BIOLOGICAL AVAILABILITY OF TRAFFIC-RELATED PLATINUM-GROUP ELEMENTS (PALLADIUM, PLATINUM, AND RHODIUM) AND OTHER METALS TO THE ZEBRA MUSSEL (DREISSENA POLYMORPHA) IN WATER CONTAINING ROAD DUST

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Abstract—The uptake and bioaccumulation of 15 road dust metals by the zebra mussel (Dreissena polymorpha) were investigated in laboratory exposure studies with emphasis on the traffic-related platinum-group elements (PGEs) palladium (Pd), platinum (Pt), and rhodium (Rh). The biological availability of the metals may depend on water characteristics, so the mussels were maintained in two types of water: nonchlorinated tap water and humic water of a bog lake, both of which contained dust of a moderately frequented road. After an exposure period of 26 weeks, soft tissues of the mussels were freeze-dried and analyzed for the metals. The metal concentrations in the mussel soft tissue ranged from several hundred micrograms per gram (e.g., for iron [Fe]) to less than 10 ng/g (for PGEs). Metal uptake from the road dust by the mussels was found for the PGEs and silver (Ag), bismuth (Bi), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), Fe, lead (Pb), and antimony (Sb). After maintenance of mussels in road dust—contaminated tap water, bioaccumulation factors (BAF = (cExposed mussels − ccontrol mussels)/croad metal, water) where c is concentration) decreased in the following order: Cu > Cd > Ag > Pd > Sb > Pb > Fc > Pt > Rh. The biological availability of most metals was enhanced by humic water as compared to tap water. Our results show a hitherto unrecognized high availability of Pd for the mussels. Thus, this metal should be monitored more intensively in the environment to assess its distribution in the biosphere.

Keywords—Bioaccumulation Platinum-group elements Zebra mussel Traffic-related metals Humic water

INTRODUCTION

Automobile traffic causes environmental contamination with different heavy metals (aluminum [Al], cadmium [Cd], cerium [Ce], chromium [Cr], copper [Cu], lanthanum [La], manganese [Mn], molybdenum [Mo], neodymium [Nd], nickel [Ni], lead [Pb], antimony [Sb], tin [Sn], vanadium [V], zinc [Zn], and zirconium [Zr]) originating, for example, from the wear of automobile tires and brake pads, the corrosion of welded metal plating, and the possible combustion of lubricating oils [1,2]. Additionally, with the introduction of automotive catalytic converters, the platinum-group elements (PGEs) palladium (Pd), platinum (Pt), and rhodium (Rh) have been emitted with exhaust fumes [3]. The noble metals are used as active components in converters for reducing the emission of hydrocarbons, carbon monoxide, and nitrogen oxides. Field studies demonstrate a cumulative increase of PGE concentrations in road dust and soils along heavily frequented roads [4–6]. However, very little has been known about a possible uptake of these catalyst noble metals by the biosphere until now. Experimental studies demonstrated that different plant species, such as Spinacia oleracea, Lepidium sativum, Urtica dioica, and Phacelia tanacetifolia, were able to take up PGEs after they were grown in soils containing these metals [7]. Analysis of grass samples from the vicinity of highly frequented roads demonstrated elevated precious metal concentrations [2,8,9]. Furthermore, a model study on rats revealed the bioavailability of fine dispersed Pt as emitted from cars [10]. In addition to terrestrial habitats, these metals also are introduced into aquatic biotopes via road runoff [11], where they accumulate in the sediment of lakes and rivers [12–14]. Sediments in runoff reservoirs at the German highway A3 near Frankfurt were found to contain up to 250 µg/kg of Pt and 50 µg/kg of Rh [15]. Surface water samples from drainage basins along highways showed a Pt level between 15 and 78 ng/L [15], although the natural background concentration of Pt in rain water ranged below 0.2 ng/L [4].

Until now, knowledge about the biological availability of PGE for aquatic organisms was derived mainly from experiments with soluble salts [13,14,16,17]. Only a small number of recent exposure studies showed that freshwater isopods (Asellus aquaticus), eels (Anguilla anguilla), and zebra mussels (Dreissena polymorpha (Pallas)) were able to take up traffic-related PGEs from road dust [14,18,19].

The main reason for the comparatively low number of studies on the uptake and accumulation of PGEs in the biosphere is that the precise quantification of very low PGE concentrations (<1 ng/g) in biological materials requires very sophisticated analytical techniques. Adsorpitive cathodic stripping voltammetry after high-pressure ashing has been widely used for the analysis of Pt and Rh in different matrices, including biological materials [20,21]. Also, the determination of Pd in biological tissues recently was made possible by a development of an extremely sensitive analytical method that uses total-reflection X-ray fluorescence analysis (TXRF) after co-precipitation of Pd with mercury (Hg) [22].

To investigate the bioaccumulation of traffic-related metals with emphasis on PGE, zebra mussels were exposed to water containing road dust of a moderately frequented road. Dreissena polymorpha is known to accumulate heavy metals, for
example, Pb and Cd [23], and is commonly used for monitoring water contamination [24,25]. Because natural water contains various ingredients that can affect the biological availability of metals for aquatic organisms, this exposure study was performed with nonchlorinated tap water (TW) and in parallel with humic water (HW) of a bog lake. This study was designed to compare the accumulation capacity of D. polymorpha for PGEs with that for common heavy metals and to examine the influence of different water types on the biological availability of the metals.

MATERIALS AND METHODS

Experimental design

Road dust used for the exposure was collected in 1999 from a moderately frequented road in the city of Karlsruhe, Germany. After collection, the road dust was dried in an oven at a temperature of 50°C and sieved (grain size < 2 mm). The PGE concentrations in the dust were determined as described below. Total-reflection X-ray fluorescence analysis was used for the determination of common heavy metal concentrations.

Zebra mussels were collected from Lake Mondsee, Austria, transported to the laboratory in Karlsruhe, Germany, and thoroughly rinsed before being divided into four groups (Table 1). Two of the groups (exposed and control) were maintained in TW and two were maintained in HW from a bog lake (Hohlohsee, Black Forest, Germany). The characteristics of the waters and the zebra mussels are given in Table 1. The natural organic matter of the water from Hohlohsee has been characterized in detail by the German interdisciplinary research project, ROSIG. The fulvic acid fraction represents about 30% of the dissolved organic carbon and the humic acid fraction represents about 20% [26].

After acclimatization, one TW group of mussels and one HW group of mussels were exposed to 10 L of aerated water containing 1 kg of road dust. The mussels were positioned on strings several centimeters above the road dust sediment. The road dust in the plastic aquariums was manually stirred once weekly to allow a better solubility of the metals. The other two groups (controls) were maintained in 10 L of aerated water without supplement. The characteristics of the tank water were determined once fortnightly. Means and standard deviations (SDs) of the results are given in Table 1. The mussels were not fed and the tank water was not changed during the exposure period. Losses of water due to evaporation were compensated once fortnightly by the addition of distilled water. After an exposure period of 26 weeks, mussels were transferred to clean water not containing road dust for 2 d to avoid contamination while sampling and to remove road dust particles from the gill and the intestine of the mussels according to the methods of Roditi and Fisher [27]. Subsequently, the mussels were thoroughly rinsed with tap water and killed by deep-freezing. Size and weight of each mussel were determined before removing the soft tissue, which was pooled for each experimental group, freeze-dried, and stored at room temperature. Aliquots of the tissue samples were analyzed for the PGEs (n = 2–3 per group) and for silver (Ag), arsenic (As), bismuth (Bi), Cd, cobalt (Co), Cr, Cu, iron (Fe), Mn, Ni, Pb, and Sb (n = 3–6 per group).

Digestion procedures

For the PGE analysis, road dust and mussel tissue were digested with high-pressure ashing. The mussel soft tissue (0.3–1.5 g, freeze-dried) or 0.5 g of the dust samples were mineralized with 4 ml of HNO3 (65%, subboiled) and 0.5 ml of HCl (30%, suprapure, Merck, Darmstadt, Germany) in 70-ml quartz vessels with a high-pressure asher (HPA®, Kärner, Rosenheim, Germany) according to the methods of Zimmermann et al. [28]. The resulting solution was evaporated to about 0.5 ml and brought to 10.0 ml with deionized water. Each digestion solution was divided into two aliquots; one for the voltammetric determination of Pt and Rh, and the other for Pd analysis by TXRF analysis after coprecipitation of the metal of interest with Hg.

For the analysis by inductively coupled plasma–mass spectrometry (ICP-MS), aliquots containing 70 to 100 mg of the freeze-dried tissue samples were digested in 1.8 ml of nitric acid (65%, suprapure, Merck) by using a microwave procedure described by Sures et al. [29]. Twelve samples of standard reference material (DORM 2, National Research Council, Canada, Promocem, Wenel, Germany), composed of dogfish (Squalus acanthias) muscle, were treated in the same manner. To determine the analytical detection limits, blanks (n = 8) were prepared without insertion of sample material.

Analysis of Pt and Rh by adsorptive cathodic stripping voltammetry

Both Pt and Rh were measured by adsorptive cathodic stripping voltammetry according to the methods of Alt et al. [20,21] and Zimmermann et al. [28] and were quantified by using the standard addition method. The detection limits were determined as three times the standard deviation of the measurement of blanks. Depending on the sample amount the detection limit of the whole procedure was calculated as 4 to 12 pg/g for Pt and 75 to 225 pg/g for Rh. The efficiency and the precision of the procedure were shown in Alt et al. [20,21].
Analysis of Pd by TXRF analysis after coprecipitation with Hg

The Pd analysis by TXRF analysis after coprecipitating Pd with Hg is described in detail in Messerschmidt et al. [22]. Absolute amounts of Pd of 55 to 100 pg were detected, whereas the absolute detection limits are below 5 pg for the procedure. The efficiency and the precision of the separation and enrichment procedure were shown in Messerschmidt et al. [22] and Sures et al. [18]. From this, the recovery for Pd was determined to >95%.

Analysis of metals by ICP-MS

We measured Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Sb in mussel tissues by ICP-MS. A high-performance quadrupole ICP-MS system (PQ ExCell, VG Elemental, Franklin, MA, USA), operating in the normal scan mode, was used for these measurements. The plasma was run at 1,350-W power with 13.1 L/min coolant gas flow, 0.75 L/min auxiliary gas flow, and 0.93 L/min nebulizer gas flow. The peristaltic pump rate was 1 ml/min. Before measurements were made, the microwave-digested solutions were diluted 1:5 with deionized water.

Element concentrations in each sample were calculated from the corresponding regression lines (correlation factor > 0.99) by using different dilutions of a standard solution (ICP multielement standard solution, Merck). Detection limits were determined to be three times the standard deviation of the measurement of blanks.

Data analysis

Metal concentrations in the mussel tissue were determined as ng/g (dry wt) for the PGEs and µg/g (dry wt) for the other metals. To estimate the biological availability of an element, the mean metal content of the control was subtracted from that of the corresponding exposed animals, to compensate for the background concentration. This difference was then divided by the total metal level in the water \( c_{\text{total metal, water}} = c_{\text{road dust}} \times 1 \text{ kg}/10 \text{ L} \), resulting in the bioaccumulation factor, \( \text{BAF} = (c_{\text{exposed metal}} - c_{\text{control metal}})/c_{\text{total metal, water}} \), where \( c \) is concentration.

RESULTS

Analysis of metals by ICP-MS

The certified values of the metal concentrations in the standard reference material DORM 2, and the values of these metals as determined in the present study, plus the accuracies and the detection limits of the ICP-MS analysis method, are given in Table 2. For 10 elements present in the standard reference material, reliable accuracies ranged from 84 to 125%; the best accuracy was associated with As. Detection limits (three times standard deviation of the blanks) for the metals, listed in order of increasing values, were Sb < Bi = Cd < Co < Ag < As < Pb < Cr < Mn < Ni < Cu < Fe. The detection limits ranged from 0.06 ng/ml for Sb to 52 ng/ml for Fe.

Element concentrations in the road dust

The Pd, Pt, and Rh concentrations in the road dust were 29 ± 1 ng/g, 244 ± 44 ng/g, and 26 ± 6 ng/g, respectively. The concentrations of the other metals were far greater. In order of decreasing values, the TXRF analysis of the dust (\( n = 3 \)) yielded metal levels (mean ± SD) of 18 ± 1 mg/g (Fe), 439 ± 45 µg/g (Mn), 101 ± 20 µg/g (Cu), 53 ± 3 µg/g (Pb), 42 ± 5 µg/g (Ni), 15 ± 4 µg/g (Sb), 8 ± 1 µg/g (As), 0.9 ± 0.3 µg/g (Ag), and 0.7 ± 0.3 µg/g (Cd). The concentrations of Bi, Co, and Cr were not determined in the road dust.

Element concentrations in the soft tissue of the zebra mussel

Metal levels in the mussel soft tissue ranged from several hundred micrograms per gram (e.g., for Fe) to less than 10 ng/g (for PGEs), with the levels of Ag, Bi and Rh of the unexposed mussels not exceeding the corresponding detection limit (Fig. 1).

For As, Co, Mn, and Ni, significant metal uptake from the road dust by the mussels was not observed. In contrast, Ag, Bi, Cu, Fe, Pb, Sb, and the PGEs were taken up from the road dust by D. polymorpha as compared to the corresponding control (RdTW vs CoTW and RdHW versus CoHW). The RdTW mussels demonstrated 1.3 (Rh), 1.4 (Fe), 1.5 (Cr), 5 (Cu), 6 (Pb), 16 (Pt), 23 (Sb), 33 (Pd), 1,700 (Bi), and 3,300 (Ag) times higher mean metal levels than the CoTW mussels. The mean Cd concentration was slightly elevated in the dust-exposed mussels. Within the elements that were taken up by the mussels, higher concentrations of metals were found in the exposed mussels of the HW group compared to the TW group. The exceptions were Bi and Sb; the levels of these metals were similar in the two exposed groups.

Metal bioaccumulation by the zebra mussel

We calculated BAFs so that we could compare the accumulation capacity of D. polymorpha for the catalyst noble metals with that for other road dust metals. The bioaccumulation factors decreased in the following order (Fig. 2): Cu > Cd > Ag > Pd > Pb > Sb > Pt > Rh for the RdTW group and Cd > Cu > Pd > Ag > Pb > Sb > Fe > Rh > Pt for the RdHW group.

Within the catalyst noble metals, Pd had the highest bioaccumulation factor. The bioaccumulation factor of Pd was very similar to that of Ag and was much greater than that of Pb, Sb, or Fe.

The water type of the treatment had substantial effects on the BAFs for the metals. The BAFs of the HW group were 1.2 (Pb), 1.4 (Cu), 1.8 (Ag), 2.2 (Pd), 3.1 (Fe), 3.7 (Cd), and
Fig. 1. Element concentrations (\(a \pm d\)) in the soft tissue of the bivalve *Dreissena polymorpha* after 26 weeks of exposure in two types of water (humic water or tap water) with or without the addition of road dust. Values are mean element concentrations (\(n = 2 \pm 3\) per group for the platinum-group elements and \(n = 3 \pm 6\) per group for the other elements). Error bars (\(a \pm c\)) represent standard deviation.

### DISCUSSION

The present study demonstrated that Ag, Bi, Cd, Cr, Cu, Fe, Pb, Sb, and the catalyst noble metals Pd, Pt, and Rh were taken up by *D. polymorpha* from road dust. Cadmium, Cu, Fe, and Pb are common traffic-related metals in road dust [1,30]. Lead is still present in street dust, although the introduction of automobile catalysts has reduced the use of leaded fuel and lowered environmental Pb concentrations [31]. Chromium is associated with the corrosion of welded joints [1], and Sb is one of the major metallic components of asbestos-free brake linings [2]. However, the sources of Ag and Bi are unclear. Traffic-related metals can enter aquatic ecosystems via road runoff or atmospheric deposition, resulting in deleterious effects on water quality, sediment quality, and biota [32]. The presence of pollutants can cause a decrease in the diversity of macroinvertebrates [32], and also could be detected by sentinel organisms such as the zebra mussel [24,25]. Our exposure studies demonstrated for the first time that *D. polymorpha* also takes up the PGEs.

The biological availability of traffic-related PGEs for aquatic animals is confirmed by exposure studies with freshwater isopods (*A. aquaticus*) and eels (*A. anguilla*) [14,18]. In the present study, the bioaccumulation of PGEs is compared with that of other metals. Mussels can take up dissolved and particulate metals [25,27], so the BAF was determined with the total metal level in the water, according to the methods of Roditi et al. [25]. The total metal level in the water was calculated from the metal amount added to the tank water at the beginning of the experiment. Because of sedimentation of the dust particles, the real metal concentration in the water is lower, resulting in greater BAFs. Roditi et al. [25] determined BAFs for the zebra mussel decreasing in the order Cd > Hg > Ag > Se > Cr; this sequence is similar to that identified in the present study. With regards to PGEs, the greatest BAF was found for Pd, followed by Pt and Rh. Experimental studies on terrestrial plants have shown that the transfer of PGEs from contaminated soils into plants also decreases in the order Pd > Pt > Rh, with a Pd transfer even surpassing that of essential trace elements such as Cu and Zn [7]. Although the mussels accumulated Pd to a lower extent than they accumulated Cu, the BAF for Pd was 10 times greater than the BAF for Fe.

The PGEs from automotive catalytic converters are emitted in particulate form [3]. An important aspect for the biological availability of pollutants in aquatic ecosystems is their solubility in water. The water solubility of PGE constituents in road dust decreases in the same order [33] as their biological availability, as determined in the present study. Other studies have shown that small but significant quantities (\(\approx 5\%\) of the total amount) of the PGE in automobile exhaust fumes are water-soluble [3]. Furthermore, humic substances can increase the solubility of PGEs in water [34,35], and results presented here show that the biological availability of the noble metals (and most of the other elements) was increased in HW compared to TW. One may assume that the humic substances enhance the biological availability of the metals. On the other hand, the two water types differed substantially in the water hardness. Exposure studies with zebra fish (*Danio rerio*) demonstrated for both humic substances and Ca a detoxification...
potential against metals [36]. Therefore, the Ca concentration may also be a decisive factor in metal uptake by *D. polymorpha*.

A model of the bioaccumulation of nonessential alkaline-earth metals interprets their uptake by mistaking them for Ca, a biologically essential element, because of their chemical similarity [37]. Strong positive associations between Ca and divalent trace metals such as Cd, Co, Cu, Mn, Ni, Pb, uranium (U), and Zn, recently reported in tissues of two species of freshwater bivalves [38], supports this model. Palladium occurs mainly as Pd(II), but Pt and Rh co-occur in different main oxidation states (Pt(II), Pt(IV); Rh(I), Rh(III)). For this reason, the predominant occurrence of Pd(II) may account for the elevated bioaccumulation tendency of this metal in particular in HW with low Ca content.

Until now, the only field data about anthropogenic PGE contamination in the aquatic biosphere refer to the freshwater isopod *A. aquaticus* [13,14]. In the present study, the concentrations of Pt and Pd in the control mussels were above the detection limit. The mussels were collected in Lake Mondev (Austria), a lake surrounded by a highway. Recent field studies demonstrated that *D. polymorpha* sampled from this lake indicated via its heavy metal content (e.g., Pb and Cd) that road runoff enters the lake [23]. Therefore, the Pt and Pd content in the control mussels may be derived from road runoff. Because of the high capacity of *D. polymorpha* to accumulate PGEs, this bivalve could be of great use as a sentinel organism for monitoring not only conventional heavy metals but also noble metals in aquatic ecosystems.

Although one would expect that PGE contaminations are restricted to traffic-rich areas, analysis of ice samples in Greenland demonstrated the global character. Barbante et al. [39] found approximately 40 to 120 times higher PGE contaminations in snow dated from the mid 1990s than in ice dated from 7,000 years ago. Combining the growing environmental contamination and the high biological availability with the toxicological and allergological potential [40], PGEs may become a new problem in the near future. Because of the increasing use of Pd in the metal mixtures of automobile catalysts and this metal’s extraordinary accumulation capacity (e.g., three to five times higher than that of Pb), Pd in particular should be of great interest for environmental impact studies.

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