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RAINWATER CONTRIBUTION TO THE DISSOLVED CHEMISTRY OF STORM RUNOFF

by

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MANAGEMENT PERSPECTIVE

Runoff from urban stormwater can contain significant amounts of pollution loads. This study, carried out under the Water Quality Modelling project, shows that the contribution of nitrogen compounds and certain metals from the rainwater was much more significant than that from the land. This information is useful for estimating pollution loadings and modelling water quality.

Acting Chief
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SOMMAIRE

Cette étude porte sur les liens entre la présence de substances dissoutes dans les eaux pluviales et dans les eaux de ruissellement qui s'écoulent dans un bassin versant urbain comprenant des installations industrielles. Une série d'échantillons d'eaux pluviales a été recueillie et analysée pour déceler la présence de substances nutritives déterminées, des principaux ions et d'oligo-éléments. On a découvert que les eaux pluviales constituaient la principale source de composés d'azote et de deux métaux (Cu et Ni). Par contre, les eaux pluviales ne renfermaient que des proportions peu importantes de phospohore (P total), d'ions majeurs et d'oligo-éléments déterminés (Ba, Cd, Cr, Pb et Zn).

PERSPECTIVE-GESTION

Les eaux de ruissellement des zones urbaines peuvent renfermer des quantités importantes de polluants. La présente étude, menée dans le cadre du projet de Modélisation de la qualité de l'eau, révèle que l'apport de composés d'azote et de certains métaux provenant des eaux pluviales dépasse de beaucoup les charges provenant du sol. Cette information est utile pour estimer les charges de polluants et pour élaborer des modèles de qualité de l'eau.

Le chef intérimaire

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ABSTRACT

The relationship between the dissolved chemistry of rainwater and urban storm runoff was studied in an urban test catchment with industrial land use. Towards this end, sequential samples of rainwater and stormwater were collected and analyzed for selected nutrients, major ions and trace metals. For nitrogen compounds and two metals (Cu and Ni), rainwater was found to be the major source. For total P, major ions and selected trace metals (Ba, Cd, Cr, Pb and Zn), the rainwater contributions were hardly significant.

INTRODUCTION

Although the early studies of urban runoff pollution assumed that the contribution of pollutants in rainwater is small or even negligible, the recent studies by Wilber et al. (1975), Malmqvist (1978), Black (1980) and Halverson et al. (1984) showed that certain pollutants found in stormwater are primarily contributed by rainwater and rainwater should be recognized as one of the sources of pollution in urban runoff.

The studies dealing with urban runoff pollution and its sources are quite numerous as documented by a recent literature survey on this subject (Ellis, 1986). It was noted, however, that only a few studies of urban runoff pollution dealt with the direct contribution of pollutants in rainwater to urban runoff pollution, although the knowledge of such a contribution and other pollution sources is important for simulation of urban runoff composition. To advance the understanding of urban runoff pollution and its sources, a study of the contributions of rainwater to the pollution of urban runoff was undertaken in Burlington, Ontario. Such contributions were measured for individual events and further examined with regard to basic storm characteristics.

STUDY AREA

The test catchment selected for the study of rainwater and runoff pollution represents an urban area of 10.3 ha with industrial land use and imperviousness of 69%. Industrial operations located in the catchment are diverse and include food processing, steel fabrication, engine oil refinery, manufacturing of wood finishing products, sheet metal finishing, and wholesale offices, showrooms and warehouses.

The test catchment is drained by a simple tree-type sewer system consisting of a main sewer with two lateral branches. The sewers are concrete pipes with diameters varying from 0.53 m to 0.69 m. The drainage density in the catchment, defined as the sewer length per unit area, is 35 m/ha.

The land surface slopes in the catchment were estimated as 0.015. The longest overland flow route was measured as 19 m. Such relatively short overland flow routes and moderate slopes contribute to a relatively fast response of the catchment. Using the kinematic wave formula, the maximum inlet times in the catchment were estimated as 5 and 15 minutes for rainfall intensities of 66 mm/hr and 37 mm/hr, respectively.

METHODS

Constituents Studied

The selection of constituents to be studied was to a large extent governed by the results of earlier studies (Randall et al. 1978) which indicated significant amounts of certain constituents in rainwater. Altogether, 18 constituents listed in Table 1 were studied. These constituents can be classified into three categories: nutrients, major ions, and metals.

Table 1. Constituents Studied: Detection Limits and Frequencies of Occurrence

Constituent	Abbreviation	Number of Samples RA[1]/ST[2]	Detection Limit (mg/L)	Frequency of Occurrence in Observed Events (%)	
				Rainwater	Stormwater
Nitrate Nitrite	NO_2/NO_3	98/180	0.005	100	100
Ammonia	NH_4	98/180	0.001	100	100
Total Kjeldahl N	TKN	98/180	0.010	100	100
Dissolved Carbon	DC	96/181	0.200	97	100
Total Phosphorus	TP	99/180	0.001	100	100
Calcium	Ca	94/189	0.200	99	100
Magnesium	Mg	94/189	0.100	99	100
Sodium	Na	97/189	0.100	78	100
Potassium	K	98/189	0.100	91	100
Sulphate	SO_4	98/198	1.000	100	100
Chloride	Cl	98/198	0.100	93	100
Barium	Ba	79/175	0.100	4	13
Cadmium	Cd	76/196	0.010	57	9
Chromium	Cr	76/196	0.010	42	45
Copper	Cu	80/196	0.010	90	82
Lead	Pb	80/195	0.010	48	48
Nickel	Ni	80/195	0.010	91	51
Zinc	Zn	61/187	0.010	100	100

1 Rainwater
2 Runoff (stormwater)

Rainwater Sampling

Rainwater samples were collected sequentially using a specially designed rainwater sampler which was described elsewhere (Ng, 1985). The depth of rainfall was recorded by a tipping-bucket rain gauge.

Runoff Monitoring

Runoff quantity and quality were observed in a manhole at the downstream end of the main sewer. Runoff flow rates were measured by means of a calibrated weir. Weir heads inside a stilling well were recorded by a float-type water level recorder. Runoff samples were collected at the same location by a Sigmamotor automatic water sampler, model 620. The sampler collects up to 24 sequential samples, 500 ml each, at preselected times.

Sample Processing and Analysis

The transfer, storage and analysis of both rainwater and runoff samples were done according to the standard procedures which are given elsewhere (Water Quality Branch, 1978; Water Quality Branch, 1981). The detection limits for various analyses were given earlier in Table 1. Because of the intermittent nature of rainfall and the sequential sampling at constant time intervals, some rainfall samples were too small to allow all chemical analyses.

Using the analytical results, mean event constituent concentrations were calculated for all events using the following expression:

$$C = \sum_{i=1}^{n} C_i V_i / V$$

where C is the mean volume-weighted concentration, C_i is the concentration in the i-th sample, V_i is the flow volume during the period from $(t_{i-1} + t_i)/2$ to $(t_i + t_{i+1})/2$, t is the time of sampling measured from the onset of sampling, n is the total number of samples and V is the sum of V_i's.

Using the mean event concentrations, the unit loading rates were calculated for both rainwater and runoff by averaging the observed loads over the runoff contributing area. For this purpose, the following expression was used:

$$L_j = 1000\ H_r C_j$$

where L is the unit loading rate for constituent j (in mg/m^2), H_r is the water volume, rainwater or stormwater, in metres (calculated as the water volume divided by the runoff contributing area), and C_j is the mean event concentration (mg/L).

RESULTS AND DISCUSSION

The data base analyzed in this study comprises 31 rainfall/runoff events, which were selected from a 2-year field record. For each event, the basic characteristics and the level of contamination were determined. The event characteristics which included the rainfall and runoff depths, and the antecedent dry weather period were given elsewhere (Ng, 1985).

For individual events, compositons of rainwater and stormwater samples were determined and used to calculate mean loadings. All data are given in Table 2. Discussion of presented data follows.

Frequencies of Occurrence

The frequencies of occurrence of the 18 constituents studied, at levels above the detection limit, are given in Table 1. It is apparent from Table 1 that all nutrients and major ions were present in a vast majority of samples at levels above the detection limit. Some differences in frequencies in rainwater and stormwater samples were noted for metals. For cadmium and nickel, the frequencies in stormwater were lower than in rainwater. This would imply that both elements are lost from rainwater during the transport through the drainage system. The opposite was true for barium which may be originating mostly in the catchment rather than from atmospheric sources.

Mean constituent concentrations and loading rates

The loadings in rainwater varied widely during the individual events as well as from one event to another. When examining the loading variations within the

Table 2. Study Results

Constituent	Concentrations (mg/L) RA[1] Mean	St.Dev.	ST[2] Mean	St.Dev.	Mean Loadings (mg/m^2) RA	ST	Mean Ratio of RA/ST Loadings[3]
NO_2/NO_3	.756	.579	.757	.690	2.7	3.4	1.0
NH_4	.585	.653	.302	.292	2.3	1.0	2.6
TKN	.827	.820	.572	.489	3.2	2.2	1.4
DC	1.753	2.255	3.824	2.580	7.5	16.6	0.4
TP	.036	.058	.122	.087	0.2	0.5	0.5
Ca	1.378	1.134	19.742	7.256	4.7	74.8	0.1
Mn	.392	.364	2.924	.830	1.4	11.9	0.1
Na	.231	.185	2.441	1.496	0.8	13.1	0.1
K	.124	.083	.755	.355	0.4	2.9	0.2
SO_4	6.106	5.499	21.687	9.979	20.7	88.6	0.2
Cl	.505	.451	3.627	2.645	1.7	12.5	0.1
Cd	.011	.004	.010	.002	0.03	0.05	0.7
Cu	.068	.077	.029	.023	0.21	0.11	2.3
Cr	.014	.021	.013	.007	0.04	0.06	0.6
Pb	.105	.298	.095	.101	0.13	0.36	0.5
Ni	.049	.034	.026	.014	0.15	0.12	2.0
Zn	.229	.216	.140	.224	0.43	1.12	0.6
Ba	.052	.032	.031	.031	0.19	0.45	0.6

[1]RA = Rainwater; [2]ST = Stormwater; [3]The mean ratio may differ from the ratio of mean loadings.

set of 31 events, the smallest variations were found for all nutrients with the exception of total phosphorus. Generally, such variations were within one order of magnitude. Nitrogen loadings were relatively consistent and high in both study years. Such findings are similar to those reported by Randall et al. (1978) for bulk precipitation samples.

The variations in total phosphorus (TP) and major ions and metals were within two orders of magnitude. In the case of TP, this was partly caused by some very low concentrations observed which is consistent with the earlier reported findings of Halverson et al. (1984).

Among the major ions, SO_4 was found in the highest loadings (23.55 mg/m^2) among all the constituents studied. The lowest loadings were noted for Na and K which indicated that most of the storms originated locally or in other inland regions and, therefore, carried low Na concentrations in comparison to those from sea coast regions (Kennedy et al., 1979). Among the trace metals studied, the loading rates of Zn, Cu, Ni, and Pb were found to be predominant in rainwater. Cd, Cr and Ba were found in considerably smaller quantities. These findings are supported by the frequencies of occurrence given in Table 1. The loading of Zn was the highest among all the trace metals studied. This finding is in agreement with the observations of Wilber et al. (1975).

The runoff loadings also showed wide variations among the constituents reported for rainwater. The loadings of SO_4 and Ca were significantly higher than those for all other constituents. The nitrogen compounds loadings were of the same order of magnitude as in rainwater.

Among all the constituents, the major ions, with the exception of K, were found at significantly high loading rates. The loadings of K were an order of magnitude smaller than all the others in this group. The SO_4 and Ca loadings were particularly high. Black (1980) reported similar finding in a study of runoff from a small parking lot.

Among the loadings of trace metals, the loading rate of Zn was the largest followed by that of Pb. In fact, the Zn loading rate was an order of magnitude greater than other loadings in this group. The mean concentrations of Zn and Pb in runoff from the study area were 0.140 mg/L and 0.096 mg/L, respectively. Such values compare well to those reported for another catchment in the same urban area (Marsalek, 1983). In this catchment which represented a shopping plaza the mean concentrations of Zn and Pb were 0.117 mg/L and 0.096 mg/L, respectively.

It was also noted that the loadings of Zn and Pb were much higher in stormwater than in rainwater and, therefore, originated primarily in the catchment.

The contributions of rainwater to runoff dissolved chemistry are presented in Table 2 which lists mean loadings in rainwater and stormwater, and their ratio. Comparisons of both loadings indicate that for major ions and most metals, some redistribution of loadings takes place as the rainwater pollutants enter the drainage system and are transported to the drainage outfall. On the other hand, for nitrogen compounds, Cu, and Ni, practically all runoff loadings possibly originated in rainwater, because the ratios of rainwater to stormwater loadings are greater than 1. The studies reported by Malmqvist (1978), Randall et al. (1978), Black (1980), and Halverson et al. (1984) concluded unanimously that rainwater is a significant source of nitrogen compounds. The presence of nitrogen compounds in rainwater is believed to result from the rainout rather than the washout, because there is abundance of nitrogen (78%) in the atmosphere. For the remaining nutrients, the rainwater loadings represented 45% and 33% of those in stormwater for TC and TP, respectively.

Among the trace metals studied, rainwater contributed most of the Cu and Ni loadings observed in stormwater. This finding for Cu confirms the data reported by Marsalek (1983) for a shopping plaza runoff. The main source of Ni seem to be smelter emissions from a heavily industrialized area located about 20 km from the study catchment. For the remaining metals, land use activities seem to be the main sources. This is particularly true for Zn and Pb which originate from traffic byproducts and only 38% and 36% of their loadings, respectively, seem to be contributed by rainwater.

Rainwater barely contributed to major ion loadings in runoff. Such contributions varied from 5% for Na to 23% for SO_4. Major ions were abundant in stormwater and this had a buffering effect on stormwater acidity. Although the average pH value for rainwater was only 4.5, the corresponding value for stormwater was 7.2.

Effects of Storm Characteristics on Rainwater and Stormwater Compositions

A limited analysis of the effects of storm characteristics on rainwater composition was also undertaken. In particular, linear correlations among the storm rainfall, antecedent dry period and the rainwater composition were studied. It was noted that there was no correlation between the storm rainfall and the antecedent dry period. Further analysis indicated that the rainwater composition did not correlate well with both the storm rainfall and antecedent dry weather period. Such findings suggest that rainwater composition, for a given storm, is a result of the rainout process.

For stormwater, the correlation between runoff composition and the antecedent dry period was investigated. The calculated linear correlation coefficients varied from -0.358 (for Cd) to 0.622 for NH_4. Such values indicate very poor correlations between both phenomena and do not support the common assumption of linear pollutant accumulation on the catchment surface as the main factor controlling runoff quality.

CONCLUSIONS

Investigations of relationships between the dissolved chemistry of rainwater and stormwater indicate that rainwater is a significant source of numerous pollutants found in stormwater. This is particularly true for various forms of nitrogen and possibly some metals (Cu and Ni). For the remaining constituents studied, TP, major ions and selected metals (Ba, Cd, Cr, Pb and Zn), rainwater contributed very little to the loadings found in stormwater. These findings should be utilized in the modelling of urban runoff quality. The pollutants in rainwater are a product of the rainout process and their concentrations are independent of the pollutant accumulation and wash off processes on the catchment surface as in runoff. These processes form the basis of the current runoff quality models. Such models should be better suited for the modelling of pollutants which originate in the catchment (TP, major ions, and most metals).

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