



Analysis of the built-up processes for volatile organics and heavy metals in suspended solids from road run-off

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ABSTRACT

Road run-off water quality can be significantly impacted by many pollutants deposited on road surfaces through vehicular activities. Any control strategy for the improvement of water quality relating to organic and inorganic pollutants should be based on a detailed knowledge of pollutant built-up processes and the relationship of pollutants to one another. Total volatile suspended solids (VSS), polycyclic aromatic hydrocarbons (PAHs) and heavy metals were estimated in total suspended solids (TSS) collected in two catchments. This study found a good relationship between total VSS and TSS and between TSS and PAHs. This relationship information can be utilized for the development of effective Best Management Practices for TSS control. However, the relationship between TSS and heavy metals was identified as being strong in only some cases.

Keywords: Storm water; Pollutant build-up; Volatile organics; Heavy metals

1. Introduction

Urban road activities are one of the major sources of storm water pollution [1,2]. The pollutants build up on a road surface slowly with time and are eventually transported to receiving water bodies with storm

water run-off during wet weather periods as part of a wash-off process. The road-deposited pollutants are broadly categorized into organic and inorganic materials. Organic pollutants include organic matter, hydrocarbons, oil and grease, whereas non-volatile inorganic pollutants include metals [2–4]. A detailed knowledge of built-up processes in road deposits is

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key to the development of effective control measures for the removal of organic and inorganic pollutants [5–7]. Few attempts have been made to correlate build-up of pollutants and influencing factors (e.g. wind, humidity, temperature, etc.) for urban dust [8,9]. Road run-off pollutants may differ from road deposit because the wash off of pollutants from the road surface is governed by storm water hydrology including rainfall run-off behaviour and the nature of pollutants [10,11]. Thus, the study of volatile and non-volatile pollutants in storm water run-off may provide an insight into their relationships. This research work investigates the relationships between suspended solids, volatile suspended solids (VSS), polycyclic aromatic hydrocarbons (PAHs) and heavy metals. Storm water sediment samples were collected during four run-off events in Sydney, Australia and during nine run-off events in Winterthur, Switzerland. This study investigated the built-up process for total suspended solids (TSS) in run-off and its relationship with VSS, PAHs and heavy metals. The outcome of this study will assist in the development of mitigation measures for the improvement of urban water quality in terms of vehicle-generated heavy metals, hydrocarbons and other organics. These mitigation measures could include road-cleaning methods, storm water retention ponds, and non-structural control and management guidelines.

2. Materials and methods

This study was undertaken in two road catchments in Europe and Australia. Storm water samples were collected at a road run-off outlet in Winterthur, Switzerland and in Sydney, Australia using autosamplers (ISCO 6712 portable samplers USA) by collecting the initial run-off volume (~2.5 mm for Sydney and ~3 mm for Winterthur) to depict the first flush, collected during an early period of run-off. The autosampler contained 24 sets of bottles and was programmed to collect the first flush volume (every 5 m³ in Sydney and every 10 m³ in Winterthur).

The collected samples were filtered through a glass fibre filter GF/C of pore size 1.2 µm. The residues on filters were investigated for VSS, PAHs and heavy metals. VSS were measured by heating the sediment at 450 °C for 15 min [12]. Selected event samples were used for PAH and heavy metals analysis. PAHs were measured by solvent extraction followed by gas chromatography/mass spectrometry measurement [13]. Non-volatile heavy metals were measured by inductive coupled plasma mass spectrometry after acid digestion [11].

2.1. Built-up process of suspended solids on roads

Sartor and Boyd [14] proposed a method to evaluate the amount of sediment that accumulates on a catchment surface and subsequently contributes to storm water run-off pollution. To evaluate the amount of pollutants in a catchment prior to a run-off event, the effective non-run-off removal process must be determined and incorporated into an accumulation function. The accumulation function simulates the net accumulation of pollutants. According to Sartor and Boyd [14], the rate of removal of pollutants in run-off, $dP(t)/dt$, decreases with the mass accumulated on the surface, as shown in Eq. (1):

$$dP(t)/dt = -kR(t) * P(t) \quad (1)$$

where k = wash-off coefficient (mm⁻¹), t = time (h) and $R(t)$ = run-off rate (mm/h).

This can also be expressed as:

$$P(t) = P_0 * \exp(-kQ(t)) \text{ or} \\ P_0 - P(t) = P_0 * (1 - \exp(-kQ(t))) \quad (2)$$

where P_0 = initial amount of pollutant on the surface and $Q(t)$ = accumulative run-off volume (mm).

3. Results and discussion

3.1. Suspended solids in urban run-off

Storm water generated from road surfaces washes off numerous types of deposited pollutants. The first flush concept is useful to relate how the early phase of the run-off can be more heavily polluted than subsequent run-off and this should define the treatment required.

Fig. 1 shows the dynamic behaviour of suspended solids from road catchments in Sydney and Winterthur. These two examples demonstrate that suspended solids and flow rate have a distinct relationship. The rising TSS peak appeared at the beginning of run-off in all events. This clearly demonstrates the presence of a first flush effect in those events (graphs of all events not shown here due to space limitations).

Fig. 2 shows the observed and calculated accumulative TSS loads in Sydney and Winterthur. The Sartor and Boyd model was used to estimate the available surface deposit of TSS (P_0) on the road from the available field data. A non-linear regression method was applied to estimate the initial TSS deposit (P_0) and wash-off coefficient (k) for both sites using the SPSS v20 statistical software. The initial TSS deposits for

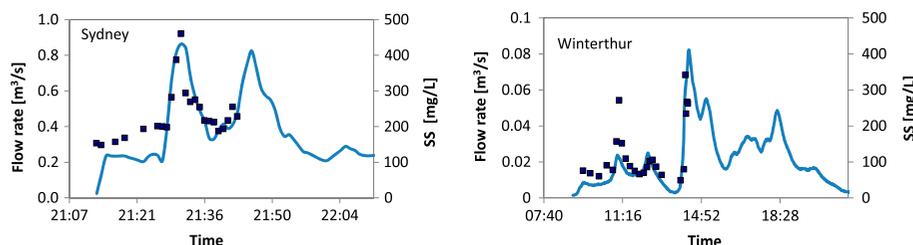


Fig. 1. Behaviour of TSS with flow rate in the first flush.

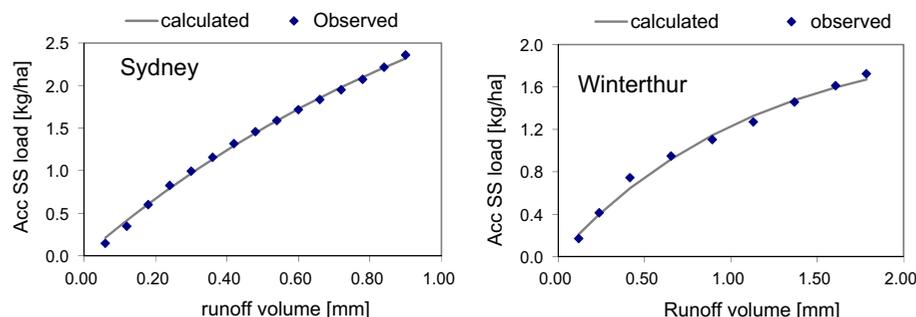


Fig. 2. TSS load calculation based on Sartor and Boyd's model for TSS concentration in the first flush.

Sydney were in the range of 0.4–4.5 kg/ha, whereas in Winterthur, it ranged from 2.1 to 12.5 kg/ha. The wash-off coefficient (k) ranged from 0.69 to 4.32 mm⁻¹ at the site in Sydney and k ranged from 0.27 to 2.55 mm⁻¹ at the site in Winterthur.

At both sites, the results showed that the k value was unstable at low flow rates. Once the flow rate increased, the estimation of the initial deposit and the k value showed some stability. In Sydney the k value was found to be 0.82 mm⁻¹, whereas in Winterthur, it was 0.39 mm⁻¹. The wash-off coefficients (k) found in the past road run-off studies were 0.18 mm⁻¹ [14] and 0.37 mm⁻¹ [15]. The relatively large variation in the k value is explained as follows.

Our findings showed that the k value can be high where the initial deposit is very low, especially during the early phase of run-off. Since the model is based on pollutant wash off, it is expected that the flow rate has

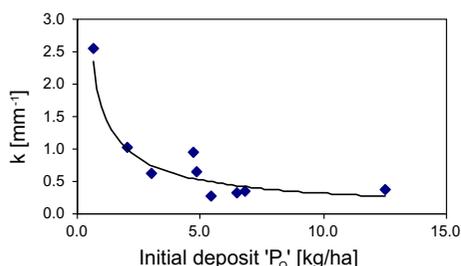


Fig. 3. Relationship between wash-off coefficient and initial deposit observed in Winterthur, Switzerland.

an impact on the establishment of the initial deposit and the wash-off coefficient. Fig. 3 shows the relationship between wash-off coefficient and initial deposit rate observed in Winterthur, Switzerland. This relationship indicates that the k value and initial deposit rate might not be estimated simultaneously during low-flow rate periods. One of the probable reasons is that fine particles are washed off at low flow rates. In other words, fine particles are less dependent on flow rate [16].

Sartor and Boyd developed a model for a single event with the pollutant concentration decreasing with the progress of time. This can be expressed as:

$$C(t) = \frac{1}{F(t)} \left(\frac{dP}{dt} \right) = -k * \frac{P(t) * R(t)}{A * R(t)} \quad (3)$$

$$C(t) = -k * \frac{P(t)}{A} \quad (4)$$

where $C(t)$ = concentration, $F(t) = A * R(t)$ = flow rate (L/s), A = area (ha), $R(t)$ = run-off rate.

Since the concentration of suspended solids may vary with time and does not necessarily decrease in all cases, the k value may differ from event to event and from catchment to catchment.

3.2. Relationship of TSS to VSS and PAHs

Fig. 4 shows the relationship between TSS and VSS and between TSS and PAH for four run-off

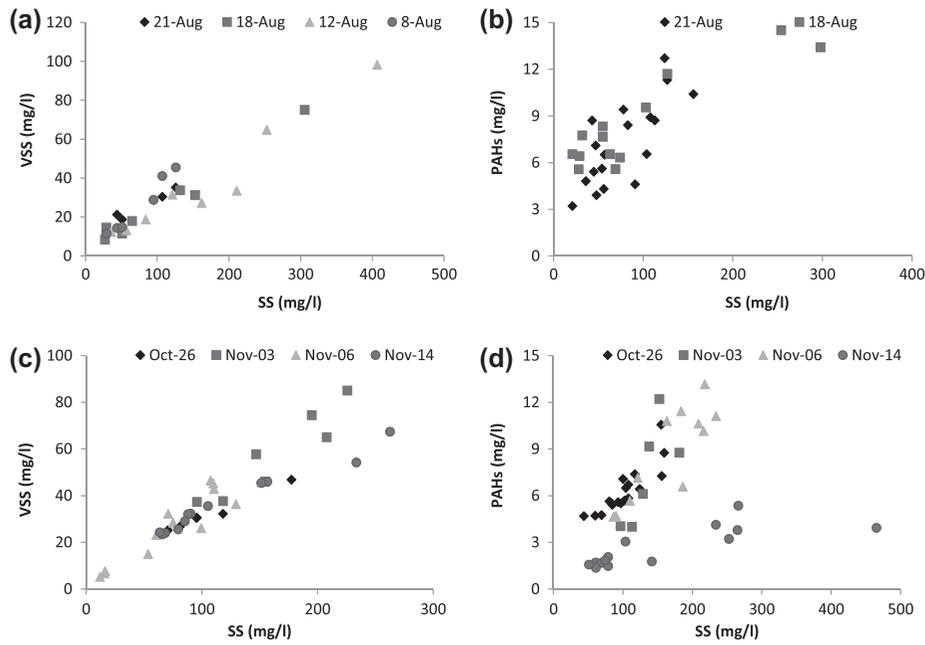


Fig. 4. Relationship between TSS and volatile SS and PAHs in Sydney (a), (b) and Winterthur (c), (d).

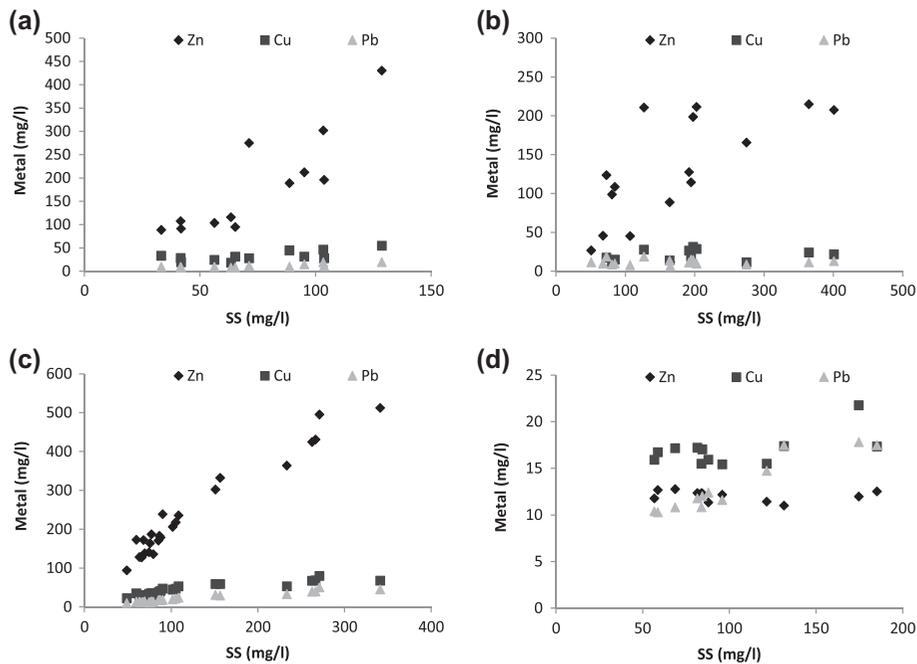


Fig. 5. Relationship between TSS and heavy metals on 11 August (a) and 18 August (b) in Sydney and 14 November (c) and 17 November (d) in Winterthur.

events in Sydney and four events in Winterthur. This shows that there is a good linear relationship between TSS and VSS ($R^2=0.85-0.95$). The result indicates that VSS is largely affected by TSS. To understand further about the role of TSS in PAHs

transport, we also plotted the relationship between TSS and PAHs ($n=7$). The correlation coefficient (R^2) was found in between 0.63 and 0.87. This indicates that the concentration of PAHs is also largely influenced by TSS in run-off.

3.3. Relationship between TSS and heavy metals

Fig. 5 shows the relationship between TSS and heavy metals in run-off in Sydney and Winterthur. Of the two events measured in Sydney, one event showed a positive correlation between TSS and three metals ($R^2=0.50\text{--}0.74$), but another event did not show a strong relationship ($R^2<0.41$). Of the four events measured in Winterthur, two events showed a good relationship between TSS and heavy metals ($R^2=0.56\text{--}0.95$), whereas the other two events did not show a strong relationship ($R^2<0.45$). These relationships between metals and suspended solids indicate that several parameters may influence the wash-off behaviour of metals. Hergren et al. [8,17] noted the strong influence of DOC along with TSS and particle size in metals run-off in urban catchments. Hallberg et al. [18] also observed a relatively strong relationship between metals and suspended solids, but more so in winter than in summer. Tuccillo [19] observed a strong relationship between size fraction and metal concentrations in urban run-off. Overall, the literature indicates that physico-chemical and meteorological factors govern the presence of metals in suspended solids.

4. Conclusion

This study investigated the pollutant build-up on road catchments in Sydney, Australia and in Winterthur, Switzerland and examined the relationships among the pollutant components in these two catchments. The important findings from this study include:

- The transport process for TSS is influenced by storm water flow rate and may vary from event to event.
- Initial TSS deposits on road surfaces estimated using the Sartor and Boyd non-linear regression model ranged from 0.4 to 4.5 kg/ha in Sydney and from 2.1 to 12.5 kg/ha in Winterthur, Switzerland.
- TSS displayed a linear relationship with VSS ($R^2=0.92\text{--}0.95$ for Sydney and $0.85\text{--}0.95$ for Winterthur) and with PAHs ($R^2=0.59\text{--}0.89$ for Sydney and $0.57\text{--}0.86$ for Winterthur).
- There was a less clear relationship between heavy metals and TSS.

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