

# ZINC, COPPER AND LEAD IN ROAD RUN-OFF

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## **ABSTRACT**

Transport activities contribute chemical contaminants to urban stormwater. The size of this contribution relative to those from other urban activities is an important consideration when attributing the costs of stormwater treatment.

As part of our efforts to estimate the fraction arising from transport we have undertaken intensive road run-off monitoring programmes at sites on Ash Street and Richardson Road in Auckland. The sites have negligible drainage onto the road from adjacent buildings and land surfaces, accessible stormwater networks that carry run-off only from easily delineated road surface catchments and high vehicle use. Weirs and flow recorders were installed in the stormwater networks and automatic run-off samplers were placed over the access manholes. Twenty four run-off samples were collected at the Ash Street site between 31 March and 14 April 1999 and 74 samples were collected at the Richardson Road site between 24 August and 18 September 2002. Vehicle numbers and size, atmospheric particulates and PAHs, gases (CO, NOx), wind speed and direction and rainfall were monitored continuously.

A contaminant accumulation/run-off model was developed and fitted to the measured metal concentrations in the road run-off to provide estimated concentrations for each minute of the monitoring periods. This model assumes a continuous linear accumulation of contaminants on the road surface; a reasonable assumption because daily vehicle numbers varied little at both sites. It also assumes that the fraction of accumulated contaminant washed off the road each minute is a function of the run-off intensity, ie mm/minute. Integration of the "instantaneous" contaminant mass loads, ie g min<sup>-1</sup>, over the monitoring periods produced estimates of the total amounts of copper, zinc, and lead washing off the road catchments. From these estimates, the vehicles counts and the lengths of the road catchments, the contributions of metals in the run-off per vehicle km were calculated.

# 1. INTRODUCTION

The contribution that transport activities make to the chemical contamination of aquatic ecosystems has long been a topic of considerable interest (and was the reason for starting the research described in this paper) but since 2000 this interest has increased many-fold. The reason for this is that by October 2000 all storm water discharges were required to have permits or "resource consents" under our Resource Management Act.

Storm waters, particularly in urban areas, are known to contain chemical contaminants that can adversely affect the aquatic ecosystems into which the storm waters are discharged. Since the purpose of the Act is to avoid, remedy or mitigate the adverse effects of activities affecting natural water, the application of the Act to storm water has prompted serious consideration of storm water treatment and, more particularly, who is going to pay for it. One line of thinking is that since vehicles produce a proportion of the contaminants in urban storm water, then vehicle users

should pay this proportion of the cost of storm water treatment. The question is; "What is the proportion?"

Against this background, our research has focussed on estimating the road transport emission rates for chemicals that end up in urban storm water.

Contaminants that occur within the road corridor originate from remote sources such as industry emissions, as well as from the vehicles within the corridor, and contaminants move from the road corridor through both atmospheric and road run-off pathways. Our research is trying to quantify the contaminant mass flows from both remote sources and vehicles and along both atmospheric and run-off pathways.

This paper describes part of this work; the mass flows in road run-off.

## 2. STUDY METHOD

#### 2.1 STUDY SITES

The main requirements for a suitable monitoring site were that:

- the road run-off drains to a single point that can be instrumented for flow and automated sampling,
- only the road run-off reaches this point i.e., no drainage from other surfaces such as house roofs,
- the road catchment is readily defined,
- there is a supply of electricity near-by,
- the site is reasonably secure.

Sites that meet all these requirements are few and far between but we found two suitable sites in Auckland; one on Ash Street and the other on Richardson Road.

Ash Street (Figure 1) is a dual carriage-way arterial road carrying about 20,000 vehicles day<sup>-1</sup>. The monitored section of road is a gentle curve about 100m long. Traffic flows freely, although slowly at peak times. This section of the road is drained by two gully traps linked to a single storm water pipe. A manhole about 5m from the road provided access to the pipe.



Figure 1. Ash Street site.

Richardson Road is a single carriage-way but carries about 17000 vehicles per day, only slightly fewer than Ash Street. The monitored section was 500m long extending from one side of a gully to the other (Figure 2). Traffic flow was interrupted by a traffic light-controlled intersection at one end. Seven gully traps drained the road to a single pipe with an accessible manhole about 30m from the edge of the road (Figure 3).



Figure 2. Richardson Road site.

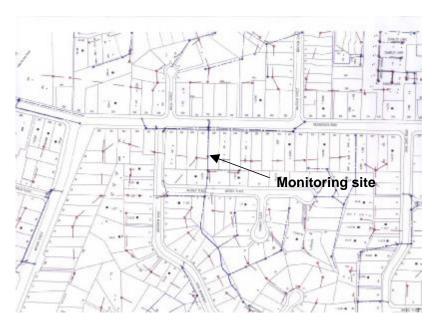


Figure 3. Storm water network at Richardson Road

#### 2.2 MONITORING PROGRAMME

At both sites, a NIWA air quality monitoring trailer was used to measure wind direction and speed, rainfall, solar radiation, temperature, humidity, continuous atmospheric CO and PAH concentrations, and to collect samples of PM<sub>10</sub>. Traffic counters recorded vehicle type, numbers, and speed. A flow recorder and automatic water sampler were installed in a cabinet attached over top of the manhole. A small weir was constructed in the storm water pipe immediately below the manhole to provide level control and a pond for the sampler intake. The samplers were programmed to be initiated by water level.

Over a two week period from 31 March to 14 April 1999, 24 samples from three rainfall events were collected at the Ash Street site and over a four week period, 24 August to 18 September 2002, 74 samples from four events were collected at the Richardson Road site.

## 3 RESULTS

#### 3.1 ASH STREET

The top section of Figure 4 shows how vehicle numbers typically vary with the time of the day reaching peak numbers during the morning and evening rush. The section of the rainfall event sampled is shown expanded in the middle section of figure with the sample collection times marked as triangles. The lower section shows the concentrations of zinc and polycyclic aromatic hydrocarbons (PAH) in the samples collected at the times shown in the middle section of the figure.

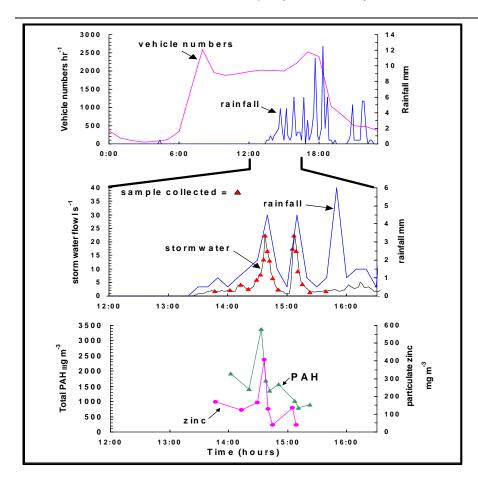


Figure 4. Results from the Ash Street site

## 3.2 RICHARDSON ROAD

The general form of the data, including the diurnal pattern of vehicle movements, collected from the Richardson Road site was the same as that shown in Figure 4 for Ash Street. Figure 5 shows the run-off discharge and the sampling times marked by dots for Richardson Road. The value of each dot on this figure is the particulate zinc concentration.

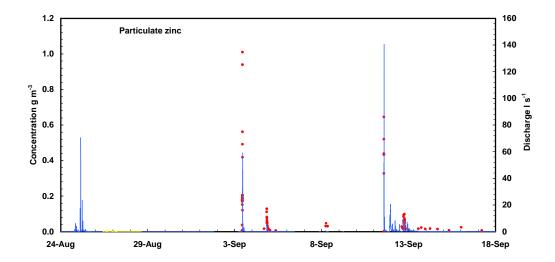


Figure 5. Particulate zinc concentrations and run-off discharge for Richardson Road.

Figure 6 shows the results for dissolved zinc. The obvious difference between the two figures is that whereas the particulate zinc concentrations decreased very rapidly after a rainfall event, the dissolved concentrations did not change much. This is an important feature of the results as explained below.

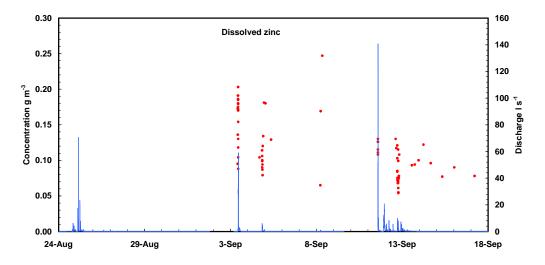


Figure 6. Dissolved zinc concentrations and run-off discharge for Richardson Road.

# 4 RUN-OFF MODELLING

The overall result that we were trying to obtain was the total mass load of metal washing off the road over a specific period of time. The mass load is obtained by multiplying the metal concentration in a sample by the discharge over the period that the sample represents. There is no problem doing this for samples collected at relatively short time intervals because neither the flow nor the concentration are likely to change much during each interval. For large gaps in the sample collection

sequence, however, the mass load cannot be calculated because the concentrations are unknown. Concentrations for these gaps need to be predicted and this is most accurately achieved by modelling.

At both monitoring sites, vehicle numbers per day did not vary much over a week although the pattern was more spread out on Sunday. Consequently, with similar numbers of vehicles every day, it is reasonable to assume that contaminants would be generated by vehicles at a roughly constant rate. Over periods of several days it is, therefore, also reasonable to assume that these contaminants would deposit on the road surface at a roughly constant rate. It would also be expected that a proportion of the vehicle-generated contaminants would be removed by wind from the road corridor. Rain falling on the road would mobilise the deposited contaminants with the proportion mobilised being some function of the rainfall, such as the rainfall intensity, i.e., the harder it rains the greater the proportion mobilised in a given space of time.

These processes were combined into the simple accumulation-wash-off spreadsheet model described below.

### **4.1 MODEL STRUCTURE**

For the accumulation module, the gross amount of a contaminant deposited on the road surface (GM,) over time interval – t (1 minute) is given by

$$GM_{t} = ((-tRA) + NM_{t-1})(1-D)$$

Where

R is the contaminant accumulation rate (g m<sup>-2</sup> - t<sup>-1</sup>)

A is the area of road surface (m<sup>2</sup>),

 $NM_{t-1}$  is the amount of contaminant (g) on the road at time t-1, i.e., the end of the previous time interval,

D is the fraction of contaminant removed from the road by non-washoff processes, mainly wind,

NM<sub>t-1</sub> is the net amount of contaminant remaining on the road at time t-1 after deposition, non-washoff removal and wash-off removal during the previous time interval.

The fraction F of the contaminant washed off the road in the time interval - t is given by

$$F = 1 - e^{K}$$

Where

$$K = -(SI)^{B}$$

S is a "slope" coefficient

I is the washoff intensity (stormwater discharge in mm/- t) B is an exponent.

The double exponential form of F ensures that F cannot exceed 1.0.

The net amount remaining on the road surface at time t (NM<sub>t</sub>) is given by

$$NM_t = GM_t (1-F)$$

The model calibration procedure involves selecting values for R, E, S and B, and adjusting these to find the minimum sum of differences between measured and modelled 1 minute loads.

#### 4.2 MODEL RESULTS FOR RICHARDSON ROAD

Figure 7 shows the best relationship that has been obtained to date for the fit of modelled to measured 1 minute run-off loads for particulate zinc. Note that both axes are logarithmic.

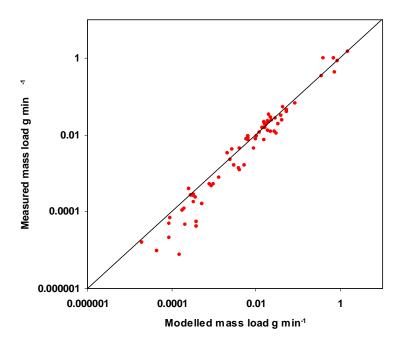


Figure 7. Model and measured 1 minute loads for particulate zinc.

This model fit gives a total run-off load of 52.8 g of particulate zinc over the 76 day monitoring period. There were 17,354 vehicles per day passing along the 0.5km monitored section of Richardson Road. The road run-off particulate zinc load was, therefore, 0.257 mg vehicle<sup>-1</sup> km<sup>-1</sup>. Best model fits for particulate copper and particulate lead gave estimates of 0.0424 mg vehicle<sup>-1</sup> km<sup>-1</sup> and 0.0463 mg vehicle<sup>-1</sup> km<sup>-1</sup> respectively.

Figure 8 shows the net accumulation of particulate zinc on Richardson Road during the monitoring period.

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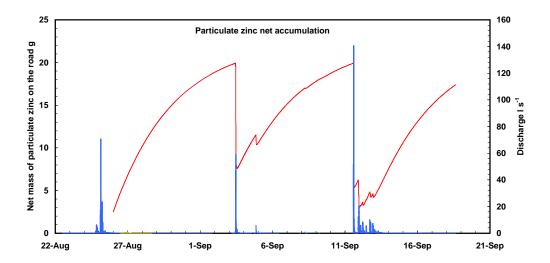


Figure 8. Net accumulation (red line) of particulate zinc on Richardson Road.

It might be expected that with Auckland's frequent rain, there would be little opportunity for contaminants to be blown out of the road corridor. A good model fit could not be obtained, however, without assuming a reasonable non-wash-off loss. This extent of this loss is shown in Figure 8 by the way the net accumulation rate decreases with time during dry periods. Similar patterns of accumulation were required to obtain good fits for particulate copper and lead.

Modelling dissolved metals was quite different. It was readily apparent from the monitoring data that dissolved metals do not follow the accumulation/wash-off concept adopted for particulate metals. Simple chemistry also tells us this. Most of the adsorption/desorption processes that occur between dissolved and particulate metals are quite fast so it would be expected that dissolved concentrations would always reflect the concentrations of metal attached to nearby sediment, i.e., mg kg<sup>-1</sup>, rather than the amount of particulate metal present, i.e., g m<sup>-3</sup>. In other words, the dissolved metal concentration in contact with sediment containing, say, 1000 mg kg<sup>-1</sup> of metal, would always be the same irrespective of how much of the sediment was present. This is exactly what we found in the road run-off and it enabled a simple approach to predicting dissolved metal concentrations.

Figure 9 shows the relationship between the ratio of dissolved to particulate zinc and the concentration of particulate zinc. Note that both axes are logarithmic.

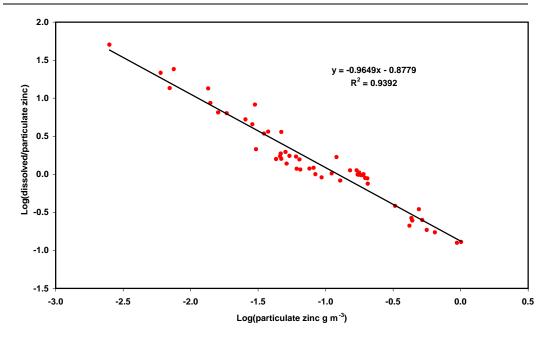


Figure 9. The dissolved/particulate zinc ratio as a function of the particulate zinc concentration.

This relationship shows that the dissolved zinc concentration varies only slightly and this can be seen from Figure 6. The best fit to this relationship enabled the dissolved zinc concentrations to be predicted from the modelled particulate zinc concentrations. The same procedure also worked well for copper. Figure 10 shows the match of modelled and measured dissolved zinc loads.

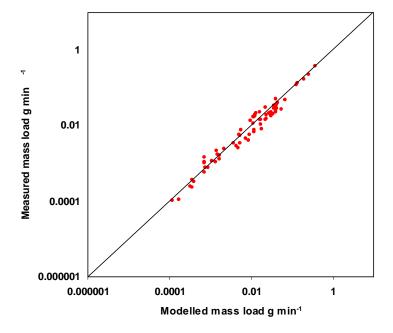


Figure 10. Measured and modelled 1 minute loads for dissolved zinc. Note that both axes are logarithmic.

Summing the 1 minute modelled dissolved zinc loads gives a total road run-off load of dissolved zinc of 38.9g over the 76 day period. This is 42% of the total zinc load; 91.7g, an important consideration when designing treatment processes for road run-off.

The particulate copper load was 8.69g and the dissolved copper load was 3.46g. The dissolved copper load was 28% of the total copper load.

The load for particulate lead was 9.5g over the monitoring period. Dissolved lead concentrations in natural waters are usually very low and this was also the case for road run-off. The load for dissolved lead was only 0.21g; 2% of the total lead load.

Table 1 presents the per vehicle loads for dissolved, particulate and total zinc, copper and lead.

Table 1. Model results for zinc, copper and lead (mg vehicle<sup>-1</sup> km<sup>-1</sup>). Estimates contained in the Auckland Region State of the Environment Report (ARC, 1999) are included for comparison.

Metal	Zinc	Copper	Lead
Particulate metal (this paper)	0.257	0.0424	0.00104
Dissolved metal (this paper)	0.190	0.0169	0.0463
Total metal (this paper)	0.447	0.0593	0.0473
Total metal (ARC, 1999)	0.70	0.16	

# 5 ROAD RUN-OFF CONTRIBUTIONS TO URBAN STORM WATER LOADS

Our research described above has provided estimates of contaminant loads washing-off roads expressed on a "per vehicle" basis, but there are two other substantial bits of information required before the transport contribution to the contaminants in urban stormwater can be estimated. Obviously, the transport contribution will vary with different catchments so catchment-specific calculations are required to obtain the most reliable estimates.

The first piece of additional information required is the total storm water contaminant load, e.g. on an annual basis, for a selected catchment. The few estimates of total loads for New Zealand urban catchments that have been published have very large uncertainties mainly because they are based on small numbers of samples. The second bit of information required is the number of vehicle km over the chosen time interval for the catchment. This can be obtained from the traffic models operated by many of the larger urban authorities.

The "back-of-the-envelope" estimates described below use very rough data for these two latter pieces of information but when better quality data become available the estimates below can be improved considerably.

There is a third bit of information required and that is the vehicle fleet composition in the selected catchment. The per vehicle loads of contaminants in road run-off will vary with the mix of vehicles, so for accurate estimates this mix must be known. Such information is available from traffic models but in the absence of data from these models, it is reasonable to assume that the 17000 or so vehicles travelling along

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Richardson Road each day are representative of the mix of vehicles on most large roads in Auckland City. For small residential roads, however, the mix is likely to be biased more towards light vehicles.

### 5.1 "BACK-OF-THE-ENVELOPE" ESTIMATES FOR AUCKLAND CITY

By a complex process of traffic counting and modelling combined with the latest census data, it is possible to estimate that the total distance travelled by vehicles in Auckland City in 2001 was 4.02 x 10<sup>9</sup> vehicle km. Multiplying this figure by the per vehicle loads estimated from our research, gives 1800 kg of zinc, 240 kg of copper and 190 kg of lead washing-off the City's roads in 2001.

The best compilation of urban catchment storm water loads for total metals is still the Urban Runoff Data Book (Williamson, 1993). In this publication, the 20<sup>th</sup>, 50<sup>th</sup> and 80<sup>th</sup> percentile loads for metals are derived from the frequency distributions of literature data reported prior to about 1990. These percentiles for zinc and copper are given in Table 2. The 20<sup>th</sup> percentile means that 20% of the urban loads reported in the literature were less than the value quoted, e.g., 250 g ha<sup>-1</sup> year<sup>-1</sup> for zinc. The area of Auckland City is about 15500 ha. Combining these data gives the values in Table 2 for the total annual loads of zinc and copper in storm water from the City. Also given are the annual road run-off loads as percentages of the total storm water loads. The actual percentage for Auckland City depends on its average urban catchment load which is probably somewhere between the 20<sup>th</sup> and 80<sup>th</sup> percentiles given in Table 2.

There have been no useful compilations of data for lead since the removal from lead from petrol in 1996.

		Zinc			Copper		
	Units	20%ile	50%ile	80%ile	20%ile	50%ile	80%ile
Urban catchment loads	g ha <sup>-1</sup> year <sup>-1</sup>	250	750	2000	20	90	200
Road run-off loads for Auckland City	kg year <sup>-1</sup>	1800			240		
Auckland City storm water loads	kg year <sup>-1</sup>	3880	11600	31000	310	1400	3100
Road run- off/stormwater for Auckland City	%	46	16	6	77	17	6

## **6 THE NEXT STEP**

The final step in our research is to estimate the contribution of remote sources to the contaminants on road surfaces. We measured the rates of particle deposition from the atmosphere adjacent to both Ash Street and Richardson Road. The rates were high close to the road and decreased exponentially away from the road to a relatively constant background. These data will enable us to estimate the remote source deposition rates on road surfaces and also to confirm the non-wash-off losses from road surfaces predicted by our wash-off models.

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# 7 ACKNOWLEDGEMENTS

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# **8 REFERENCES**

ARC, (1999). Auckland Region State of the Environment Report. Auckland Regional Council.

Williamson, R. B. (1991). Urban Runoff Data Book. Water Quality Centre Publication No 20.)