The toxicity and chemical composition of urban stormwater runoff

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The effects of land use on the chemical composition of urban stormwater runoff and its subsequent acute toxicity to the aquatic invertebrate *Daphnia pulex* have been investigated in the Brunette drainage basin of Burnaby, British Columbia. Both land use and interval between rainfall events influenced the chemical composition and toxicity of the stormwater. The industrial and commercial land use sites were the major source of those trace metals most often considered toxic to aquatic invertebrates, with runoff from the commercial sites proving most frequently toxic to the test organism. Toxicity followed the sequence commercial > industrial > residential > open space. A detailed study of a single storm event indicated that while the "first-flush" of the storm contributed to toxicity—through the physical scouring of insoluble pollutants—some soluble pollutants, which were washed out of the watershed later in the storm event, also proved to be toxic. This finding has implications for the collection and treatment of stormwater runoff. Laboratory bioassays with synthetic stormwater composed of the trace metals Cu, Fe, Pb, and Zn at concentrations observed in field samples demonstrated that pH and suspended solids helped to regulate the toxicity of trace metals, and implicated the importance of these factors in natural stormwater toxicity.

Key words: stormwater, street surface sediments, land use, buildup time, trace metals, toxicity, *Daphnia* bioassays, pH, suspended solids effects.

Les effets de l'utilisation du sol sur la composition des eaux de ruissellement en milieu urbain et leur importante toxicité pour l'invertébré aquatique *Daphnia pulex* ont été examinés dans le bassin versant Brunette à Burnaby en Colombie-Britannique. L'utilisation du sol et l'intervalle entre les précipitations influent sur la composition chimique et la toxicité des eaux de ruissellement. On a constaté que les sites à utilisation industrielle et commerciale constituaient la source principale des métaux en traces le plus souvent déclarés toxiques pour les invertébrés aquatiques et que les eaux de ruissellement provenant des sites commerciaux s'avéraient le plus souvent toxiques pour l'organisme à l'étude. La toxicité suivait la séquence suivante : utilisation commerciale > utilisation industrielle > utilisation résidentielle > espace vert. L'étude détaillée d'une précipitation à permis de constater que bien que la « chasse initiale » de la précipitation ait contribué à la toxicité par l'affouillement des polluants insolubles, certains des polluants solubles entraînés plus tard hors du bassin versant se sont également révélés toxiques. Ces résultats ne sont pas sans conséquences pour la collecte et le traitement des eaux de ruissellement. Une série de tests biologiques en laboratoire à l'aide d'eau de ruissellement synthétique composée des métaux en traces Cu, Fe, Pb et Zn à des concentrations similaires à celles d'échantillons recueillis sur le terrain, ont indiqué que le pH et les matières en suspension avaient contribué à contrôler la toxicité des métaux en traces, en plus de démontrer l'importance de ces facteurs pour la toxicité des eaux de ruissellement naturelles.

Mots clés : eaux de ruissellement, sédiments de surface des rues, utilisation du sol, temps d'accumulation, métaux en traces, toxicité, tests biologiques sur *Daphnia*, pH, effets des matières en suspension.

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Introduction

Contamination of the aquatic environment from point sources of pollution has been well documented and is readily amenable to control processes. However, as many investigators have pointed out, pollution from nonpoint sources can account for over half of the contaminant load entering waterways (Whipple *et al.* 1974; Wanielista *et al.* 1977). Without planning considerations to treat this nonpoint pollution source, for some pollution problems very little abatement may occur. For example, Colston (1974) concluded from his study on nonpoint sources that, even if 100% removal of organic matter and suspended solids from raw municipal wastewater took place, the total reduction of contaminants discharged to the receiving creek would only be 52% for chemical oxygen demand (COD), 59% for 5-day biochemical oxygen demand (BOD_5), 5% for suspended solids, and 9, 6, 11, 21, 12, and 43% for the trace metals Cr, Cu, Fe, Pb, Ni, and Zn respectively. In the urban environment the largest contributor of nonpoint pollution is urban stormwater runoff. In fact, the United States Environmental Protection Agency (U.S. EPA) suggests that urban runoff may rival agriculture as the worst contributor of nonpoint pollution, and may be a far more serious polluter in many areas (Barton 1978).

The contaminants in urban runoff include toxic metals (Wilber and Hunter 1979), hydrocarbons (Hunter *et al.* 1979; Hoffman *et al.* 1982), nutrients (Bedient *et al.* 1980), and pesticides (Murphy and Carleo 1978). In a recent study, which included 51 catchment areas, Cole *et al.* (1984) found that the U.S. EPA organic priority pollutants posed little risk at the levels detected in stormwater based on criteria for levels considered safe to aquatic life. However, the most prominent toxic trace metals, namely, copper, lead, and zinc, exceeded the freshwater acute toxicity criteria 50, 27, and 12% of the time. In a nationwide assessment of urban runoff impacts on receiving-water quality, Heaney and Huber (1984) found that there was often a weak linkage between surface runoff and impairment of the beneficial uses of the receiving water. They concluded that most impacts were relatively subtle and that more refined studies and sampling efforts were needed to develop reliable cause–effect relationships.

Many factors can affect the quantity and quality of stormwater runoff. Studies have been conducted to investigate factors (such as land use, traffic intensity, rainfall intensity, and climate) that affect the buildup and transport of pollutants in stormwater (Pitt and Amy 1973; Hall *et al.* 1976; Helsel *et al.* 1979; Bedient

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NOTE: Written discussion of this paper is welcomed and will be received by the Editor until May 31, 1988 (address inside front cover).

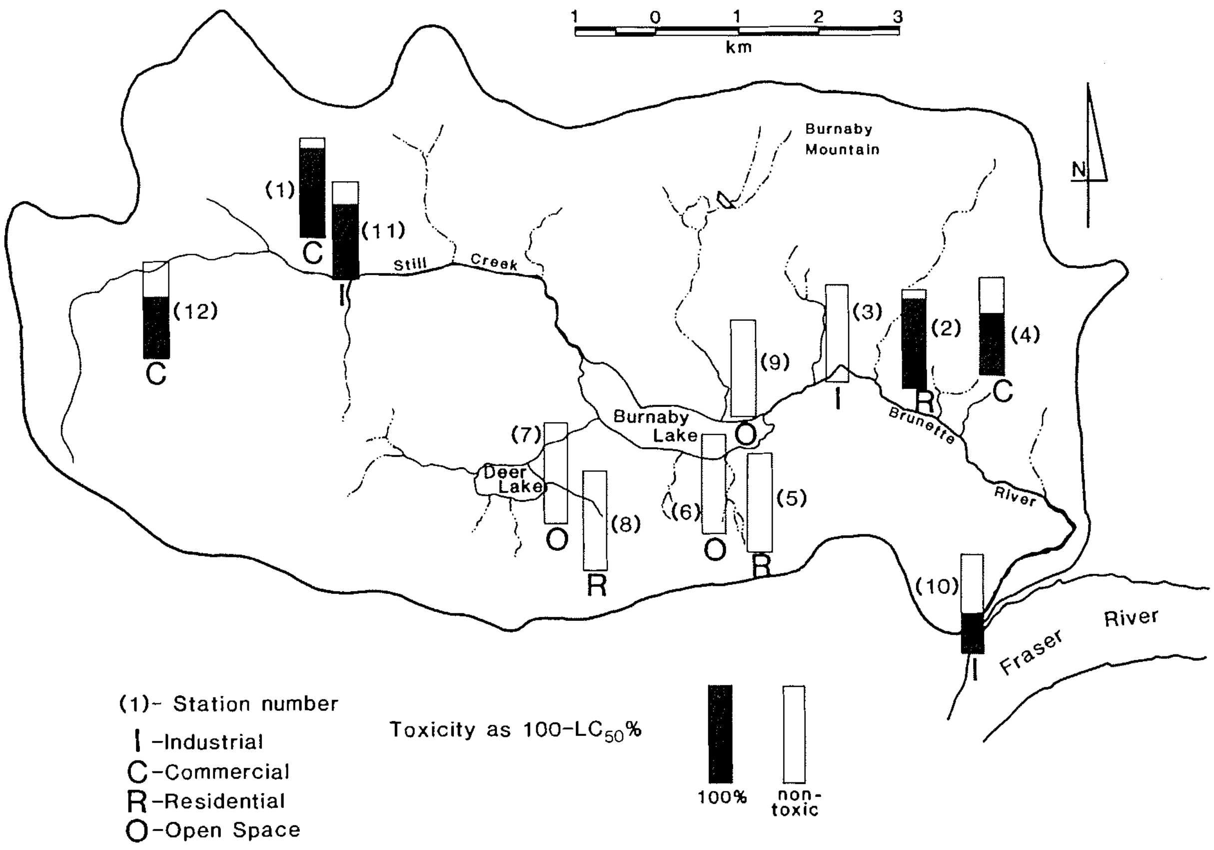

FIG. 1. Study area, sampling stations, and toxicity of urban stormwater in the Brunette watershed.

et al. 1980). Very little research has been conducted to determine the impact of stormwater on organisms in the aquatic environment.

The purpose of the research reported here is to address the toxicity of stormwater runoff from the urban environment and to try to relate this toxicity to land use, and the chemical composition of the runoff.

Methodology

Study area and sampling

This research was carried out in the Brunette River drainage basin, which is a highly urban and industrialized area within the municipalities of Burnaby, Vancouver, and New Westminister, B.C. The major water bodies within the basin include two shallow lakes, namely, Burnaby Lake (120 ha) and Deer Lake (32 ha); Still Creek, the main tributary entering the west end of Burnaby Lake (58% of the flow); and the Brunette River (with an average flow of 2.7 m^3/s), which enters the Fraser River at New Westminister (see Fig. 1). The Greater Vancouver Regional District has utilized the natural drainage of the watershed for stormwater collection to such an extent that some reaches of Still Creek are contained completely within storm sewers.

The total area of the watershed is 6060 ha, which can be divided into four predominant land uses, namely, 42% residential, 31% open space and forested, 15% commercial and institutional, and 5.5% industrial. The commercial and institutional land uses are scattered throughout the basin, while the heavy industrial areas are concentrated along the middle reach of Still Creek and the north side of Burnaby Lake. The most extensive area of open space is on the steeper slopes of Burnaby Mountain, the edge of Burnaby and Deer lakes, and the poorly drained lower reaches of Still Creek. Approximately 15% of the total land area is taken up by highways, streets, and alleys. This includes two major highways (Highway 401 and the Lougheed Highway), which follow the lower elevation contours around both sides of Burnaby Lake and form the major east–west corridor between Vancouver and the Fraser Valley.

Twelve stormwater sampling sites, three in each of the major land use areas, were selected for this study (see Fig. 1 for their location). It was realized that each site encompassed a variety of land uses; however, the predominant land use was estimated to make up at least 75% of the drainage area sampled.

Water samples were collected with an ISCO automated water sampler, which was manually activated at the onset of a rainfall event to collect 500 mL of stormwater at 20 min intervals over the storm period. In the case of multiple sampling of a single storm event, the automated sampler was used at one site and the other sites were sampled manually. A composite sample made of all the individual samples collected during a storm event was used for the toxicity testing and chemical analysis. An antecedent dry period of at least 24 h was required before samples were collected.

Street surface sediments were collected from the curbs of paved roadways from different land use areas throughout the watershed during one sampling period (buildup time = 15 days). Sediments were placed in plastic bags and frozen (−20°C) until analysis.

Analytical procedures

Most analytical procedures followed the methods outlined in *Standard methods for the examination of water and wastewater*

(American Public Health Association *et al.* 1980). The analytical measurements included total suspended solids (TSS), conductivity, pH, total alkalinity, total and calcium hardness, and chemical oxygen demand (COD). Hydrocarbons were quantified by the infrared C—H stretching frequency (3300–2600 cm^{-1}) of a carbon tetrachloride extract on a Perkin–Elmer Model 247 infrared spectrophotometer. Results were reported as equivalent isooctane (Gruenfeld 1973). The trace metals in stormwater (Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn) were determined by direct aspiration of acid-digested (HNO_3, 5% by volume) concentrated (5:1) samples on a Jarrell Ash Model 810 atomic absorption spectrophotometer. A nonabsorbing line was used to correct for interference. For soluble metal estimation, samples were filtered through Whatman No. 4 filters prior to acidification.

Street sediments were dried at 110°C for 48 h, dissaggregated in a mortar, and sieved through a No. 80 mesh (177 μm) nylon screen. One gram of sieved sediment was digested in 10 mL of nitric perchloric acid mixture (a 4:1 mixture of conc. HNO_3 and 70% $HClO_4$). The samples were refluxed for 1 h, evaporated to dryness until no white fumes evolved, cooled, and diluted in 1.5 *M* HCl (20 mL) for aspiration into the atomic absorption spectrophotometer.

A laboratory acclimated population of *Daphnia pulex*, originally obtained from Deer Lake, was selected as the bioassay organism. *Daphnia* was selected because considerable research has been conducted on metal toxicity to this organism (Biesinger and Christensen 1972; Kaiser 1980) and these cladocerans are comparatively sensitive to metal toxicity (Baudouin and Scoppa 1974). Daphnid neonates less than 24 h old were collected from mature females for all bioassays, to ensure a uniform sensitive organism for the acute toxicity tests. Five neonates were placed in each serial dilution of stormwater, which had been allowed to acclimate to ambient test chamber temperature (20°C), and the motile daphnids enumerated at 24, 48, and 96 h. The quantal method, in which mortality of the test organism was recorded at fixed times from a series of logarthmic dilutions and the LC_{50} derived by interpolation from the resultant curve of percent mortality vs. log percent effluent concentration, was used to measure the acute toxicity of the stormwater (Brown 1973; Sprague 1969, 1970).

Toxicity over a storm event was measured on one occasion to study the "first-flush" phenomenon, where it has been estimated that most pollutants are removed from the street surface during the first hour of rainfall (Wilber and Hunter 1977; Kaufman and Lai 1980). Grab samples were collected manually at 20 min intervals over the 4 h storm period to avoid the problem of a 10 min integrated sample collected by the automatic sampler.

Some laboratory toxicity bioassays were conducted on *Daphnia* using synthetic stormwater, prepared with soluble solutions of Cu, Fe, Pb, and Zn prepared at the "worst-case" concentrations found in the stormwater. The toxicity of these metals was measured at different pH and at different suspended solids levels, to estimate the effects of these parameters on toxicity. These toxicity tests were all done by making the appropriate additions to filtered Deer Lake water. The toxicity of Zn, Pb–Zn, and Cu–Pb–Zn combinations was measured at pH's of 5.0, 5.5, 6.0, 6.5, 7.5, and 8.0. The toxicity of the same metal combinations was measured in association with total solids concentrations of 50, 100, and 200 mg/L (diatom filter powder—Vortex Products). The combined effects of total solids (50, 100, and 200 mg/L) at three pH's (5, 6, and 8) on the toxicity of Pb–Zn and Cu–Pb–Zn to *Daphnia* were also measured, to try and elucidate some of the complexitie involved in the interpretation of environmental toxicit measurements.

Statistical analysis

The University of British Columbia triangular regressio package (Le and Tenisci 1978) was used to determine the partia correlation coefficients between the stormwater chemistry and toxicity. In addition, the program STREG was used to generate multiple regression equations for toxicity as a function of all statistically significant parameters. The Marking–Dawson additivity index (Marking and Dawson 1975) was used in the synthetic stormwater study, to evaluate the contribution of each component to the overall toxicity of the mixture, and to determine synergistic and antagonistic effects.

Results and discussion

General chemical characteristics of stormwater

The general physical–chemical characteristics of the composite stormwater samples obtained at the 12 sampling sites are presented in Table 1. Chemical oxygen demand (COD) was best correlated ($r^2 = 0.81$) to the buildup time. The residential areas contained the highest loading rate (36 mg/L per day), with the industrial and commercial sites having similar values (23 and 26 mg/L per day respectively). This was probably due to greater amounts of vegetal material from gardens, lawns, and trees in residental areas. Although open and (or) green space areas also generate large amounts of vegetal matter, they contain a smaller percentage of impervious surface area and much of the soluble organic matter leached from vegetation can be adsorbed by the soil (Rimer *et al.* 1978).

The hydrocarbons (1.8–9.2 mg/L) were not an important component of the total COD. There was a weak relationship ($r^2 = 0.49$) between hydrocarbons and buildup time for the complete data set. However, when two relatively high concentrations (8.8 and 9.2 mg/L) at industrial sites were not included in the correlation analysis the relationship was very good ($r^2 = 0.86$). These two sites produced stormwater with high suspended solids levels (444 and 1868 mg/L) owing to heavy construction activity. Apparently, these solids help to scavenge hydrocarbons from the drainage area. Eganhouse and Kaplan (1981) and Hoffman *et al.* (1982) both found that most of the hydrocarbons were associated with the particulate phases in stormwater, demonstrating that suspended solids were important in hydrocarbon transport.

Total dissolved solids in stormwater, as estimated by conductivity measurements, showed a weak relationship to buildup time ($r^2 = 0.48$). The dissolved solids level of open space (av. conductivity 159 μS/cm) was very close to that of lakes (<150 μS/cm) in the watershed.

Many investigators have attempted to relate the quality of stormwater runoff to the number of antecedent dry days (Bedient *et al.* 1980; Hoffman *et al.* 1982; Owe *et al.* 1982). As these studies demonstrated, the relationship was usually poor. This poor relationship between buildup time and quality may be attributable to the varying intensity and duration of the rainfall, and its ability to scour the contaminants from the street surfaces during a storm event. This serves to point out the "storm-specific" nature of this type of research, and the limitations of a generalized extrapolation of the data.

Trace metal contamination of stormwater

The highest degree of contamination of those trace metals considered most toxic to aquatic organisms (Cd, Cr, Cu, Ni, Pb,

TABLE 1. Chemical analysis of stormwater

			Analytical parameters						
Station*	Class†	Buildup time (days)	COD (mg/L)	pH	TSS (mg/L)	Total alkalinity (mg/L $CaCO_3$)	Total hardness (mg/L $CaCO_3$)	Conductivity (μS/cm)	Hydrocarbons‡ (mg/L)
1	C	33	1031	5.70	129	52	327	496	6.7
2	R	18	763	5.80	64	34	142	512	5.8
3	I	17	269	6.00	16	63	82	96	4.6
4	C	1.5	108	5.82	55	12	12	15	2.0
5	R	4	57	6.80	15	33	29	130	2.4
6	O	4	70	6.55	22	12	15	84	1.8
7	O	4	78	5.82	76	8	17	58	3.2
8	R	4	99	6.28	122	20	19	109	2.6
9	O	7	46	6.96	151	22	54	73	1.8
10	I	15	430	8.10	1868	122	85	470	9.2
11	I	15	406	7.52	444	64	92	693	8.8
12	C	15	169	7.34	33	154	142	587	4.3

*See Fig. 1 for location.
†C = commercial, R = residential, I = industrial, O = open space land uses.
‡As isooctane.

and Zn) occurred in the runoff from the industrial and commercial land use areas (Fig. 2). The open and (or) green space areas all showed lower trace metal concentrations in stormwater, which may be indicative of background levels or removal due to a more permeable surface. These stormwater data are biased somewhat by higher buildup times for the commercial and industrial land use areas (see Table 1). To separate land use and buildup time effects on contaminant generation in the watershed, street surface sediments, all collected at one time during a constant buildup period, were analyzed for trace metals. These data are included in Fig. 2 so that a relative comparison can be made to the trace metal trends observed in stormwater. With the exceptions of Cr, Fe, and Mn, there were similar land use trends for the trace metals in both stormwater and street sediments.

Trace metal concentrations in stormwater and street sediments from the industrial, commercial, and residential areas are compared with the green and (or) open space areas in Table 2 to determine the relative level of contamination. This table assumes a significant difference to be values greater than the arithmetic mean + 2 standard deviations ($\chi + 2s$) of the green space trace metal values. Oliver and Agemian (1974) used similar criteria to show relative levels of contamination as opposed to natural occurrence for trace metals in river sediments. These data indicate that copper, nickel, lead, and zinc in both stormwater and street sediments are consistently higher in industrial and commercial land use areas. The residential areas generally show lower levels of trace metal contamination. In a stormwater study near Washington, DC, Helsel *et al.* (1979) also found that trace metal presence in stormwater runoff was related to land use, with a general increase in most toxic trace metals (Cu, Cr, Pb, and Zn) as the intensity of land use (agriculture to residential to commercial) and traffic volume increased.

It can readily be seen that there is a high degree of variability in metal concentrations associated with stormwater from any single land use area (Fig. 2). Some of this variation can be attributed to sampling during different rainfall events. The natural discontinuities in time and space during different rainfall events and their effects upon meaningful data comparison have been assessed by Griffin *et al.* (1980). However, it is very expensive to sample numerous sites during a single rainfall event, in terms of both manpower and equipment costs. As such, these data present a first examination of a localized stormwater runoff pollution problem.

Fe, Cr, and Ni were linearly related ($r^2 > 0.75$) to the total suspended solids content of the stormwater, whereas Cu, Pb, and Zn showed a definite linear correlation with buildup time ($r^2 > 0.83$). Owe *et al.* (1982) also found a good correlation between buildup time and the surface accumulation of contaminants such as trace metals (Cu, Pb, Zn). Therefore, many factors, such as land use, suspended solids concentration, and buildup time appear to be important in regulating the levels of trace metals in stormwater. Other factors that were not investigated, such as intensity of rainfall, traffic density, runoff flow velocity, and percent of area curbed (which can affect sediment transport), could also influence the trace metals in stormwater (Wilber and Hunter 1979; Helsel *et al.* 1979).

Toxicity of stormwater

The acute toxicity of the composite stormwater samples to *Daphnia pulex* is summarized graphically on a map of the drainage basin in Fig. 1. Six of the twelve sites produced stormwater that was toxic to some degree. Three of these were commercial sites, two industrial, and one residential. Stormwater from all open and (or) green space areas was nontoxic to *Daphnia* in static 96-h tests. Therefore, the frequency of occurrence of toxicity in stormwater, in relation to land use, appeared to be commercial > industrial > residential > open space. A commercial site and a residential site contributed stormwater with the highest toxicity, requiring only 11.5 and 10% dilution respectively to give a lethal toxic response.

An examination of the pattern of toxicity in the watershed showed higher toxicity in the upper (sites nos. 1, 11, and 12) and lower (sites nos. 2, 4, and 10) reaches of the basin; those sites in the middle of the basin all had runoff that was nontoxic. In general, these middle reaches of the basin are at the lower, gently sloping elevations, close to the main water bodies and have been predominantly used for residential and open and (or) green space land uses.

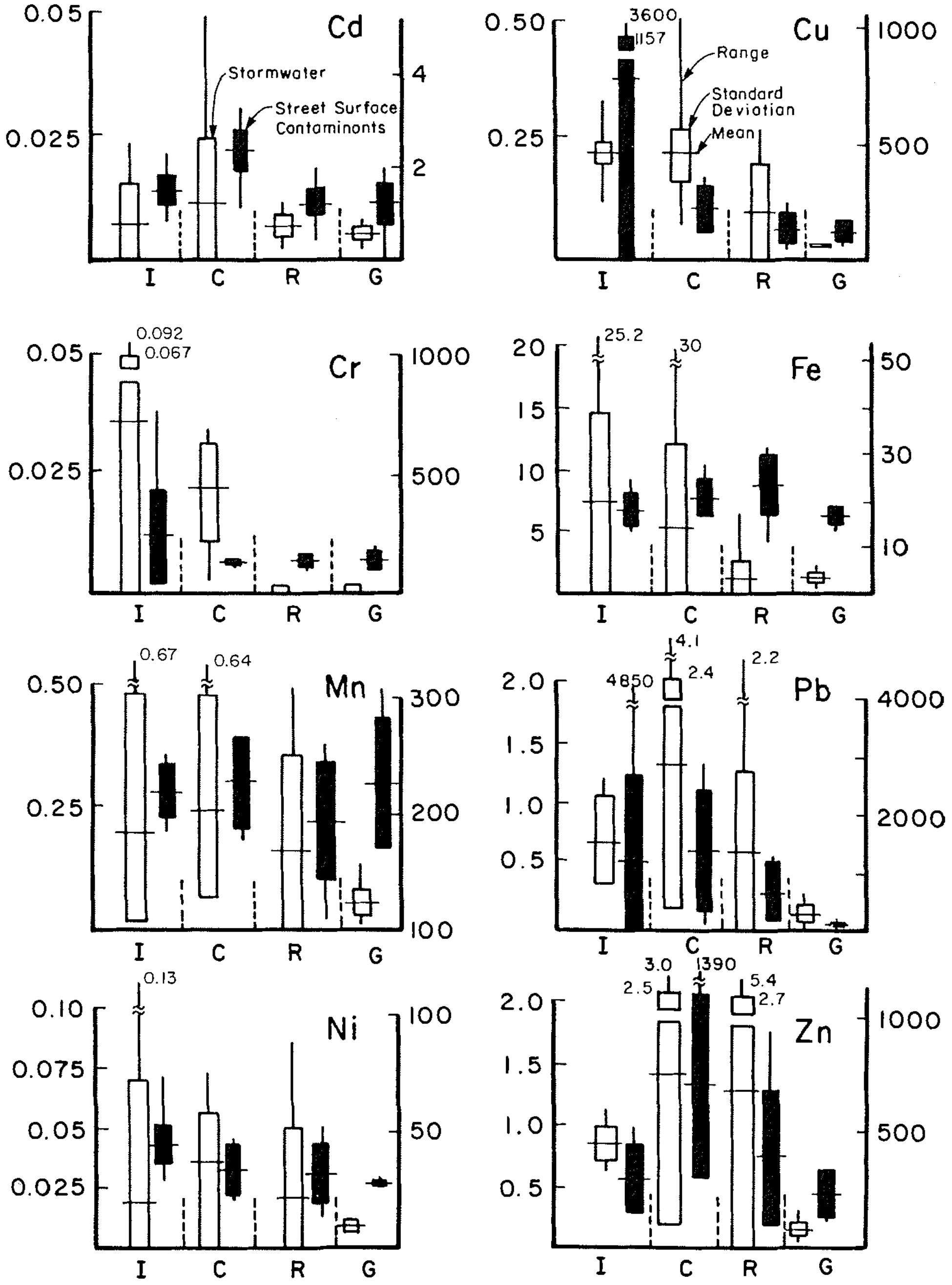

FIG. 2. Trace metal content of stormwater runoff and street surface sediments from different land use areas (all stormwater values in mg/L, on the left axis; all street surface sediment values in mg/kg dry weight on right axis, iron values as mg/kg × 10^3 on right axis; I = industrial, C = commercial, R = residential, G = green and (or) open space).

TABLE 2. Trace metal contamination significantly different from green space areas

	Trace metal significant difference*															
	Cd		Cr		Cu		Fe		Mn		Ni		Pb		Zn	
Land use	SW	SS	SW	SS	SW	SS	SW	SS	SW	SS	SW	SS	SW	SS	SW	SS
Industrial	33	0	66	13	100	88	100	13	66	0	100	63	100	88	100	25
Commercial	33	50	66	0	66	33	100	17	66	0	66	50	100	83	100	66
Residential	33	0	0	0	33	25	33	13	33	0	33	50	66	75	66	25

*A significant difference is considered to be $>\bar{x} + 2s$ of the trace metal levels in green and (or) open space where $\bar{x}$ = arithmetic mean and s = standard deviation. The values are expressed as a percent of the values from the different land use areas that exceed the $\bar{x} + 2s$ green and (or) open space values. SW = storm water, SS = street sediments. For all stormwater land use areas, $n = 3$; for street sediments, $n = 4$ for green and (or) open space, $n = 8$ for industry, $n = 6$ for commercial, and $n = 8$ for residential.

A statistical analysis, which determined partial linear regression coefficients for all individual chemical parameters and toxicity according to specific land use classification, did not show any significant positive correlation to trace metal concentrations. However, when all land use sites were considered collectively, Cu and Zn showed positive correlations to toxicity, with values of 0.88 and 0.74 respectively. The buildup time and pH were also related to toxicity over all land uses, with partial linear regression coefficients of 0.85 and 0.89. Multivariate stepwise regression analysis of all the chemical data in relation to toxicity didn't provide any better relationships than were found by partial regression analysis. Toxicity at the commercial sites was related only to zinc, while toxicity at the residential sites was related to buildup time. When all sites that showed toxicity were considered independent of land use, lead appeared to have the strongest influence on toxicity. To provide a much stronger statistical validation of these cause–effect relationships would require a larger data base, with sampling at several stations during numerous single rainfall events.

Very few studies have assessed the toxicity of surface runoff. Couillard (1982) used the green alga (*Selenastrum capricornutum*) to assess the toxicity of snowmelt water runoff. He found that the runoff was more toxic during a period of snowmelt without rainfall, while rainfall addition caused dilution and lower toxicity. The toxicity was associated with the soluble components that complex with EDTA, which indirectly implicated the soluble trace metals. In a nationwide survey of urban runoff impacts, Heaney and Huber (1984) reported that fish kills were a problem, but in many cases the cause–effect relationships were weak.

First-flush analysis

A single storm event at a commercial land use site (station no. 1) was monitored over a 4 h period, to delineate the toxicity and chemical composition of stormwater during different stages of the storm. The period of rainfall, stormwater toxicity, and relative distribution of soluble (as estimated by conductivity measurements) and particulate materials, at 20 min intervals, are presented in Fig. 3. Toxicity values of 100 indicate that the stormwater was nontoxic to *Daphnia*, whereas a value of less than 100 indicates the percent dilution of stormwater that was toxic. The first-flush of the storm event, which is usually considered to occur during the first hour (Wilber and Hunter 1977; Kaufman and Lai 1980; Black 1980), transported a large proportion of the insoluble material past the sampling point; the first sample collected during this period was toxic.

A much longer period of toxicity occurred in the middle of the storm event and it appeared to be associated with a peak of soluble material in the stormwater. Hunter *et al.* (1979) also reported that soluble materials (in this case hydrocarbons) lagged behind the particulate-associated components during a detailed study of hydrocarbons in runoff. Although it was difficult to associate this toxicity to any specific element in the soluble fraction of the stormwater, the soluble concentrations of Cu, Ni, Pb, and Zn all exceeded 10 μg/L during this period. Copper has been shown to be acutely toxic to *Daphnia hyalina* at these concentrations (Baudouin and Scoppa 1974). Perhaps the availability of the metals in this soluble fraction is the important factor regulating toxicity at this time. Wilber and Hunter (1979) found that between 10 and 20% of the total Cu, Pb, and Zn found associated with stormwater solids could be considered available, since they were associated with the soluble and exchangeable phases.

The timing of transport of these soluble materials during the storm event could be a function of many factors, including solubility equilibria, exchange capacity, and adsorption–desorption processes associated with solid materials that are deposited in different areas of the stormwater system. If the toxicity results reported here are applicable to a wide variety of storm events in different areas, the proposed methods of collection and treatment of the "first-flush" component of the storm to reduce detrimental effects to aquatic life should be reevaluated (Oberts 1977; Swain 1985).

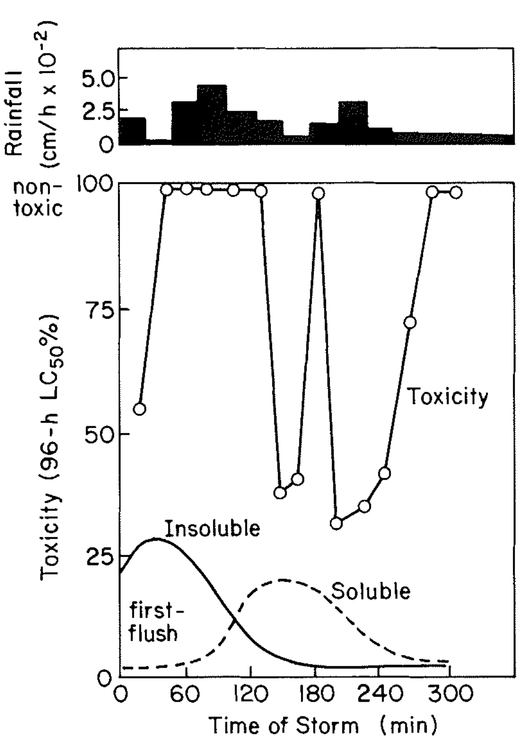

FIG. 3. Toxicity over a storm event.

Laboratory bioassays with synthetic stormwater

The "worst-case" concentrations of Cu, Fe, Pb, and Zn found in stormwater (0.45, 30, 4.14, and 3.2 mg/L respectively) were used to study the impacts of metal combinations, suspended solids, and pH upon trace metal toxicity to *Daphnia*. The resultant 96-h LC$_{50}$ values for the trace metals run individually and in combination are summarized in Table 3.

The most obvious trend in these data was the extremely low toxicity of iron and the reduction of toxicity of other metal combinations, when iron was added. The Marking–Dawson index confirmed the high degree of antagonism between iron and the other trace metals. Precipitation of iron at the neutral pH and the binding or adsorption of other trace metals to the precipitate could have been the main factor in toxicity reduction. While all trace metal combinations used in the bioassays were toxic, the Marking–Dawson additive index indicated that most metal combinations were less toxic than the individual trace metals. Only the Pb–Cu and Pb–Zn combinations showed a synergistic toxic response.

There was an increase in toxicity with a decrease in pH between 8.0 and 5.0 (Fig. 4). The effect was very pronounced for Zn and the Pb–Zn combination but did not appear to affect the Cu–Pb–Zn toxicity. The reduced toxicity at pH 5 for the Cu–Pb–Zn combination may have been an experimental artifact, since subsequent experiments with these metals demonstrated higher toxicity at a lower pH (Fig. 5). At a lower pH, most of the trace metals are more available, since they

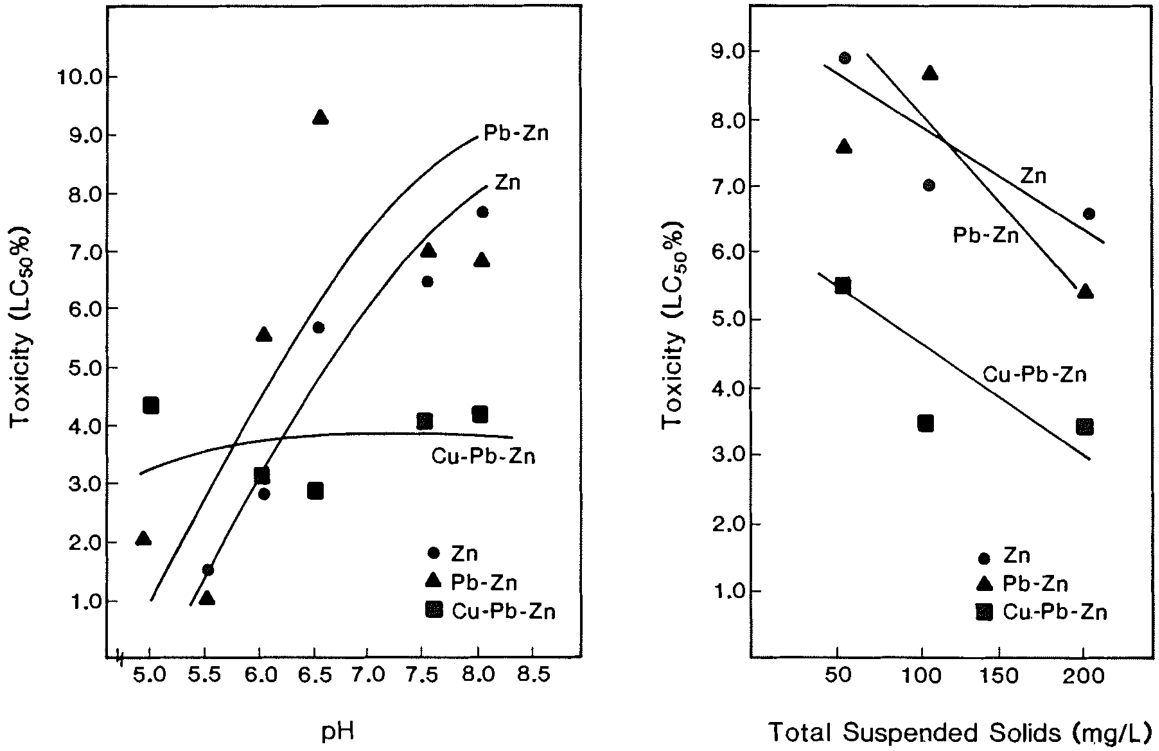

FIG. 4. Trace metal toxicity of synthetic stormwater at different pH's and suspended solids concentrations.

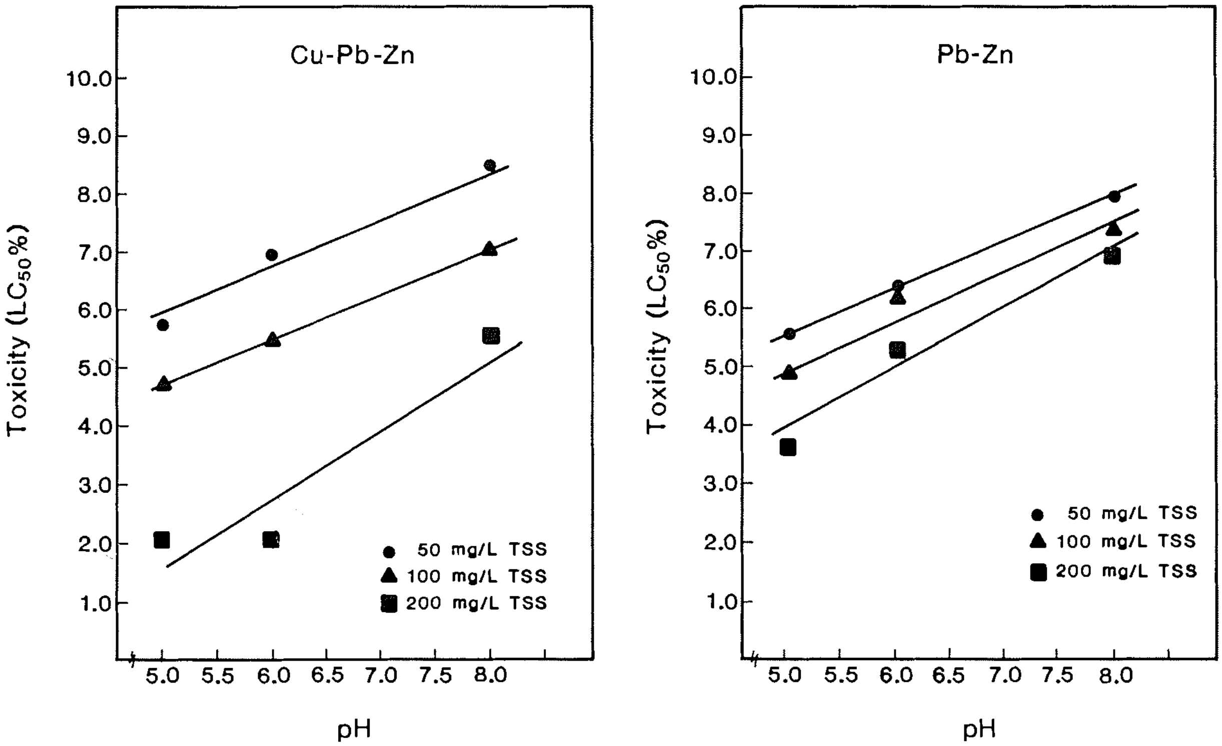

FIG. 5. Trace metal toxicity of synthetic stormwater when different pH's and suspended solids concentrations are combined.

usually exist in a free ionic form, whereas when pH increases, insoluble hydroxides and oxides can form (Gadd and Griffiths 1978).

There was an increase in toxicity as the level of suspended solids increased from 50 to 200 mg/L (Fig. 4). This trend was apparent for the Zn, Pb–Zn, and Cu–Pb–Zn trace metal combinations. This concentration range of suspended solids, when tested alone, was not toxic, although Muller (1982) has reported that dextran and cellulose particles can influence the reproductive rate of *Daphnia magna*. As suggested in the literature (Gadd and Griffiths 1978; Wilber and Hunter 1979), a high proportion of trace metals are readily bound to suspended solids, which would generally make them less available to organisms. However, since the test organism is essentially a

TABLE 3. Toxicity of synthetic stormwater*

Number of metals	Trace metal combinations				Toxicity (LC$_{50}$)†
	Cu	Fe	Pb	Zn	
1	—	—	4.14	—	35.8
	0.45	—	—	—	9.2
	—	30.0	—	—	85.8
	—	—	—	3.2	6.4
2	0.45	—	4.14	—	1.0
	—	—	4.14	3.2	2.4
	—	30.0	4.14	—	85.9
	—	30.0	—	3.2	9.6
	0.45	—	—	3.2	8.2
	0.45	30.0	—	—	92.0
3	—	30.0	4.14	3.2	47.5
	0.45	—	4.14	3.2	3.5
	0.45	30.0	—	3.2	24.8
4	0.45	30.0	4.14	3.2	16.6

*All values in mg/L, bioassays run at pH 7.0, TSS = 0 mg/L.

†Percent of trace metal solution toxic to 50% of *Daphnia*.

filter feeder, it would be expected to ingest adsorbed trace metals as it removes particulate material from the water column. Other studies have reported similar results with respect to pesticide adsorption and toxicity (U.S. EPA 1972).

A comparison of the combined effects of pH and suspended solids on metal toxicity (Fig. 5) demonstrated that the pH effects tended to dominate the toxicity response but that higher levels of suspended solids were also important. In addition to its effect upon the form of the metal, pH could alter the character of the adsorption sites on the particles. Caution should be used in general application of these toxicity observations, since the characteristics of natural suspended solids can vary considerably (organic content, cation exchange capacity, and particle size) and differences in water quality (dissolved organics, alkalinity, and hardness) could affect the toxicity response that is observed.

While a comparison between lab-derived and field bioassay data has many constraints, these results provide some confirmation of trace metal toxicity associated with stormwater. The field data generally produced a lower acute toxicity value than the lab-derived data; this would be expected for a number of reasons: (1) the laboratory data were derived from experimentation using the "worst-case" conditions based on composite field data, (2) soluble trace metals were used in the laboratory studies, and (3) natural interferences such as hardness could lower the overall toxicity. On the other hand, additional physiochemical properties of stormwater, which are not easily adaptable to this kind of bioassay testing, could contribute to stormwater toxicity. These include relatively insoluble organic contaminants such as hydrocarbons (Eganhouse and Kaplan 1981), chlorinated pesticides (Hall *et al.* 1976), and polycyclic aromatic hydrocarbons (Morton 1983), which have been found to be largely associated with the particulate material in a stormwater catchment area.

Conclusions

Factors regulating the chemical composition and toxicity of stormwater are very complex. Stormwater from intensively used commercial and industrial sites contained the highest levels of pollutants, such as oxidizable organic matter (COD) and trace metals. The levels of some metals (Cu, Pb, and Zn) were correlated to the buildup time, although factors such as intensity of rainfall, and morphology of the drainage area could affect the transport of these materials. There was no direct relationship between the toxicity level of the stormwater and land use, but runoff from commercial and industrial sites was more frequently toxic to *Daphnia*. When all land uses were considered collectively, copper and zinc showed the highest correlation with toxicity.

The "first-flush" of a storm event transported a large proportion of the insoluble material and the first sample collected during this period was toxic. A much longer period of toxicity occurred in the middle of the storm event and it was related to soluble material in the stormwater.

In laboratory bioassays with *Daphnia*, the toxicity of iron was low and it reduced the toxicity of other metals (Cu, Pb, and Zn). Lead increased the toxicity of copper and zinc. There was an increase in metal toxicity as pH decreased from 8 to 5, and toxicity increased when suspended solids concentrations increased from 50 to 200 mg/L. These laboratory experiments begin to explain the variable nature of stormwater toxicity and provide an understanding of why field measurements of toxicity in stormwater can change rapidly, as a storm flushes particulate and soluble materials from the watershed.

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