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# Prediction of the wash-off of traffic related semi- and non-volatile organic compounds from urban roads under climate change influenced rainfall characteristics

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ABSTRACT

Traffic generated semi- and non-volatile organic compounds (SVOCs and NVOCs) pose a serious threat to human and ecosystem health when washed off into receiving water bodies by stormwater. Climate change influenced rainfall characteristics makes the estimation of these pollutants in stormwater quite complex. The research study discussed in the paper developed a prediction framework for such pollutants under the dynamic influence of climate change on rainfall characteristics. It was established through principal component analysis (PCA) that the intensity and durations of low to moderate rain events induced by climate change mainly affect the wash-off of SVOCs and NVOCs from urban roads. The study outcomes were able to overcome the limitations of stringent laboratory preparation of calibration matrices by extracting uncorrelated underlying factors in the data matrices through systematic application of PCA and factor analysis (FA). Based on the initial findings from PCA and FA, the framework incorporated orthogonal rotatable central composite experimental design to set up calibration matrices and partial least square regression to identify significant variables in predicting the target SVOCs and NVOCs in four particulate fractions ranging from >300 to 1 μm and one dissolved fraction of <1 μm. For the particulate fractions in >300–1 μm range, similar distributions of predicted and observed concentrations of the target compounds from minimum to 75th percentile were achieved. The inter-event coefficient of variations for particulate fractions of >300–1 μm was 5–25%. The limited solubility of the target compounds in stormwater restricted the predictive capacity of the proposed method for the dissolved fraction of <1 μm.



## 1. Introduction

Traffic related semi- and non-volatile organic compounds (SVOCs and NVOCs) are primarily associated with diesel fuels, fuel oils, heavier engine oils and lubricants [1]. Homologous series of n-alkanes from decane to tetracontane are amongst the most common constituents of these products, which are widely used in motor vehicles, and have the potential to pollute the urban water environment through deposition and wash-off from urban roads [2]. Rainfall characteristics such as, intensity, duration and frequency or average recurrence intervals (ARIs) are predicted to undergo significant changes as a result of climate change. In this context, the Commonwealth Scientific and Industrial Research Organisation (CSIRO) has forecasted longer periods of dry weather with fewer, but more intense storms in Australia due to climate change [3]. Such climate change driven changes in the rainfall characteristics will affect the wash-off processes of various stormwater pollutants including the SVOCs and NVOCs.

The detrimental effects of SVOCs and NVOCs on human health have been widely reported in research literature. Mutagenic evidence in mammalian cells caused by diesel engine exhaust particles has been cited by Bao et al. [4]. Morgan et al. [5] attributed the long term exposure to diesel engine exhaust particles to respiratory allergy, cardiopulmonary mortality and risk of lung cancer. Petroleum related activities have also been attributed to significant wetland loss in the Mississippi Delta [6]. While studies on the impacts of traffic generated volatile organic compounds such as BTEXs (benzene, toluene, ethylbenzene and xylene) in urban roads [7] and ambient atmosphere have commonly been undertaken [8,9], such pollutants have only been characterised in terms of concentrations and modelled for the ambient atmosphere [10]. However, it is important to note that pollutants present in the urban atmosphere are not necessarily deposited on the urban roads due to various climatic factors. Therefore, compartment-based multimedia models (e.g. separate wash-off models from pervious and

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impervious surfaces) are particularly suitable in rationalising the differences in environmental fate and transport of pollutants in a defined environment [11]. Nevertheless, the wash-off phenomenon from urban roads becomes complex when the changed rainfall characteristics due to climate change affect the wash-off processes of such pollutants. In this context, the current state of knowledge on traffic generated semi- and non-volatile organic compounds (SVOCs and NVOCs) available on roads for wash-off is very limited.

Mahbub et al. [12] recently proposed a prediction model for the build-up of five traffic generated volatile organic compounds on urban roads. However, their model did not investigate the uncertainties involved in the wash-off of the wide range of traffic generated pollutants from roads under climate change driven changes to rainfall characteristics. Accurate estimations of the concentrations of available SVOCs and NVOCs on roads in wash-off under climate change are required in order to undertake mitigation measures for the management of such pollutants in stormwater runoff. Accordingly, this research study presents a framework for predicting the concentrations of traffic generated SVOCs and NVOCs in wash-off under climate change influenced rainfall characteristics. This approach is expected to contribute to overcome the uncertainties inherent in the wash-off estimation of traffic generated SVOCs and NVOCs by predicting these pollutants based on the significance of individual predictors and consequently, strengthening the appropriate measures for pollution mitigation.

## 2. Materials and methods

### 2.1. Site selection

Four road sites within a 5 km radius from a meteorological gauging station were selected as the wash-off study sites. The station was located at 27.90°S and 153.31°E at an elevation of 6 m above mean sea level with daily rainfall data recorded since 1894. The selected road sites were situated in three relatively new suburbs in the Gold Coast region, Australia with the transport infrastructure developed in the last decade. The sites were in different land uses such as residential, commercial and industrial in order to incorporate a mix of vehicular traffic characteristics. The locations, traffic and pavement characteristics of the selected sites are provided in the supplementary data. Due to their close proximity to the rain gauging station, it was hypothesised in this study that the predicted changes in the rainfall characteristics at the four study sites resulting from climate change are similar to that at the rain gauging station.

### 2.2. Rainfall simulation incorporating climate change

The research study used a rainfall simulator [13] to replicate the design rainfall events resulting from climate change. The rainfall simulation was based on the studies of Abbs et al. [14] who predicted the average fractional change for extreme rainfall intensities at 2, 24 and 72 h durations for the Gold Coast area in Australia for 2030 and 2070 using CSIRO general circulation model known as CC-MK3 and CSIRO regional downscaling model known as RAMS. Several climate change studies [3,15] have predicted that the probability of occurrence of shorter duration (<2 h) events with a large change in precipitation intensities is very high.

Mahbub et al. [16] used the outcome from the Abbs et al. [14] study and proposed the following three scenarios to describe the climate change influenced rainfall characteristics in the Gold Coast region:

- Shorter duration, with higher intensity with ARI constant;
- Shorter ARI, shorter duration with intensity constant; and
- Shorter ARI, with higher intensity while duration becomes shorter.

The current study incorporated these scenarios by simulating the 2009 and 2030 rainfall characteristics in the Gold Coast region of Australia according to the study by Mahbub et al. [16]. As the subsequent chemometric data analyses and interpretations require referencing to these simulated rainfall events, Table 1 is reproduced in this paper.

A total of twenty-two rain events were simulated in the four selected road sites. It was not feasible to simulate all twenty-two rain events simultaneously at all four sites due to time restrictions imposed by the city council on road lane closures. Therefore, the simulation events were distributed among the four study sites in different sets of intensity ranges of 24.6–39.3, 58.3–63, 75–77 and 119–125 mm/h.

### 2.3. Wash-off sample collection

The rainfall simulations were undertaken over a 2 month period from April to May 2009. Wash-off samples resulting from the simulations were collected using a commercially available vacuum cleaner. The weather was dry and the temperature during the sampling ranged between 22 °C and 25 °C. The collection plots were 3 $m^2$ in size and were located in the middle of the traffic lanes at the study sites, marked with permanent markers, and thoroughly cleaned with deionised water. Then the plots were left for seven dry days to allow for traffic generated pollutants to build-up. This allowance of seven dry days was in conformity with the findings of Egodawatta [17] who noted that the pollutant build-up on road surfaces asymptote to an almost constant value after an antecedent dry period of 7 days. The collection plots were connected to a collection trough [13]. The runoff water in the collection trough was vacuumed continuously into 25 L plastic containers. The plastic containers were washed thoroughly inside out with 10% HCl followed by Decon 90® detergent wash and rinsed throughout with deionised water. The containers were then dried at 40 °C for 48 h before collecting samples from the field. A photo of the sample collection procedure is provided in the supplementary data.

After collection, the runoff samples were transported to the laboratory for sub-sampling immediately. As pollutant concentrations can vary by orders of magnitude during a runoff event, the flow weighted average or event mean concentration (EMC) samples were found to be appropriate for evaluating the impacts of stormwater runoff on receiving waters [18]. In this study, 500 mL EMC samples in amber glass bottles were prepared in the laboratory using a churn splitter. The required volumes at a particular duration constituting an EMC sample were determined from the percentages of the total runoff collected in different containers for that duration and mixed together to obtain the 500 mL EMC sample for an event.

The particle size distributions of the suspended solids in the subsamples were determined using a Malvern Mastersizer S Particle Size Analyser capable of analysing particles between 0.05 and 900 μm diameter. The particle size distributions of the subsamples were used as a guide for maintaining homogeneity in the sub-samples throughout the sample splitting process. Based on the particle size distribution, the total particulate analytes in the 500 mL EMC subsamples were fractioned into four size ranges, namely, >300 μm, 150–300 μm, 75–150 μm, 1–75 μm using wet sieving. The filtrate passing through a 1 μm membrane filter was considered as the total dissolved fraction. In each case, 500 mL homogeneous sub-samples were prepared using deionised water, collected in 500 mL amber glass bottles with a PTFE seal, preserved with 5 mL of 50% HCl at 4 °C in the laboratory and analysed within 40 days of collection. A total of 110 wash-off samples were