

First flush effect of metals and anions in stormwater runoff from roads in mid-Sweden

B. B. Lind¹, M. Bäckström² and E. Geisler¹

¹*Swedish Geotechnical Institute, Sweden*

²*Man-Technology-Environment Research Centre, Örebro University, Sweden*

Abstract

The first flush effect of metals and anions was studied in stormwater runoff from one highway and one local urban road. The runoff events followed upon a dry period of three days. The results indicate that 50-60% of the total mass of Zn, Cu, Pb, Ni, Co, Cd and As was transported with the first 30% of runoff. At the highway site the first flush concentrations of Cu exceeded the target values for small watercourses by a factor of 3. At the local urban road site the runoff concentrations were considerably higher, but might be affected by the road materials, the rain intensity and by vehicles stopping at the traffic lights. It is concluded that the first flush effect from single rain events can cause high concentrations of, for example, Cu and Pb, which may be toxic to the biota.

1 Introduction

Road traffic and road materials are the source of a number of pollutants hazardous to the environment and the concentration of pollutants in stormwater runoff from roads and highways has been studied in several research projects during the last 20 years. The EU-project POLMIT is an ambitious effort to obtain an overall picture of the spreading and dispersal mechanisms of pollutants from the European road network. Knowledge of mean concentrations and the total load of different constituents in the runoff water is thus fairly good. However, the concentrations of pollutants vary a great deal within each runoff event, causing a first flush effect with high concentrations during the first minutes of the runoff. The concentration of pollutants during the first flush may exceed the target values for water quality and cause damage to the environment (Bjerkås & Lindmark [1]).

The first flush phenomenon was studied using automatic sampling more than 15 years ago in the UK (Colwill, *et al.* [2]) and more recently in the USA (Sansalone & Bushberger [3]). It has been shown that both dissolved and particulate metals show first flush effects. Dissolved metals, such as Cd, begin to show first flush effects at relatively low rainfall intensity whereas particulate metals, Pb for example, show the same effect at higher rainfall intensities. However, the chemical composition of stormwater changes over time as other fuels and materials come into use. There is a need for continuous follow-up of the first flush effect and its environmental load compared with the average runoff load.

This paper presents the results from a study of stormwater quality and pollution load from first flush runoff from a Swedish highway. The results are discussed in relation to mean stormwater quality and also compared with a complementary study of first flush effects from an urban road with vehicles stopping at traffic lights.

2 Methods and Sampling

2.1 Field sites

The highway studied, site A, is the European E4 highway at Norsholm, about 21 km NE of Linköping in the middle of Sweden (the monitored site F within the POLMIT project). This is a four-lane (2+2) highway with separated driving lanes in each direction. The speed limit is 110 km/h and the traffic density (ADT) is 17 900 vehicles per day, of which 3 000 (17 %) are heavy vehicles. The highway was opened to traffic in November 1992 and the asphalt cover is the original since that time.

Stormwater runoff was captured in a PVC-gutter, 1 m long, 15 cm wide and 5 cm deep, installed adjacent to the asphalt edge. From the gutter the water was channelled into a pipe for sampling. The runoff area to the gutter was defined as a 1 m wide strip crossing the road slightly obliquely, see Fig. 1. The runoff area to the gutter is 12 m².

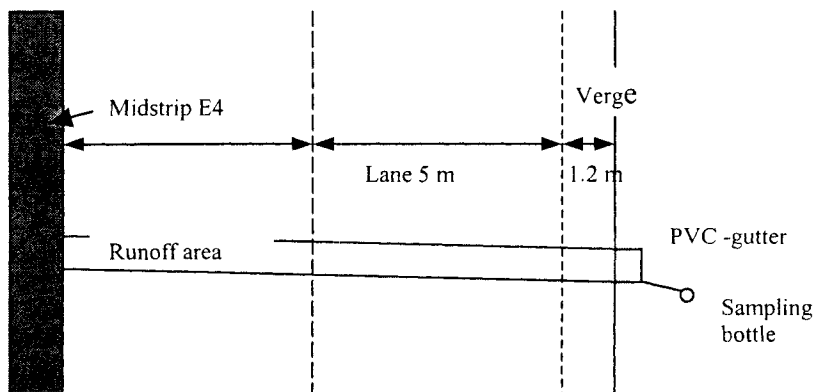


Figure 1. Schematic map of the studied field location - highway E4 at Norsholm.

One storm event was monitored for a period of 1.5 h from the beginning of the first rainfall until 45 min of the generated runoff had been captured. The rain started at 9 am on October 31 and lasted for 2 h with a total of 5 mm rainfall, measured in a precipitation gauge c. 100 m from the road. The runoff from the road started 30 minutes after the beginning of the rain and the first 2 mm (24 l runoff) of the precipitation was sampled. There had been three days (72 h) of clear weather before the actual rain event.

Samples were taken in 250 ml, acid-rinsed, bottles and before sampling the PVC-gutter and pipes was carefully washed with clean water. Samples were taken 0, 2, 3, 5, 7, 10, 15, 20, 30 and 45 minutes after the start of the runoff. The flow intensity was calculated from the filling time of the 250 ml bottles. The traffic intensity during the sampling period was calculated approximately by extrapolation from counting over two-minute periods.

In addition to the study of the highway runoff a similar, complementary study, was made on runoff from a traffic light-regulated urban road, site B, with traffic density of ADT 11 500 vehicles per day. After three days (72 h) of dry weather the road area 15 m ahead of the traffic lights was wetted by artificial rain. Water, from the public water supply at Linköping, was spread with an intensity of approximately 0.2 mm/minute for 50 minutes. The road was seven metres wide and the wetted runoff area was marked and measured to be 14 m². A total of 140 l of water was spread with the aid of two watering-cans. The runoff water was collected on a washed plastic sheet placed under the asphalt edge at the side of the road. Sampling and sample treatment were in accordance with the highway study.

2.2 Sample treatment and analysis

All sample bottles had been washed in a bath of 7M HCl solution for one week and then rinsed three times with ultrapure water (18 Mohm/cm). After the sampling events the samples were brought to the laboratory immediately, where the pH and conductivity were measured. Each sample then was divided into three parts. The combined colloidal and dissolved fractions, as defined conventionally, were separated from the particulate fraction by filtration on an 0.45 µm membrane (Teflon filter, PTFE/H) and acidified to pH 1-2 using conc. HNO₃ for further analysis by ICP-MS at XRAL Laboratories Canada (method MS 200). The non-filtered parts of the samples were sent for analysis to XRAL (total metal analysis) and Örebro University (anion analysis) respectively, see Fig. 2. The separated fraction < 0.45 µm includes the dissolved matter but it has also been reported (Randall, *et al.* [4]) that an average of 80% of the total suspended solids in urban runoff had a diameter of less than 25 µm, and 57% had diameters of less than 15 µm.

Capillary zone electrophoresis (CZE) analysis of the anions chloride, sulphate and nitrate was performed on a HP ^{3D}CE system (Hewlett Packard) equipped with a diode array detector. The carrier electrolyte consisted of 5 mM chromate buffer at pH 8 with 0.5 mM tetradecyltrimethylammoniumbromide (TTAB) (Jones & Jandik, [5]; Romano, *et al.* [6]). Injection was done hydrostatically at

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10 mbar for 30 seconds. Before the samples were injected they were filtered through 0.40 μm PC filter.

Dissolved organic carbon (DOC) was measured with catalytic oxidation followed by IR detection using a Formacs^{HT} TOC Analyzer (Skalar Analytical). Prior to analysis the samples were filtered through a 0.40 μm PC filter.

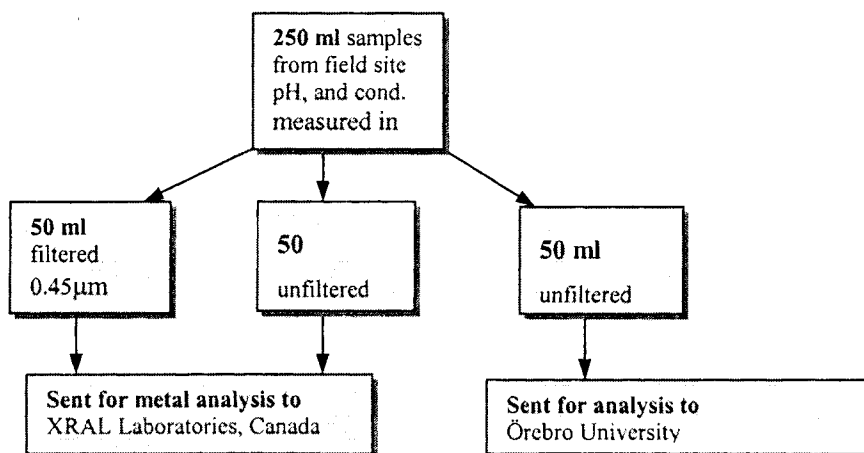


Figure 2. Sampling and analysis strategy.

3 Results and discussion

The runoff from the E4 highway (site A) started 30 min. after the beginning of the rain and the discharge intensity varied from about 0.002 l/s (0.000167 l/sm²) initially to a peak of 0.014 l/s (0.00117 l/sm²) after 15 min and then slowly falling to 0.005 l/s at the end of the sampling period. The discharge from the urban road (site B) was on average 0.0467 l/s (0.0033 l/sm²) although the flow fluctuated somewhat due to the watering technique. The traffic density at site A was measured to be 10 vehicles per minute in the two lanes adjacent to the gutter, i.e. approximately 450 vehicles during the sampling period. At site B the density was approximately four vehicles per minute or around 180 vehicles during the sampling period. The chemical composition of the Linköping tap water used as artificial rain at site B is presented in Table 1.

A common opinion has been that the longer the dry period, the more pollutants are accumulated on the road, thus causing a larger first flush effect of pollutants when the rain eventually comes. However, it has also been argued that the antecedent dry period length is insignificant in explaining any variation in pollutant load (Ellis, *et al.* [7]) and that an equilibrium between accumulation and wind-removal of pollutants will occur on the road after a few days of dry weather (Harrison & Wilson [8]; Colwill, *et al.* [2]). The first flush effect will thus be the same after a few days of dry weather compared with weeks of dry weather.

Table 1. Chemical composition of Linköping tap water.

Parameter	Concentration	Parameter	Concentration
Zink (ppb)	5.7	Vanadium (ppb)	0.15
Copper (ppb)	76.7	Cobalt (ppb)	<0.1
Lead (ppb)	0.15	Chloride (ppm)	11.18
Chromium (ppb)	0.55	Sulphate (ppm)	19.99
Nickel (ppb)	1.0	Nitrate (ppm)	2.69
Cadmium (ppb)	0.03	DOC (ppm)	3.79
Arsenic (ppb)	0.45		

The results from the pH and conductivity measurements are presented in Fig. 3 and Fig. 4. The pH is in the range of common values for road runoff (Malmqvist [9]; POLMIT [10]). The study was made before any salting for the season on the highway, site A, and the conductivity was in the range of summer values measured at this site within the POLMIT project. The initial values at site B were more in the range of winter values compared with the POLMIT results. The declining conductivity trends at both site A and site B indicate the first flush effect, however, the conductivity at site B is much higher. This difference in chemical content is largely considered to be associated with the chloride and particulate phase as reflected in the chemical analysis below. The interpreted cause of this is the higher "rainfall" and runoff intensity at site B, in combination with differences in road material and traffic.

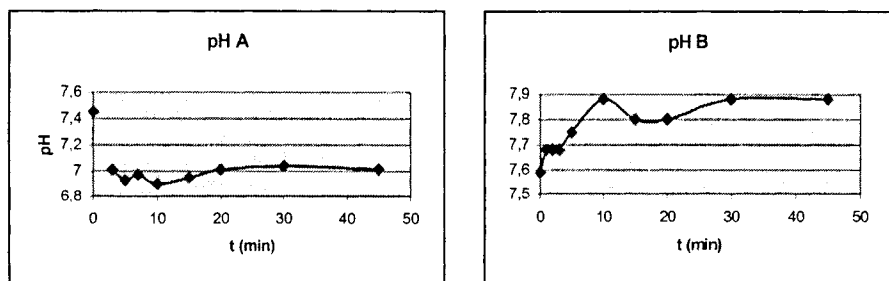


Figure 3. pH variations in unfiltered samples from site A and site B.

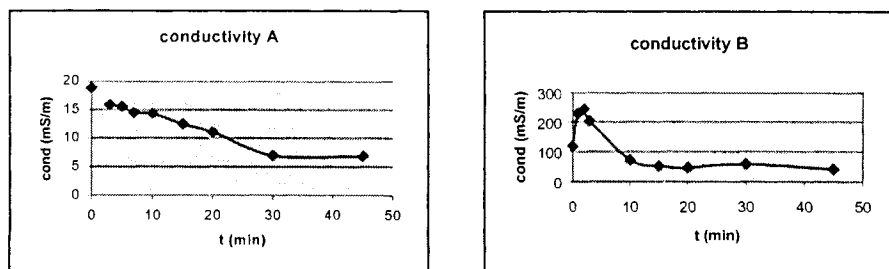


Figure 4. Conductivity in unfiltered samples from site A and site B

The concentrations of the anions Cl^- , SO_4^{2-} , NO_3^- (Fig. 5) and DOC (Fig. 6) follow the same decreasing trend as the conductivity, although the pattern at site B is quite disturbed.

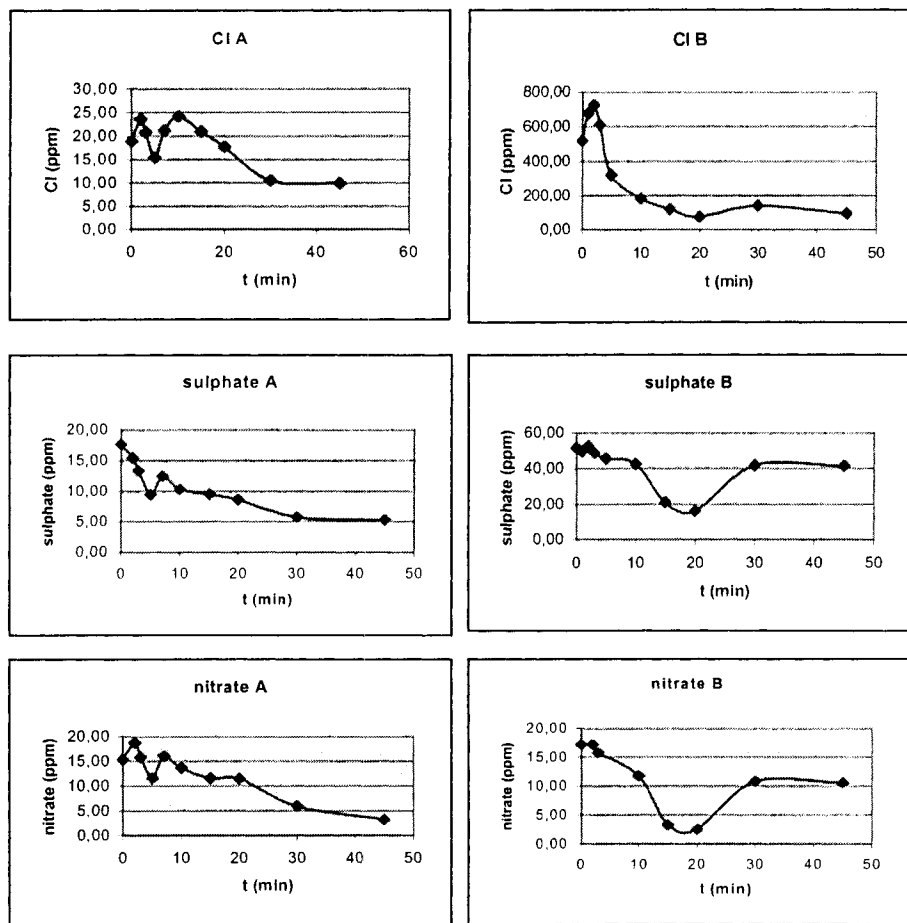


Figure 5. Chloride, sulphate, and nitrate at sites A and B

The analysis results for selected metals are presented in Fig. 7. All elements in series B and most elements in series A show a significant first flush effect. The metal concentrations fall rapidly during the first 15-20 minutes of runoff and the more stable long-term concentrations are in many cases around 30% of the original concentrations. Considering the intensity and duration of the rain at site A it was calculated that approximately 50-60% of the total mass of the metals Zn, Cu, Pb, Ni, Cd, Co and As was transported during the first 30 minutes, representing about 30% of the total runoff volume. Similar results were calculated for all elements at site B. This is much in agreement with results

reported by Beckwith *et al.* [11], Hvitved-Jacobsen & Yousef [12] and Sansalone & Buchberger [3].

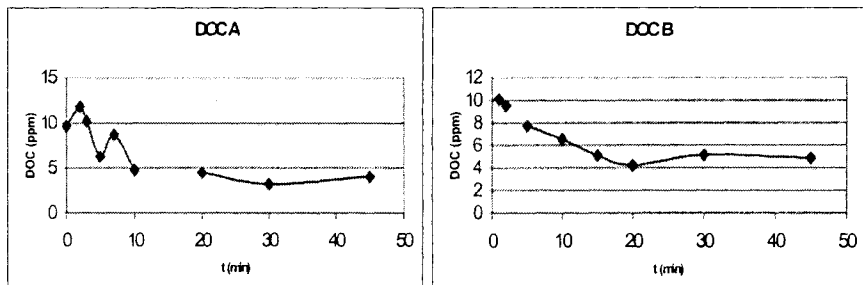


Figure 6. Concentrations of dissolved organic carbon at sites A and B

In series A 97% of the Pb was associated with particles $> 0.45 \mu\text{m}$ and as much as 99.5% in series B. 35-50% of the Zn content, 20-30% of the Cu, 30-60% of the Ni and 65-90% of the Co was found as particles $> 0.45 \mu\text{m}$. The first flush effect were present both in the particulate fractions $> 0.45 \mu\text{m}$ and in the finer "dissolved" fraction. The concentrations of Cr were low at the beginning of series A but increased rapidly after about 20 minutes of runoff and reached high values. The increase was the result of the addition in the fraction $< 0.45 \mu\text{m}$. There was little difference between the "dissolved" and colloidal fractions for As, except for the initial phase, whereas the Cd concentrations in series A fluctuated.

The toxicity and environmental load of metals depend both on the concentrations and on the total load of metals. In Table 2 the initial and long-term concentrations of selected metals are listed together with the calculated total metal loads from the first 30 minutes as part of the total load over the whole rain event, site A 120 minutes and site B 50 minutes. Also listed are the seasonal average values for the runoff, calculated from one-year measurements within the POLMIT project, literature values for road stormwater, average values for rain in the region and actual target values for pollution influence on small watercourses.

From the comparison in Table 2 it can be concluded that the first flush accounts for a major part of the pollution transport with the stormwater runoff. However, at site A the metal concentrations were moderate and even during the initial runoff phase most values were below the calculated seasonal mean values. Copper seems to have the most severe first flush effect of the metals studied. There is an obvious risk that the first flush of Cu can cause concentrations well above the target values in small watercourses.

4 Conclusions

This investigation shows that a significant first flush effect occurred both at the highway site and the urban road site. The runoff concentrations of metals and

Table 2. Comparison of values found in this study with values found in the literature and within the POLMIT project.

ppb	Site A, Fraction, unfiltered			Site B Fraction, unfiltered			Aver.	Aver.	Rain ^β	Target values [#]
	Init. Conc.	Long. conc.	Tot. % 30 min	Init. Conc.	Long.	Tot. % 30 min	Site A ^α	Lit.		
Zn	100	40	60	400	100	59	250	300*	7-30	130
Cu	55	20	52	150	80	57	30	50-100**	1.2-6.6	18
Pb	10	4	58	45	18	56	20	100- 200**	1.7-4.6	35
Cr	3	15	40	7	2.5	57	4	2.6***		11
Cd	0.1	0.05	55	2.0	0.2	63	1	2-4**	.05-0.1	2.5
Ni	4	1.5	56	9	4	56		2.6***	0.2-0.4	16

*Larm 1994; **Malmqvist 1994; ***Bjelkås & Lindmark 1994; [#]According to "heavy influence from point source on small watercourses in S Sweden", NV 4918 1999; ^βIVL; ^αcalculated as the mean of the Sept. Nov. and Dec. POLMIT samples.

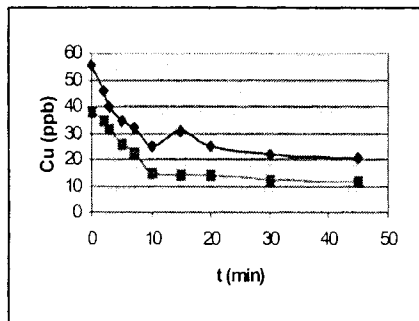
anions studied at site A (highway) were moderate and it may be concluded that not very much pollutants had accumulated during the three-day period of dry weather before the actual rain event. The concentrations at site B were considerably higher for all elements, except for nitrate and chromium. The results from this investigation indicate that 50-60% of the total mass of dissolved and particulate pollutants may be transported with the first 30% of runoff in a single rain event lasting a few hours. The first flush effect from single rain events during dry periods can cause high concentrations of Cu and Pb for example, which may be toxic to the biota.

5 Acknowledgement

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SERIES A



SERIES B

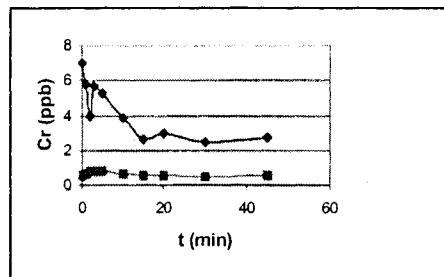
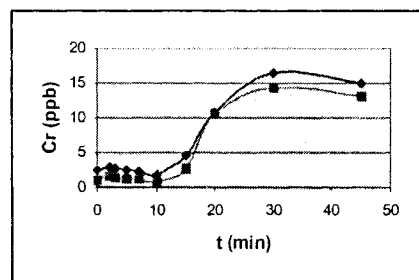
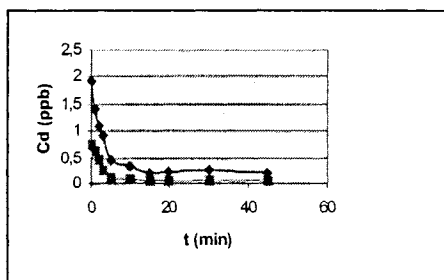
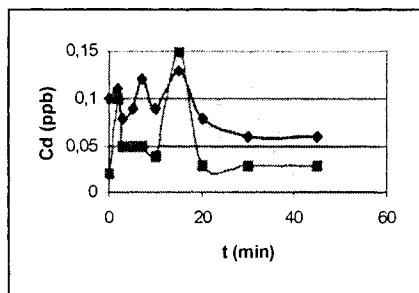
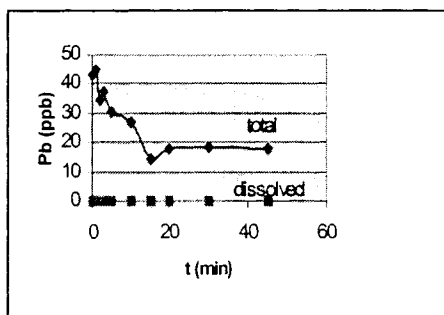
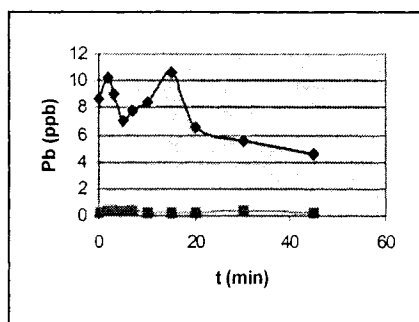
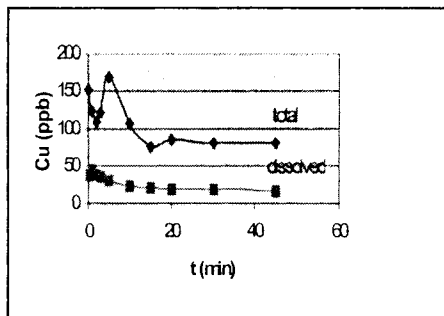
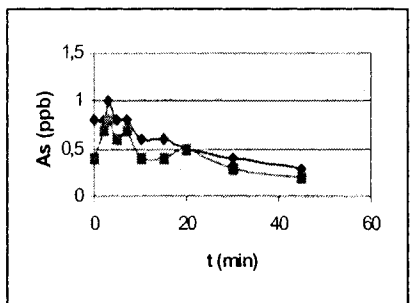
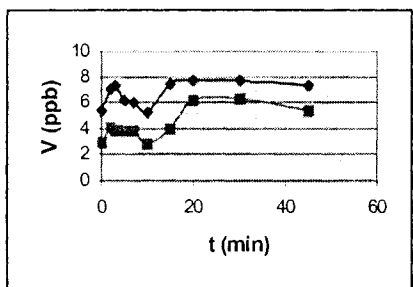
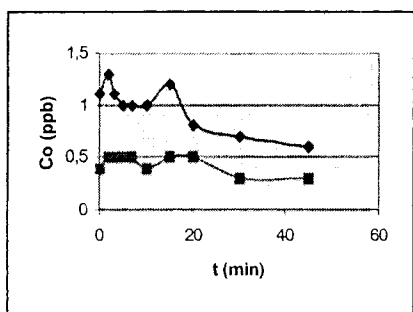
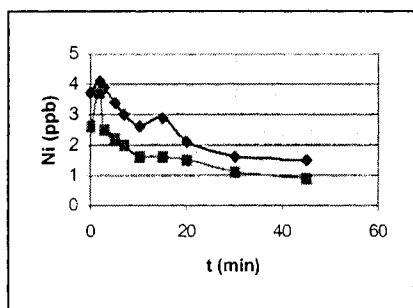


Figure 7. Metal concentration in filtered (square symbols) and unfiltered (diamond symbols) samples from site A (highway) and site B (urban road).



SERIES A



SERIES B

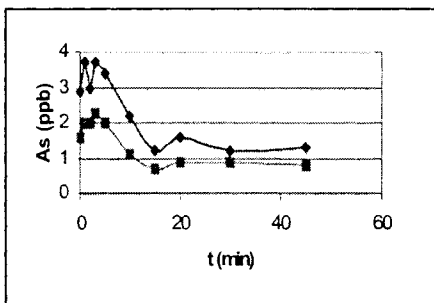
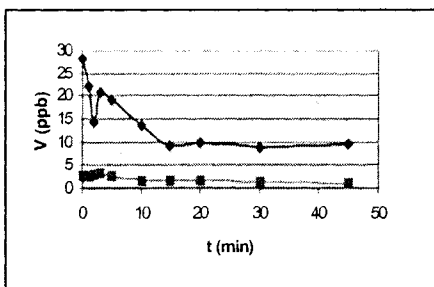
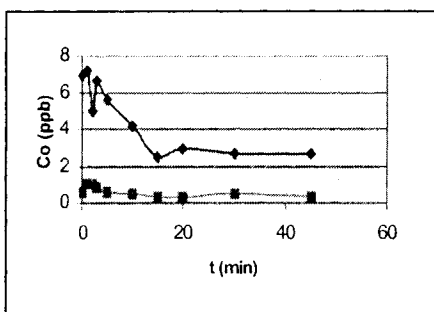
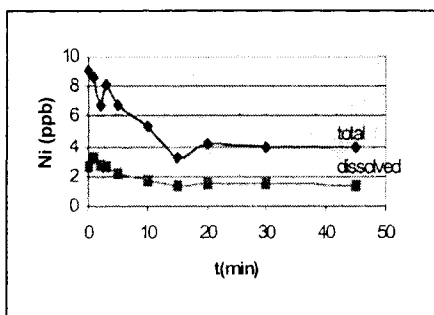


Figure 7- cont. Metal concentration in filtered (square symbols) and unfiltered (diamond symbols) samples from site A (highway) and site B (urban road).



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