Effects of Climate Change on the Wash-off of Volatile Organic Compounds from Urban Roads

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Abstract

The predicted changes in rainfall characteristics due to climate change could adversely affect stormwater quality in highly urbanised coastal areas throughout the world. This in turn will exert a significant influence on the discharge of pollutants to estuarine and marine waters. Hence, an in-depth analysis of the effects of such changes on the wash-off of volatile organic compounds (VOCs) from urban roads in the Gold Coast region in Australia was undertaken. The rainfall characteristics were simulated using a rainfall simulator. Principal Component Analysis (PCA) and Multicriteria Decision tools such as PROMETHEE and GAIA were employed to understand the VOC wash-off under climate change. It was found that low, low to moderate and high rain events due to climate change will affect the wash-off of toluene, ethylbenzene, meta-xylene, para-xylene and ortho-xylene from urban roads in Gold Coast. Total organic carbon (TOC) was identified as predominant carrier of toluene, meta-xylene and para-xylene in <1µm to 150µm fractions and for ethylbenzene in 150µm to >300µm fractions under such dominant rain events due to climate change. However, ortho-xylene did not show such affinity towards either TOC or TSS (total suspended solids) under the simulated climatic conditions.

Keywords:

Volatile organic compounds, rainfall characteristics, climate change, total organic carbon, pollutant wash-off

1. INTRODUCTION

Rainfall characteristics such as intensity, duration and frequency are predicted to change throughout the world due to climate change. In Australia, longer periods of dry weather with fewer, but more intense storms are forecast (CSIRO 2007). This is compounded by the fact that population growth rates in coastal regions of Australia are consistently high (ABS 2010). In recent years, many coastal local government authorities in Australia have experienced growth rates in the range of 50% to 60% higher than the national average.

This rapid population growth coupled with changes in rainfall characteristics will significantly impact on coastal communities. In this respect, the effects of population growth and land use on ecosystem health, particularly on coastal water quality, have drawn much attention both locally (Burnley and Murphy 2004; Gurran et al 2006) as well as globally (Kimura 1988; Decembrini et al. 1995; Benson et al. 2008). However, current knowledge on the dynamic effects of climate change on the water quality in highly urbanised coastal areas is very limited.

Abbs et al. (2007) predicted high risk of floods spanning large areas of developed flood plains in the Gold Coast region due to extreme rainfall events resulting from climate change. A report by the European Environment Agency, EEA (2003) suggested some possible effects of climate change on water quality including increased pollutant discharges (during floods), rising temperature and oxygen depletion (during droughts) and changes in aquatic ecology. This in turn will exert a significant influence on the discharge of pollutants to receiving estuarine and marine waters. CSIRO (2007) also noted some possible effects of climate change on water quality in Australia in terms of changes to micro fauna and flora as well as the processes that transport pollutants into streams and aquifers. Most of these studies are generalised without particularly focussing on the coastal regions.

Vehicular traffic is one of the most significant sources of toxic and carcinogenic pollutants deposited on urban roads. These pollutants are washed-off from road surfaces during rainfall-runoff events and eventually transported to water bodies. The major pollutants that are generated by vehicular traffic include polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPHs), volatile organics and heavy metals (Hoffman et al. 1982, 1984; Sansalone & Buchberger 1997a). Amongst these different pollutants, benzene, toluene, ethylbenzene and xylene commonly referred to as BTEX are a special family of pollutants that are volatile organic compounds or VOCs with boiling points ranging from 50-260 $^{\circ}$C (Ayoko 2004) and primarily generated in the urban environment from vehicle exhaust, brakes, engine oils, evaporative emissions, indoor air pollution activities and equipments. These compounds are listed as carcinogenic or possibly carcinogenic to humans (IARC 2009). Herngren et al. (2005a) studied the wash-off relationships of traffic generated pollutants with solids and organic carbon. However, the wash-off relationships between VOCs and the physico-chemical parameters of runoff have not featured prominently in the literature.

The Gold Coast region of Australia is a popular tourist destination and subject to high population growth. From the period of 2001 to 2007 the region recorded a 3.7% annual population growth, which is higher than the current Australian population growth and a concomitant increase in vehicle usage (ABS 2010). An in-depth understanding of traffic generated pollutant wash-off processes in Gold Coast will help in the development of wash-off models influenced by climate change. This paper discusses a research study undertaken to investigate the wash-off processes of toluene, ethylbenzene, meta-xylene, para-xylene and ortho-xylene under predicted changes in rainfall characteristics due to climate change in the Gold Coast region. The wash-off relationships of these VOCs with total suspended solids (TSS) and total organic carbon (TOC) was also investigated to establish surrogate parameters during VOC wash-off.

2. MATERIALS AND METHODS

2.1 Site selection

Four road sites in three suburbs in the Gold Coast were selected as the wash-off study sites. Table 1 describes the study sites with their topographic and pavement characteristics. These study sites are located within 1.5 to 5 km distance from the meteorological gauging station 40166. This station has recorded daily rainfall data since 1894 and is located at 27.90° S and 153.31° E at an elevation of 6 m. All of these study sites and the rainfall gauging station 40166 are located within a radial distance of 12 km from the shoreline.

Insert Table1

According to Table 1, the Billinghurst Crescent and Discovery Drive are situated in residential areas, Shipper Drive is situated in an industrial area, whilst Lindfield Road is situated in a commercial area. The selected sites also represent the transport infrastructure developed in the Gold Coast region in the past decade.

Egodawatta (2007) found that the pollutant build-up on road surfaces asymptote to an almost constant value after a minimum antecendent dry period of seven days. Hence, seven dry days were allowed at each site before collecting the wash-off samples for this study. A total of twenty two rain events were simulated at the four sites. The distributions of these events per site are discussed in the subsequent sections.

2.2 Wash-off sample collection

The research study used a rainfall simulator (Herngren et al. 2005b) to replicate the design rainfall events on the road surfaces and a commercially available vacuum cleaner was used to collect the wash-off samples. The rainfall simulator was based on the design of simulators used in agricultural research as described by Floyd (1981) and Loch et al. (2001). It consisted of an A-frame structure made of aluminium tubing of 40-mm diameter. Three Veejet 80100 nozzles, spaced 1 m apart are mounted on a stainless steel boom at a height of 2.4 m. This is the prescribed height for creating terminal velocities similar to natural rainfall for all drop sizes (Herngren 2005b). Further details on the design of the simulator can be found in Herngren et al. (2005b) and Loch et al. (2001).

The plot area for rainfall simulation was separated by a frame connected to a collecting trough. The runoff water in the collecting trough was vacuumed continuously into 25 L plastic containers. The water pressure through the nozzles was maintained at 41 kPa which was found to be the most appropriate pressure to create drop size distribution near natural rainfall for the given height of the nozzles above the road surface (Bubenzer 1979).

The runoff samples were transported to the laboratory for sub-sampling immediately after collection. As pollutant concentrations can vary by orders of magnitude during a runoff event, the flow weighted average or event mean concentration samples (EMC) were found to be appropriate for evaluating the impacts of stormwater runoff on receiving waters

(Sansalone & Buchberger 1997b). In this study, 500 mL EMC samples were prepared in the laboratory using a churn splitter. The required volumes at a particular duration constituting an EMC sample was calculated from the percentages of the total runoff at that duration and mixed together to get 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 to 900 µm diameter. Based on the particle size distribution, the total particulate analytes 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 at 4°C in the laboratory and analysed within 14 days of collection.

2.3 Simulation of rainfall incorporating climate change impacts

The rainfall simulation was based on the studies of Abbs et al. (2007) who used a dynamic downscaling technique incorporating the CSIRO CC-MK3 and CSIRO RAMS climate models to generate 2030 and 2070 average fractional change for extreme rainfall intensities at 2, 24 and 72 hour durations for the Gold Coast area. The published results from that study for the Gold Coast region are summarised in Table 2 below.

Insert Table 2

It is clear from Table 2 that higher changes in the rainfall intensities are projected for shorter duration events in the 2030 and 2070 predictions for the Gold Coast region. Several climate change studies (CSIRO 2007; IPCC 2007) have predicted that the probability of occurrence of shorter duration (<2 hr) events with large change in precipitation intensities is very high.

Mahbub et al. (2010a) used the outcome from the Abbs et al. (2007) study to propose three scenarios of changes in rainfall characteristics for the Gold Coast region. The current study used all of these scenarios to simulate the 2030 rainfall in Gold Coast. Table 3 shows the rainfall simulation plan according to the study by Mahbub et al. (2010a). For simplicity and due to Gold Coast City Council restrictions on lane closure times, the simulation events were distributed in the four study sites as per their intensities which ranged from 25-39, 58-63, 75-77 and 119-125 mm/hr.

Insert Table 3

2.4 Sample testing

The pH and electrical conductivity (EC) of the wash-off samples were determined initially. Subsequently, the samples were subjected to testing for VOCs namely, toluene, ethylbenzene, ortho-xylene, meta-xylene and para-xylene. These tests were undertaken according to the USEPA Method 5035 and 8260B (EPA 2008) using purge and trap extraction followed by Gas Chromatography/Mass Spectrometry (GC/MS). A specially built Zebron® ZB624 GC column of 20 m length, 0.18 mm internal diameter and 1.00 µm film thickness was used. The initial oven temperature was set at 40°C, held at that temperature for 2 min., followed by an increase of 10°C per min. until the oven temperature reached 200°C. The injector temperature was kept at 200°C with a 50:1 split mode. Ten different calibration standards (Chemservice® THM501 – 1RPM) at 1, 2, 5, 10, 20, 50, 100, 150, 200 and 250 µg/L concentrations were prepared for each target analyte. Volatile internal standards (Chemservice® IS-8260ARPM) consisting of flourobenzene, chlorobenzene-d5 and 1, 4- dichlorobenzene-d4 were added to each sample and standards at 50 µg/L concentration. Field blanks were used during each field trip and all results were blank corrected.

Three quality control standards at 10, 50 and 100 µg/L concentrations were prepared independently of the calibration standards and were included in each batch for comparison with the calibration standards. One laboratory control sample from each batch was spiked with another quality control standard at a concentration of 20 µg/L. The percentage recoveries of the spikes were estimated using the following equation:

$$R = (C1 - C2) / C1 \times 100 \qquad (1)$$

where R= percent recovery, C1= initial spike concentration in µg/L before extraction, C2= final spike concentration in µg/L.

The percentage recoveries were found to be within 90%-95%. The limit of detection for each individual compound was established as 0.01 µg/L for the test method.

The total and dissolved organic carbon (TOC and DOC) concentrations and total and dissolved suspended solids (TSS and TDS) concentrations were also determined according to methods 2540C and 2540D in APHA (2005). The particle size percentages (PSP) were calculated using the Particle Size Analyser software (Malvern 1994).

2.5 Data analysis

The data matrices consisted of twenty two objects and twelve variables for each of the five size fractions. The twenty two objects were numerically defined starting from 1. After initial observation of the probability distribution of the objects, normalisation of all objects was undertaken so that each object had the same relative or absolute size. As the variables were measured in different units, standardisation of each variable was also undertaken as a pre-treatment measure so that each variable could be treated with equal importance at the beginning of the data analysis.

The data analysis was designed to investigate the impact on wash-off of volatile organics from urban roads due to changes in rainfall characteristics. Hence, the twenty two rainfall simulation events described above were taken as objects. The attributes of rainfall events such as intensity, duration and average recurrence interval (ARI) along with the target VOCs, TSS, TOC, PSP, EC and pH were considered as variables in the data analysis. Multivariate chemometrics methods such as principal component analysis (PCA), preference ranking organisation method for enrichment evaluation (PROMETHEE) and geometrical analysis for interactive aid (GAIA) were employed for the data analysis.

Factor /component extraction processes such as PCA (Jartun et al. 2008) and multicriteria decision making processes such as PROMETHEE and GAIA (Herngren et al. 2005a; Ayoko et al. 2007) have been used widely to characterise the incorporation of pollutants in stormwater runoff from urban roads, to correlate suspended solids with heavy metals in runoff and to model the pollution impacts on physico-chemical properties of surface water and groundwater. In this study, the combined use of these three methods applied to investigate stormwater quality from road runoff were expected to provide the generic patterns of behaviour of stormwater pollutants underpinned by specific decisions based on different criteria. Detailed discussion of these techniques can be found in the referenced literature (e.g., Keller et al. 1991; Mareschal & Brans 1988).

2.5.1 PCA

PCA is a pattern recognition technique employed to understand the correlations among different variables and clusters among objects. The PCA technique is used to transform the original variables to a new orthogonal set of Principal Components (PCs) such that the first PC contains most of the data variance and the second PC contains the second largest variance and so on. Though PCA produces the same amount of PCs as the original variables, the first few contain most of the variance. Therefore, the first few PCs are often selected for interpretation. This reduces the number of variables without losing useful information contained in the original data set. The number of PCs to be used for interpretation is typically selected using the Scree Plot method described by Jackson (1993).

The application of PCA to a data matrix generates a loading for each variable and a score for each object on the principal components. Consequently, the data can be presented diagrammatically by plotting the loading of each variable in the form of a vector and the score of each object in the form of a data point. This type of plot is referred to as a 'Biplot'. The angle between variable vectors is the indicator of the degree of correlation. Clustered data points in a biplot indicate objects with similar characteristics. Detailed descriptions of PCA can be found elsewhere (Jackson 1993). In this study, SIRIUS2008 software (Sirius 2008) was used to perform the exploratory PCA procedures.

2.5.2 PROMETHEE

PROMETHEE is designed to rank a number of objects in terms of the data criteria (Brans et al. 1986; Keller et al. 1991). The ranking for each variable or criterion is performed by a user specified preference function. The study used DecisionLab 2000 software (Decision 2000) to perform PROMETHEE analysis. The steps involved in the application of PROMETHEE are as follows:

1. For each variable all objects or actions in the data matrix compared pairwise, in all possible combinations by subtraction, and thus a difference, d , matrix is generated;
2. A preference function $P(a,b)$ is chosen for each variable. It describes how much outcome a is preferred to outcome b . In the DecisionLab2000 software, one of six such functions along with corresponding threshold values may be chosen by the user. It is also necessary to specify whether top-down (maximized) or bottom-up (minimized) ranking of objects for each variable is preferred. In addition, each variable can be weighted in importance, but in general, most modelling initially uses the default weighting of 1. In this work, the affinity of the target VOCs with the TSS and TOC was studied and hence, variables were maximised. The Gaussian preference function (P) described below was applied:

   $$P(a,b) = 0 \text{ for } d \leq 0 \quad (2)$$

   $$P(a,b) = 1 - e^{-d^2/2\sigma^2} \text{ for } d \geq 0 \quad (3)$$

   where d is the difference for each pairwise comparison and σ is the threshold, which was set at the value of the standard deviation of each criterion (Brans et al. 1986). This was the smallest deviation in terms of the target VOCs affinity towards TSS or TOC that would be considered as decisive by the DecisionLab2000 software. The choice of the Gaussian function was based on the suggestion by Brans et al. (1986) as they showed that the function provides the least discontinuities and guarantees the most stable results out of the six different preference functions. All the variables were weighted equally at the beginning of the procedure.

3. The products of each preference function $P(a,b)$ and the weights for the corresponding variables are summed up to generate a preference index table. These indices correspond to the pairwise comparison of the objects or actions.
4. To compare each action one-to-one with the others systematically, preference flows are computed. The DecisionLab2000 software supported three types of preference flows namely, positive outranking flow (ϕ^+), negative outranking flow (ϕ^-) and the net outranking flow (ϕ). The positive outranking flow (ϕ^+) is associated with the degree of preference with which one action is preferred on average over the other actions and the negative outranking flow (ϕ^-) is associated with the degree of preference with which the other actions are preferred on average to that action. The higher the ϕ^+ and the lower the ϕ^-, the more preferred is the action. This procedure results in a partial pre-order, called PROMETHEE I ranking.
5. There are certain circumstances as described by Keller et al. (1991) when two actions a and b may not be comparable. Then, the net outranking flow (ϕ), which is the algebraic difference between the positive and negative outranking flows, needs to be calculated. This procedure, known as PROMETHEE II, was used in this study to eliminate any incomparability between actions or objects.

2.5.3 GAIA

GAIA facilitates a sensitivity analysis technique for multicriteria decision methods such as PROMETHEE (Keller et al. 1991; Mareschal & Brans 1988). GAIA provides a graphical view of the actions and variables for net outranking flow (ϕ) in the form of a PCA biplot by decomposing the ϕ values from PROMETHEE II into unicriterion flows for each variable. The advantages of GAIA over a PCA biplot is that it also produces a decision axis that takes into account the weights associated with the variables. This helps the decision-maker with an enriched understanding of the problem in terms of the detection of clusters of actions, conflicts in variables, inability to compare between actions and so on (Mareschal & Brans 1988). This study used DecisionLab 2000 software (Decision 2000) to perform GAIA analysis.

3. RESULTS AND DISCUSSION

3.1 Exploratory PCA

In the five wash-off data matrices (four for different particulate size fractions and one for the dissolved fraction described above), the twenty two rainfall objects were considered having object attributes such as intensity, frequency and duration that were responsible for generating the wash-off of volatile organics, TSS and TOC from urban roads. EC, pH and PSP were also considered as parameters that influence the wash-off of volatile organics. The concentration ranges were 0.03 to 0.13 µg/L for toluene, 0.01 to 0.03 µg/L for ethylbenzene, 0.02 to 0.06 µg/L for meta and para-xylene and 0.01 to 0.03 µg/L for ortho-xylene. The pH ranged between 6.99 to 7.2 and EC ranged between 22.8 to 63.4 µs/cm. In order to get a better understanding of the generic data patterns, PCA was performed on each of the pre-treated wash-off data matrices. Figure 1 shows the PCA biplots of the five wash-off size fractions.

Insert Figure 1

In Figure 1, it was identified that the target volatile organics formed a group (group A) in wash-off from urban roads for all the five size fractions. In Figure 1(a), 1(b), 1(c) and 1(d), the correlations of the group (A) variables with TOC are stronger than with TSS. However, in the dissolved form in Figure 1(e), the correlation of the group (A) variables with TDS is stronger than with DOC. This suggests that organic carbon acts as the predominant medium for the target volatile organics wash-off in the particulate fraction from >300 μm to 1 μm, but in the dissolved fraction of <1 μm, TDS is the predominant medium of volatile organics.

In all of the fractions in Figure 1, pH has much stronger correlations with the group (A) organics than EC. This suggests that VOCs are washed-off as non-ionic compounds for all fractions. Amongst the three rainfall attributes, average recurrence interval (ARI) has the strongest correlation with the group (A) organics than duration and intensity. However, ARI always has negative correlations with the group (A) organics for all fractions whilst PSP has positive correlations with them in the four particulate fractions. This suggested that for the four particulate size fractions, low ARI events were able to significantly wash-off the corresponding particle fractions of the group (A) organics from urban roads. The influence of duration and intensity on the particulate wash-off of group (A) organics was not significant in Figures 1(a) through to 1(d) as they had low correlation with the group (A) organics. In Figure 1(e), the PSP as well as the intensity and duration are nearly orthogonal to the group (A) organics suggesting that in the wash-off of the dissolved fraction of VOCs, these parameters are not significant.

The scores for the events 19, 20 and 21 were significantly positive along with positive loadings from the group (A) organics on PC1 for all five size fractions. This suggested that the occurrence of VOC wash-off during these events were predominant than in the case of the other events. The investigation of these events in Table 3 revealed that intensity ranging from 59 to 63 mm/hr, duration ranging from 25 to 69 minutes and ARI from 1 to 5 years were the attributes of these predominant events in the wash-off of VOCs. However, the PCA did not incorporate all the five size fractions together. Hence, this PCA outcome is suggestive of important rain events during VOC wash-off. However, a detailed investigation of the predominant rain event clusters under changed climatic conditions is beyond the scope of PCA. Mahbub et al. (2010b) suggested several rain event clusters under changed rainfall characteristics due to climate change. This study has incorporated those clusters and used multicriteria decision making analysis to investigate their effect on VOC wash-off.

3.2 PROMETHEE AND GAIA

The PROMETHEE rankings were performed in order to establish the predominant rain events as well as the predominant surrogate carrier (either TSS or TOC) in terms of VOC wash-off. Subsequently GAIA was used to perform sensitivity analysis of the PROMETHEE outcome. The twenty two rain events were classified into five clusters namely, low, low to moderate, moderate, high and extreme events. This classification was based on a study by Mahbub et al. (2010b). The events with intensity <40 mm/hr with relatively low ARI were classified as low events; those having intensity between 50 to 100 mm/hr but with relatively higher ARIs of up to 50 years were classified as moderate events; events having intensities >100 mm/hr with very high frequency were classified as high events whilst events with similar intensities to moderate and high with extremely rare occurrence (ARI $\geq$ 100 years) were classified as extreme events. Events which manifested the attributes of both low and moderate events were classified as low to moderate events.

Consequently, events 1, 2, 3, 4, 5, 6 were classified as low events; events 19, 20, 21 were classified as low to moderate events; events 14, 15, 16, 22 were classified as moderate events; 7, 8, 9, 10, 11 were classified as high events; 12, 13, 17, 18 were classified as extreme events. The study also defined the affinity of the target VOCs towards TSS and TOC as 'µg of VOC/ mg of TSS or TOC'. Accordingly, two PROMETHEE data matrices were constructed.The first one consisted of the classified rain events described above as actions and all the variables described in the PCA as criteria while taking all five size fractions as different scenarios. Figure 2 presents the PROMETHEE outranking flows for VOC wash-off.

Insert Figure 2

In Figure 2(a), events 1, 2, 3, 8 and 19 were not comparable in the partial outranking flows of PROMETHEE I and as such are shown at the beginning. Event 7 was outranked by events 8 and 19 whilst event 4 was outranked by events 1 and 2. In Figure 2(b), the complete outranking flow of PROMETHEE II is presented. This confirms that the top ten rain events in terms of VOC wash-off are 8, 19, 1, 2, 3, 4, 9, 7, 10 and 20. Interestingly, these events are composed of low, low to moderate and high rain events. Hence, the PROMETHEE rankings show that the attributes of low and high rain events would affect VOC wash-off from urban roads more predominantly than moderate and extreme events. The quality of these decisions was investigated using the GAIA biplot as shown in Figure 3.

Insert Figure 3

In Figure 3, the decision axis (pi) is located within the vicinity of the low, low to moderate and high rain objects. This suggests that low, low to moderate and high rain events are the predominant events in the combined rainfall scenario due to climate change. This decision was tested for its stability by changing the weights of the criteria interactively for the maximum achievable net outranking flows of the actions as shown in Figure 2(b). It is also evident from the loadings of the five size fractions in Figure 3 that these fractions were mainly present in the low, low to moderate and high rain events.

The second PROMETHEE data matrix was constructed by taking the affinity of VOCs towards TSS or TOC (expressed as µg of VOC/ mg of TSS or TOC) as the actions, whilst the previously described five rain events cluster as criteria for all five size fractions. The PROMETHEE outranking flows are shown in Figure 4.

Insert Figure 4

In Figure 4(a), the partial outranking flows of the VOC affinity towards TSS or TOC revealed that the affinity of toluene and meta and para-xylene towards TOC were stronger than towards TSS. The affinity of ethylbenzene towards TOC and meta and para-xylene towards TSS were not comparable. However, the complete outranking flows in Figure 4(b) revealed that toluene, meta and para-xylene as well as ethylbenzene are more strongly associated with TOC than TSS. The affinity of ortho-xylene towards either TSS or TOC were very weak.

GAIA biplots for the five rain events clusters as well as the five different size fractions were analysed for the affinity of VOCs towards TSS and TOC. Figure 5 presents the GAIA outcomes.

Insert Figure 5

In Figure 5(a), five rain clusters (low, high, low to moderate, moderate and extreme) are presented as the criteria whilst the VOC affinity is presented as the actions with the size fractions combined. The decision axis is very strongly inclined towards the affinity of toluene towards TOC indicating that toluene might form the strongest bond with organic carbon during wash-off. Moreover, the affinity of toluene, meta and para-xylene as well as ethylbenzene towards TOC are mainly present in low, low to moderate, or high events in Figure 5(a). This finding is quite significant in the sense that initially in Figure 3, these rain events were found to be the predominant clusters for the transport of the five different size fractions during VOC wash-off. Here in Figure 5(a), these are also the predominant rain event clusters confirming the affinity of VOCs towards TOC except for ortho-xylene. The wash-off of ortho-xylene was found to be independent of any of the rain event clusters.

In Figure 5(b), the affinity of VOCs were analysed for five different size fractions. The correlations of the affinity of toluene, meta and para-xylene towards TOC with the loading vectors for <1 µm, 1-75 µm and 75-150 µm were stronger than those for 150-300 µm and >300 µm on the horizontal axis. This suggested the fact that the two finer fractions 1-75 µm and 75-150 µm as well as the dissolved fraction <1 µm represent the affinity of toluene, meta and para-xylene towards TOC during wash-off. The affinity of ethylbenzene towards TOC was mainly present in 150-300 µm and >300 µm size fractions in Figure 5(b). Ortho-xylene's affinity towards either TSS or TOC could not be observed in any of the size fractions. In both cases of Figure 5(a) and 5(b), the decisions were tested for their stability by changing the weights of the criteria interactively for the maximum achievable net outranking flows of the actions as shown in Figure 4(b).

4. CONCLUSIONS

This study has characterised the wash-off of toluene, ethylbenzene, meta and para-xylene and ortho-xylene under simulated rainfall characteristics on urban roads due to climate change, in the Gold Coast region. The following findings were drawn from this investigation:

- Low, low to moderate and high rain events due to climate change would be the predominant events in terms of toluene, ethylbenzene, meta and para-xylene and ortho-xylene wash-off from urban roads in the Gold Coast region. Highly urbanised coastal areas with similar effects due to climate change on rainfall characteristics are expected to demonstrate similar wash-off phenomena.
- Toluene, ethylbenzene and meta and para-xylene show a stronger affinity towards TOC than TSS during their wash-off under the changed climatic conditions for the particulate fraction 1µm to > 300 µm. Hence, TOC could be regarded as the predominant carrier of VOCs in wash-off under changed climatic conditions in these particulate fractions. The removal of these pollutants from stormwater runoff could be achieved by specifically targeting the removal of TOC in the corresponding particulate fractions.
- Ortho-xylene did not show any affinity towards either TSS or TOC during wash-off. Hence, no surrogate carrier could be established for the wash-off of ortho-xylene. The removal of ortho-xylene from stormwater runoff may require independent measures from that of toluene, ethylbenzene and meta and para-xylene for both particulate and dissolved fractions. Due to very low concentration of ortho-xylene at ppb level in the stormwater runoff, this study proposes only periodic monitoring at the inlet to storage reservoirs at this stage. However, further studies on mitigation measures need to be undertaken if the ortho-xylene concentration in the stormwater runoff exceeds the safe concentration limit.

- Under the combined size fraction scenario, the affinity of toluene and meta and para-xylene towards TOC were more predominant in the two finer fractions of 75-150 µm and 1-75 µm as well as the dissolved fraction of <1 µm and the affinity of ethylbenzene towards TOC was mainly present in 150-300 µm and >300 µm. Hence, the effectiveness of the removal of these pollutants could be enhanced by targeting only the removal of the corresponding fractions. This approach enables a priority based removal of toluene, ethylbenzene and meta and para-xylene from stormwater runoff depending on the existing concentration levels.
- Under combined size fraction scenario, VOCs affinity towards TOC was predominantly observed in low, low to moderate and high rain events clusters. The importance of this finding could be realised by targeting the removal of TOC in <1µm to 300µm fraction from the runoff from such rain events as described in this study. This type of adaptation will enable authorities involved in stormwater quality mitigation strategies to cope with the changed rainfall characteristics due to climate change in highly urbanised coastal regions.

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6. FIGURE CAPTIONS

Figure 1 PCA biplots for (a) >300 µm; (b) 150-300 µm; (c) 75-150 µm; (d) 1-75 µm; and (e) <1 µm size fractions for the wash-off of toluene (TOL), ethylbenzene (ETB), meta and para xylene (MPX) and ortho xylene (OX)

Figure 2 PROMETHEE partial ranking (a) and complete ranking (b) for the twenty two different rainfall events in terms of VOC wash-off

Figure 3 GAIA biplot of the rain events under the combined scenario of five size fractions

Figure 4 PROMETHEE partial ranking (a) and complete ranking (b) for the VOC affinity matrix during wash-off from urban roads

Figure 5 GAIA biplots for five pre-defined rain events clusters (a) and five different size fractions (b) in terms of VOC's affinity towards TSS and TOC

7. TABLES

Table 1 Topographic and pavement characteristics of the four study sites for the VOC wash-off sample collection

Site Name	Land Use	Geographic Locations	Distance from the Nearest Rain Gauging Station, Km	Elevation from the Sea Level, m	Surface Texture Depth (STD), mm	Age of the Road Section, yr	Surface Coating
Billinghurst Cres	Residential	27.856°S 153.298°E	4.97	18	0.7015	10	DG10[b]
Shipper Drive	Industrial	27.861°S 153.332°E	5.04	3	0.6788	6	DG14[a]
Lindfield Road	Commercial	27.922°S 153.334°E	2.96	19	0.9417	10	DG10[b]
Discovery Drive	Residential	27.899°S 153.327°E	1.51	12	0.6957	2	DG14[a]

[a]Dense Grade Bitumen Asphalt with 5.1% aggregate binder

[b]Dense Grade Bitumen Asphalt with 5.3% aggregate binder

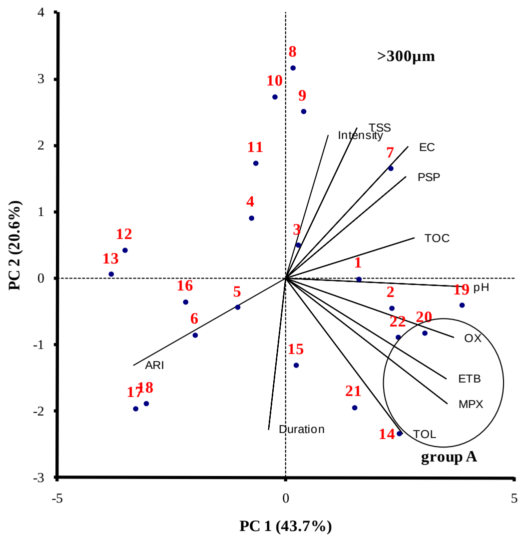
Table 2 Average percentage change in extreme rainfall intensity for the Gold Coast region: adapted from Abbs et al. (2007)

Duration	Region	2030		2070	
		% change of mean intensity	Range between 10^{th} and 90^{th} percentile (%)	% change of mean intensity	Range between 10^{th} and 90^{th} percentile (%)
2	*All Gold Coast*	53	26-89	48	4-91
	Coastal	50	33-65	35	6-72
	Mountains	56	22-96	65	27-97
24	*All Gold Coast*	17	8-29	16	5-28
	Coastal	15	8-23	13	0-26
	Mountains	19	8-32	19	9-30
72	*All Gold Coast*	8	0-17	14	4-23
	Coastal	6	-2-13	10	-4-23
	Mountains	10	0-20	17	9-24

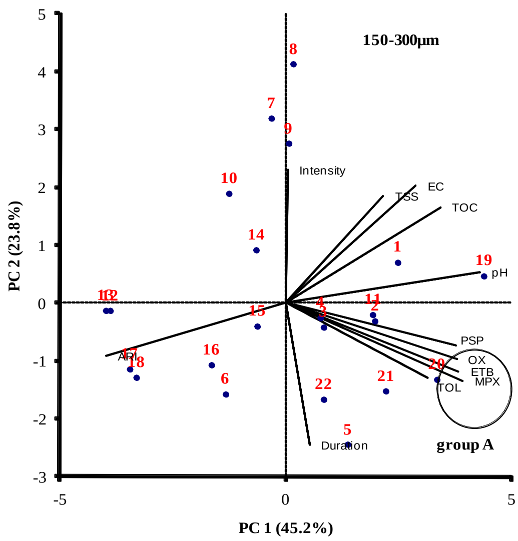
Table 3 Future simulation events based on the normal daily rainfall intensity in the Gold Coast region for 2030: adapted from Mahbub et al. (2010a)

Scenario	Current simulation events for Gold Coast region					Future simulation events for Gold Coast region for 2030				
	ARI (year)	**Duration (min)**	**Intensity (mm/hr)**	**Runoff (L)**	**Simulation Event Number**	**ARI (year)**	**Duration (min)**	**Intensity (mm/hr)**	**Runoff (L)**	**Simulation Event Number**
Shorter duration, with higher intensity while ARI constant	1	60	39	55	1	1	25	63	64	19
	2	90	39	89	3	2	43	61	107	20
	5	133	39	136	5	5	69	59	175	21
	10	160	39	166	6	10	85	58	216	22
	100	105	75	182	18	100	49	115	185	13
	-	-	-			1	65	37	62	2
Shorter ARI, shorter duration while intensity constant	100	45	125	163	12	1	5	125	9	7
	-	-	-			1	120	25	121	4
Shorter ARI, with higher intensity while duration getting shorter	10	53	77	82	14	5	16	125	68	10
	20	68	77	106	15	10	21	122	88	11
	50	87	77	147	16	2	11	120	44	9
	100	101	77	175	17	1	6	119	23	8

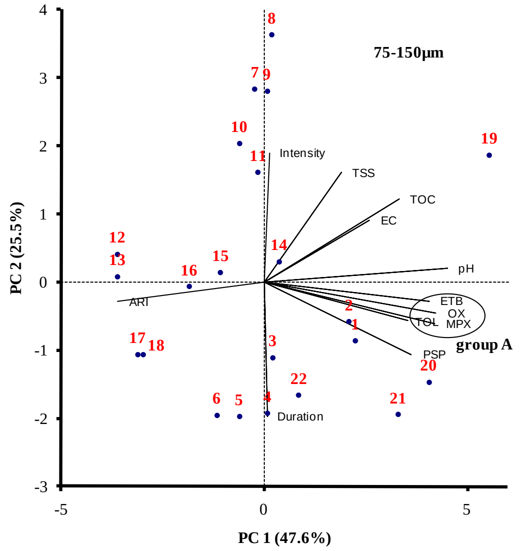
8. FIGURES



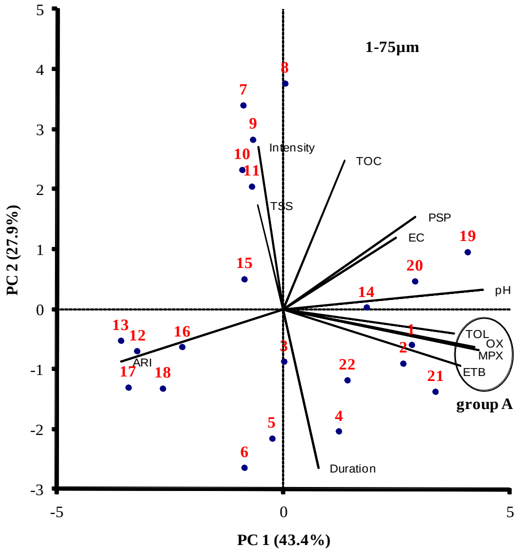
(a)



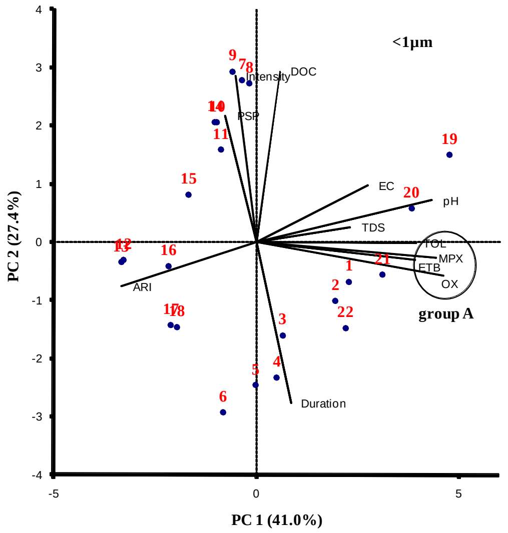
(b)



(c)

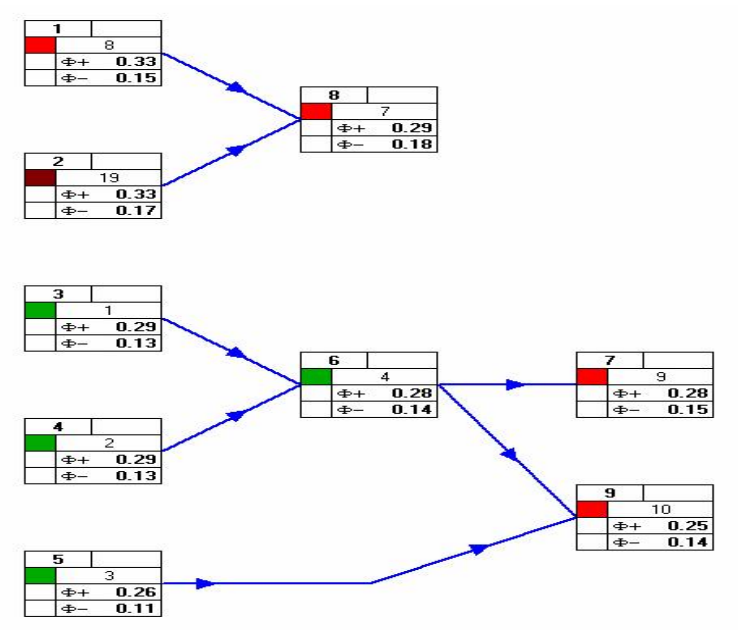


(d)

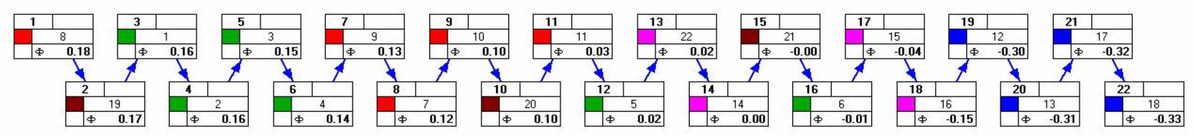


(e)

Figure 1



(a)



(b)

Figure 2

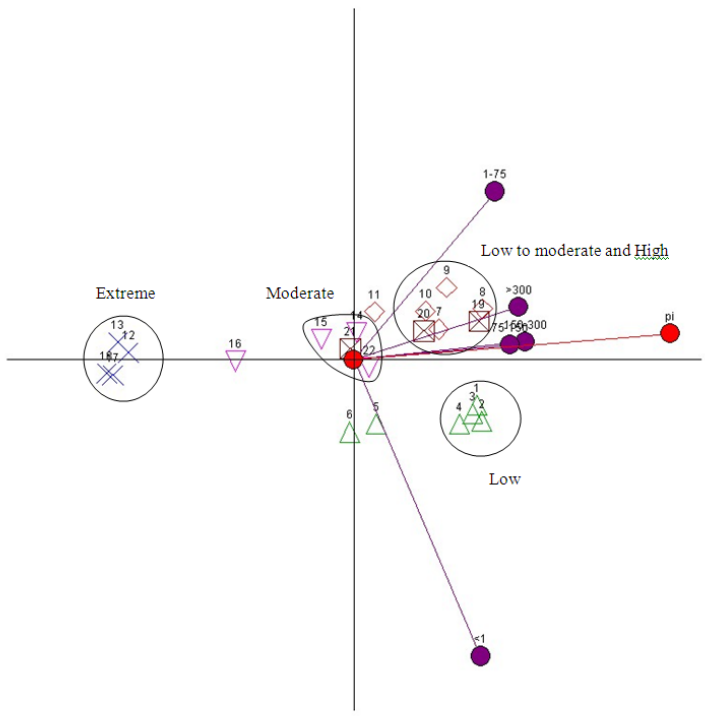
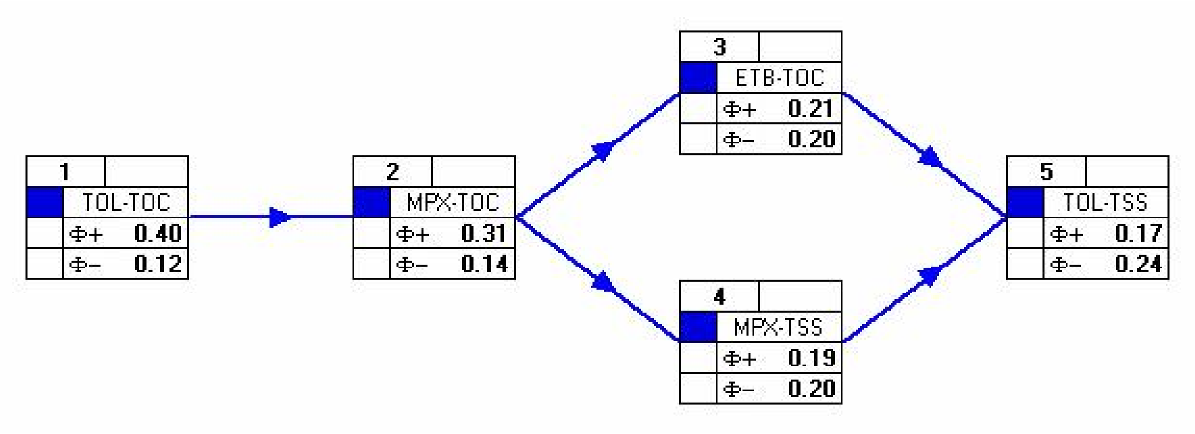
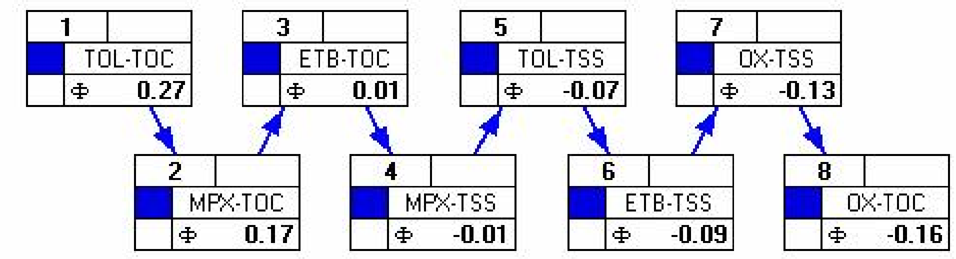


Figure 3

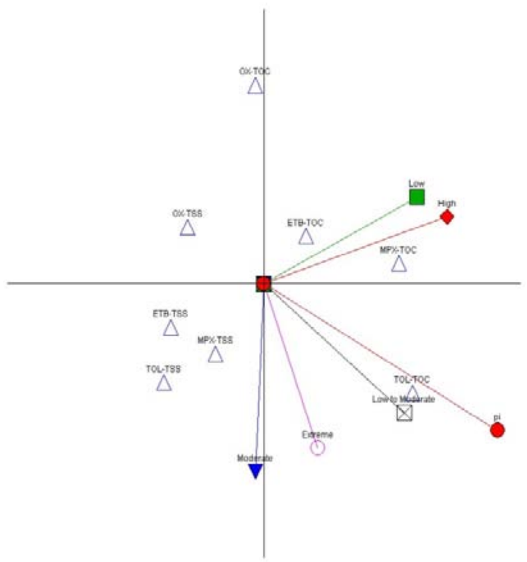


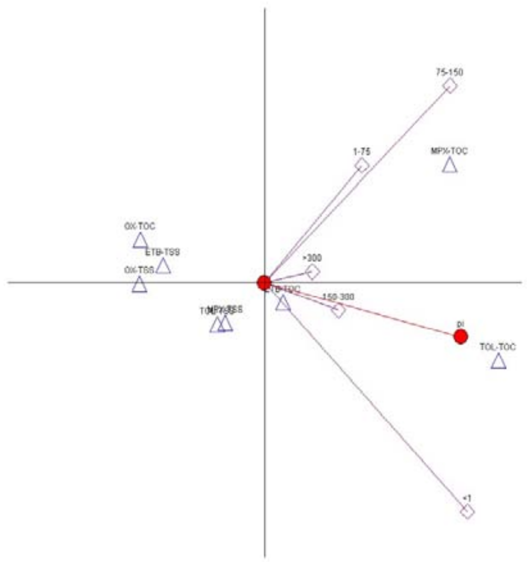
(a)



(b)

Figure 4





(a) (b)

Figure 5

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