Report for 2005MD89B: Chemical and Biological Availability of Zinc in Road Runoff Entering Stormwater Retention Ponds

Publications

- There are no reported publications resulting from this project.

Report Follows

Problem and Research Objective

Growth in urban areas leads to the development of new roads, highways, and other types of impervious surfaces. With this increase in impervious surfaces there is a growing concern about the contaminant contributions of roadway runoff during storm events. Runoff carries with it any pollutants and particulates that have built up on the road. Of these pollutants, heavy metals are of growing concern due to their presence at increased levels in urban stormwater. There can be a number of sources of heavy metals in stormwater runoff including building siding, building roofing, wet and dry deposition, automobile parts, and gas and oil (Davis et al. 2001, Breault and Granato 2000, Councell et al. 2004). The metals that were found from these sources were Zn, Pb, Cu and Cd in order from highest estimated annual loads to lowest. Brake wear was found to be the biggest contributor of Cu while brick buildings and tire wear were the biggest contributors of Zn. The importance of automobile parts as sources of these metals has been previously studied. Councell et al (2004) estimated that tires are composed of 1% Zn by weight and they estimated that in 1999 alone, a total of about 11,000 tons of Zn was released from tire wear nationwide. Davis et al (2001) estimated from the literature a discharge estimate of 75 ug Cu/km-vehicle from brake pads.

Stormwater retention ponds are becoming a common tool in managing stormwater runoff and in the state of Maryland they are an acceptable best management practice (BMP). Retention ponds allow suspended sediments to settle and pollutants to contact and adsorb to the surface of pond sediments (Lawrence et al 1996). Since runoff often contains high concentrations of heavy metals it is expected that these ponds will also contain high levels of metals. Liebens et al (2001) studied 24 ponds that were located in residential and commercial areas. In all 24 ponds metal concentrations were higher than in control ponds. The work also suggested that older ponds had higher concentrations than younger ponds. Pond sediment concentrations ranged from 0.27-622 mg/kg of Zn and bdl-55 mg/kg of Cu. Casey et al (2004) also quantified trace metals in retention pond sediments. They found Zn concentrations ranging from 53-1155 mg/kg and Cu concentrations ranging from 18-341 mg/kg. In both these studies it appears that the ponds are removing and storing at least some of the heavy metals that are coming off of the roadway.

The presence of heavy metals in these ponds is a concern due to their effects on the organisms that inhabit the area. Toxicity due to heavy metals has been studied in a variety of organisms including fish, amphipods, mussels and amphibians (Bailey et al 1998, Karouna-Renier et al 1997, Anderson et al 2004, Lefcort et al 1998). Throughout all of these studies, the specific effects that are seen in the organisms vary a great deal. Differences in type of organism, type and concentration of the metal(s), the pH of the environment, bioavailability, and the sediment characteristics that are present are all factors that have been found to influence toxicological effects (Karouna-Renier and Sparling 2001, Anderson et al 2004). There is a growing push to look at metal toxicity and accumulation in amphibians, especially anuran juveniles as well as adults. Because of their presence in many urban streams and ponds, studying these amphibians is important in determining if they will be negatively affected by the metals in their environment. Metals have been found to decrease hatching success (Haywood et al 2004), reduce the growth of tadpoles (Haywood et al 2004) and reduce tadpole survival (Haywood et al 2004, Lefcort et al 1998). Lefcort et al (1998) also found that in a laboratory study, metals reduced the fright response of *Rana luteiventris,* which could decrease the rate of survival of the tadpoles in natural environments. Even when metal exposures did not cause substantial lethal or sub-lethal affects, tadpoles accumulated heavy metals in their tissues and guts when exposed to metal contaminated water and/or sediment (Sparling et al 1996, Lefcort et al 1998, James et al, Loumboudis et al 1998). The high concentration of metals accumulating in the bodies of the tadpoles could result in trophic transfer to organisms that prey on them (Sparling et al 1996, Haywood et al 2004).

Study Objective

The purpose of the present study was to determine if Cu and Zn were major constituents of stormwater runoff, roadway dust, and retention pond sediments and then to determine if they were in a form that was easily available for uptake by biota.

Materials and Methods

Background Soils:

Background soil samples were taken throughout the study site along 4 transects (Figure 1). In each transect, samples were taken approximately 15 m apart. At each sampling point a surface sample was taken down to a depth of about 3 cm. Periodically a bulk sample was also taken down to a depth of about 8 cm.

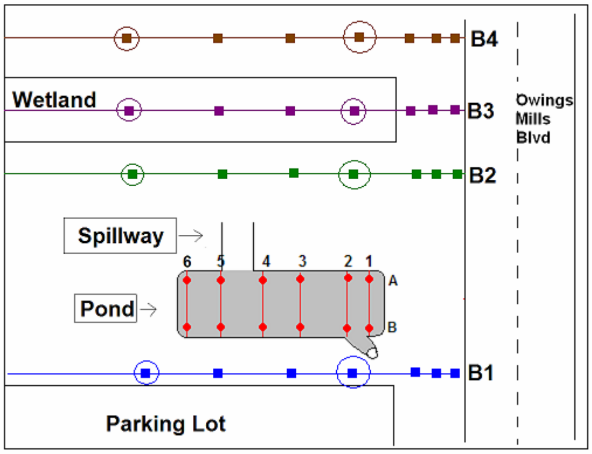
All samples were dried in an oven at 70˚ C. A portion of each dried soil sample was ground using a SPECS Mixer/Mill 2500. The mixer/mill was cleaned between each sample using DI water and methanol. The ground samples were used for the determination of trace elements by XRF (X-Ray Fluorescence). For XRF preparation, ground samples were pressed into pellets using the SPEC X-Press. Approximately 7 g of sample and 0.7 g of a cellulose binder were mixed together and placed into the pressing die. Each pellet was then kept in a desiccator until analyzed by the XRF. NIST SRM 2709 (San Joaquin Soil) was used during

XRF analysis for QA/QC. The samples were analyzed for copper, chromium, nickel, lead, vanadium, and zinc.

Pond Sediments:

Sediment cores were collected from within the pond along six transects. Each transect was sampled twice, once on the left side of the pond and once on the right side of the pond (Figure 1). Final core depths varied between 50 and 90 cm. Sediment cores were collected using a McCauley peat sampler. There was an unconsolidated, organic top layer that was difficult to collect using the peat sampler. For this top layer, a PVC pipe was used. Sediment cores were separated according to depth and placed into plastic bags for transport and storage.

Figure 1: Sampling Map



The wet mass of each core was determined to allow for subsequent estimates of metal storage in each area of the pond and a sub-sample was then used for dry weight determination.

For ICP-MS analysis, approximately 60 mg dry sample was placed into a clean Teflon vial. Samples were acidified using 1 ml of HF and 3 ml of HNO3 and placed on a hot plate overnight. Both acids were of trace metal grade. The samples were dried and 3 mL of hydrogen peroxide was added to the vessels and placed onto the hot plate. The samples were again dried and HF and HNO3 was added in the same proportions as before and placed onto the hot plate.

This extra digestion step was to ensure that the samples were completely digested. Finally samples were dried and an internal standard solution of 2% HNO3 containing 10 ppb of germanium and 1 ppb of indium was added to each vial and samples were put back onto the hotplate for re-digestion. Samples were then analyzed by ICP-MS for total metal concentrations. The NIST standard reference material 2709 (San Joaquin Soil) was also analyzed with the sediment samples to monitor external reproducibility.

Using the mass of the sediment cores, the surface area of the sampler, and the area of the sampling grid, total pond storage was estimated for Cu and Zn.

Selected pond sediments also underwent sequential extraction process to determine the possible bioavailability of the metals within the pond. The method used was based on the work published by Tessier et al. (1979).

Road Dust

Road dust was sampled from the roadway surface around the storm drains leading into the retention pond. Dust was obtained using a forensic vacuum with a 0.2 μm filter. Samples were collected starting in the spring of 2005, and were collected at least once every season over the next year. Total metal concentrations were determined in the same manner as the pond sediments. The road dust was also separated by wet sieving using a <63 um nylon sieve and a <5 um nylon sieve. Each of these fractions underwent total digestion as well as sequential extractions.

Storm Events:

An ISCO sampler was installed at the outflow of the storm pipe that leads directly into the drainage pond. The sampler activated when a specified flow was reached and continued to collect samples on a time basis. For storms 1-7, samples were collected every 20 minutes throughout the duration of the storm. Beginning with storm 8, bottles 1-12 collected samples every 4 minutes, the remainder of the bottles collected samples every 30 minutes. Samples were recovered and returned to the lab. Five mL of sample was filtered through a 0.45 um nylon filter and then acidified to 0.2N using 6N HNO3. This represents the truly dissolved metals in the sample. Another 5 mL of the same water sample was acidified to 0.2N using 6N HNO3 and then filtered through a 0.45um nylon filter. This represents the truly dissolved plus particulate bound metals. These water samples were then analyzed by ICP-MS along with the NIST standard reference 2096 (Mussel Tissue) to validate calibration and reproducibility. The runoff concentrations along with the discharge during the storm were used to determine the total runoff load for both the dissolved and particulate bound Cu and Zn.

For storms 1-3, the remainder of the storm sample was vacuum filtered through Whatman ashless 25 um filter paper to determine total suspended solids. Starting with storm 4, samples were filtered through a preweighed 0.45 um cellulose nitrate filter. A small number of these filters underwent total digestion. Filters were placed into clean Teflon vials and digested as described above. Samples were analyzed by ICP-MS for Cr, Ni, Cu, Zn, As, Se, Cd, and Pb.

Sediment Bioassay:

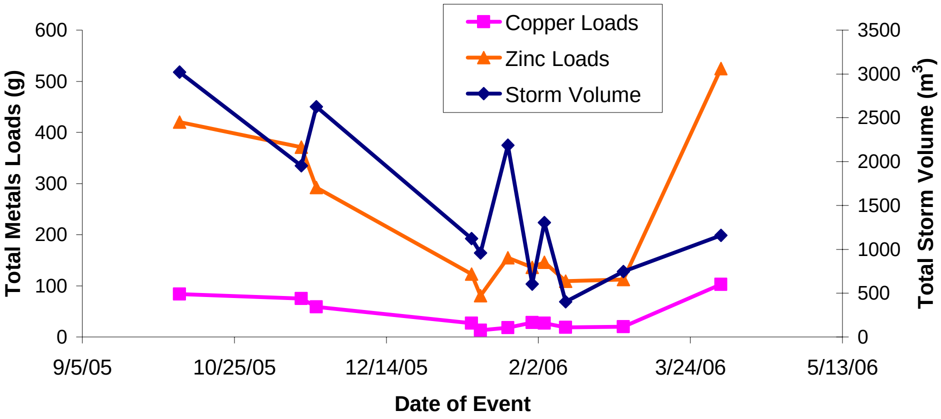
To assess the toxicity of stormwater pond sediments to early developmental stages of amphibians potentially utilizing stormwater ponds as breeding sites we exposed eggs and larvae to pond sediments and clean sand controls in laboratory microcosms. Developing wood frog eggs (*Rana sylvatica*) and subsequent larvae were exposed to either pond sediments or clean sand in the first experiment. In the second experiment American toad eggs (*Bufo americanus*) were exposed to pond sediments or clean sand and evaluated for hatching success and subsequent time to metamorphosis.

Principal Findings and Significance

Storm Events

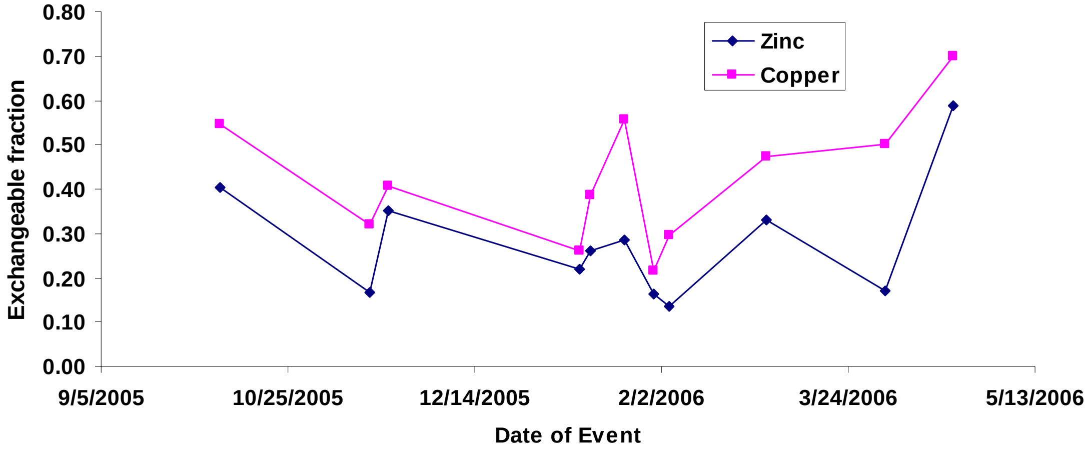
A total of 12 storm events were collected and analyzed. Average total metal concentrations for each storm were between 6-36 ug/L for Cu and 23-169 ug/L for Zn. Within each storm however, concentrations were as high as 366 ug/L for Zn and 80 ug/L for Cu. Along with metal concentrations, storm loads were also determined for both Cu and Zn (Figure 2). Zinc loads were generally 2-4 times higher than copper loads.

Figure 2: Total zinc and copper loads from stormwater entering the retention pond in storm runoff



Exchangeable and total metal concentrations were also determined for each storm. Both copper and zinc were mainly particulate bound, however the fraction of dissolved copper was higher in all storms compared to zinc (Figure 3). It is important to determine the speciation of the metals entering the pond because dissolved metals are more available to biota. Since the culvert drains only the roadway, it is likely that Cu and Zn largely originate from automobile wear such as brake pad particulates and tire particulates. Therefore these data are consistent with metals being mainly particulate bound.

Figure 3: Fraction of exchangeable metal loads out of the total metal loads entering the retention pond in storm runoff.



<u>Pond Sediments</u>

The next step of the project was to determine metal concentrations within the retention pond sediments. Cores were taken down to a depth of at least 50 cm, however the majority of the metal concentrations were found to be in the top 10 cm of the sediments cores (Figure 4 and 5). The top 10 cm consisted mainly of unconsolidated organic matter. Concentrations of Zn in this top layer ranged from 136-1031 mg/kg and for Cu ranged from 99-215 mg/kg. Pond sediment concentrations were substantially higher than background concentrations indicating that there was an input of both Cu and Zn into the pond from the roadway. Comparison with background levels indicates that some vertical transport of Zn and Cu may be occurring at these sites given the elevated concentrations below the immediate depositional zone.

<u>Road Dust</u>

Trace metal concentrations in road dust were determined for three separate size fractions. These fractions were bulk road dust, the less than 63 micron fraction and a less then 5 micron fraction. The highest concentration of both copper and zinc was in the less than 5 micron fraction. A comparison of the road dust fractions with the pond sediments and background soils are shown in Figures 6 and 7. Pond sediments represent mixing between background soils and the influx of particulates from the roadway. In this case, it appears that the pond sediments are a mixture of the background soils and the <5micron and <63 micron fractions.

Figure 4: Zinc depth profile for pond sediments. Solid vertical line represents mean background concentration and dotted vertical lines represent +/- one standard deviation.

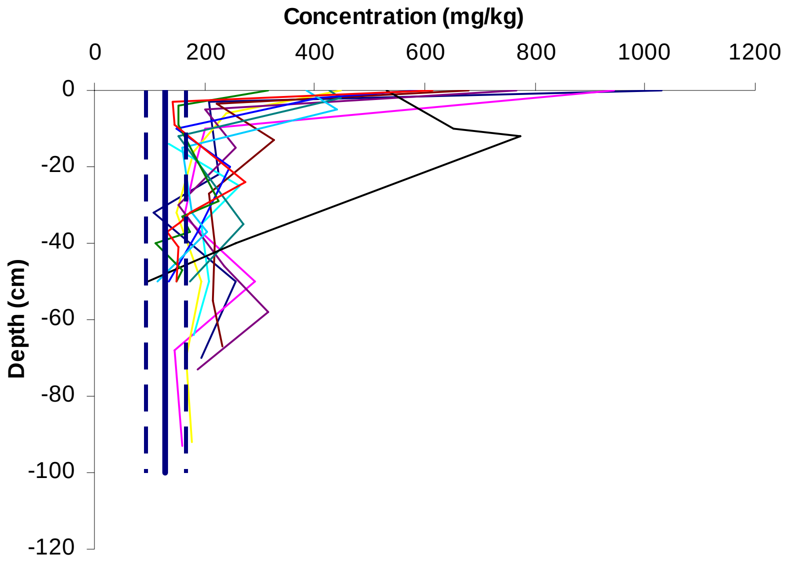


Figure 5: Copper depth profile for pond sediments. Solid vertical line represents mean background concentration and dotted vertical lines represent +/- one standard deviation.

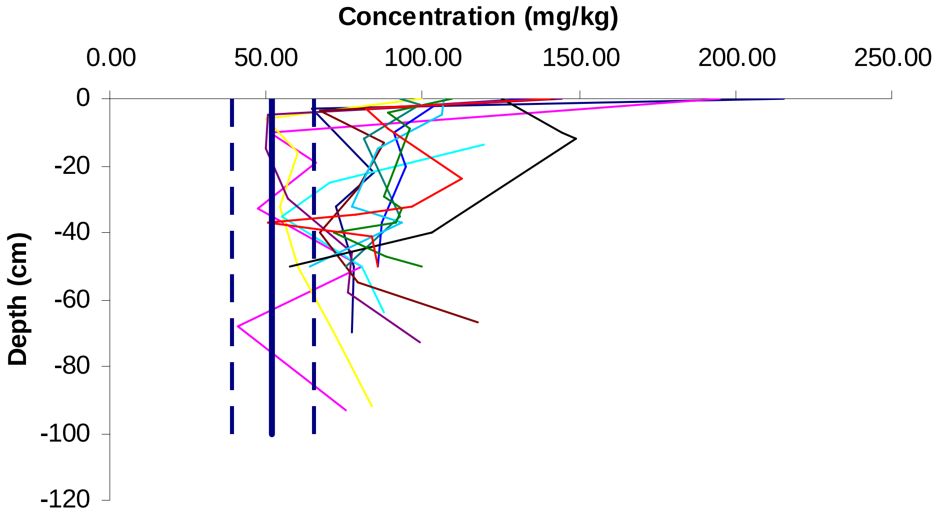


Figure 6: Total zinc levels in road dust in comparison with background and pond surface sediments.

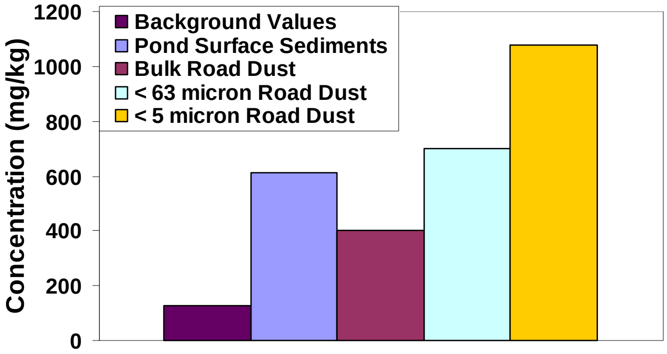
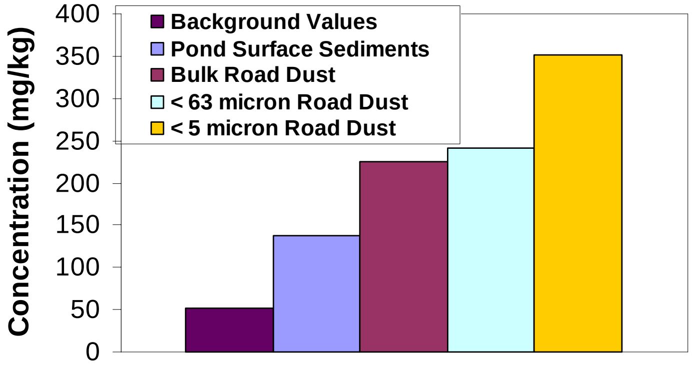
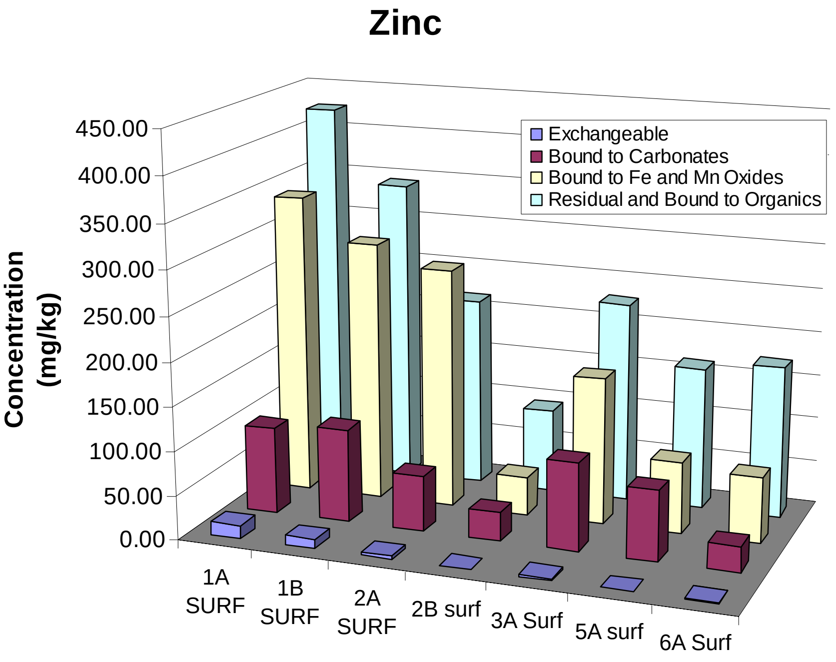


Figure 7: Total copper levels in road dust in comparison with background and pond surface sediments.



Sequential extractions were performed on pond sediments and the bulk and <5 micron road dust fractions (Figures 8 and 9). The extractions performed on the pond sediments revealed that there was little to no available copper in the sediments. In all surface sediments, copper was in the most recalcitrant fraction. For zinc, there was a small amount bound to carbonates and Fe and Mn oxides. Depending on the conditions that these sediments undergo, these fractions could release zinc into the water column. For the most part however, Zn is in the most recalcitrant fraction.

Figure 8. Sequential extraction of zinc and copper from surface stormwater pond sediments.



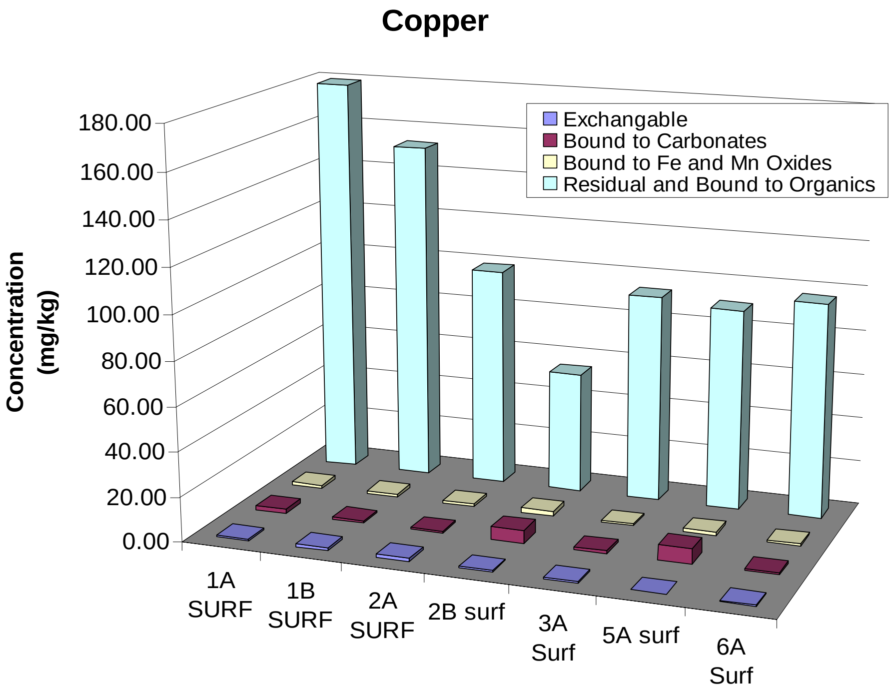
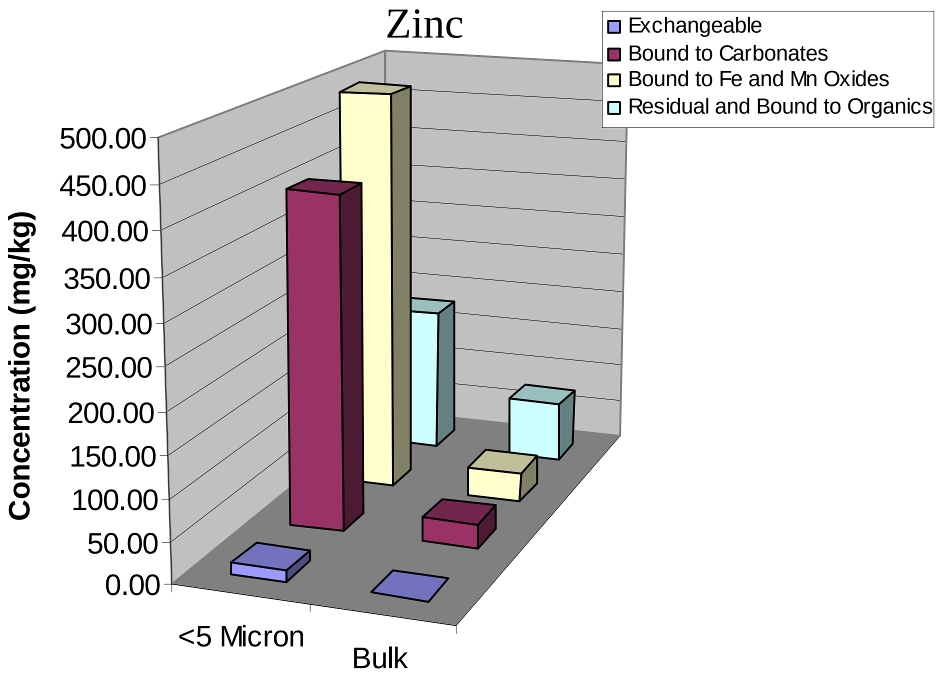
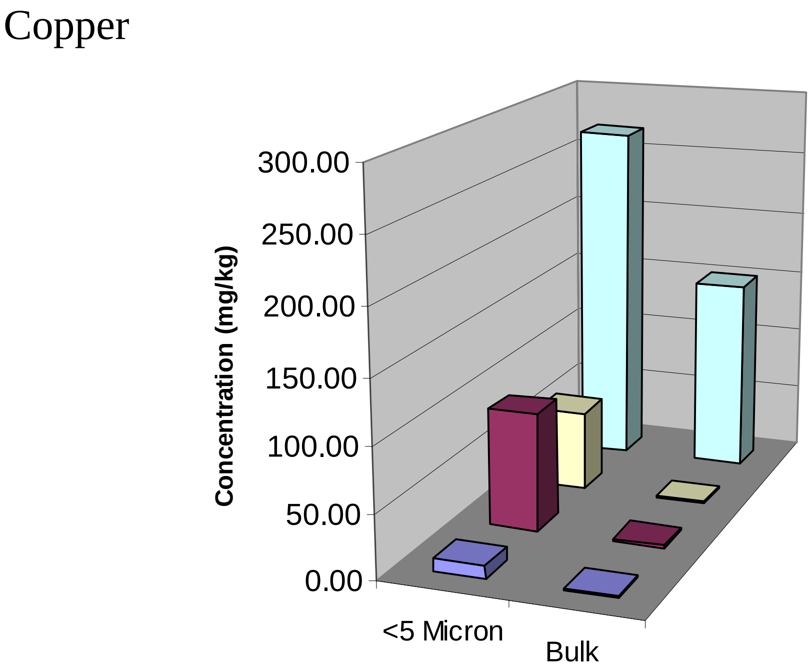


Figure 9. Sequential extraction of zinc and copper from road dust.





With the road dust extractions the <5 micron fractions for both Cu and Zn had metals that were bound to carbonates and bound to Mn and Fe oxides (Figure 9). The highest concentrations of zinc were found in these two fractions. While there was some Cu in both of these forms, most of it was in the residual and organic bound forms. For the bulk road dust, the majority of both Cu and Zn were not readily available.

Finally, pond sediment cores were used to determine total pond storage and compared to storm loads to determine how well the pond is retaining these pollutants. Zn storage within the pond is approximately 16.5 kg while Cu storage is approximately 6.0 kg. For Zn, this represents about 73 storm events while for Cu this represents close to 140 storm events using the average loads in storm inflow determined in this study.

Sediment Bioassay

Developing wood frog eggs (*Rana sylvatica*) exposed to pond sediments experienced reduced hatching success in comparison to controls and no larvae exposed to pond sediments survived to metamorphosis (Figure 10). In contrast, hatching success of American toad eggs (*Bufo americanus*) exposed to pond sediments was high and similar to eggs exposed to clean sand. Furthermore, while metamorphs showed sublethal effects of exposure to pond sediments (Figure 11), metamorphic success was similar between larvae exposed to pond sediments and those exposed to clean sand. Analyses of trace metal levels and water chemistry in the microcosms suggested contamination of sediments from road salting was responsible for the lethal effects observed among developing wood frogs embryos and larvae (Figure 12). Overall, our results suggest contamination of stormwater ponds with road salt is a factor in reducing the wildlife habitat quality of ponds and the role of ponds as ecological traps for pond-breeding amphibians warrants further investigation.

Figure 10. Mean percentage of embryo and larval wood frogs surviving as a function of days of exposure to clean sand (control) and sediment from a stormwater management pond in Owings Mills, Maryland.

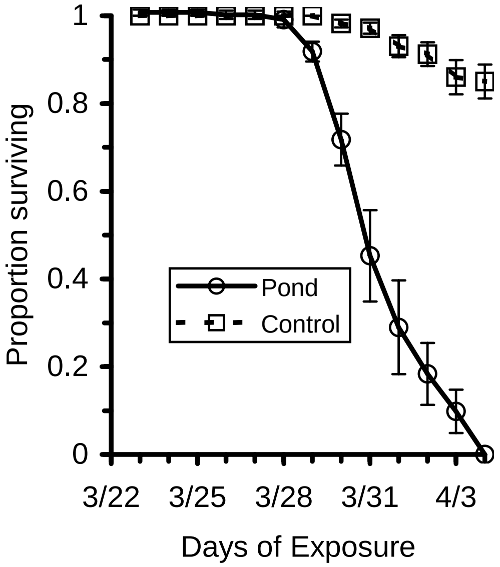


Figure 11. Mean size at front limb emergence and metamorphosis of American toad larvae exposed to sediments from two stormwater management ponds and clean sand (controls).

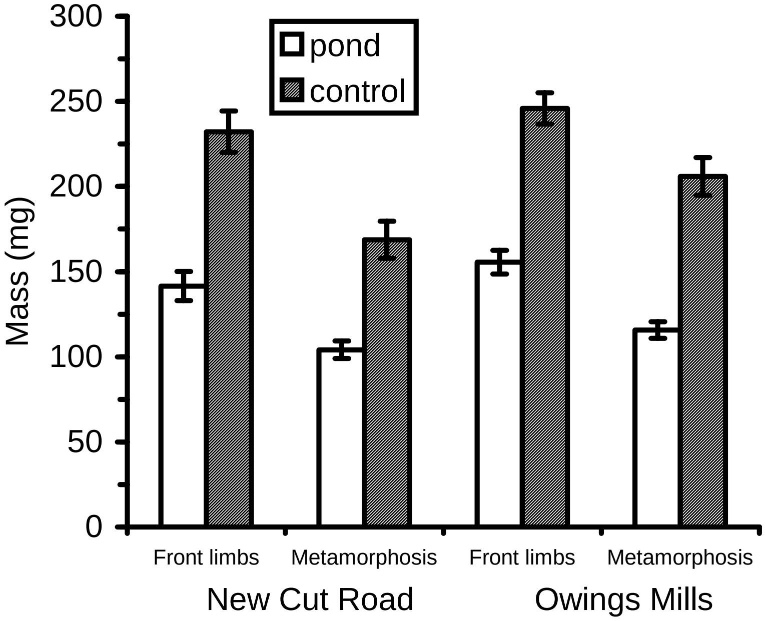
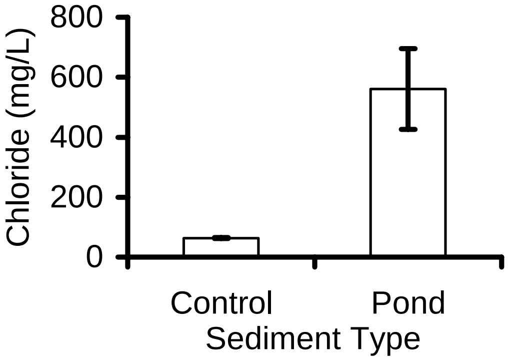


Figure 12. Mean concentration of chloride in water from bins used in wood frog exposures.



Discussion

The high concentrations of both Cu and Zn metals in stormwater runoff are likely the result of automobile wear debris. Zinc concentrations in stormwater runoff were also higher than copper concentrations for all storm events. This is consistent with numerous other studies that have looked at these metals in stormwater runoff (Drapper et al 2000, Sansalone and Buchberger 1997, Kayanian et al 2003). Metal concentrations and metal loadings varied a great deal between storm events. Storm intensity, storm duration and antecedent dry periods can all influence these differences in metal concentrations.

The fraction of Cu and Zn that is dissolved in runoff also varied a great deal within storms and between storms. On average 30% of the zinc was dissolved and about 40% of the copper. Other studies have shown that 53-95% of zinc present in runoff is dissolved and 31-56% of copper present is dissolved (Legret et al 1999, Sansalone et al 1997). The fraction of dissolved zinc is lower in this study than previous studies, however a major factor that influences these fractions is the source of the metal. Galvanized railings, roofing material, and building siding are all contributors of zinc to stormwater runoff. Areas where these are major contributors of zinc could have higher dissolved fractions of the metals. Runoff from buildings and galvanized railings were not major contributors at this site which may explain the low dissolved fraction of zinc.

Retention pond sediment metal levels were substantially higher than background soils. Dissolved metals that enter the pond from the roadway may be adsorbing onto the sediment surfaces contributing to these elevated concentrations. The mean concentration of copper in the pond surface sediments was 131 mg kg^{-1} and for zinc the mean sediment concentration was 611 mg kg^{-1}. Other studies that have looked at retention pond sediments have shown similar concentrations of both zinc and copper. In comparison with general consensus-derived sediment quality guidelines (MacDonald et al. 2000), levels of Cu and Zn in the pond sediments exceed threshold effects concentrations (TEC; Cu = 31.6 mg kg^{-1}; Zn = 121 mg kg^{-1}) as well as probable effects concentrations (PEC; Cu = 149 mg kg^{-1}; Zn = 459 mg kg^{-1}) above which adverse effects are likely to occur. However sequential extraction data indicate that while metal concentrations are high, there is a relatively small amount that would be readily available for uptake by organisms inhabiting the pond.

One of the most important observations of biotic impact at this site has been the presence of elevated levels of salt from deicing operations persisting into the summer months. Levels up to 45,000 μS (approximately 0.5 M chloride) were found in the water column through the last sampling event in June. No amphibian larvae were observed in the pond during the spring and toxicity tests conducted with sediment from the site demonstrated that wood frog (*Rana sylvatica*) eggs and larvae were severely impacted by the elevated salt levels. In contrast, American toad (*Bufo americanus*) eggs and larvae showed no impact on hatching success or survival when exposed to the salt-contaminated sediments in a subsequent experiment. This suggests that the habitat value of this pond is controlled more by road salt application than the metal content of roadway runoff. The elevated salt level in this pond may also affect transport of metal ions due to increased formation of metal complexes and may have contributed to the vertical transport of metals through the pond sediment profile.

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