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Multimedia Evaluation of Trace Metal Distribution Within Stormwater Retention Ponds in Suburban Maryland, USA

R. E. Casey,[1] A. N. Shaw,[1] L. R. Massal,[2] J. W. Snodgrass[2]

[1] Department of Chemistry, 8000 York Road, Towson University, Towson, MD 21252-0001, USA
[2] Department of Biological Sciences, Towson University, Towson, MD 21252-0001, USA

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Stormwater retention ponds are used to promote infiltration and decrease flooding during storm events, especially in regions with extensive impervious surfaces. These ponds can retain suspended solids including particulate-associated contaminants such as metals, pesticides, polycyclic aromatic hydrocarbons and nutrients (Pitt, 1999; Bishop, et al. 2000; Karouna-Renier and Sparling, 2001; Datry, et al. 2003). Retention ponds are often used by wildlife in suburban regions, however the extent to which pollutants degrade retention pond function as wildlife habitat remains unclear (Campbell 1994; Helfield and Diamond 1997). The occurrence of significant pollutant levels has been documented in stormwater runoff entering ponds (e.g., Hall and Anderson 1988; Hares and Ward 1999) and in sediments within ponds (e.g., Wigington et al. 1983; Bishop et al. 2000; Karouna-Renier and Sparling 2001). Bishop et al. (2000) documented adverse effects of exposure to retention pond sediments among northern leopard frog (*Rana pipiens*) eggs and larvae. In contrast, Karouna-Renier and Sparling (1997) found no effects of exposure of an amphipod (*Hyalella azteca*) to sediments from Maryland retention ponds.

The contaminant burden in these ponds is particularly relevant for aquatic breeding amphibians. Amphibian breeding in retention ponds can result in the exposure of adults, eggs and larvae to pollutants accumulated in ponds. Moreover, the relatively permeable skin and benthic feeding habits of many larval amphibians allows accumulation of significant concentrations of pollutants in their tissues (e.g., Grillitsch and Chovanec 1995), which can be transferred out of ponds when the larvae metamorphose or are consumed by semi-aquatic wildlife such as snakes and wading birds.

This study was conducted to determine the distribution of trace metals in stormwater retention ponds in a watershed experiencing rapid residential growth and urbanization.

MATERIALS AND METHODS

We investigated trace metal levels in comparison with published water quality criteria and effects thresholds for water, sediments and larval amphibians utilizing

Correspondence to: R. E. Casey

stormwater retention ponds. Stormwater retention ponds were located in the Red Run branch of the Gwynns Falls watershed in Baltimore County, Maryland, USA. Water column, sediment and tadpole samples were obtained from six ponds in summer 2001. Four ponds were sampled again in 2002; the remaining two ponds from 2001 were either dry or contained no tadpoles, due in part to an uncharacteristically dry year in 2002. One additional retention pond from the same watershed was added in 2002.

Two water column and sediment samples were obtained from each pond, one each from the pond inlet and outlet (where discernible). Sediment samples were obtained from the top 5 – 8 cm. Three to 25 tadpoles were collected using dip nets and seines so as to collect enough biomass for 5 replicate analyses of tadpole tissue; for smaller tadpoles, up to 5 organisms were composited to create an individual replicate. All samples were placed on ice for return to the laboratory where tadpoles were identified to species (with the exception of distinguishing between *Hyla versicolor* and *H. chrysoscelis*) using keys and field books (Altig 1970; Travis 1981; Gibbons and Semlitsch 1991; Johnson 2000) and then, along with sediment samples, frozen (-20°C) until sample preparation. Water samples were acidified to pH < 2 with trace metal grade HNO_3 (Fisher Scientific) then filtered through 0.45 μm PTFE syringe filters. Sediment samples were mixed by hand then analyzed in triplicate by digestion in 6 M trace metal grade HNO_3 overnight at 150°C followed by filtration through 0.45 μm PTFE syringe filters.

Tadpoles were dissected into separate compartments. In previous studies, the stomach and intestinal track to vent (referred to as the gut coil) were removed from tadpoles due to the presence of sediments and undigested matter that were not necessarily incorporated into the tadpole tissue (Sparling and Lowe 1996; Burger and Snodgrass 2001). Burger and Snodgrass (2001) also separated the tail from the remaining body to differentiate between tissue containing primarily muscle and skin (the tail) and tissue containing organs (the head and abdomen). In this study the gut coil and tail were dissected and the remainder (head, abdomen and organs) was referred to as the "head". Tissues were dried at 70 °C then digested in 6 M trace metal grade HNO_3 overnight at 150°C, followed by high purity 30 % H_2O_2 (Ultrex II grade, J.T. Baker) on a hotplate for 3 h. Hydrogen peroxide was not added to gut samples because the peroxide decomposed immediately upon addition. Instead, an additional 2 mL of 6 M nitric acid was added to the gut samples to further digest organic matter in the gut. Samples were evaporated and the residue was dissolved in trace metal HNO_3. Method blanks were prepared for water, sediment and tissue analyses. Duplicate digestions of NIST SRM 2976 (mussel tissue) were included in each batch of digestions. Average recoveries for SRM 2976 were as follows: Cr 112%; Ni 97%; Cu 86%, Zn 88%; Cd 84%; Pb 94%. Recoveries for Cr, Ni, Cd and Pb were within the certified confidence ranges; Cu and Zn were within 90% of the lower limit of the certified range.

Sediments, tissues and water samples were analyzed using a Thermo Elemental Plasma Quad ExCell inductively coupled plasma mass spectrometer (ICPMS) with In as an internal standard. External calibrations were performed using commercial mixed standards (SPEX CertiPrep, Inc., Claritas PPT grade). Cu, Cr, Pb, Cd, Zn, and Ni were determined for all samples with the exception of Zn in water samples. For sediments and tissues, concentrations are reported in terms of dry weight (mg kg^{-1} dry weight).

To assess relationships between metal levels, tadpole species and tissue types, we used a mixed model approach to a block design two-way ANOVA with ponds treated as a random block effect and tissue type and species considered fixed effects. Data were log transformed prior to analysis. For the purposes of statistical analysis, values below the detection limit were replaced with half the detection limit. This occurred in one tail sample each for Pb and Ni. Cd concentrations were below the detection limit in 47% of gut samples and 28% of head and tail samples. As a result, Cd was not included in the statistical analysis and we only report ranges for this metal.

RESULTS AND DISCUSSION

In all ponds mean water column concentrations of Cd, Cr, Ni, and Pb were below US EPA National Recommended Water Quality Criteria (US EPA 1999) for both indefinite exposures (criterion continuous concentration, CCC) and short-term exposures (criteria maximum concentration, CMC; Table 1). This is consistent with previous findings that metals are generally associated with particulates and not freely dissolved (Campbell 1994). There were two instances where Cu levels (9.6 and 13.3 $\mu g\ L^{-1}$) exceeded the CCC of 9.0 $\mu g\ L^{-1}$. The second instance also slightly exceeded the CMC of 13 $\mu g\ L^{-1}$. Water column metal levels were generally similar to levels found in studies of ponds from other regions. Cr, Cu and Pb in the water column were similar to concentrations in ponds studied by Bishop et al. (2000) and Mayer et al. (1996). Although Ni levels were slightly higher in this study compared to Bishop et al. (2000), levels of Ni reported by Shutes et al. (2001) and Mayer et al. (1996) were comparable to concentrations at the sites we studied. Cu levels were also similar to those reported by Karouna-Renier and Sparling (2001) for another set of retention ponds in Maryland.

Mean trace metals in sediments were compared to the consensus-based sediment quality guidelines derived by MacDonald et al. (2000) (Table 2). Pond means for sediment Cu and Ni often exceeded the threshold effect concentrations (TECs) and Ni exceeded the probable effect concentrations (PECs) in 36% of ponds. All metals exceeded the TEC in at least one site, except for Cd, which was below detection in all samples. While trace metal concentrations often fell between the TEC and PEC, Cr, Cu, Ni and Zn were higher than reference trace metal values (anticipated typical concentrations, ATCs) for soils in central Maryland (Maryland Department of the Environment 2001). Trace metal retention is one of the goals in stormwater pond designs (Wigington et al. 1983) so this may be a consequence of intended retention pond function. Cd was not detected in sediments and Pb was generally at or below the central Maryland ATC value. Sediment levels of Cu, Pb and Zn were generally higher than values reported by Karouna-Renier and Sparling (2001). Otherwise levels of Pb were lower in this study compared to Mayer et al. (1996), Liebens (2001) and Datry et al. (2003). For the remaining metals (Cr, Cu, Cd, Ni and Zn), values in this study are within the range of sediment metal levels reported in other studies (Mayer et al., 1996; Liebens 2001; Bishop et al., 2000; Datry et al., 2003).

Table 1. Mean water column trace metal concentrations (for quantifiable samples). Limit of quantitation (LOQ): 1 $\mu g\ L^{-1}$ for all metals.

	Mean	Range	% < LOQ
	$\mu g\ L^{-1}$		%
Cd	1.3	< LOQ – 1.3	91
Cr	4.0	< LOQ – 4.6	91
Cu	6.0	< LOQ – 13.3	45
Ni	6.0	< LOQ – 32.7	27
Pb	1.9	< LOQ – 2.3	82

Table 2. Sediment trace metal concentrations and ranges (of pond means) in relation to consensus-based sediment quality guidelines. Limit of quantitation (LOQ) is 5 mg kg^{-1} for all metals. TEC = threshold effect concentration; PEC = probable effect concentration; NA = not applicable (all samples < LOQ).

	Retention Ponds		Consensus Sediment Quality Guidelines			
	Mean	Range	TEC		PEC	
	mg kg^{-1}		mg kg^{-1}	% Ponds Exceeding	mg kg^{-1}	% Ponds Exceeding
Cd	< LOQ	all < LOQ	0.99	NA	4.98	NA
Cr	53	18 – 252	43.4	18	111	9
Cu	74	18 – 341	31.6	73	149	9
Ni	61	19 – 267	22.7	82	48.6	36
Pb	26	9 – 116	35.8	9	128	0
Zn	211	53 – 1155	121	36	459	9

We collected three species of tadpoles: *Rana clamitans*, *R. palustris* and *H. versicolor/chrysoscelis*. Mean trace metal concentrations, averaged over all species, were generally highest in the gut, followed by the head and were lowest in the tail (Table 3). However, the magnitude of differences among tissues varied among species ($P < 0.053$ for the species x tissue interaction). When broken down by species, this trend continued with a significant tissue effect ($P < 0.0001$) for all metals (except Cd for which statistical analysis was not performed). There was a significant species effect for Zn ($P < 0.001$) with the hylids having generally higher levels in each tissue type compared to the ranids. Whole body levels of Cr, Cu, Ni, and Pb were similar among the species (Table 4).

Metal levels in tadpole tails were less than 10% and in some cases less than 1% of the concentration in sediments, whereas heads had metal concentrations similar to those of sediments. Metal levels in tadpole gut coils were on average 2 – 3 times greater than concentrations in sediments, similar to findings of Sparling and Lowe (1996) and Burger and Snodgrass (2001). This could indicate bioconcentration in the intestinal tract, which has been previously demonstrated for adult ranids (Papadimitriou and Loumbourdis 2003). Alternatively, gut contents may be composed of a higher fraction of fine sediment (silts and clays) or algae, either of which could have trace element levels present in greater concentrations than the bulk sediment.

Table 3. Trace metal concentrations averaged over all tadpoles by compartment. The reported range is the range of pond means. Limit of quantitation (LOQ): 1 mg kg^{-1} for the gut; 0.2 mg kg^{-1} for the head and tail.

	Gut		Head		Tail	
	Mean	Range	Mean	Range	Mean	Range
			mg kg^{-1}			
Cd	1	<LOQ – 3	2	0.3 – 4.7	1	<LOQ – 3.0
Cr	56	22 – 88	12	2 – 32	8	1 – 47
Cu	82	43 –135	33	13 – 50	10	4 – 17
Ni	73	30 – 255	16	4 – 55	6	1 – 19
Pb	35	16 – 76	6	1 – 14	2	1 – 5
Zn	342	90 – 1025	147	69 – 310	104	45 – 233

Table 4. Mean whole body metal concentrations in tadpoles reconstructed from tissue compartments.

	R. clamitans	*R. palustris*	*H. versicolor/ chrysoscelis*
		mg kg^{-1}	
Cd	0.7	1.6	1.0
Cr	26	18	28
Cu	43	38	44
Ni	27	20	56
Pb	15	10	18
Zn	136	127	268

Pauli et al. (2000) compiled data from an extensive number of amphibian and reptile studies. In comparison with reported values for tadpoles, Cu and Cr concentrations were higher in tadpoles from our study site than the general range of values in Pauli et al. (2000). It is possible that Cr levels are higher at our site due to the proximity of a serpentine outcrop rich in Cr minerals adjacent to the watershed. The reasons for elevated Cu levels are less clear. Our data were within the ranges of reported values for Zn and Pb and reported Cd values were similar to the limit of quantitation in this study. No Ni values were present in Pauli et al. (2000) for tadpoles.

Whole body metal concentrations in tadpoles were reconstructed from individual tissue compartments (Table 4). In comparison with a study by Birdsall et al. (1986) of tadpoles from highway drainages in Maryland and Virginia, sediment Pb levels were slightly higher in their study, but the Pb levels in whole tadpoles were similar to values obtained here. In contrast, tadpoles from ponds in Michigan with agricultural and woodland land uses had much lower sediment concentrations and much lower tissue metal concentrations than those in this study (Gillilland et al. 2001). This is consistent with laboratory experiments in which body burdens increased with increasing sediment exposures (Sparling and Lowe 1996). Whole body levels can also be used for initial estimates of risk to terrestrial predators based on published effects studies. Levels of Pb, Ni and Zn in tadpoles at these sites were lower than dietary exposures found to have substantial effects in birds (Eisler 1988, 1993 and 1998). Effects of dietary exposures in avian wildlife for Cu, Cd and Cr are limited so additional data are need for risk estimates.

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