11]. Morever, the present study has demonstrated that *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.* have not exhibit hyperaccumulation for Sb, Pb, Cd, Cu and Zn. This may be due to the heavy metals of target parts at the end of the growing season for these 5 species. Therefore, an increase in antimony translocation towards the epigeal biomass results in the loss of an increasing fraction of the yearly absorbed antimony[3].

Concequently, present results suggest that *Phalaris arundinacea, Junculus inflexus, Polygonum percicaria, Carex riparia* and *Spirogyra sp.* can not use as a bioindicator for Sb, Pb, Cd, Cu and Zn accumulation. Simultaneously, Sb, Pb, Cd, Cu and Zn levels remained below levels at which toxic effect would be likely to occur in potential concern for macroinvertebrate and fish.

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