

Consequential Species of Heavy Metals in Highway Runoff

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ABSTRACT

Speciation of heavy metals in aquatic systems plays a key role in their transport, chemical reactions, and bioavailability. Those physical and chemical forms that may cause significant consequences, known as consequential species, should be identified before the potential environmental impact of the metal can be determined. Species of dissolved lead, zinc, copper, and cadmium were identified by using anodic stripping voltametry for rainfall, highway and bridge runoff, and receiving streams at the intersections of Maitland Interchange and I-4, and US-17-92 and Shingle Creek in the central Florida area. Natural water systems reduce ionic species by complexation of incoming trace metals, which results in the reduction of their toxic effects. Most of the heavy metals in highway runoff that are discharged into detention/retention ponds similar to the Maitland site are concentrated in the upper layer (approximately 5 to 6.8 cm) of the bottom sediments. The potential for their release is unlikely if an aerobic environment of the sediment is maintained.

Highway stormwater runoff contains significantly higher concentrations of trace metals, particularly lead (Pb), zinc (Zn), iron (Fe), cadmium (Cd), chromium (Cr), nickel (Ni), and copper (Cu), than the adjacent water environment (1,2). As these metals reach the ecosystem, they will undergo physical, chemical, and biological transformations. They may be adsorbed on clay particles, taken up by plant and animal life, or remain in solution. Particulate fractions will settle to the bottom sediments, and heavy metals may resuspend or redissolve back into solution if the environmental conditions permit. Fate and transformations of trace elements in natural environments follow complex processes and much information is needed before their impact can be predicted.

Environmental scientists realize that the total concentration of a particular metal in natural waters can be very misleading. A water with high total metal concentration may be, in fact, less toxic than another water with a lower concentration of different forms of that metal. For example, ionic Cu is far more toxic toward aquatic organisms than organically bound Cu. Also, biotoxicity of Cu complexes decreases as their stability increases. Therefore, it is of prime importance to fully understand different dissolved metal species in an aqueous environment and to study the impact of those species on existing biota.

Information on consequential species of metals in highway runoff after their introduction into aquatic systems is essential to enhance the understanding of their impact and better evaluate measures for their control. This paper contains a summary of the results obtained from the following field and laboratory investigations:

1. Analysis of major constituents and trace metals in water samples of rainfall, stormwater, and water from a detention pond that receives highway and bridge runoff, and Shingle Creek, which flows beneath that bridge;
2. Partitions of trace metals between the bottom sediments and overlying water column;
3. Biotoxicity for various metal species; and
4. Speciation of trace metals in natural water by using a computerized chemical model (WATEQ2).

STUDY SITES

Two sites were selected to investigate the consequential species of heavy metals in highway stormwater runoff: (a) the intersection of Interstate 4 and Maitland Interchange and (b) the intersection of US-17-92 and Shingle Creek, south of Kissimmee, Florida. The traffic on I-4 at the Maitland site exceeds 50,000 vehicles per day and the traffic on US-17-92 at the Shingle Creek site exceeds 12,000 vehicles per day. The average daily traffic (ADT) count at each site for the past 3 yr was provided by David Harrell of the Florida Department of Transportation (FDOT) in personal communication in 1984, and is presented in Table 1.

TABLE 1 Daily Traffic Count for Selected Sites to Study Consequential Species

| Site Location | Traffic Lanes | Average Daily Traffic | | |
|---|---------------|-----------------------|--------|--------|
| | | 1981 | 1982 | 1983 |
| NE I-4 and Maitland Interchange | Eastbound | 36,013 | 38,717 | 51,454 |
| | Westbound | 35,430 | 39,288 | 50,023 |
| SW I-4 and Maitland Interchange | Eastbound | 45,207 | 47,456 | 54,482 |
| | Westbound | 43,705 | 50,008 | 52,810 |
| Maitland Avenue at SR 427 | Eastbound | 12,506 | 14,305 | 15,833 |
| | Westbound | 12,896 | 13,965 | 15,683 |
| US-17-92 and Shingle Creek, St. #3, SW Kissimmee City Limit | Combined | 12,856 | 12,117 | 12,254 |

Stormwater runoff from I-4 is delivered by overland flow over grassy swales to storm drain inlets or detention ponds A, B, and C (Figure 1). Stormwater runoff from the Maitland Boulevard bridge that crosses over I-4 is conveyed directly off the roadway surface through stormwater inlets to culverts that ultimately discharge into Pond A. The ponds are interconnected and the water from the west pond flows over a wooden weir at its southern end, which is connected to Lake Lucien by means of a culvert and a short, densely vegetated ditch (Figure 1). The west pond is triangular in shape, with a surface

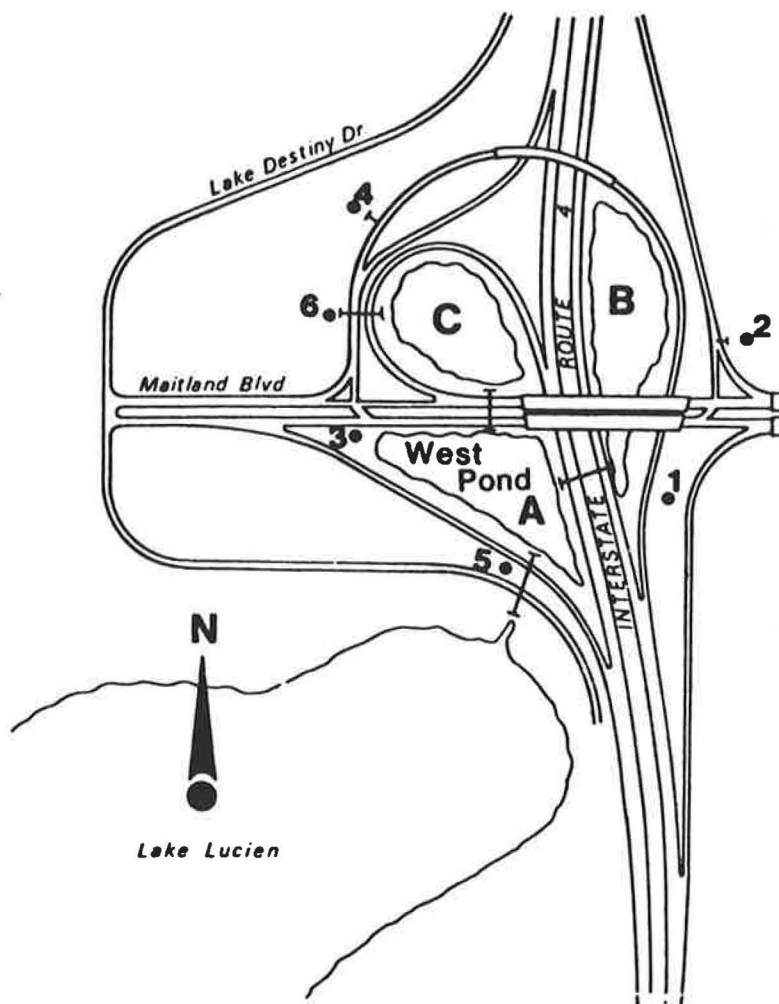


FIGURE 1 Sampling site for highway runoff at Maitland Interchange and Interstate 4.

area of approximately 1.2 ha (3 acres) and a depth of 1.5 to 2 m.

US-17-92 crosses Shingle Creek south of the Kissimmee city limit, approximately 1 mile from Lake Tohopekaliga. The roadway is a two-lane undivided highway with a 1983 ADT count of 12,250 vehicles. Stormwater runoff is removed from the bridge area by a system of numerous 10-cm scupper drains that empty onto the underlying wetland areas (Figure 2).

FIELD AND LABORATORY PROCEDURES

Water samples were collected for heavy-metal analysis from the west pond at the Maitland Interchange and from the surrounding drainage area as shown in Figure 1. Sampling locations, shown in Figure 2, were selected beneath the bridge from the scupper drains (S-1) and from the Shingle Creek water near the bridge site (S-2) to study metal speciation in the highway bridge runoff and receiving stream.

Water samples were also collected from rainfall, highway runoff, and the detention pond at the Maitland Interchange and I-4 intersection for analysis of particulate and dissolved metal content. Similar analyses were performed on water samples collected from highway bridge runoff and the receiving stream at US-17-92 and Shingle Creek. Various metal species of Pb, Zn, Cu, and Cd in solution were determined by

using anodic stripping voltammetry (ASV) techniques that followed the proposed scheme by Bately and Florence (3). These metals are the most abundant in highway runoff and received the most study (4). Together, these accounted for approximately 90 to 98 percent of the total metals observed, with Pb and Zn accounting for 89 percent. Speciation of other metals by using the same technique has not been fully developed. However, available computer programs may assist in the determination of various species of additional metals that exist under a known set of environmental parameters (5).

A detailed discussion of site description, sampling collection, and utilized procedures is presented in a recent report submitted to the Florida Department of Transportation (FDOT) (6).

WATER ANALYSIS

Water samples were collected in duplicate, filtered in the field, and stored inside ice-packed chests. Five sets of the water samples, collected on April 6, May 13, June 7, July 5, and August 1, 1983, were analyzed by both the U.S. Geological Survey (USGS) Water Resources Laboratory in Ocala and the Chemistry and Environmental Engineering Laboratories at the University of Central Florida (UCF) in Orlando. The samples were preserved and stored in the refrigerator at the laboratory until analysis, as speci-

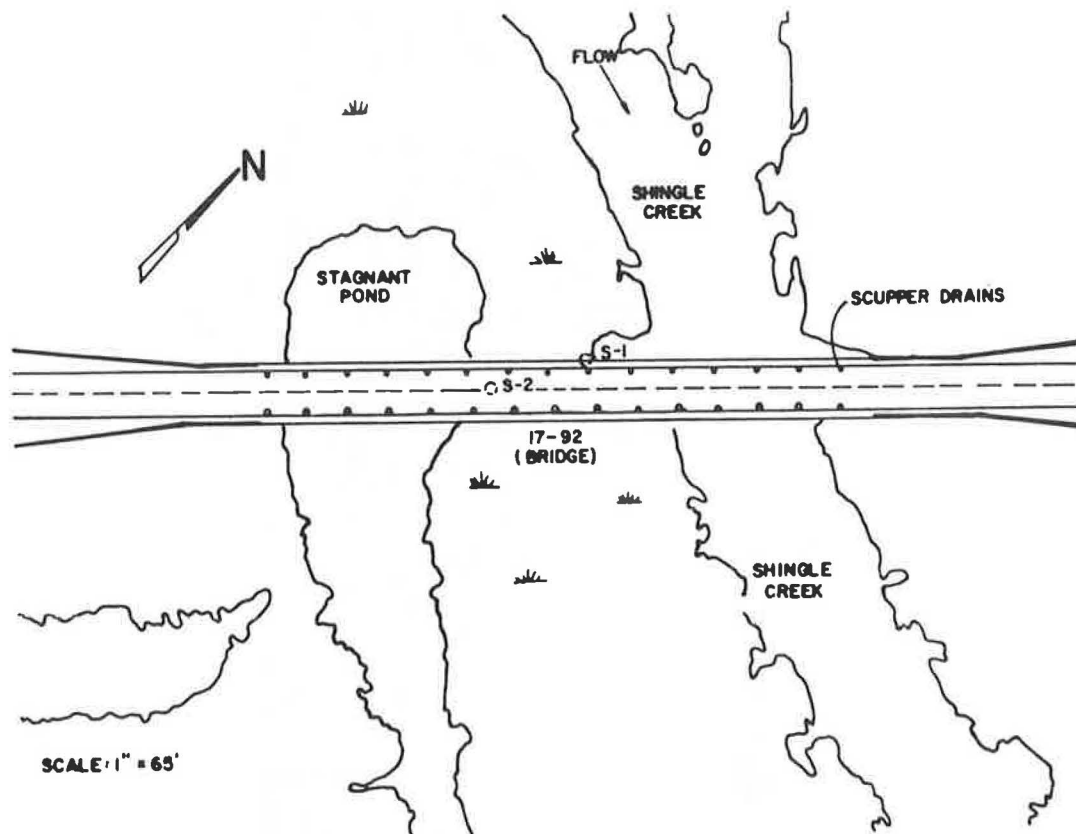


FIGURE 2 Locations of sample sites at US-17-92 and Shingle Creek.

fied in a report by the U.S. Environmental Protection Agency (7). The analysis included major anions, cations, and trace metals. The overall averages of the results from the USGS and UCF analyses are presented in Table 2.

The average pH values from rainfall samples were

slightly higher than 5; however, other water samples tested were close to neutral. The acidic rainfall was generally neutralized as it flowed over the drainage basin. Also, runoff water picked up dissolved solids, which was evident from the increase in specific conductance and dissolved solids mea-

TABLE 2 Overall Average Dissolved Water Quality Parameters

| Parameter | Maitland Interchange | | | | | | US-17-92 and Shingle Creek | | | |
|---|----------------------|----------------|-----------|----------------|-----------|----------------|----------------------------|----------------|-----------|----------------|
| | Rainfall | | Runoff | | Pond | | Shingle Creek | | Runoff | |
| | \bar{x} | $\bar{\sigma}$ | \bar{x} | $\bar{\sigma}$ | \bar{x} | $\bar{\sigma}$ | \bar{x} | $\bar{\sigma}$ | \bar{x} | $\bar{\sigma}$ |
| pH (lab) | 5.2 | 0.7 | 6.9 | 0.2 | 6.8 | 0.2 | 6.8 | 0.2 | 7.2 | 0.2 |
| Special conditions ($\mu\text{mho/cm}$) | 18.0 | 4.0 | 123.0 | 52.0 | 186.0 | 21.0 | 210.0 | 64.0 | 237.0 | 101.0 |
| Color units | 1.0 | 2.5 | 10.0 | 9.0 | 10.0 | 7.0 | 220.0 | 69.0 | 50.0 | 36.0 |
| Dissolved solids | 9.8 | 2.1 | 75.9 | 39.9 | 113.3 | 10.4 | 159.9 | 40.8 | 173.3 | 95.4 |
| Alk (CaCO_3) | 1.0 | 1.0 | 44.4 | 16.2 | 50.4 | 9.5 | 40.4 | 15.4 | 74.5 | 22.1 |
| TH (CaCO_3) | 4.3 | 2.1 | 48.8 | 25.6 | 70.8 | 9.9 | 60.6 | 12.6 | 95.5 | 49.2 |
| NCH (CaCO_3) | 3.3 | 2.2 | 8.0 | 6.6 | 20.2 | 2.4 | 20.2 | 5.3 | 23.5 | 24.9 |
| HCO_3^- | 1.5 | 1.3 | 54.2 | 20.2 | 61.7 | 12.0 | 49.2 | 19.1 | 91.0 | 26.9 |
| SO_4^{2-} | 2.7 | 1.4 | 11.9 | 10.2 | 26.6 | 5.5 | 23.3 | 7.0 | 28.1 | 30.2 |
| Cl^- | 1.6 | 0.7 | 2.9 | 1.5 | 5.1 | 1.0 | 21.8 | 5.3 | 10.8 | 9.3 |
| TH as N | 0.66 | 0.50 | 0.79 | 0.18 | 0.51 | 0.16 | 1.37 | 0.42 | 3.15 | 2.16 |
| Organic N as N | 0.27 | 0.13 | 0.32 | 0.18 | 0.38 | 0.14 | 1.02 | 0.45 | 1.78 | 1.38 |
| $\text{NH}_4\text{-N}$ | 0.11 | 0.10 | 0.09 | 0.07 | 0.04 | 0.02 | 0.14 | 0.11 | 0.69 | 1.03 |
| $\text{NO}_2\text{-N}$ | 0.01 | 0.0 | 0.02 | 0.01 | 0.01 | 0.0 | 0.01 | 0.0 | 0.07 | 0.08 |
| $\text{NO}_3\text{-N}$ | 0.31 | 0.26 | 0.33 | 0.26 | 0.15 | 0.26 | 0.26 | 0.24 | 0.48 | 0.77 |
| TP-P | 0.02 | 0.0 | 0.05 | 0.01 | 0.01 | 0.0 | 0.22 | 0.13 | 0.12 | 0.03 |
| OP-P | 0.01 | 0.0 | 0.03 | 0.02 | 0.0 | 0.0 | 0.22 | 0.10 | 0.09 | 0.04 |
| Ca^{+2} | 1.6 | 1.0 | 27.0 | 28.3 | 20.5 | 3.4 | 17.3 | 4.1 | 27.8 | 19.2 |
| Mg^{+2} | 0.2 | 0.1 | 1.17 | 1.34 | 4.5 | 0.4 | 4.2 | 1.0 | 0.9 | 0.9 |
| Na^{+2} | 2.2 | 2.6 | 2.9 | 2.3 | 5.6 | 0.9 | 17.3 | 9.9 | 3.7 | 2.2 |
| K^+ | 0.5 | 0.4 | 1.7 | 1.6 | 4.3 | 1.6 | 2.6 | 1.0 | 3.9 | 5.6 |
| SiO_2 | 0.1 | 0.1 | 1.9 | 1.4 | 1.2 | 1.2 | 4.5 | 1.7 | 3.0 | 0.8 |
| Humic acids | 1 | 0.5 | 5 | 4 | 4 | 2 | 18 | 14 | 10 | 9 |

Note: All concentrations are expressed in milligrams per liter.

surements between rainfall and runoff samples. Rainfall samples averaged approximately 10 mg per liter of dissolved solids, whereas runoff samples averaged between 76 and 173 mg per liter. There was little difference between values measured in runoff water and those measured in receiving water. Dissolved solids concentrations can be expressed in terms of specific conductance. The ratios of dissolved solids concentration to specific conductance averaged 0.54, 0.62, 0.61, 0.76, and 0.73 for rainfall, highway runoff, the Maitland ponds, Shingle Creek water, and bridge runoff, respectively. Water characteristics for the Maitland site showed distinct differences from those for the Shingle Creek site. Also, dissolved solids, alkalinity, and total hardness in the Maitland pondwater were higher than the same parameters in runoff water, presumably because of their concentration by evaporation of the pondwater.

The average total nitrogen (TN) and phosphorus (TP) concentrations in Maitland pondwater were lower than those in rainfall and runoff waters. Inorganic nitrogen was the major component of rainwater and organic nitrogen was the major component of pondwater. The average inorganic nitrogen and total phosphorus concentrations in the Maitland pondwater samples did not exceed 30 percent of the average concentrations in highway runoff water. The pond appeared to be very efficient in the removal of inorganic nitrogen and phosphorus species from highway runoff water. The same conclusions were reached during a detailed analysis of the pondwater (8).

The TN in the bridge runoff water was higher than the TN in Shingle Creek water although the TP was lower. Shingle Creek is a flowing stream that receives municipal wastewater effluent, agricultural runoff, and urban runoff. The creek water is highly colored, averaging 220 color units caused by humic substances from the decay of vegetation. The humic substance concentration averaged 18 mg per liter in Shingle Creek water and 4 mg per liter in the Maitland pondwater. Similarly, silicon dioxide (SiO₂) concentration averaged much higher values in Shingle Creek water than the Maitland pondwater.

The analysis indicated that rainwater washed off deposits on highway surfaces and dissolved the contaminants in stormwater runoff. Major cations, particularly Ca, Mg, Na, and K, were dissolved in surface runoff water. The quality of runoff appeared to be improved by retention/detention in the Maitland pond. The calcium concentration in the pondwater was lower than in runoff water; however, Mg, Na, and K concentrations were higher in the pondwater than in the runoff water. Calcium may be reduced by precipitation and removal from the water column, and other cations are concentrated by evaporation.

METAL SPECIATION IN WATER SAMPLES

The analysis followed the speciation scheme by Batley and Florence (3), which required several treatment steps to separate the various species of labile and nonlabile trace metals. Labile species may include organic colloidal and inorganic soluble and colloidal forms. Also, nonlabile species may include organic soluble and colloidal and inorganic soluble and colloidal forms. The peak heights measured from current (I) versus voltage (E) diagrams for Zn, Cd, Pb, and Cu in water samples before and after Chelex-100 treatment and before and after exposure to ultraviolet light should allow the speciation determination of various metals. The data indicate that the average dissolved concentrations in Maitland rainfall, runoff, and pondwater were 2.49, 1.61, and 1.05 µg of Cd per liter; 8.15, 23.0, and 10.8 µg of Zn per liter; 8.7, 40.7, and 20.4 µg

of Pb per liter; and 66.1, 26.6, and 16.6 µg of Cu per liter, respectively. Also, Shingle Creek water and bridge runoff averaged 1.76 and 2.92 µg of Cd per liter; 14.5 and 15.3 µg of Zn per liter; 18.8 and 27.7 µg of Pb per liter; and 8.86 and 18.6 µg of Cu per liter, respectively. The average metal concentrations in Maitland pondwater were lower than those detected in rainfall and runoff water. The pond is efficient in the removal of metals that accumulate in the bottom sediments. The average metal concentrations in the Shingle Creek water were similar in that they were lower than those detected in the highway bridge runoff that crossed over the creek at US-17-92.

The relative distribution of various dissolved species of trace metals that were detected in water samples collected during this study is presented in Table 3. The data showed that labile, organic, and colloidal fractions averaged 82.0, 5.3, and 32.9 percent for Cd; 92.2, 0.3, and 42.7 percent for Zn; 60.9, 22.1, and 55.6 percent for Pb; and 63.7, 48.9, and 69.8 percent for Cu, respectively, in all water samples tested. The organic fraction for dissolved Cu in water samples was the highest among all metals tested. The organic fraction in all metals tested followed a decreasing order: Cu > Pb > Cd > Zn. The labile fraction followed a similar decreasing order: Zn > Cd > Cu > Pb. Also, the colloidal fraction followed a decreasing order of Cu > Pb > Zn > Cd. It can be concluded, then, that Zn and Cd from highway runoff are more reactive in natural environments than Cu and Pb. Zn and Cd, however, may exist in ionic forms and are more readily available to biota in natural systems.

TABLE 3 Relative Distribution for Various Dissolved Species of Trace Metals in Water Samples

| Metal | Form | Percentage in Water from | | | | |
|-------|--------------|--------------------------|--------|------|---------------|---------------|
| | | Maitland Interchange | | | US-17-92 | |
| | | Rainfall | Runoff | Pond | Bridge Runoff | Shingle Creek |
| Cd | Labile | 85.9 | 84.7 | 86.3 | 78.1 | 75.2 |
| | Nonlabile | 14.1 | 15.3 | 13.7 | 21.9 | 24.8 |
| | Organic | 1.1 | 4.3 | 4.2 | 3.4 | 13.3 |
| | Inorganic | 98.9 | 95.7 | 95.8 | 96.6 | 86.6 |
| | Colloidal | 19.3 | 36.4 | 31.7 | 38.3 | 38.8 |
| | Noncolloidal | 80.7 | 63.6 | 68.3 | 61.7 | 61.2 |
| Zn | Labile | 93.7 | 92.5 | 96.3 | 92.5 | 89.5 |
| | Nonlabile | 6.3 | 7.5 | 3.7 | 7.5 | 10.5 |
| | Organic | 0.0 | 0.7 | 0.3 | 0.3 | 0.2 |
| | Inorganic | 100 | 99.3 | 99.7 | 99.7 | 99.8 |
| | Colloidal | 45.8 | 23.6 | 83.7 | 29.2 | 31.0 |
| | Noncolloidal | 54.2 | 76.4 | 16.3 | 70.8 | 69.0 |
| Pb | Labile | 65.6 | 72.7 | 55.4 | 43.8 | 67.2 |
| | Nonlabile | 34.4 | 27.3 | 44.6 | 56.2 | 32.8 |
| | Organic | 14.6 | 15.4 | 17.3 | 44.0 | 19.3 |
| | Inorganic | 85.4 | 84.6 | 82.7 | 56.0 | 80.7 |
| | Colloidal | 63.3 | 36.7 | 54.2 | 68.7 | 54.9 |
| | Noncolloidal | 36.7 | 63.3 | 45.8 | 31.3 | 45.1 |
| Cu | Labile | 84.0 | 45.9 | 81.0 | 58.7 | 49.0 |
| | Nonlabile | 16.0 | 54.1 | 19.0 | 41.3 | 51.0 |
| | Organic | 38.3 | 56.6 | 53.8 | 33.4 | 62.2 |
| | Inorganic | 61.7 | 43.4 | 46.2 | 66.6 | 37.8 |
| | Colloidal | 59.8 | 75.6 | 72.1 | 62.0 | 79.7 |
| | Noncolloidal | 40.2 | 24.4 | 27.9 | 38.0 | 20.3 |

SPECIATION OF TRACE METALS IN SEDIMENTS

Concentrations of trace metals measured in the incoming highway runoff appear to exist predominantly in association with particulate matter. Particulate fractions accounted for 42 percent of the total Cd, 86 percent of the total Zn, 47 percent of the total

TABLE 4 Comparison of Average Heavy-Metal Concentrations in Stormwater Runoff and in the Retention Basin (West Pond) at Maitland Interchange

| Parameter | Average Incoming Stormwater Quality (N=16) | | | Average Retention Basin Water Quality (N=34) | | | Percent Change Through Retention Basin | |
|-----------|--|---------------------------|-------------------|--|---------------------------|-------------------|--|-------|
| | Dissolved ($\mu\text{g/L}$) | Total ($\mu\text{g/L}$) | Percent Dissolved | Dissolved ($\mu\text{g/L}$) | Total ($\mu\text{g/L}$) | Percent Dissolved | Dissolved | Total |
| Cd | 1.1 | 1.9 | 58 | 0.8 | 1.0 | 80 | -27 | -47 |
| Zn | 50 | 347 | 14 | 5.8 | 6.4 | 91 | -88 | -98 |
| Cu | 32 | 60 | 53 | 14 | 16 | 88 | -56 | -73 |
| Pb | 43 | 723 | 6 | 16 | 22 | 73 | -63 | -97 |
| Ni | 3.2 | 28 | 11 | 1.8 | 2.3 | 78 | -44 | -92 |
| Cr | 3.3 | 10 | 33 | 2.3 | 3.4 | 68 | -30 | -66 |
| Fe | 48 | 1176 | 4 | 20 | 61 | 33 | -58 | -95 |

Cu, 94 percent of the total Pb, 89 percent of the total Ni, 67 percent of the total Cr, and 96 percent of the total Fe, as shown in Table 4. All the soluble and particulate fractions in the pondwater were lower than those detected in the incoming stormwater. The reduction in concentrations varied between 27 and 88 percent in the dissolved fraction and between 47 and 98 percent in the total metal concentration.

The results previously presented indicate that the fate of a large portion of both the suspended and dissolved fractions of stormwater-associated heavy metals is the ultimate deposition of a wide variety of mechanisms into the bottom sediments of the receiving water body. After several years of this continual deposition, a large accumulation of heavy metals may develop in the sediments. This concentrated layer of heavy metals may present a potential pollution hazard if leaching occurs. To investigate the potential movement of sediment-deposited heavy metals, the vertical distribution of heavy metals in 43 sediment cores collected from the Maitland ponds was examined and the average metal concentrations in sediment layers of 0 to 0.8, 0.8 to 2.8, 2.8 to 4.8, and 4.8 to 6.8 cm were calculated.

The heavy-metal content in the 4.8 to 6.8-cm layer was similar to heavy-metal concentrations measured in nearby soils that were unaffected by stormwater runoff. Therefore, these concentrations were considered equal to background values and subtracted from each of the others. The vertical distributions of Zn, Pb, Cr, Ni, Cu, and Fe in sediment cores that were collected in the West pond are shown in Figure 3. This figure shows that the metal concentrations decreased in an exponential fashion with a correlation coefficient of 0.99 or better. Accumulated heavy metals were quickly attenuated during movement through sediment material. Attenuation of the metals was found to occur in the top 5.0 to 6.8 cm with normal background concentrations below that depth.

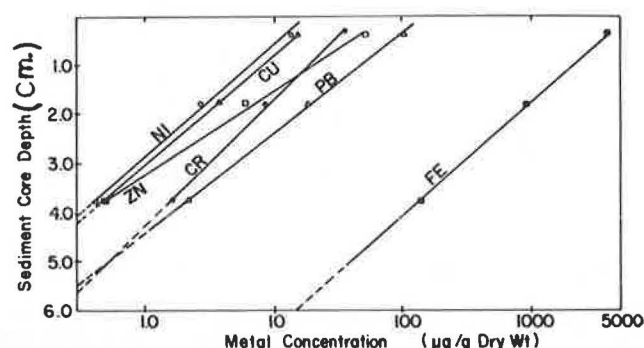


FIGURE 3 Transports of heavy metals through bottom sediments of retention/detention pond at Maitland Interchange.

It can be concluded, therefore, that heavy metals, after reaching the sediments, are transformed into stable associations that remain near the sediment surface and decline rapidly in concentrations with increasing depth.

Most previous studies that deal with particulate metal fractions have measured total metal concentrations, whereas relatively few attempts have been made to evaluate the speciation of particulate metals. The use of total metal concentration as a basis for evaluating particulate matter or sediments implies that all forms of a given metal are equal in terms of their toxicity, biological and physiological availability, mobility, and origin. Obviously, this assumption is not valid.

Theoretically, it is chemically possible to partition solid material into specific metal fractions by using appropriate procedures and an improved sequential extraction procedure for the speciation of particulate trace metals that had been reported (9). In this procedure, six fractions can be identified that eliminate many of the problems previously reported in single extraction procedures.

The data indicate that very little or none of the trace metals in the sediments is soluble in distilled deionized water. Pb appears to exist primarily in exchangeable form and associated with Fe-Mn oxides. Cu, Fe, Cr, Ni, and Zn are mainly bound to Fe-Mn oxides and with organic matter in the sediments. Also, most of the Cd in sediments appears to be exchangeable. Therefore, the potential of trace metal release by natural water is very limited or unlikely if aerobic conditions are maintained. Under aerobic conditions, hydrous Fe-Mn oxides act as a sink for trace metals that result from specific adsorption and coprecipitation.

PREDICTION OF METAL SPECIATION

The speciation of trace elements in natural waters is important in the assessment of the potential for biological uptake. Most of these analytical techniques measure gross parameters such as total dissolved Pb or Cu but give no clue as to the actual form of their existence in the environment. One of the methods used to gain insight into this area is computer modelling. One widely used computerized chemical model for trace and major element speciation and mineral equilibria of natural waters is WATEQ2 (5). This computer model can be used to predict the average dissolved metal species present in water samples of known chemical composition. The predicted average dissolved metal species in water samples from the study area are shown in Table 5.

The predicted speciation shows that Zn and Cd exist mainly as free ions below pH 8 and are controlled by carbonates at higher pH values. Pb exists as free ions, bicarbonate, and carbonate forms below

TABLE 5 Predicted Average Dissolved Metal Species in Water Samples from Study Areas Using WATEQ2 Model

| Metal | Major Species | Average Concentration ($\mu\text{g/L}$) | | | | |
|-------|--------------------|---|----------------|------------|---------------|---------------------|
| | | Rainwater | Highway Runoff | Pond Water | Bridge Runoff | Shingle Creek Water |
| Zn | Zn^{+2} | 8.1 | 19 | 9.3 | 11.3 | 12.8 |
| | ZnHCO_3^+ | 0.1 | 2.3 | 0.9 | 1.7 | 1.2 |
| | ZnCO_3 | — | 1.2 | 0.4 | 1.6 | 0.5 |
| | Total | 8.2 | 23.0 | 11.0 | 15.0 | 15.0 |
| Cd | Cd^{+2} | 2.46 | 1.28 | 0.82 | 2.15 | 1.44 |
| | CdHCO_3^+ | 0.04 | 0.16 | 0.08 | 0.30 | 0.13 |
| | CdCO_3 | — | 0.10 | 0.05 | 0.40 | 0.06 |
| | Cd-Fulvate | — | 0.02 | 0.01 | 0.06 | 0.06 |
| | Total | 2.50 | 1.60 | 1.00 | 3.00 | 1.80 |
| Pb | Pb^{+2} | 36.6 | 5.7 | 3.8 | 1.8 | 3.7 |
| | PbHCO_3^+ | 0.7 | 4.3 | 2.4 | 1.8 | 2.2 |
| | PbCO_3 | 0.2 | 30.3 | 13.0 | 23.8 | 12.1 |
| | Total | 38.0 | 41.0 | 20.0 | 28.0 | 19.0 |
| Cu | Cu^{+2} | 34.4 | 2.4 | 1.8 | 0.8 | 3.4 |
| | Cu-Fulvate | 30.0 | 16.1 | 9.8 | 10.8 | 7.7 |
| | Cu(OH)_2 | — | 2.4 | 1.2 | 3.2 | 0.2 |
| | CuCO_3 | — | 3.9 | 1.9 | 3.3 | 0.3 |
| | Total | 66.0 | 27.0 | 16.0 | 19.0 | 9.0 |
| Ni | Ni^{+2} | 0.99 | 0.87 | 0.76 | 0.45 | 1.17 |
| | NiCO_3 | — | 2.00 | 1.13 | 2.46 | 1.68 |
| | Total | 1.00 | 3.00 | 2.00 | 3.00 | 3.00 |

pH 6.5 and is controlled mainly by the carbonate concentration above pH 7. Ni exists mainly as the free metal ion below pH 6, is divided between the free ion form and NiCO_3^0 between pH 6 and 7.5, and is controlled solely by carbonate concentration above pH 7.5. Finally, Cu exists mainly as Cu-fulvate between pH 5 and 7, is divided between Cu-fulvate and Cu(OH)_2^0 between pH 7 and 8, and is controlled by Cu(OH)_2^0 exclusively above pH 8.

The predicted species show specific compounds that are based on thermodynamic data, and the measured species using ASV are grouped in classes on the basis of behavioral characteristics. However, for the purpose of comparison, it may be assumed that free metal ion is represented by the measured class of soluble labile and that fulvate-humate compounds represent the organic fractions measured by ASV. The predicted and measured speciation indicated that Zn and Cd existed mainly as free metal ions in natural waters. Cu is strongly influenced by organic matter present and exists mainly as organic complexes. However, organic Pb complexes are measured by ASV and are not predicted by WATEQ2 as a result of the lack of sufficient thermodynamic data for organic lead compounds.

Of course, it is very difficult to find in the literature the thermodynamic data on metal complexes that are associated with fulvic and humic substances in the natural environment. As more information becomes available, the computer program can be modified and improved. The organic Pb complexes varied between 15 and 44 percent of the metal in solution measured by ASV. The labile Pb fraction appears to include ionic forms as well as organic and inorganic complexes. Also, most of the labile fraction of Cu in the aquatic environment may be associated with organic complexes.

The presence of organic substances in natural waters and the role of the sediments in the removal and retention of trace metals that are released to receiving streams tend to detoxify the metals associated with highway runoff. Most of the metals are retained by the bottom sediments on a permanent basis if aerobic conditions and high redox-potential

(Eh) values are maintained. The ability of natural waters to detoxify trace metals was demonstrated by the higher lethal concentrations for 50 percent kill (LC-50) for mosquito fish in retention/detention pondwater as compared with the LC-50 values in de-ionized tap water (10).

CONCLUSIONS

Trace metals in aqueous systems are partitioned between the overlying water column and the accumulated sediments beneath it. Heavy metals that are bound within the crystal lattice of clay particles are considered unavailable, whereas materials dissolved in interstitial or surface adsorbed ions that may be easily displaced by ion exchange are considered available. Between those two extremes, heavy metals may be present in chemical forms that are potentially available to organisms. There are several similar classification schemes for dissolved heavy metals in natural water systems. These schemes may assist in the identification of the most toxic species in solution that are available to biota. It is realized that biotoxicity is dependent on the available species and not on the total metal concentration. During this study, the following conclusions were reached:

1. Retention/detention ponds similar to the Maitland ponds are effective in nutrient and heavy-metal removal from highway runoff. The bottom sediments concentrate the heavy metals and nutrients that are discharged into the pond.

2. The average dissolved Cd, Zn, Cu, Pb, Ni, Cr, and Fe in the Maitland ponds are 73, 12, 44, 37, 56, 70, and 42 percent of those detected in the incoming highway runoff, respectively. Similarly, the total Cd, Zn, Cu, Pb, Ni, Cr, and Fe concentrations in the Maitland ponds averaged 53, 2, 27, 3, 8, 34, and 5 percent of those measured in the incoming highway runoff. Most of the metals in highway runoff appear to be in particulate form.

3. Bottom sediments in the Maitland ponds have heavy-metal concentrations in the top 5 to 6.8 cm. Accumulated heavy metals are attenuated very quickly during movement through sediment material. Most of the metals are mainly bound to Fe-Mn oxides and organic matter. A fraction of Pb and Cd appears to be exchangeable. Therefore, the potential of trace metal release to solution by natural water is very limited or unlikely if aerobic conditions are maintained.

4. More than 70 percent of the soluble Cd and Zn in rainfall, highway runoff, Maitland pondwater, and Shingle Creek water exists in ionic form (M^{+2}). Most of the Pb exists as PbCO_3^0 , and a significant fraction of the Cu is associated with organic complexes if humic substances are present.

5. Existing standards for trace metals do not specify chemical speciation of those metals or their bioavailability. The detoxifying effect of some water quality parameters on trace metals should be reflected in the standards.

6. Determination of existing chemical speciation by computerized models can be a useful tool for planning purposes in the prediction of potential environmental impacts.

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Removal of Highway Contaminants by Roadside Swales

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ABSTRACT

Removal of highway contaminants by roadside swales was investigated at the Maitland and EPCOT Interchanges with Interstate 4 (I-4) in Orange County, Florida. Runoff samples from highway and grassy swale areas at Maitland Interchange were collected for 8 months for comparison of highway runoff with runoff that passed through a grassy swale. Also, a controlled water flow from adjacent detention/retention ponds was dosed with nitrogen, phosphorus, and heavy metals to produce concentrations typical of highway runoff. The mixture was allowed to flow for a period of 3.0 to 5.5 hr over selected areas of adjacent roadside swales. Periodic grab samples were collected from several locations along the swale throughout the flow period and were analyzed to determine concentration and mass removal rates for various pollutants under several values of flow rates and experimental conditions. Hydraulic, hydrologic, and water quality parameters were evaluated. Removal efficiencies for dissolved heavy metals appeared to be higher than for nitrogen and phosphorus. Pollutants may be retained in swale areas by sorption, precipitation, coprecipitation and biological uptake processes; however, occasional increases in concentrations of highway contaminants were observed at intermediate stations during the swale experiments. Mass removal of heavy metals, nitrogen, and phosphorus was directly related to infiltration losses and on-site storage.