BEHAVIOR OF RUNOFF-DERIVED METALS IN A WELL DEFINED PAVED-CATCHMENT/RETENTION POND SYSTEM

BY

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ABSTRACT

A well defined suburban parking lot runoff-retention system was intensively studied to better understand the removal and fate of heavy metals in retention ponds. Over six-hundred individual water, particulate, and sediment samples were collected in this project, documenting runoff and pond behavior during the summer dry period and, subsequently, during and after three major rain events in the fall and winter wet season. We have developed a general picture of heavy metal inputs and outputs for the ponds, and have identified the pattern of metal sedimentation and remobilization.

Our results indicated that relatively high levels of Cu were present in both water and sediments. Cd was present at negligible levels in the water and at only modest levels in the sediments. Pb levels in runoff particles and sediments were significantly higher than in the native soils but were not as high as expected. Cu was identified as a useful "model" toxic metal that occurred in substantial concentrations and was relatively easy to analyze. We chose to study Cu in detail; other toxic metals were measured in selected samples. Given the time and resource constraints, our strategy was to learn as much as possible about the overall behavior of Cu rather than to gain only limited information about a suite of different metals.

Dissolved metal concentrations varied during the course of the sampling but were not dramatically different among three ponds. Dissolved metal concentrations were generally highest in the input pond and lowest in the discharge pond, suggesting relatively rapid removal in the first pond. Suspended particles did not constitute a significant mass of Cu in the water column but Cu and other metals accumulated rapidly in the pond sediments. These

observations are consistent with a fast mean-settling time for particles which of course translates into a short particle residence-time in the water.

The first storm of autumn washed high concentrations of metals into the runoff from which they were rapidly removed by sedimentation in the first pond. Little metal entered the sediments of the second and third ponds. Effluent concentrations to the receiving stream were relatively low. Thus, ponds serve as a buffer to the Cu flux. When Cu inputs were high, the ponds removed metals and ameliorated the concentrations exiting to the receiving waters. When input concentrations were very low, the ponds occasionally became a *source* of Cu to the stream because the steady ("buffered") outflow concentration was at times higher than the input. The adsorption/desorption processes of the sediments appear to play a key role in regulating metal discharges.

Because sediment concentrations of metals declined so precipitously from the input pond to the subsequent ponds, we investigated the spatial distribution of metals in the sediments **within** the input pond. Interestingly, we found that most metals were concentrated in relatively narrow "plumes" in the sediments extending axially from each of the storm-sewer inlet pipes. Concentrations of metals in the sediments at the periphery of the input pond were much lower than at the center, and were comparable to the low levels of the second and third ponds. This showed that a relatively small pond (perhaps half the size of the input pond) can remove most metals from parking-lot runoff, and demonstrated the desirability of constructing small, inexpensive ponds at the outlets of suburban parking lots in order to preserve the integrity of receiving streams.

FOREWORD

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It is Institute policy to make available the results of significant water-related research conducted in Oregon's universities and colleges. The Institute neither endorses nor rejects the findings of the authors of such research. It does recommend careful consideration of the accumulated facts by those concerned with the solution of water-related problems.

ACKNOWLEDGMENTS

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1. INTRODUCTION

WATER QUALITY PROBLEMS AND URBAN RUNOFF

Urban stormwater runoff severely degrades the quality of streams and other receiving waters. Although suspended solids, bacteria, and nutrients are major parts of the problem, heavy metals are the priority pollutants in runoff that present the greatest risk to aquatic biota and human health. Continued urbanization in the Northwest, as elsewhere, increases non-point-source runoff pollution from roads, parking lots, and other impervious surfaces. Although detailed studies specific to the climate of this region are scarce, data from other areas of the country suggest that urban runoff is extensively degrading the biological integrity of streams in and near urban centers, and that escalating inputs of Pb, Zn, Cd, and other toxic metals are primarily responsible for this damage.

Non-point-source pollution such as urban runoff is difficult to control. Runoff is especially problematic in suburban areas where centralized storm-water drainage systems are non-existent. Retention basins are frequently advocated as a cost-effective way of reducing the acute impacts of runoff from isolated catchments such as parking lots. While it is relatively easy to design a retention pond that allows the bulk of suspended solids to settle out, fine-colloidal and dissolved components may remain in the water that is discharged. Much research has indicated that aqueous heavy metals are primarily associated with fine particles and with natural humic chelating materials. Thus retention ponds, as currently designed, may be ineffective at reducing the input of priority pollutants to receiving waters.

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PURPOSE AND OBJECTIVES

The behavior of heavy metals in runoff retention ponds was characterized through an intensive physical and chemical study of a hydrologically well defined parking-lot/retention-pond system in Beaverton, Oregon. Total concentrations of priority-pollutant metals were measured in pond influent, effluent, and sediments during a one-year sampling program. These data allow an overall understanding of the behavior of metal contaminants in the system.

Our purposes in conducting the study were: 1) to quantify the amounts of metal pollutants that a non-industrial, suburban parking lot system contributes to receiving waters in the climate of the maritime Northwest, 2) to determine the efficacy of removing these metals in retention ponds, and 3) to better understand the fate of metals retained in these ponds. We were fortunate to have an excellent study site immediately adjacent to our laboratories. The pond system was newly constructed, had no pre-existing sediments, was almost certainly oversized with respect to solids and metals removal, and was divided into three discrete basins so that spatial variation in metal sedimentation could be easily identified. Although constraints of time and money precluded an exhaustive study of the complex physical and chemical processes governing metal behavior in the system we were able to achieve the goals we had set.

Our objectives in this report are to:

1) briefly review the most significant and relevant research reported in the literature on toxic metals in parking-lot runoff;

2) describe the physical attributes of the study area, explain the approach used in the project, and discuss the rationale for the methods employed;

3) determine the overall metal-removal efficiency of the OGC retention ponds throughout the seasonal variation in precipitation typical of the Pacific Northwest;

4) describe the spatial and temporal patterns of accumulation of a model heavy metal (Cu) in the sediments of the OGC runoff-retention ponds;

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5) examine pond sediments as a possible *source* of heavy-metal pollutants for the receiving waters;

6) address the feasibility of designing retention ponds expressly for the purpose of reducing the discharge of priority-pollutant metals from parking facilities and other impervious structures.

BACKGROUND AND RELATED RESEARCH

Although treatment of point-source wastes has improved the quality of many major rivers in recent years, small streams draining urban areas have continued to decline in quality, a decline that is almost entirely attributable to non-point-source runoff [Brown and Green 1980; Cole et al. 1984; McConnell 1980]. Heavy metals appear to be the most important toxic substances of a suite of contaminants found in urban runoff [Cole et al.1984] and most of the metals are attributable to automobile activity [Pitt and Bozeman 1980]. In addition to possible human health effects, metals in runoff seriously damage natural populations of algae and aquatic animals [Jones and Redfield 1984; Madeiros et al. 1984]. Suburban areas often have serious runoff contamination from large paved parking lots that are remote from any centralized collection and treatment system. These parking lots collect heavy metals from oil and gas drippings, exhaust emissions, rust, debris from tires, brakes, metal and rubber mechanical components, disintegrating vehicle bodies, mud and dust attached to vehicles [Pitt and Bozeman 1980] as well as collecting pollutants from air and rainfall [Halverson et al. 1984]. A study of a shopping mall parking lot [Owe et al. 1982] revealed Pb, Zn, and Cu concentrations in runoff in the range of 1 - 3 ppm, and Cd up to 0.3 ppm, levels that are acutely toxic to aquatic biota and an order of magnitude or more greater than maximum permitted levels in drinking water.

So-called "low-structural" management practices such as small detention ponds often have been advocated as the most cost-effective control strategy

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for urban runoff [Finnemore and Lynard 1982] but these ponds are primarily designed to reduce peak runoffs and thereby minimize the impact of pulses of suspended solids and BOD in receiving streams [Griffin et al. 1980]. Such ponds are frequently misapplied as a solution to all aspects of runoff pollution [Jones and Jones 1984]. In particular, detention ponds are likely to be ineffective at removing very fine particles unless long retention times are designed. It is well known that metals in aquatic systems are primarily associated with particles [Santschi 1984; Baccini 1984] and that the amount of metals bound to particles varies inversely with grain size: the smallest particles contain the greatest proportion of metals [Horowitz and Elrick 1984]. This also is true in urban runoff. Sartor and Boyd [1972] studied particle transport across paved surfaces and found the largest percentage of the total heavy metals (28%) in the smallest particle-size range (< 43 μm). It also was observed that the smallest particles were carried across surfaces much faster than large ones and that the smallest particles moved rather independently of the surface type or rainfall intensity. Thus, even small rainfall events may be important in transporting metals since the smallest particles contain the highest concentrations of metals. In addition, metals are an example of contaminants that are not only "acute" pollutants (like excess BOD), but also have impacts that are cumulative over time as they build up in the sediments and the aquatic biota. Thus, reducing the peak of flow intensity by a retention basin may not, by itself, eliminate the impact to the receiving stream. Finally, metals in both particulate and dissolved forms tend to build up in surface slicks and microlayers [Armstrong and Elzerman 1984; Elzerman 1982; McNaught 1982; Pellenbarg 1981]. Surface films will tend to carry heavy metals out of a detention basin.

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Although many studies have documented the presence of heavy metals in parking lot runoff, very few investigations have been made of the effectiveness of retention ponds in reducing metal inputs to streams. While ponds are not currently designed for metal removal, it is known that long retention times allow metal-bearing particles to coagulate and settle out [Randall et al. 1981; Santschi 1984]. Thus it may be possible to design cost-effective ponds that would remove metals during times of low hydraulic loading, i.e., during periods of intermittent rain, or during extended periods of low-intensity rain. The maritime Northwest is an area where such precipitation patterns tend to dominate, in contrast to the high-intensity convective storms and snowmelt runoff of other regions. Therefore it was important to quantitatively investigate the feasibility of using detention ponds to mitigate heavy metal contamination in this region.

2. METHODS AND PROCEDURES

STUDY AREA: OGC RUNOFF-RETENTION PONDS

The study area was a connected series of three retention ponds, constructed on the campus of the Oregon Graduate Center (OGC) in December 1986 (Fig. 1). OGC is located in a suburban/rural setting west of Beaverton, Oregon and 11 miles west of downtown Portland. The ponds receive runoff from a catchment area of 43,546 m². About 65% of this area is paved parking lots, roofs of building, and other impervious surfaces. Parking lots constitute 33% of the total catchment and 52% of the impervious surfaces. The parking lots are used daily by approximately 500 automobiles and delivery trucks. The pervious areas are vegetated and largely enclosed by curbing so contribute little to overland runoff. The ponds have only about 3,000 m² of "natural" adjacent watershed and most of this is pervious lawn with little direct runoff to the ponds. The areas of various catchment surfaces were obtained by digitizing construction maps of the area (Table 1).

Table 1. *Catchment areas for the OGC runoff-retention ponds, broken down by surface category.*

Category	Surface Area (m²)	% of Total Area
Roofs: Bldg. D2	4,202	9.6%
Bldg. D3	4,223	9.7%
Bldg. D4 (NW section)	1,517	3.5%
Subtotal: roofs	9,942	22.8%
Streets:	3,424	7.9%
Parking Lots:	14,282	32.8%
Subtotal: Impervious Area	27,648	63.5%
Vegetation	15,898	36.5%
TOTAL CATCHMENT AREA	43,546	100.0%
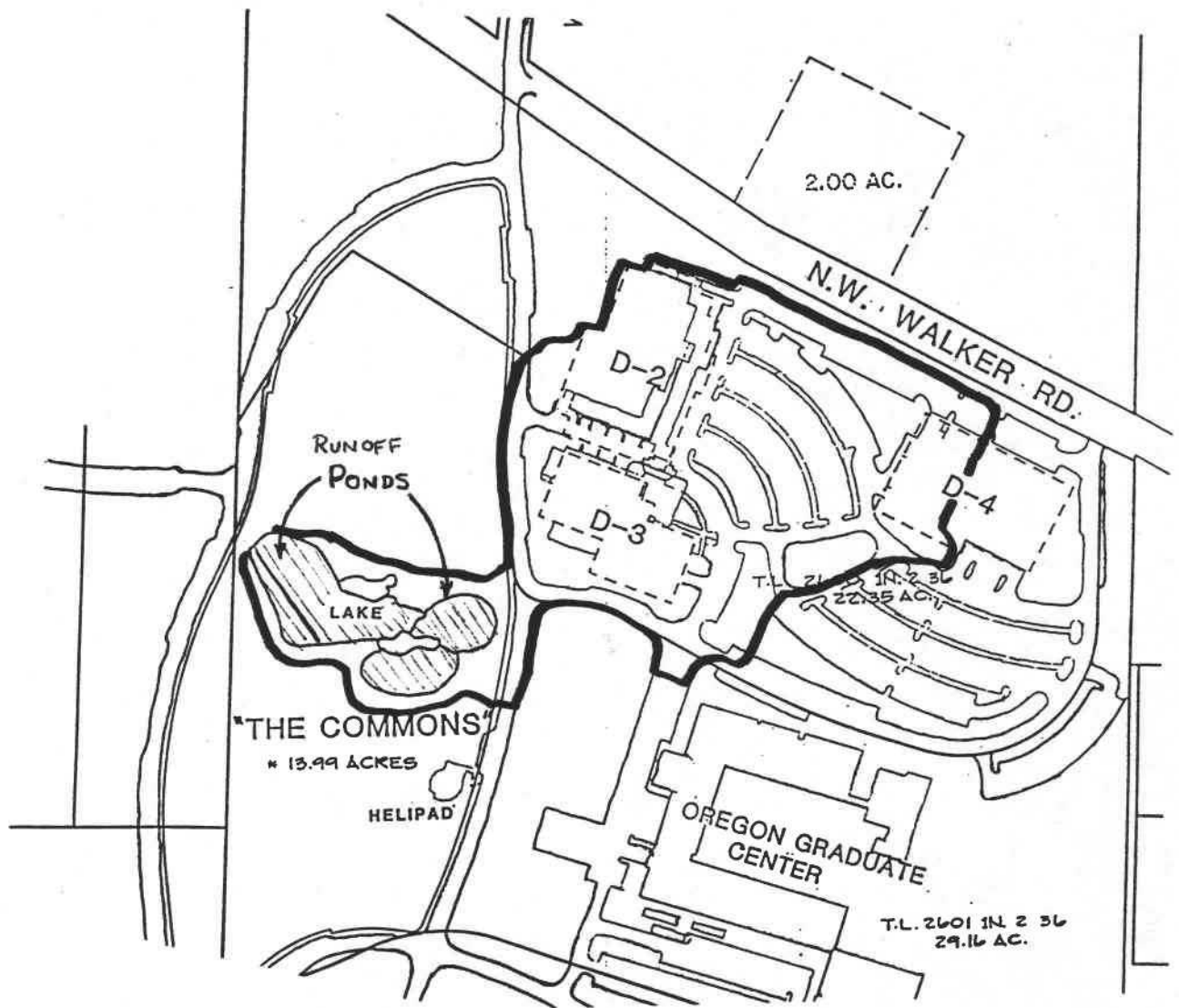
Fig. 1. Map of the catchment of the OGC runoff-retention pond system showing parking lots and other impervious areas. The catchment is outlined with a dark line.

The ponds discharge into a small stream which flows for approximately 0.5 km before entering Rock Creek. Rock Creek is a fourth-order stream and is a tributary of the Tualatin River.

All runoff is channelled into Pond B and flows over small artificial-rock "weirs" into Pond C (Fig. 2). The ponds are designed to serve an aesthetic function, as well as for hydraulic retention, and therefore have small fountains and pumped recirculation. Water is withdrawn from just below the weirs in Pond C at 75 m^3/h and pumped up to a small fountain and a submerged outlet in the center of Pond A. From Pond A it returns both to Ponds B and C but the pump inlet near the entrance of Pond C probably intercepts most of the return-flow (see Fig. 3). Therefore, Ponds A and B are always slowly recirculated (at approximately one pond-volume per day) whereas most of Pond C is relatively quiescent except for the runoff flowing through the system.
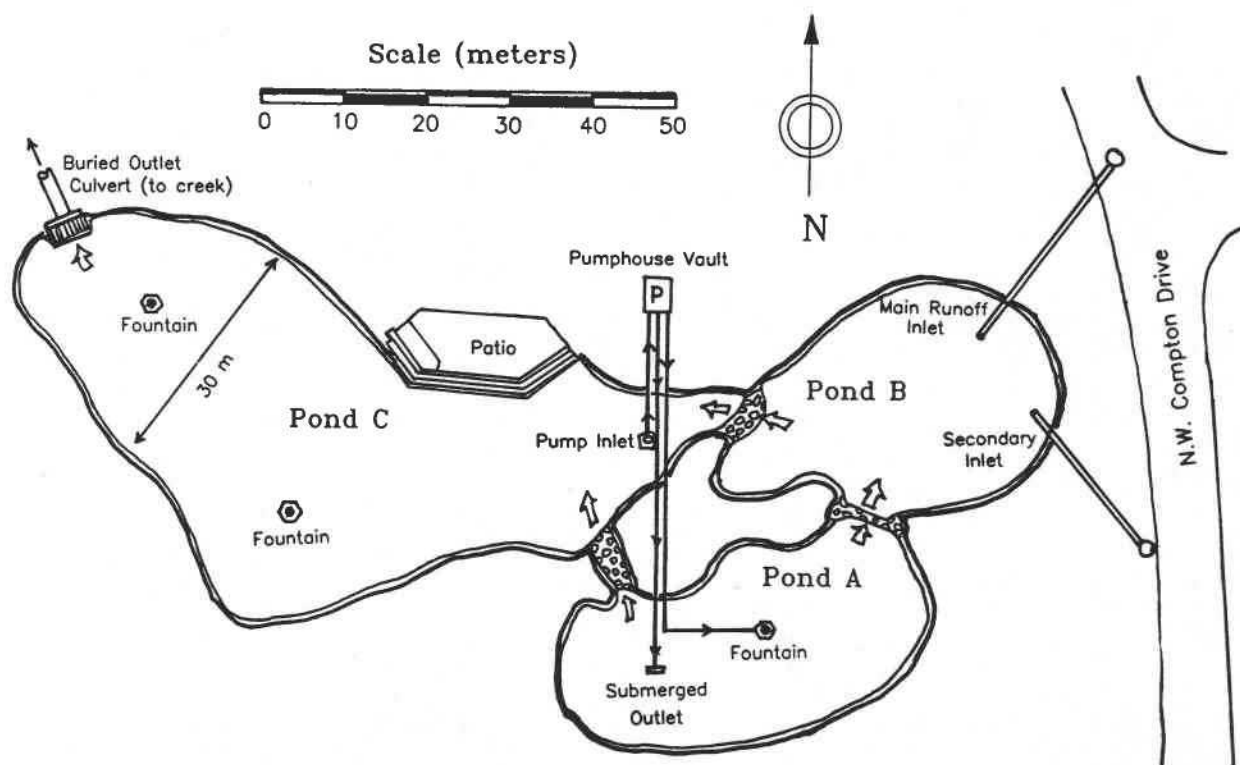
Fig. 2. Map of the OGC runoff-retention ponds. Main inlet receives nearly all of the runoff; secondary inlet drains only a few hundred meters of Compton Drive.

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Pond C does have two vertical fountains but the inlets are at the base of the outlets, and therefore these fountains serve mostly to aerate the water rather than effect complete mixing (Fig. 3). All piping in the pumped system is PVC plastic.
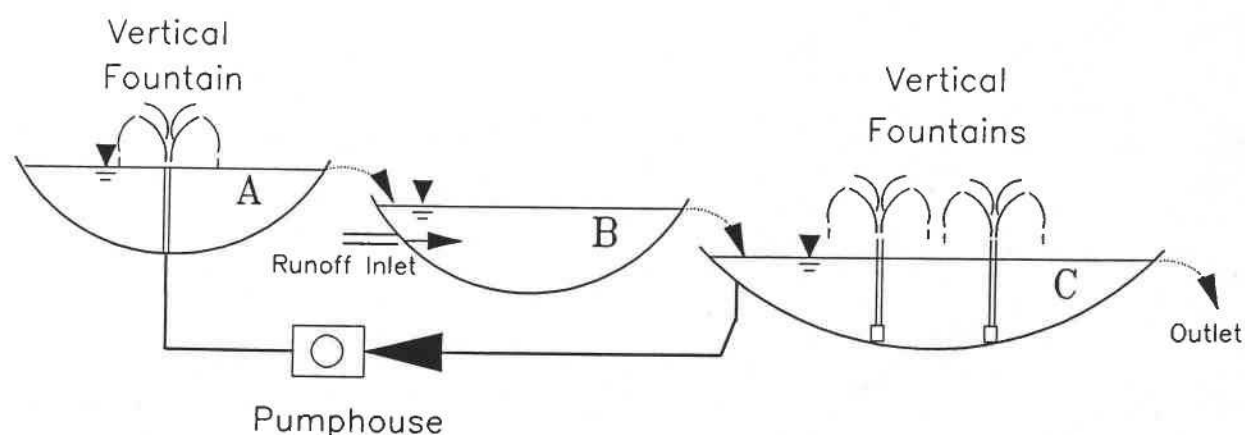
Fig. 3. *Side-view of the pond system showing the pumped recirculation system. Direct connection between Ponds A and C omitted for clarity.*

Ponds A and B are roughly circular with diameters of about 30 m. Pond C is oblong, averages about 30 m wide and 80 m long. The area, depth, and volume data for the ponds were calculated from digitizing architectural plans and are presented in Table 2.

We can define an approximate hydraulic residence time as the pond volume divided by the volumetric flow rate. The calculation is approximate because the runoff hydrograph tends to integrate and time-lag the small-time-scale variations in rainfall intensity so that runoff-inflow does not instantaneously mirror the rainfall intensity. For practical purposes we use rainfall inten-

Table 2. *Physical dimensions of the OGC runoff-retention ponds. "Low" surface elevations are the minimum for no-flow conditions, "High" elevations are for the maximum design capacity of water. Elevations are in feet above mean sea level. Volume given is for the no-flow condition, which is close to the average water-level observed.*

Pond	Surface Area (m²)	Volume (m³)	Surface Elev. (ft)		Maximum Depth (m)
A	895	1,130		193.00	1.83
B	821	905	Low -	190.21	1.83
			High-	190.46	
C	2,786	4,520	Low -	188.00	2.44
			High-	190.46	

sities that are averaged over a period of many hours as estimators of volumetric input flow rate. We can relate the approximate hydraulic residence time (T_r in h) to average rainfall intensity (I in cm/h) for a total impervious catchment area (A_{iT} in m^2) and a total pond volume of V (in m3) by the equation $T_r = V / (A_{iT} \times I \times 10^{-2})$. So, for example, a rainfall of one inch (2.54 cm) in 24 h yields T_r = 224 h (9.3 days) for the OGC system.

For individual ponds, the pumped recirculation complicates the calculation (and the physical meaning) of hydraulic residence times. Because Pond A receives no direct input, its T_r is fixed by the fountain pump rate at a constant 14.6 h. Thus the volume of Pond A is recirculated roughly 1.5 times a day. Residence times for Pond B are a result of both pumping and runoff input. Under no-input conditions (pumped flow only), T_r for Pond B is 23.4 h. Rainfall input decreases this residence time. At an average rainfall intensity of 3.4 cm/day (1.3 in/day) the input flow equals the pumped flow and the residence time is halved to 11.7 h. Note that under no-input conditions Ponds A and B together are essentially a closed, slowly recirculating system, and collectively have an infinite hydraulic residence time. Pond C

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is not significantly recirculated to other ponds and its residence time depends only on the flow rate of runoff passing through the system.

One additional complication that prevents an exact calculation of residence times is the apparent input of ground water as "base flow" to the ponds. This seems to occur only after prolonged rain events and is evidenced by a continued, slow outflow from the system for a week or more after the end of such a rain event. Apparently the local water table south of the ponds rises above the level of at least the lowest pond (Pond C) after prolonged rain. We were not equipped to sample or accurately measure this periodic base flow but we estimated that it contributes on the order of 10% to the total input of water to the ponds during the rainy season. We believe the base flow is probably a negligible source of heavy metals, but it may be a significant source of nutrients derived from lawn fertilizer and is a potential source of pesticides.

The OGC pond system was advantageous for a detailed study of heavy metal behavior in retention ponds. The catchment is well defined and consists of only impervious surfaces that are entirely on the property of the Graduate Center. The prime inputs of pollution to the catchment are restricted to automotive sources, air pollutants, and rain contaminants. Access is guaranteed at all times and the proximity of the ponds to laboratories meant that samples could be immediately size-fractionated and analyzed. This minimized artifacts due to storage and transport to the laboratory, and logistically was far easier than attempting on-site sample analysis at a remote location. Because the ponds were newly constructed, there was minimal accumulation of sediments by the onset of the project in Summer 1987. This greatly simplified interpretation of sediment data acquired in the following study year.

FIELD SAMPLE COLLECTION

Water was sampled from two depths (surface and near-bottom) at single locations near the centers of Ponds A and B, and at two locations in Pond C, termed C-east (C_e) and C-west (C_w). Sediment samples were collected from the same locations as the pond water samples. Triplicate samples were collected for all times and locations. The sampling "stations" were marked by lengths of polypropylene rope tethered to the bottom by a small concrete pier (patio or deck support pier) and held near the surface by plastic fishing floats. Samples were taken from a plastic inflatable two-person boat. The boat was maintained in position in the pond by tying up to the marker rope. For a special, detailed sampling of Pond B in the spring, sediments at eleven different locations within the pond were sampled, as is described in the Results and Discussion section below.

Surface pond samples were obtained by hand-filling 125-mL polypropylene bottles just below the surface. Depth samples in the ponds were collected using polypropylene bottles attached to a plastic extendable wand. The bottle was closed with a cork connected to a length of nylon monofilament line. The apparatus was lowered to just above the pond bottom and the cork pulled by a tug on the monofilament line. The bottle was narrow-mouthed and was quickly returned to the surface so very little mixing of water in the bottle occurred with near-surface water. All sample bottles were acid-washed.

Sediment samples were taken with a spring-jawed bottom-sampling dredge. The dredge was approximately 30 cm wide with a cylindrical diameter of 10 cm. It was constructed entirely of brass but was painted with epoxy paint to isolate any metal from the sample. The dredge was opened into a glass tray and funneled into a sample bottle for temporary storage. Each sediment sample was thus a homogenized average of the top ~10 cm of the sediments.

In addition to pond samples, samples were taken of influent water entering Pond B from the catchment, effluent water discharging from Pond C after a storm event, and water discharging into the receiving stream after passing through a 100 m concrete culvert. Influent and effluent discharges were collected with a length of Tygon tubing attached to a hand-cranked peristaltic pump, or in some cases, by grab-sampling with a polypropylene bottle.

Two different temporal sampling patterns were conducted, depending on the weather. In August through October there was essentially no rain so three samplings were made to collect baseline data on the status of the ponds after a summer period of little runoff input. In these samplings, no influent or effluent water samples could be taken but water and sediment samples were collected. In September a single significant rainfall event occurred. With this event we began a sampling pattern used several times in the fall and winter. The sampling pattern centered around each rain event. Water and sediment samples were taken, if possible, prior to the event. Influent and effluent samples were taken within a few hours of the beginning of the event. Several influent samples were taken to provide a time-series of samples of the input of pollutants to the ponds. Just after the conclusion of the event, water and sediment sample were taken with the boat and additional effluent samples were taken. Water, sediment,and effluent samples were taken on the following day, and again two or three days later.

SAMPLE PREPARATION

Within one or two hours of collection, water samples of either 50 mL or 100 mL were vacuum-filtered through acid-washed Whatman GFC glass-fiber filters (25 mm diam.), with a nominal particle-size cutoff of 1.2 μm. The filters were retained and extracted as described below for the sediment samples.

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Filtered water samples were then placed in 125 mL acid-washed polypropylene bottles, acidified with 100 μL of SupraPur concentrated nitric acid (EM Science) and stored in a cold room at 4°C for later analysis (Fig. 4).

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┌──────────────┐              ┌──────────────────┐
│ WATER SAMPLE │              │ SEDIMENT SAMPLE  │
└──────┬───────┘              └────────┬─────────┘
       │                               │
┌──────┴─────────────┐        ┌────────┴──────────┐
│ FILTRATION(100ml)  │        │   WET SIEVING     │
│ 1.2 μm fiber glass │        │ 63 μm & 125 μm    │
└──────┬─────────────┘        └────────┬──────────┘
       │                               │
       │                      ┌────────┴──────────┐
       │                      │ DRYING at 50-60 ℃ │
       │                      └────────┬──────────┘
  ┌────┴────┐  ┌──────────┐  ┌─────────┴──┐ ┌──────────────┐
  │"soluble │  │particulate│  │fraction<63 │ │ fraction<125 │
  │ phase"  │  │  phase   │  └─────────┬──┘ └──────┬───────┘
  └────┬────┘  └────┬─────┘            │           │
       │            │        ┌─────────┴───────────┴──┐
       │            └───────→│      DIGESTION         │
       │                     │ HNO3/H2O2/NH4ac        │
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       │                          ┌──────┴──────┐
       │                          │ CENTRIFUGE  │
       │                          └──────┬──────┘
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       └────────→│ AAS  │←───────────────┘
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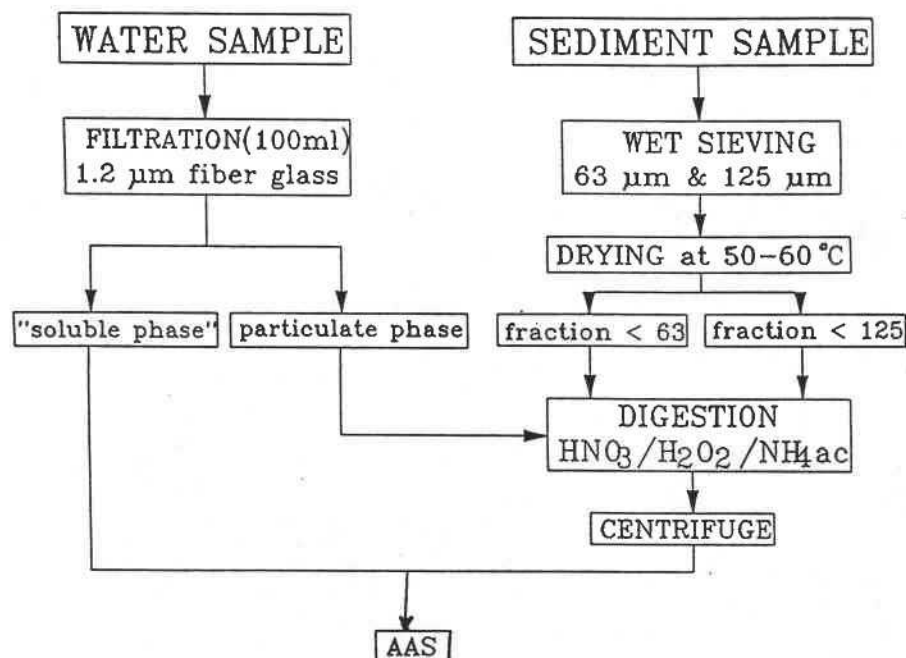
Fig. 4. *Sample-handling protocol for all types of samples.*

Sediments were stored initially in polypropylene bottles. Within the same day as sampling, each sediment sample was wet-sieved into three size fractions using sieves constructed of 8-cm diameter acrylic rings fitted with polyester mesh of 125 μm and 63 μm effective pore diameters (Gilson, Inc.). These sizes correspond to the standard particle-size cutoff diameters for fine sand and silt respectively. The fractions with grain sizes $d < 63$ μm (silt and clay) and $d < 125$ μm (clay, silt, fine sand) were retained. Fractionated samples were transferred to watch glasses and dried in an oven at 50-60°C. Each dried sample was scraped off the glass and 50-100 mg were weighed out and transferred to a polypropylene snap-cap microcentrifuge tube.

The sediment sample (or filter) was extracted overnight at room temperature in 0.5 mL of 30% hydrogen peroxide and 0.5 mL of 6.5% M nitric acid (SupraPur, EM Science). After centrifugation for 5 min at 13,000 rpm the supernatants of all extracted samples were diluted tenfold with 0.1 M ammonium acetate (Fig. 4).

This extraction procedure liberated most of the metal bound to particles by sorption to iron or manganese oxides, clay or aluminum oxide surfaces, organic matter, or precipitated as carbonate or phosphate minerals. The procedure was a modification of the standard method used for sediments by the U.S. Geological Survey and was based on the methods of Ulrich Förstner [see for example Kersten and Förstner 1986]. Because all such extractions are operationally defined, we systematically varied the extraction time and the solids-to-extractant ratio in order to more fully characterize the scheme we employed. This study is described in the Results and Discussion below.

ANALYTICAL METHODS

Metals in all samples were analyzed using a Varian Techtron atomic absorption spectrophotometer (AAS) in either an air-acetylene flame (for sediment digestates) or with a Varian Model 63 graphite furnace (for the greater sensitivity required by particulate and dissolved samples). All samples were analyzed for Cu. Selected samples were analyzed for Pb and Cd. Water samples were analyzed directly in the graphite furnace AAS. Sediment and particulate samples were first extracted according to the protocol described above and diluted to a satisfactory concentration range with 0.1 M ammonium acetate/0.6% HNO_3. Ammonium acetate minimized major-ion interferences in the graphite-furnace atomization procedure, in part because it allowed Na^+ and Cl^- ions to be volatilized in the ashing step as ammonium chloride and sodium acetate.

3. RESULTS AND DISCUSSION

METALS IN RUNOFF AND IN POND EFFLUENTS

Dissolved Metals

Dissolved metals, as operationally defined by the filtration process, were measured in the water entering and leaving the ponds from late summer through early winter. Most Cu in the water was dissolved and the dissolved concentrations of this metal were studied in detail throughout the sampling program. Selected samples early in the program were analyzed for dissolved Pb and Cd, metals which were found to be more predominantly associated with solid phases. Triplicate analyses of dissolved metals exhibited very little variance and the standard error was almost always less than 10%. Thus, error bars have been omitted from the graphs of dissolved metals for the sake of visual clarity.
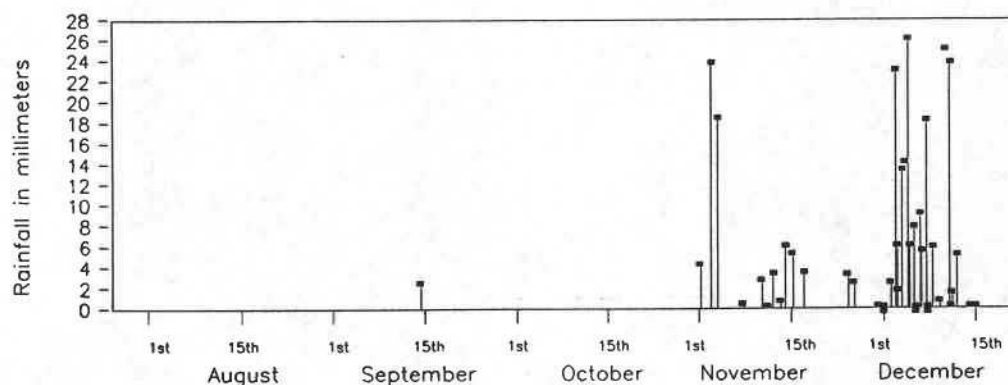
Fig. 5.   *Rainfall data for the Oregon Graduate Center study area. Data was collected on site daily with a standard rain gauge.*

Metal concentrations in runoff water were especially high during the first storm event of the fall season and declined during the rest of the sampling campaign. As shown in Fig. 5, the first significant rain event of late summer 1987 occurred on September 14. Although the total rainfall was

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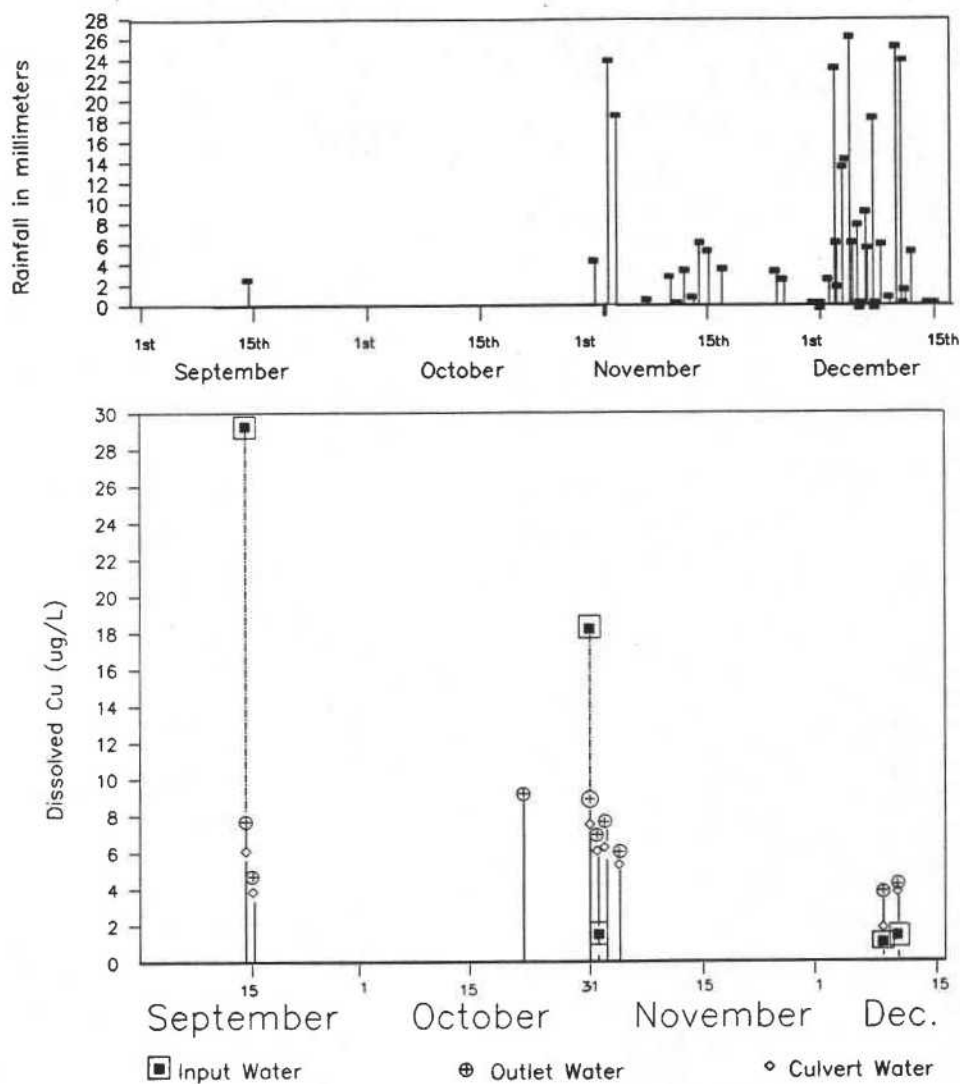
Fig. 6. *Concentrations of dissolved Cu in water from the main inlet (input), from the outlet from Pond C, and from the end of the culvert discharging into the receiving stream.*

only 3 mm, the duration was short and the intensity of the storm was correspondingly high. A grab-sample taken at the end of this storm contained dissolved concentrations of Cu at 29.3 μg/L, Pb at 1.2 μg/L, and Cd at 3.0 μg/L (Fig. 6). These levels were the highest observed in any water samples during the project and presumably reflect the wash-off of several months of accumulated pollutants in the catchment area.

Several studies made in other climates suggest that the time between rain events, if longer than about two weeks, does not affect the concentration of metals in runoff. However our findings indicate that the almost rain-free late-summer of 1987 allowed sufficient metals to accumulate such that the "first flush" of the season produced a concentrated pulse of pollution. A long dry spell followed by strong rain is not unusual in the maritime Northwest and is comparable to weather all along the Pacific coast. Hence, a concentrated pulse of runoff metal pollution in the first storms of fall or winter may be common in the far west of the United States.

The concentrations of metals in the outlet from the ponds and at the culvert entering the receiving stream were 73% - 98% lower than in the input of runoff to the ponds (Table 3). This is a natural consequence of the relatively large pond volume and hydraulic residence time. As will be shown later, the input of metals was diluted in the ponds, but also was diminished by relatively rapid removal to the sediments. Effluent continued to flow for about a day after the 9/14 storm and effluent samples taken on 9/15 show uniformly lower dissolved metals than at the end of the storm.

We suspected that most of the metals in the runoff would be associated with the particulate phase. Of the metals analyzed, Cd and especially Pb were mostly bound to particles on a total concentration basis. In contrast, Cu was primarily found in the (operationally defined) dissolved state.

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Table 3. *Dissolved and particulate concentrations of Cu, Pb and Cd in the inputs and outputs of the OGC runoff retention ponds. There was no runoff (input) on Sept. 15. All concentrations are in µg/L.*

	Inlet		Outlet	
	Dissolved	Particulate	Dissolved	Particulate
Sept. 14				
Cu	29.3	3.5	7.7	3.8
Pb	1.2	9.2	<0.1	0.2
Cd	3.0	4.4	0.12	0.16
Sept. 15				
Cu	n.a.	n.a.	4.7	<0.1
Pb	n.a.	n.a.	0.1	0.8
Cd	n.a.	n.a.	<0.01	0.02

In the 9/14 runoff influent, dissolved Cu was 90% of the total Cu, dissolved Cd was 40% of total Cd, and dissolved Pb was only about 10% of total Pb (Table 3.). These ratios were of comparable magnitude to those in the effluents from the ponds and in water samples taken from the ponds.

After a period of immeasurably-low drizzle in mid-October a small outflow was observed at the Pond C outlet and a sample was taken on 10/22 for Cu analysis. No significant parking-lot runoff was observed during this period and the outflow probably stemmed from direct input of rain and perhaps a small amount of baseflow. Dissolved Cu was 9.2 µg/L, which was about twice the level of the 9/15 sample and 20% higher than the 9/14 sample. As will be shown later for the samples from Pond C itself, dissolved Cu generally diminished in the water column in the period following the pulse-input from the 9/14 storm. The apparent increase in effluent Cu probably results from

the initial expulsion of relatively clean water from Pond C during and immediately after the 9/14 storm, giving low Cu values. After the mixing and equilibration of the ponds, the 10/22 effluent was higher by comparison, even though the Cu levels in the ponds were gradually decreasing in the period between samples.

Cu concentrations were monitored in the influent and effluent during and following a major storm on October 31-November 2 (termed the "11/1 storm"). A graphical summary of the input/outlet Cu data for this and the other two storms monitored in 1987 is presented in Fig. 6. As with the 9/14 storm, the 11/1 storm produced a pulse of elevated Cu in the input runoff. The value of 18.2 μg/L measured near the beginning of the storm on 10/31 (during the first strong flushing of runoff) was about 40% lower than that of the first storm of the season. Note however that the total rainfall was 47 mm, over fifteen times the volume of the 9/14 event. Because of the greatly increased runoff, the total mass of metals added to the ponds during the 11/1 storm was probably larger than from the 9/14 event, although an exact mass calculation is not possible without nearly continuous data and sample collection during the event. The lower Cu concentration on 10/31 reflects a greater dilution of the runoff as well as an initially cleaner catchment compared to 9/14. A second sampling, done on the second day of the storm (11/1), revealed that dissolved Cu had declined to less than 2 μg/L. This is typical of large storms: the first flush removes most pollutants within a short time and subsequent runoff is relatively dilute.

Effluent Cu concentrations during and after the 11/1 event closely resembled those of the 9/14 event, both in magnitude and in diminution with time (Fig. 6). The initial value at 8.9 μg/L was almost identical to the

prior sample taken on 10/22, reflecting a fairly stable concentration in the ponds. As before, the effluent Cu declined in the period following the storm.

Mid-November brought a series of weak rain events without distinct intervening dry periods. We did not attempt to sample during this time because a single event could not be clearly isolated, as was possible in earlier fall, and the weather was not yet fully characteristic of winter. Instead we waited until December in order to sample a storm that was well into the winter pattern of strong, frequent rains. On December 9, after a period of two days with little rain, a major two-day event deposited 48 mm of rain. Rain on the following four days was 5.2 mm, 0.2 mm, 0 mm, and 0.2 mm. Thus the "12/9 storm" was reasonably isolated as a discrete event, but followed a two-week period of heavy winter-type rains.

Samples taken on the morning of 12/10 at the height of the storm exhibited low dissolved Cu at 1.0 μg/L. This increased insignificantly to 1.4 μg/L on the following day. Effluent concentrations on these days actually *exceeded* the input concentrations. Dissolved Cu at around 4 μg/L on both days again reflected the relatively stable, but gradually declining Cu in the pond system. In this circumstance of low input levels, the buffering effects of the ponds caused them to become, in a sense, a source of Cu relative to the highly dilute runoff. Thus, while the ponds provide a valuable reduction in peak loadings of pollutants, they store metals rather than eliminate them from the system, and in fact contribute some of this stored material to the receiving waters in the form of desorbed or resuspended material. This has the net effect of flattening the peak fluxes of metals from the catchment, but also can elevate the minimum fluxes during the winter wet season.

Particulate Metals

Particulate metals were obtained by digestion of filters with a nominal size cutoff of 1.2 μm, as described above. In contrast to the high precision of the dissolved-metal measurements, particulate-metal analyses showed a wide range of values among most sets of triplicates. Our samples always had relatively low concentrations of suspended solids and apparently the heterogeneous distribution of particles in dilute suspension induced sampling variability. As a result it is more difficult to discern trends or statistically significant differences among the particulate-metal data. This was another reason for focusing primarily on the behavior of Cu which largely was present in the more precisely measured dissolved state. In all of the accompanying figures, vertical bars representing the range of measured values are shown bracketing the mean data points.

As discussed above, particles in the input runoff and outlet flow from the 9/14 event contained only about 10% of the total Cu, but most of the Pb and Cd (Table 3). Reliable particulate-metal data could not be obtained for the 11/1 storm so a detailed sampling was made of input and outlet water for particulate Cu during a series of storm events from December 1 to December 10. These storms were preceded by a four-week period of intermittent light rain and drizzle, as described above. The inlet concentrations of particulate Cu are not especially high at any point during the sampling (Fig. 7) and are only slightly higher than the outlet levels. This approximated the behavior of dissolved Cu during the protracted rainy period in December and confirms the conclusion that the inputs of runoff metals by early December had dramatically diminished in intensity compared to the first storms of late summer and early fall. Although somewhat lower in the outlet compared to the input, particulate Cu was at comparable levels in both the inlet and outlet flows,

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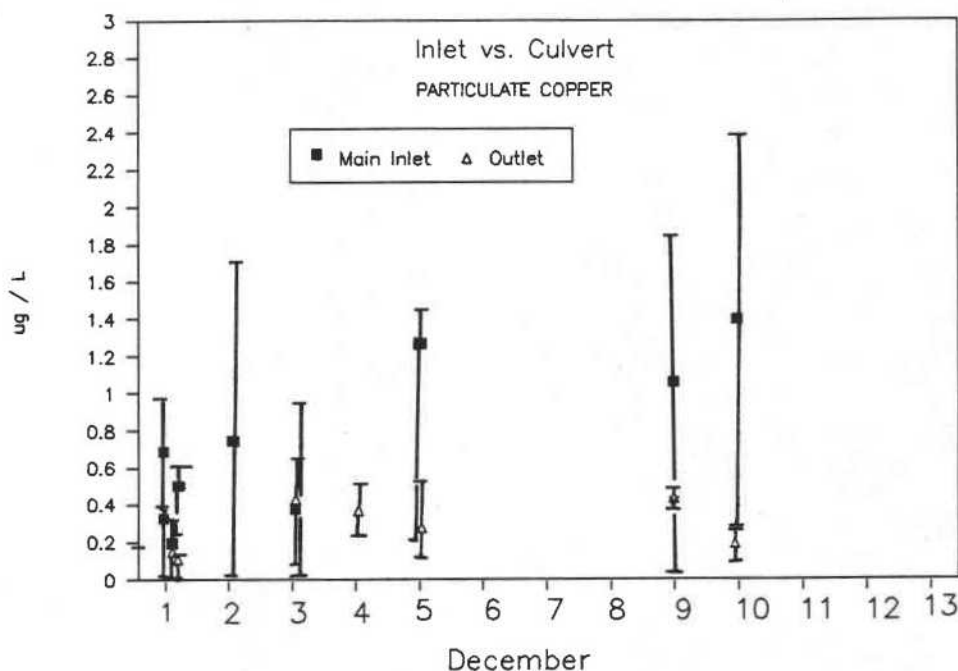
Fig. 7. *Particulate Cu in the main runoff inlet and in the outlet water from Pond C.*

indicating that the ponds did not substantially reduce the already low, mid-winter fluxes of metals to the receiving stream.

Particulate Cu was sampled at both the outlet from Pond C and approximately 100 m downstream at the point the culvert entered the receiving stream. As shown in Fig. 8, no significant differences were noted at these two points although the initial flow from the culvert may have been enriched with Cu due to a flushing of particles settled within the culvert. In later samples, the output from the culvert appears to be slightly lower in particulate Cu than the input to the culvert from Pond C. A small amount of particle sedimentation may occur within the culvert during moderate flows but this accumulated matter is probably washed out in large storm flows.

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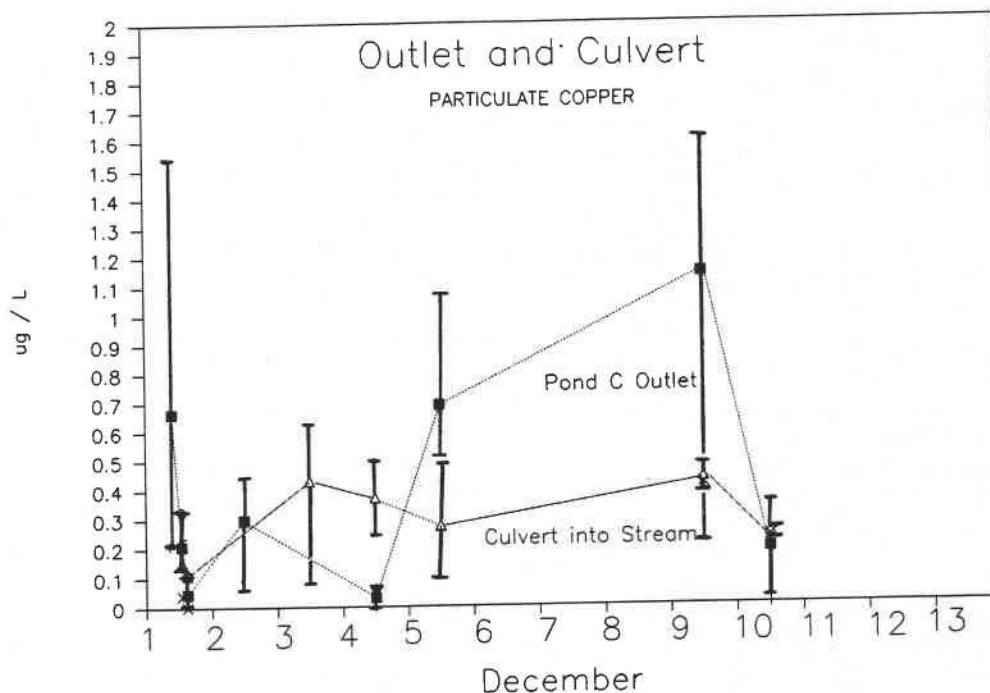
Fig. 8. *Particulate Cu in the outlet water from Pond C and at the end of the culvert entering the receiving stream.*

METALS WITHIN THE RETENTION PONDS

Dissolved Metals

Dissolved Pb and Cd were very low in all samples taken from the ponds and were most often below the detection limits (i.e., Cd < 0.05 μg/L, Pb < 0.5 μg/L). Some representative values are presented in Table 4. By comparison, dissolved Cu was greater than 1.0 μg/L in all samples, occurred frequently at 3 - 10 μg/L, and occasionally was as high as 15 μg/L. The time-course profiles of dissolved Cu for Ponds A and B are presented in Figs. 9a and 9b. The samples from the surface (0m depth) have approximately the

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Table 4. *Representative concentrations of dissolved and particulate Pb and Cd in OGC runoff retention ponds. Concentrations are in ug/L.*

| Location	Dissolved		Particulate	
	Pb	Cd	Pb	Cd
Pond A	<0.5	<0.1	0.5	1.1
Pond B	<0.5	<0.1	0.6	0.9
Pond C_e	0.5	<0.1	0.5	0.4
Pond C_w	<0.5	<0.1	0.5	0.2

same Cu concentrations as the samples taken just above the sediments (2m depth) indicating that the ponds were well mixed. The only exception to this pattern is for samples taken during the 9/14 storm in which the surface samples in Pond B have substantially higher Cu than the bottom water. In Fig. 10, the data for both Ponds A and B at both depths is plotted on the same graph to show that, within a certain amount of scatter, the dissolved Cu levels at all four stations are quite similar as a function of time. This confirms our notion that Ponds A and B are essentially a single body of water due to the pumped recirculation through these ponds. The similarity among samples also reflects the relatively high precision and accuracy of the dissolved Cu analyses.

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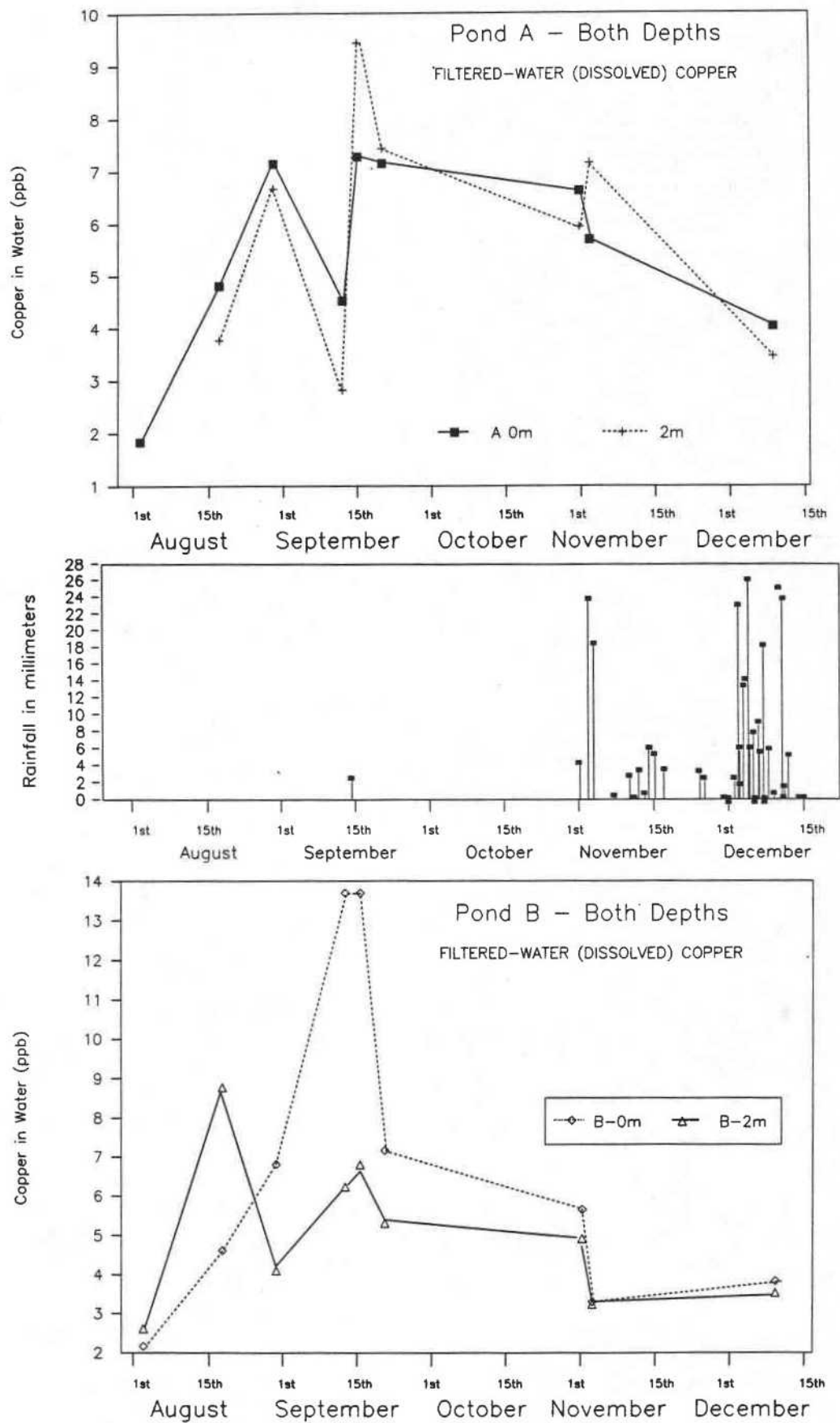
Fig. 9. a) *Dissolved Cu at 0m and 2m depths in Pond A.*
b) *Dissolved Cu at 0m and 2m depths in Pond B.*
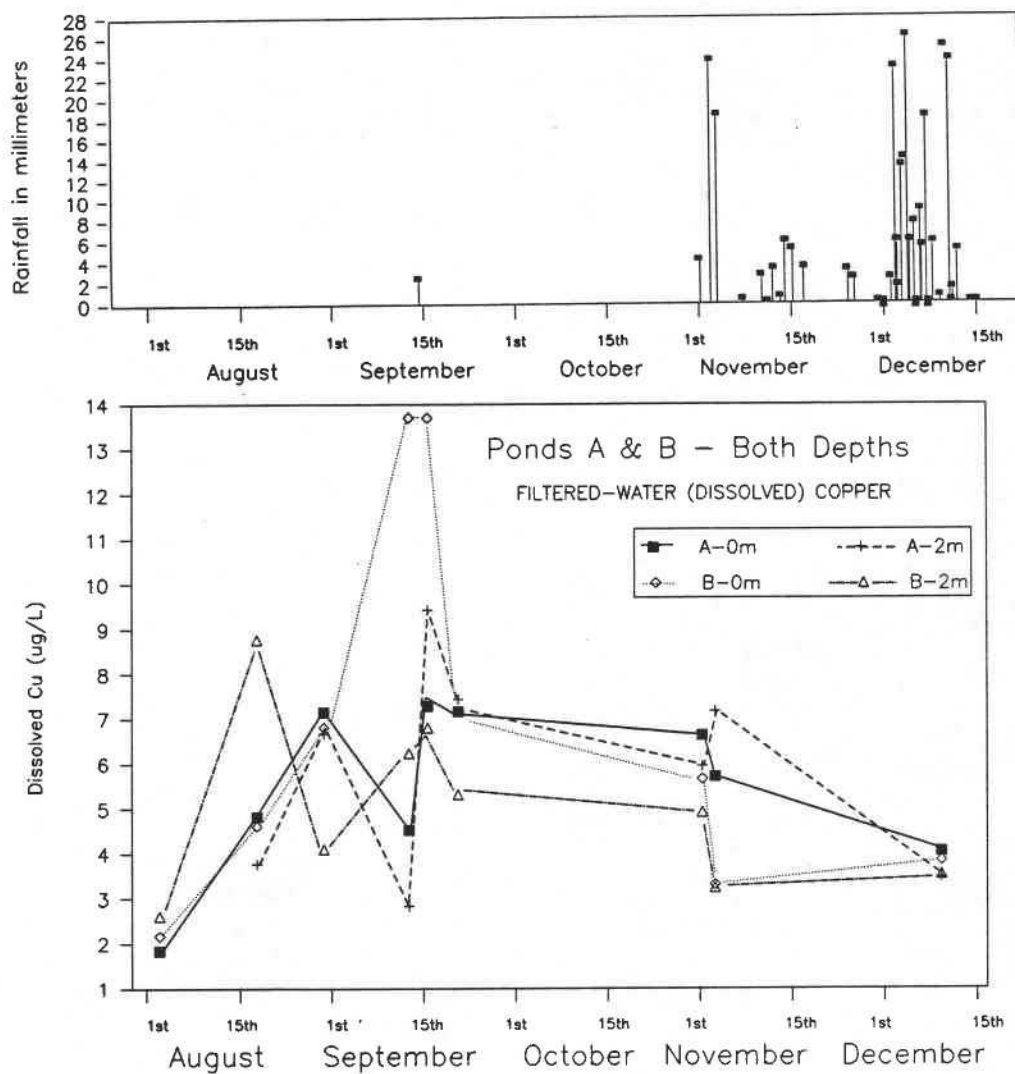
Fig. 10. *Dissolved Cu at 0m and 2m depths in Ponds A and B.*

Dissolved Cu concentrations plotted in Figs. 11a and 11b show that both the east and west sampling stations in Pond C, and both sampling depths at these points, exhibit very similar variations with respect to time. This mirrors the behavior of Cu in Ponds A and B. In fact, a comparative plot of Cu variations in Pond B and in Pond C (Fig. 12) shows that Cu in both ponds follows very much the same pattern during the late-summer to early-winter
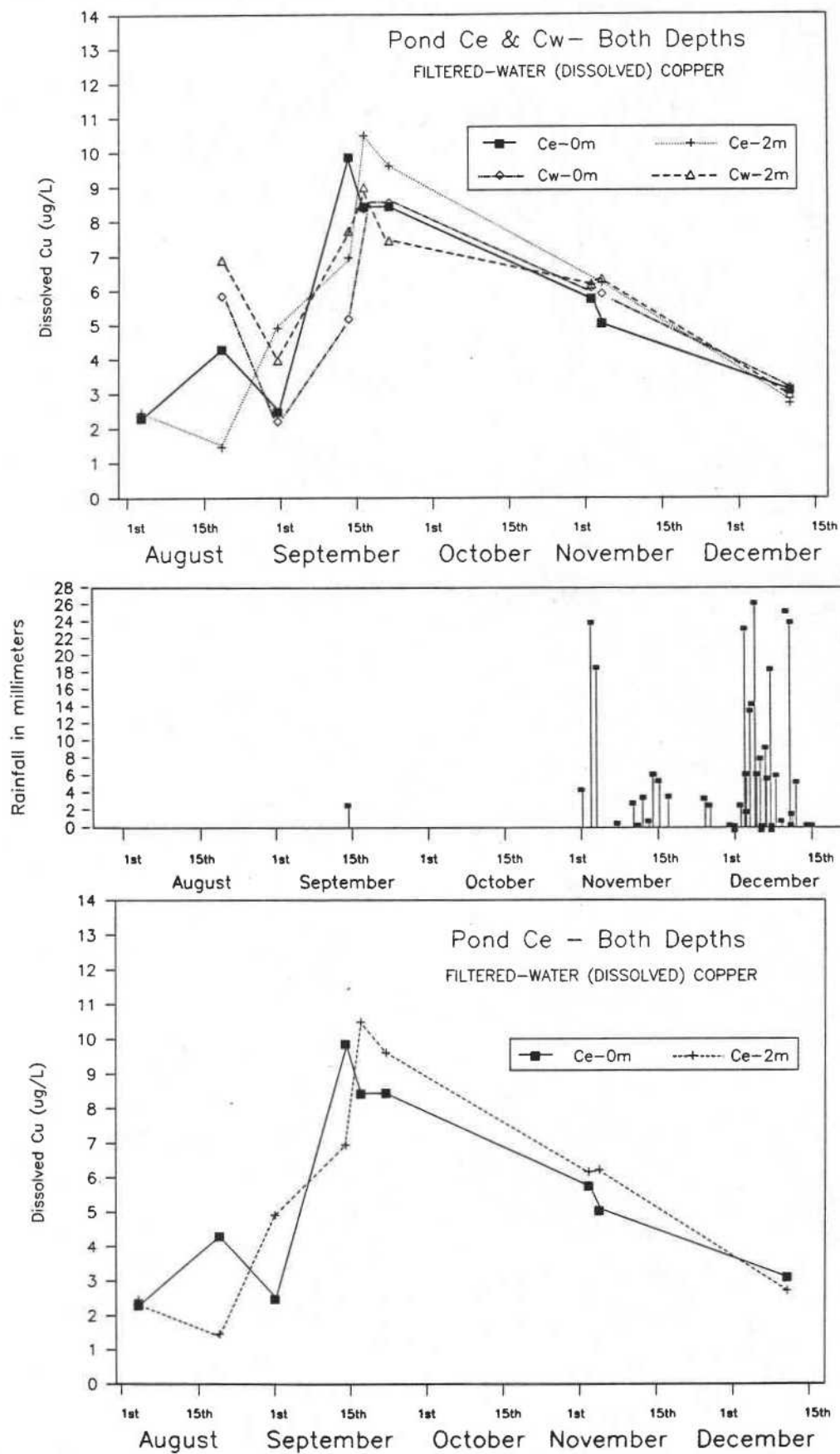
Fig. 11. **a)** *Dissolved Cu in Pond C at the east sampling station* (C_e).
b) *Dissolved Cu in Pond C at the west sampling station* (C_w).
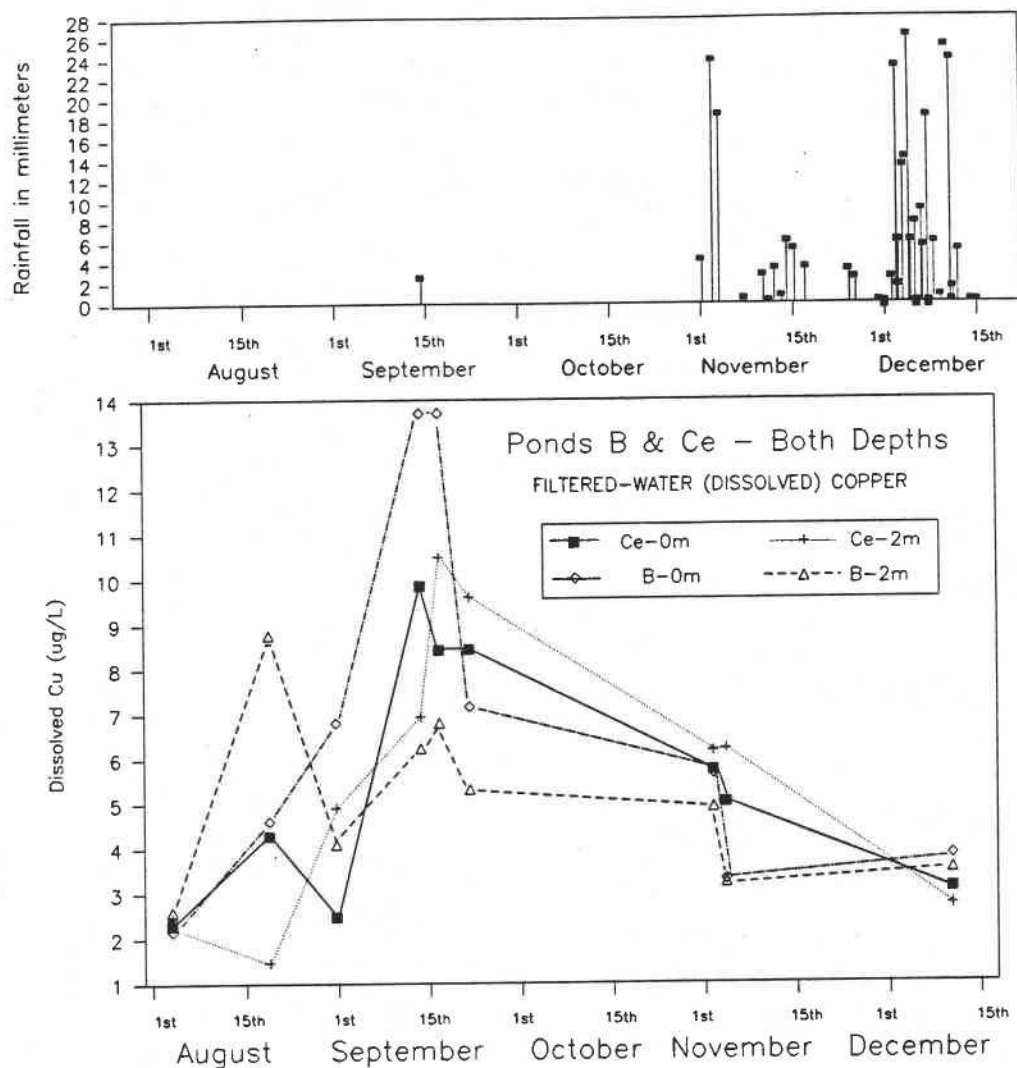
Fig. 12. *Dissolved Cu at 0m and 2m depths in Ponds B and C.*

sampling campaign. Thus, all three ponds are a relatively homogeneous water body with respect to dissolved Cu, and probably are similarly homogeneous for other dissolved components as well. As we will see in a later section of this report, the sediments of the three ponds are fairly *heterogeneous* and there is clearly not a direct correlation between Cu in sediments and Cu in the overlying waters.

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For all three ponds at the first sample-time (8/5), Cu was low in all samples. Concentrations rose significantly by the 8/21 sample-time. At most locations, Cu continued to increase to the 9/1 sampling. This period of increasing Cu in the absence of measurable runoff is not readily explained. However, during this time we observed a substantial surge in the algal population of the ponds; mats of decaying algae were noted. The sediments in Pond B took on a noticeably anaerobic odor, probably due to an accumulation of algal organic matter. We hypothesize that the onset of anoxic sediments in at least Pond B caused the dissolution of ferric oxyhydroxides and manganese oxides in the mineral phase of the sediments. These oxides are strongly adsorbent so the anaerobic dissolution could have liberated previously adsorbed Cu. It is also possible that the decay of the algae directly liberated Cu bound up in the biomass.

Cu concentrations fluctuate somewhat in early September, possibly as a result of cycling through growing and decaying algal biomass. Input from the 9/14 rain caused a pronounced increase in dissolved Cu in all three ponds. Samples from the 11/1 and 12/9 storms show very similar Cu values in all ponds. Thus, the ponds become very homogeneous as the wet season advances. The homogeneity stems from a combination of elevated hydraulic through-put and the enhanced mixing from fall and winter winds. In all samples we note a steady decline in dissolved Cu as the season advances, with levels of only about 3 μg/L in all ponds on December 11. Occasional grab samples taken in the spring (not shown on the plots in Figs. 9-12) revealed that the Cu concentration declined to less than 1 μg/L and remained constant near the detection limit of the analysis (0.5 μg/L) through the last sampling on May 2, 1988.

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From these data we conclude the following summary of metal behavior. Late summer is a dynamic time for Cu in the water column, probably as a result of uptake and release by blooming algae and because of redox-coupled cycling of Cu in the sediments. The first rainstorms of early fall introduce a dramatic pulse of Cu and other metals into the ponds by washing off the summer's accumulation of dust and dirt in the catchment. By "absorbing" the pulse of contaminants at this time the ponds provide the most critical protection of water quality in the receiving waters. If the OGC runoff were routed directly to the natural drainage system, this pulse of pollutants would shock-load the small receiving stream and Rock Creek to which the stream connects. The contaminant pulse ultimately would add incrementally to the toxic-metal loading of the Tualatin and Willamette Rivers. Later in the fall season, as the rains become more frequent, metal concentrations in the runoff decline to low levels and the metals in output from the ponds may actually exceed the input loading. During the winter the ponds undergo a prolonged period of stable concentrations and gradual dilution. By late spring, metals are at very low levels in the ponds. Although we were not able to verify this in a one-year study, we suspect that Cu and possibly other metals are mobilized from the sediments in the summer and the cycle we observed will repeat.

Particulate Metals

As stated above, particulate Cu was rarely observed to be more than 10% of the total Cu in any of the summer or fall water samples. Nevertheless, in conjunction with the detailed input/output sampling of particles during early December, we measured particulate Cu in the ponds to determine if there were any significant fluctuations in concentrations. In particular we suspected that winter storms might stir up sediments, thereby increasing suspended
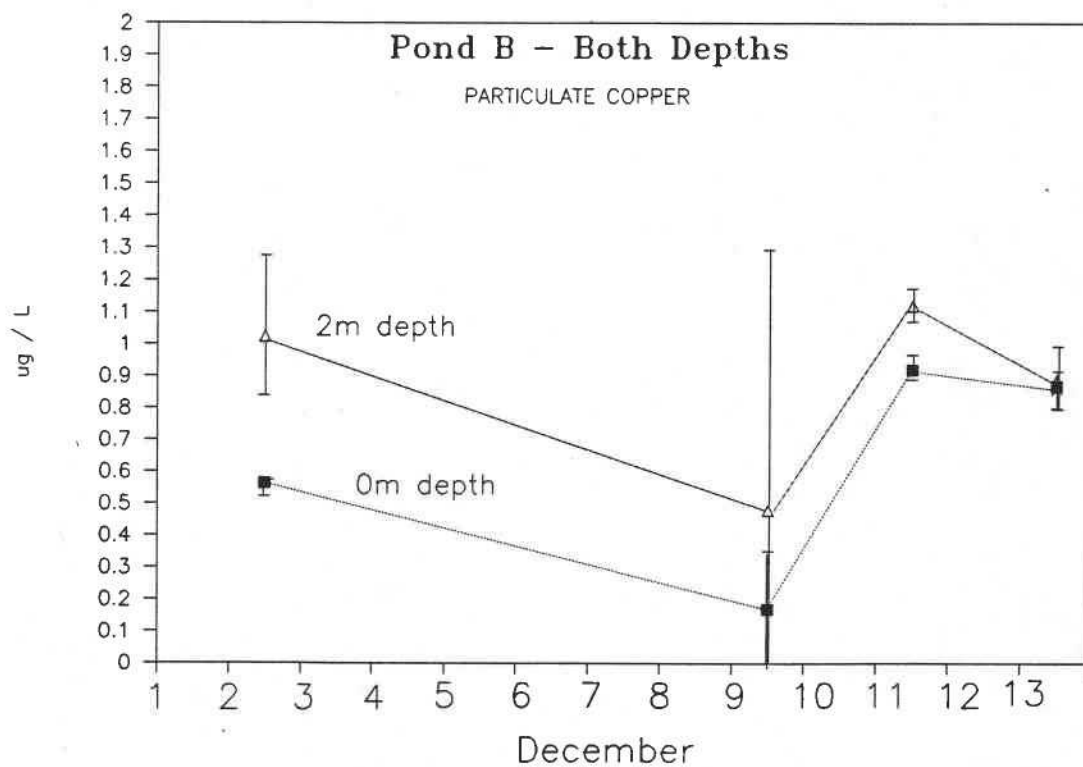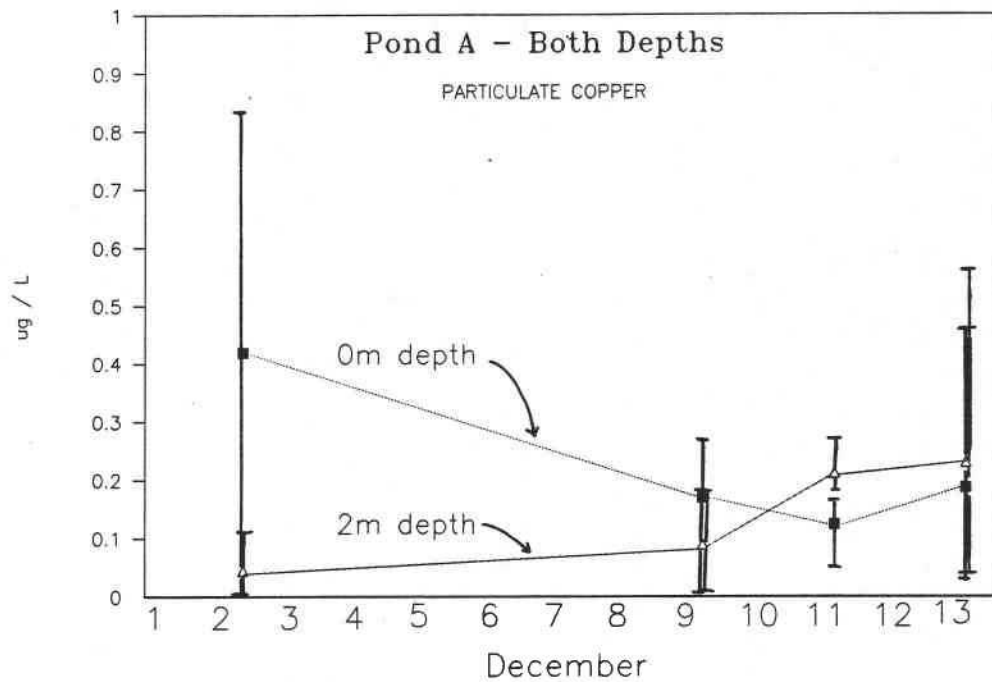
Fig. 13. a) *Particulate Cu in Pond A during early December.*
b) *Particulate Cu in Pond B during early December.*
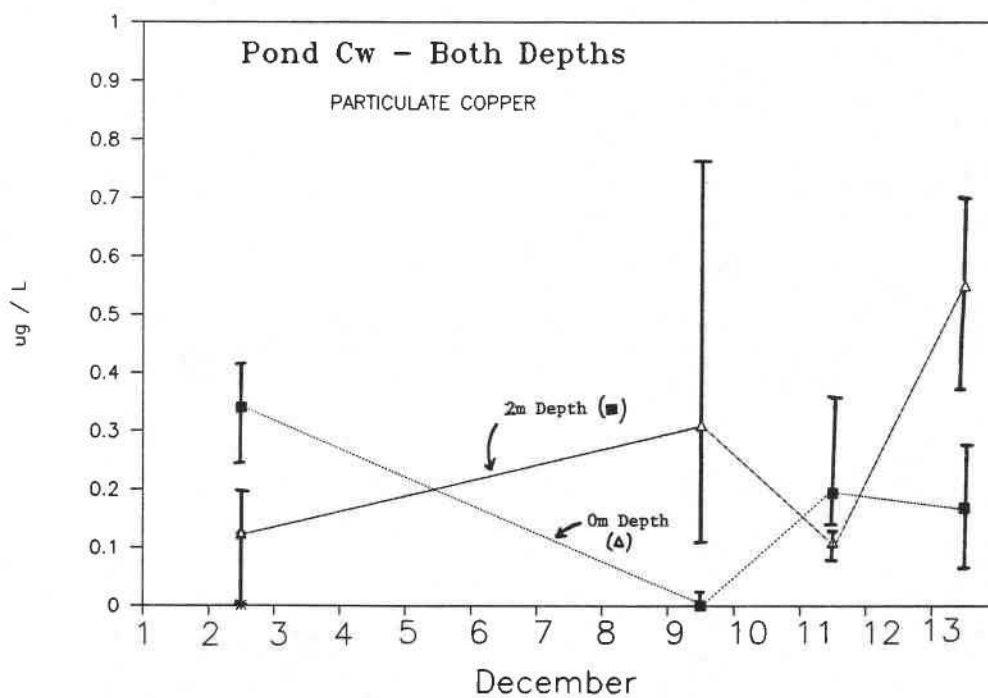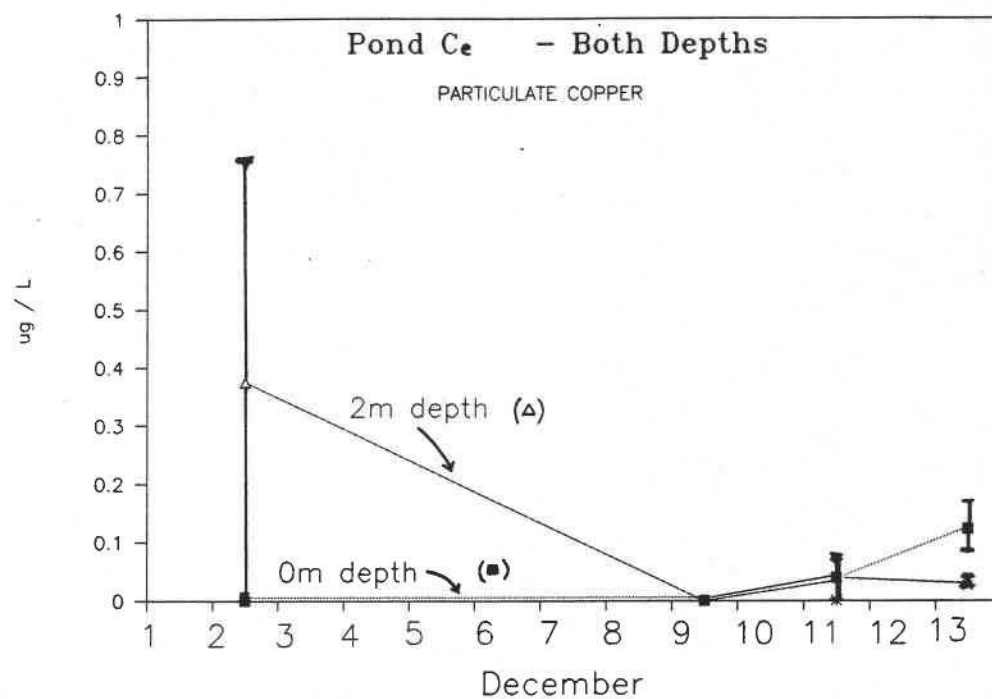
Fig. 14. **a)** *Particulate Cu in Pond C_e during early December.*
b) *Particulate Cu in Pond C_w during early December.*

solids in the water column. As is shown in Figs. 13 and 14, we found no evidence of substantial sediment resuspension during this storm period. Particulate Cu fluctuates within a few tenths of a μg/L in all ponds but these levels are not significantly higher than at any other time of year. Particulate Cu in Pond B is somewhat higher on the average than in Ponds A or C and approaches 30% of the total Cu in the water. As will be shown below, the sediments of Pond B are greatly enriched in Cu compared to Ponds A and C so the slightly elevated levels of particulate Cu in Pond B probably reflect a small degree of sediment resuspension.

METALS IN THE POND SEDIMENTS

Grain-Size Effects

Sediments in all three ponds exhibited a moderate inverse dependence of metal concentrations on the mean grain size. We obtained the most complete data for Cu although the patterns seem to hold for Pb and Cd. Sediments passed through a 125 μm sieve contain, on the average, 84% as much Cu as sediments passed through a 63 μm sieve (Table 5). The data on which these

Table 5. *Ratios of the concentration of Cu in <125 μm sediments divided by the concentration of Cu in <63 μm sediments. Mean values and standard deviations for all sediment samples.*

Pond	Mean	Std. Deviation
A	0.84	0.10
B	0.85	0.17
C_e	0.83	0.11
C_w	0.83	0.12

Pond B Sediments
(Copper)
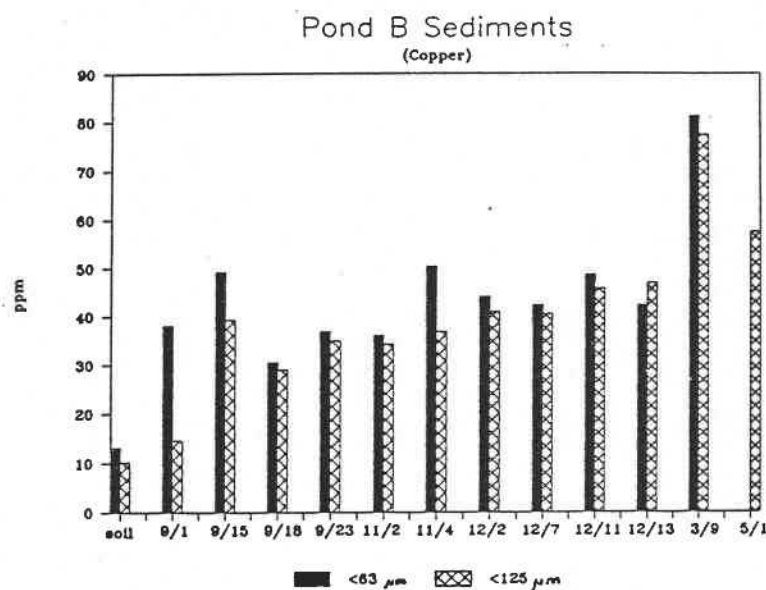
Fig. 15. *Representative sediment concentrations from Pond B in two particle-size classes.*

averages are based are typified by the bar graph presented in Fig. 15 which shows a comparison of Cu concentrations in the two size fractions for the sediments of Pond B.

Although the Cu content of different grain-size fractions does not appear to be large, these data indicate that particles between 63 μm and 125 μm must be significantly depleted in Cu. Note that over 70% of the mass of the sediments is found in the smaller (<63 μm) size fraction, as shown in Fig. 16. Only about 10-15% of the mass of the sediment is in the 63-125 μm (fine sand) range, yet the inclusion of this small amount of material in the <125 μm fraction causes a 15% difference in Cu between the <63 μm and the <125 μm

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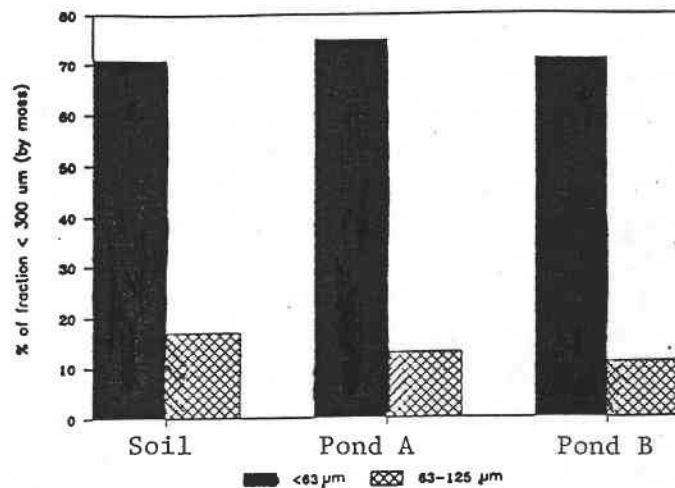
Fig. 16. *Percentages of total mass of sediments and native soil in two size classes (d < 63 μm and 63 μm < d < 125 μm).*

fractions. By mass balance considerations we can therefore determine that the size fraction >63 μm contains only negligible amounts of Cu. Thus it is important to sieve samples to a uniform size class (say <63 μm) in order to minimize variability that is due only to the percentage of the larger particles in the sample, and not due to intrinsic variation in contamination.

Extraction Procedures and Metal Recoveries

Sediment samples in this study were extracted with nitric acid and peroxide rather than subjected to total digestion. Total digestion of the entire sediment, including mineral matrix, yields all metals present, including metals that are completely bound into the matrix and that are unlikely to be available to biota under any circumstance. A partial extraction of the type

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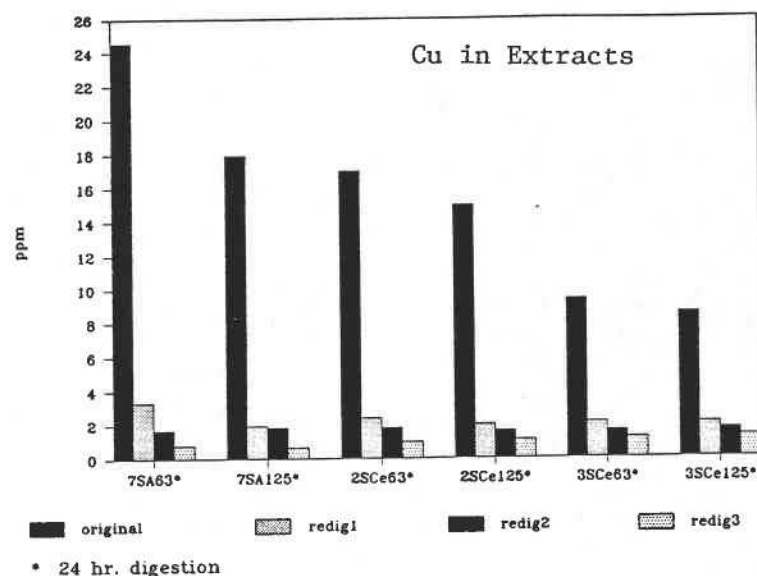
Fig. 17. *Effect of repetitive extractions of sediment samples. Each sample was extracted four times, 24 h each extraction.*

described in the Methods section measures metals that are more likely to be potential hazards in the environment. However, partial extractions for sediments are operationally defined and produce varying recoveries of metals. We believed the best compromise was to choose an extraction scheme that removed nearly all metal that could conceivably be bound to the surface by adsorption or precipitation, and then to be certain that the method always removed that fraction in a consistent manner. Specifically, we tested our method to determine the extent to which the time of extraction and the ratio of sediment to extractant affected yields of Cu. That is, we wanted to be certain that variations in the amount of Cu in our extractions were mainly due to actual

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differences in Cu in the samples, and not due simply to small variations in the extraction time or in the amount of sediment mixed with extractant.

In the first experiment, sediments of both size classes (<125 μm and <63 μm) from three pond samples were extracted for the proposed standard 24 h period. The extractant solution was removed and the sediment samples rinsed twice with water which was pooled with the extractant for analysis. The sediments were placed in fresh extractant for 24 h. Samples were re-extracted three times in this fashion. As shown in Fig 17, each re-extraction always removed a small additional amount of Cu from the sediment. Interestingly, this residual Cu was largely independent of the amount of Cu in the original sediment. For example, sample "7SA63" (from Pond A) shown in Fig. 17 yielded the equivalent of 24.5 mg/kg of Cu on the first extraction, followed by 3.4 mg/kg, 1.6 mg/kg, and 0.8 mg/kg. Sample "3SCe63" (from less contaminated Pond C) initially yielded only 9.3 mg/kg, yet the re-extraction sequence was very similar to sample 7SA63: 2.0 mg/kg, 1.5 mg/kg, and 1.0 mg/kg.

We then examined the effect of extraction time in combination with re-extraction. Two sediment samples were each divided into three aliquots. The first pair were extracted for 24 h and re-extracted three times for 24 h each, as before. The second pair of aliquots was extracted for 48 h and again triply re-extracted for 24 h per extraction, and the third pair extracted for 72 h with triple, 24-h re-extraction. For both sediment samples there was no significant difference in the 24 h, 48 h, or 72 h extraction schemes (Fig. 18). For each sediment sample the results of all extraction sequences were nearly identical, including the amounts of residual Cu in the re-extractions.

From these experiments we concluded that our standard 24 h extraction time gave reproducible results and was not sensitive to small variations in extraction time. Furthermore, the only significant variation among samples
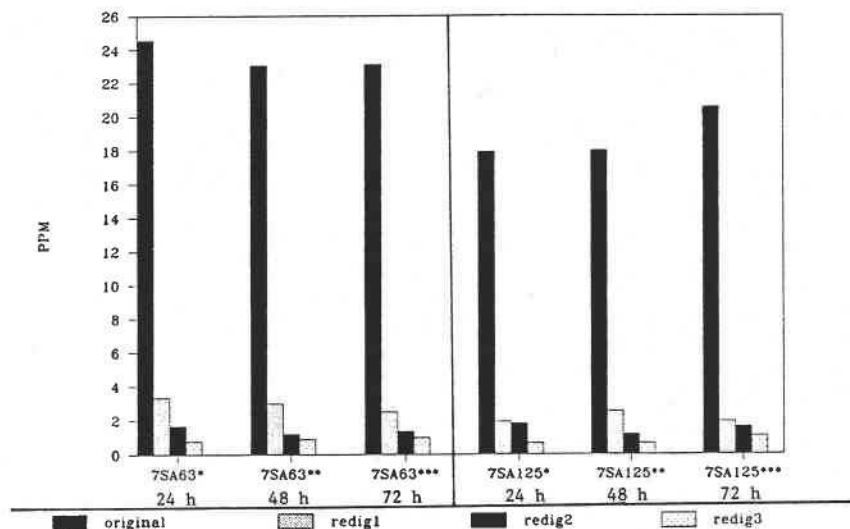
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Fig. 18. *Effect of extraction time on metal recovery. Multiple extrac-
tions with 24 h, 48 h, and 72 h extraction periods.*

could be detected in the first extraction; in subsequent extractions all
samples looked virtually alike, and only insignificant metal was removed in
the fourth extraction.   From this we concluded that the first extraction
liberated the most "available", surface-bound metals and that metals in sub-
sequent extractions were simply the result of a gradual leaching of metals
tightly bound to the surface.   The residual Cu was so consistent that we
were able to calculate an accurate mean value for the Cu removed in three
subsequent extractions (= 4.9 mg/kg).   We concluded that the concentration
from a single, 24 h extraction, corrected by addition of the mean-residual-
Cu would produce the desired information about metals in the pond sediments.

in extraction: the ratio of sediment mass to extractant solution volume. The absolute mass of sediments does not affect the accuracy of the extraction procedure as long as it is above the minimum mass of sediment that can be easily handled. The important variable is the *ratio* of sediment to extractant. A high ratio yields a larger concentration of metal in the extractant, which can be analyzed more accurately. However, a high sediment/extractant ratio may "saturate" the extraction capability of the solution and yield artificially low concentrations of metal. Conversely, a low ratio gives maximum extraction yields, but results in low concentrations of metals that may be difficult to distinguish from a blank. Either an optimal ratio range must be found, or else a correction factor determined if the optimal ratio is not suitable.

Four aliquots of a sediment sample were prepared with masses of 25 mg, 50 mg, 100 mg, and 150 mg. Each was added to 1.0 mL of extractant and subjected to the quadruple (24 h) extraction scheme described above. In the first extraction of each sample there appeared to be a distinct decline in extraction yield with increasing mass of sediment or decreasing sediment/extractant ratio (Fig. 19). This experiment was repeated for several different samples, always with the same general results. The ratio of 25 mg/1.0 mL gave the maximum yield, but 25 mg was a small and unwieldy sample mass that could introduce errors in routine analyses. Increasing both the mass and the extractant volume was an option, but would necessitate devising a extraction vessel different from the clean, disposable 1.5 mL microcentrifuge vials used in the procedure, and, would consume proportionally more of the expensive, high-purity acid and peroxide.

We found that the sediment/extractant ratio effect was reproducible enough that we could formulate a regression function to make the small cor-

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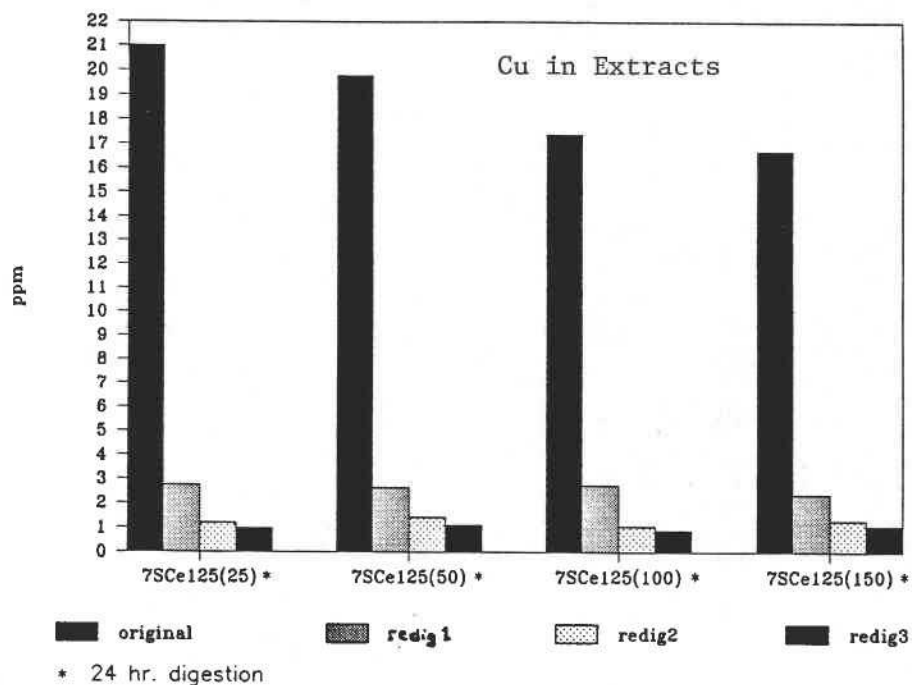
Fig. 19. *Effect of the ratio of sediment mass to extractant volume on metal recovery. Masses of 25 mg, 50 mg, 100 mg and 150 mg in 1.0 mL of extractant.*

rection necessary for samples larger than 25 mg. We found that extractions of 50 mg or 100 mg samples gave satisfactory analyte concentrations and were relatively easy to handle, so the appropriate ratio correction factor was applied to all analyses.

Pond Sediment Data

Triplicate sediment samples were obtained on the same days as pond-water samples between September 1, 1987 and December 13, 1987. An additional spring sampling was conducted at all stations on March 9, 1988, and a set was taken from Pond B on May 1, 1988. In order to get a sense of the non-contaminant,
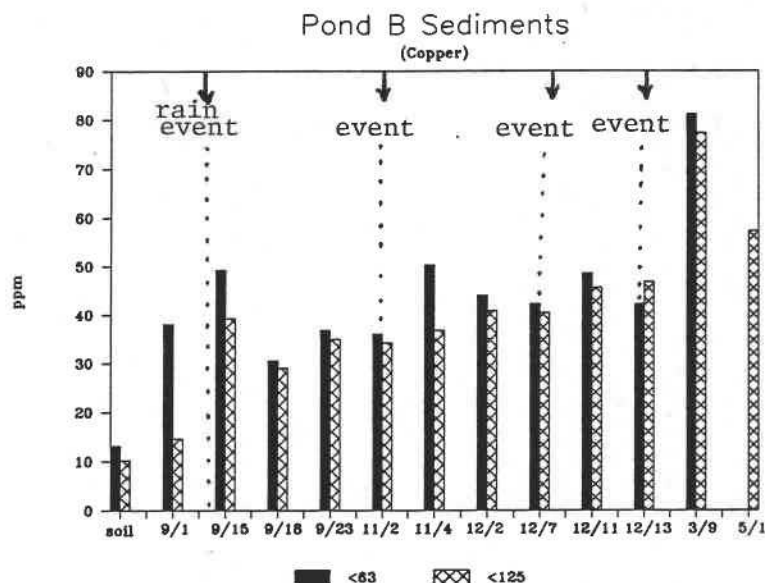
Fig. 20. *Cu in sediments of Pond B throughout the sampling period for both size fractionations. Concentrations are given as mg Cu per kg dry-weight of sediment.*

background levels in the sediments a triplicate set of "native" soil samples were taken from the surface directly adjacent to the ponds. Extractions were performed as described in the Methods section and the results were corrected as described above.

Sediments at all four sampling locations (A, B, C_e, and C_w) had Cu concentrations that were at or above the levels in the native soil, and these concentrations increased significantly throughout the sampling period. Not surprisingly, the greatest amounts of Cu were found in Pond B, the pond receiving direct input (Fig. 20). The first samples taken from Pond B in September contained about three to four times the Cu in native soil. These Cu
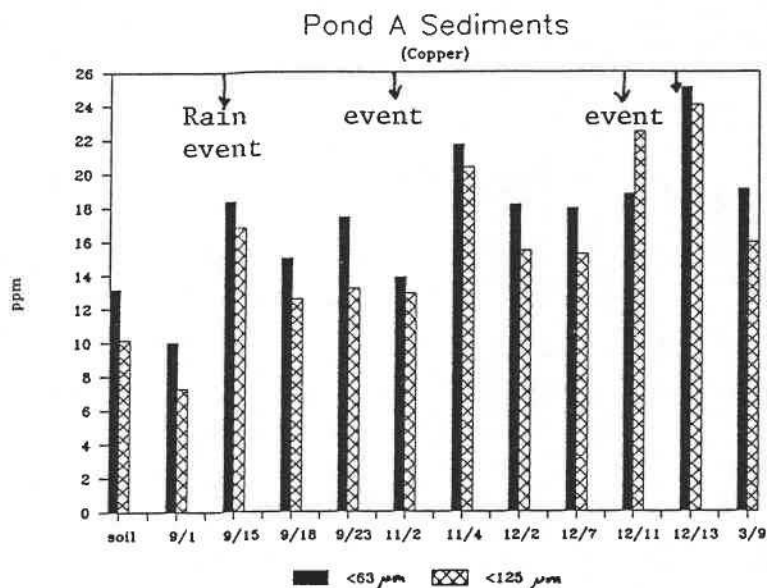
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Fig. 21. *Cu in sediments of Pond A throughout the sampling period for both size fractionations. Concentrations are given as mg Cu per kg dry-weight of sediment.*

concentrations gradually increased during the subsequent six-month sampling period and reached a peak of 80 mg/kg in the 3/9 sample, or almost seven times the background level. In the 5/1 sample Cu had dropped back to 55 mg/kg, but, overall, the data indicated a general trend of relatively rapid increase. The first sample at Pond A contained slightly less Cu than the native soil, but concentration increased in the following three months, approximately doubling by December 13 (Fig. 21). The data for Pond C_e and C_w sites were almost identical in magnitude and trend to the data from Pond A (Figs. 22 a,b).

Taken collectively, these data clearly indicate that significant amounts of Cu built up in the sediments in only a few months but that the great bulk
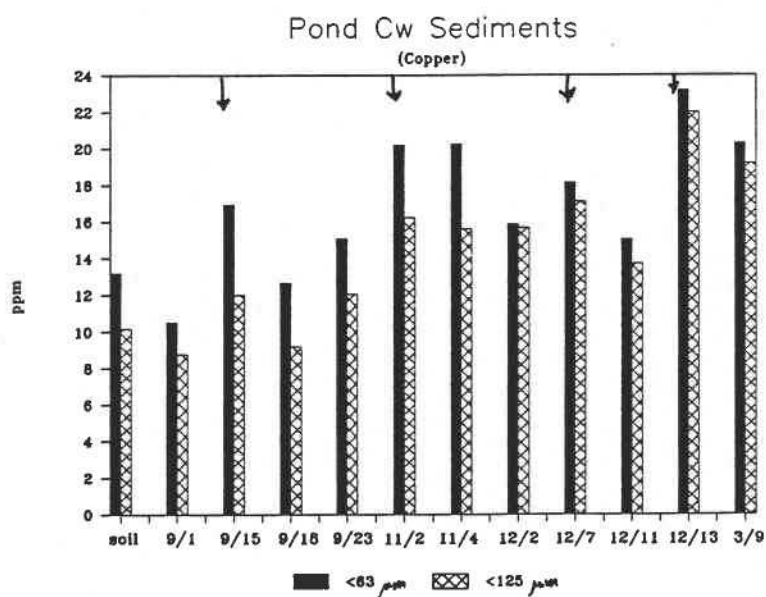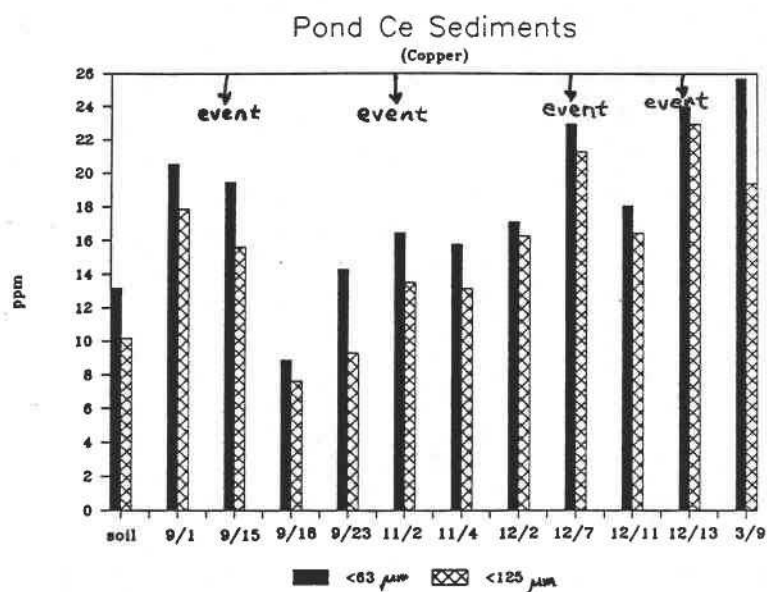
Fig. 22. a) *Cu in sediments of Pond C_e throughout the sampling period for both size fractionations.*
b) *Cu in sediments of Pond C_w. All concentrations are given as mg Cu per kg dry-weight of sediment.*

Log of the Ratio of [Diss. Cu]/[Sediment Cu]
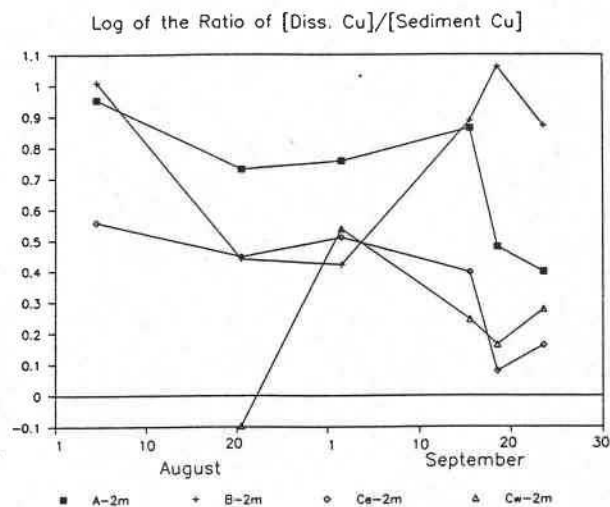
Fig. 23. *Logarithm of the distribution coefficient (K_d) for Cu in Pond B. K_d is defined as Cu in sediment divided by Cu in water at 2m depth.*

of the Cu was deposited in the first pond in the system, Pond B. Because input and pond-water data indicated that the Pb and Cd are roughly five to ten times more associated with particulate matter than is Cu, these metals are almost certainly building up in the sediments of Pond B, although at rates proportional to the smaller input fluxes.

It is interesting to note that Cu is deposited in substantially greater amounts in Pond B compared to Ponds A and C, even though the dissolved Cu concentrations are similar for all three ponds. Presumably much of the input Cu settles relatively rapidly in Pond B while the dissolved Cu circulates through all three ponds, and may re-equilibrate with all sediments. A simple coefficient (K_d) is often used to describe the distribution of organic con-

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taminants between water and sediments. A plot of the logarithm of the ratio of sediment-bound Cu to dissolved Cu (log K_d) for Pond B as a function of time shows that K_d varies rather widely (Fig. 23). Obviously, an empirical coefficient like K_d is of no use in predicting sediment-water distributions. Unfortunately, even the sophisticated models of metal adsorption currently available are still too primitive to provide accurate predictions in complex natural sediments.

Close inspection of the bar graphs in Figs. 20-22 reveals that Cu in the sediments of all ponds increased immediately after a storm event (marker arrows in Figs. 20-22) and then declined slightly in the subsequent inter-event period. Thus we conclude that most Cu-bearing particles settle in Pond B, but particles which escape Pond B settle rapidly throughout the other ponds. The slight declines in sediment Cu between events could result from desorption of Cu from the sediments into the dissolved form. Although we usually observed a decrease in dissolved Cu after storm-induced pulses, base-flow input of relatively Cu-free water may have provided enough dilution to allow desorption and diminishing dissolved Cu to occur simultaneously. Another explanation, at least for September and October is that algal growth contributed enough mass to dilute the Cu concentration in the sediments. Declines of sediment-Cu in November and December are unlikely to be caused by algal sedimentation but the throughput of diluting water during that wet period was high enough to carry off desorbed Cu or Cu on resuspended sediments.

Cu Depositional Pattern in Pond B

Because most Cu deposition occurred in the sediments of Pond B, we undertook a spatially detailed sampling of those pond sediments in May 1988. The eleven sample points were selected to form longitudinal transects along the

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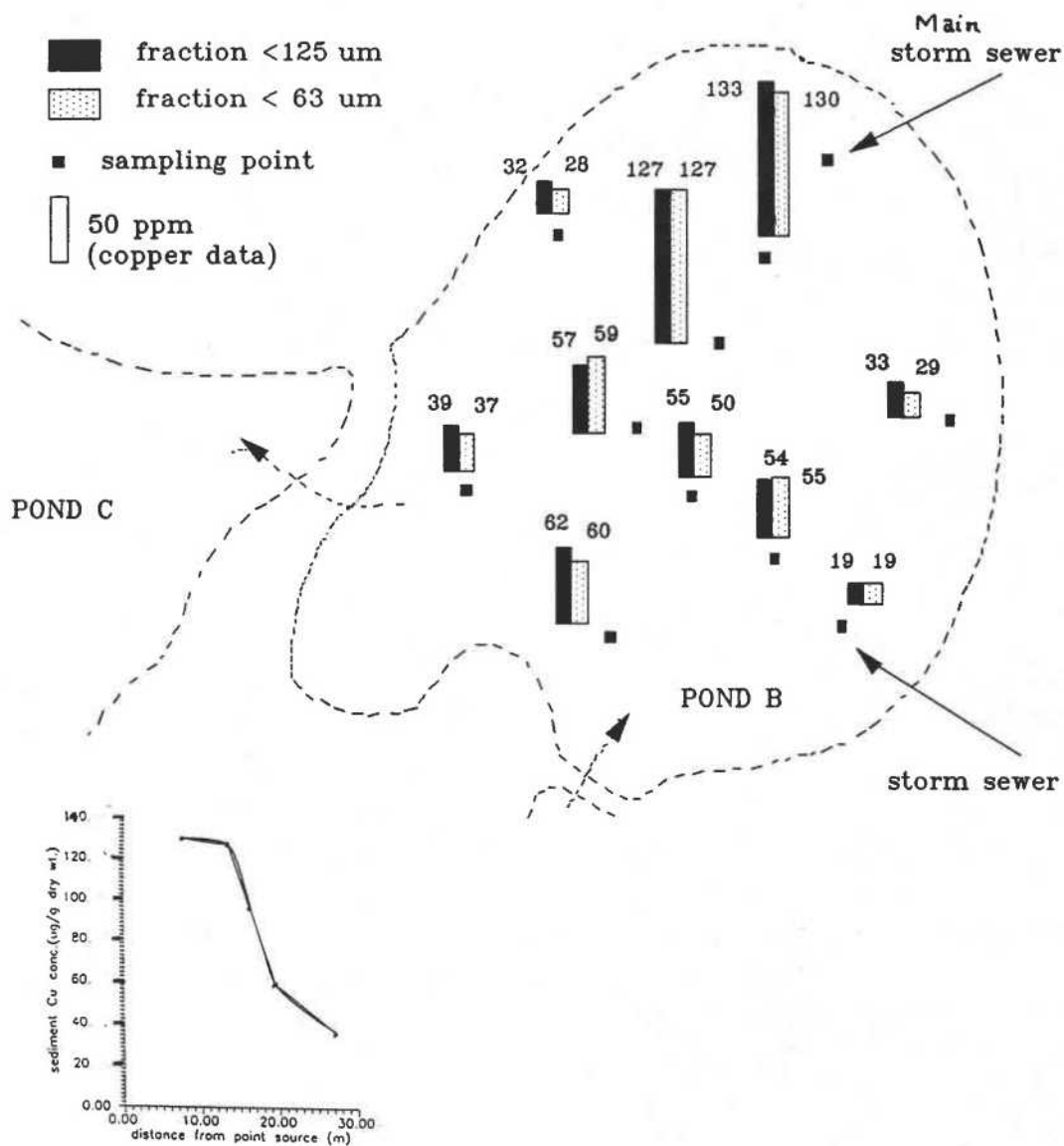
Fig. 24. *Locations and concentrations for the detailed sampling of Cu in sediments of Pond B for both size fractionations. Concentrations are given as mg Cu per kg dry-weight of sediment.*

axes of the main and secondary storm-sewer inlets, and at peripheral points around these transects. The secondary-inlet axial transect also served as a perpendicular transect to the axis of the main inlet (see Fig. 24). Sediments taken from the point closest to the main inlet proved to be entirely gravel and coarse sand, indicative of the high inlet velocities during storm events. This gravelly sample was not extracted or analyzed. Samples taken at 7 m and 13 m axially from the inlet showed extremely high concentrations of 133 mg/kg and 127 mg/kg (<63 μm fraction) respectively. The fourth sampling point along this axis, 19 m from the inlet, was the central position at which all of the routine samples were taken; it had a sediment concentration of 57 mg/kg which was comparable to all previous samples taken at that point. As can be seen in Fig. 24, this transect and all the remaining samples reveal a plume of highly contaminated sediments extending along the axis of the main inlet, with perhaps a minor plume emanating from the secondary inlet. This plume is surrounded by peripheral sediments that have much lower Cu concentration. In fact, the peripheral levels of Cu (20 - 30 mg/kg) are very similar to those found in Ponds A and C. Thus, deposition of Cu occurs so rapidly that many Cu-bearing particles do not even mix uniformly through the relatively small area of Pond B but settle within 20 m of the source. However the remaining particles settle much slower, slow enough to be distributed uniformly through all three ponds, giving a very uniform concentration of sedimented Cu outside of the central plume.

4. CONCLUSIONS

1. Runoff from suburban parking lots such as those studied for this project can contain concentrations of Cu that are high enough to be considered hazardous to the biota of natural streams. On the order of 90% of total Cu in runoff and outputs from the pond was in the dissolved state and not associated with particles. Pb concentrations were generally very low and were observed at lower concentrations than has been noted in the previous literature. We believe this is a result of declining use of lead in gasoline. Much of the Pb appears to be associated with the particulate phase. Cd was occasionally found at total levels in excess of 3 ug/L. Although this is a low level, the high toxicity of Cd indicates that Cd may now be a more important runoff contaminant than Pb. Cd was roughly evenly distributed between particles and solution.

2. In the climate of the maritime Northwest, long, relatively dry periods in the late summer and early fall allow substantial build-up of metals on catchment surfaces. The first major storms of the fall produce runoff that flushes high concentrations of contaminants off the catchment. Subsequent storms generate runoff with progressively lower peak concentrations. By late fall or early winter the runoff is highly dilute and metal concentrations are on the order of 1 ug/L or less. Metals in runoff remain low throughout the winter and spring, presumably until the following fall.

3. Retention ponds are very effective at removing the high pulses of metals associated with early autumn storms. The effluents from the OGC ponds were generally three to ten times lower in metals content than the input runoff in those events. Most of the mass of metals appears to settle out very rapidly and there is dilution of the dissolved components. For a catchment of the type and dimensions studied, a relatively small pond, perhaps 20 m in diameter would probably provide removal efficiencies equal to those for the complete pond system studied at OGC. We recommend that regulatory agencies investigate the use of such low-cost ponds as mandatory management practices for large suburban parking lots that discharge runoff to receiving lakes and rivers.

4. We did not observe any significant remobilization of removed metals in concentrated form. That is, we did not observe large-scale resuspension and wash-out of contaminated sediments during major winter storm events, nor was there evidence of substantial metal efflux by other processes such as surface films. We found preliminary evidence that Cu leaches gradually from the sediments, maintaining a low but possibly significant level of metal in the ponds and the pond effluent. During the winter months, pond effluent may therefore contain more Cu than the dilute runoff input. Overall, however, the tendency of the ponds to buffer the output concentrations of metals at low and relatively steady values is of great value in preserving the integrity of receiving waters.

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