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Analysis of the build-up of semi and non volatile organic compounds on urban roads

Parvez Mahbub [a,*], Godwin A. Ayoko [b], Ashantha Goonetilleke [a], Prasanna Egodawatta [a]

[a] School of Urban Development, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Queensland, Australia
[b] Chemistry Discipline, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Queensland, Australia

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ABSTRACT

Vehicular traffic in urban areas may adversely affect urban water quality through the build-up of traffic generated semi and non volatile organic compounds (SVOCs and NVOCs) on road surfaces. The characterisation of the build-up processes is the key to developing mitigation measures for the removal of such pollutants from urban stormwater. An in-depth analysis of the build-up of SVOCs and NVOCs was undertaken in the Gold Coast region in Australia. Principal Component Analysis (PCA) and Multicriteria Decision tools such as PROMETHEE and GAIA were employed to understand the SVOC and NVOC build-up under combined traffic scenarios of low, moderate, and high traffic in different land uses. It was found that congestion in the commercial areas and use of lubricants and motor oils in the industrial areas were the main sources of SVOCs and NVOCs on urban roads, respectively. The contribution from residential areas to the build-up of such pollutants was hardly noticeable. It was also revealed through this investigation that the target SVOCs and NVOCs were mainly attached to particulate fractions of 75–300 μm whilst the redistribution of coarse fractions due to vehicle activity mainly occurred in the >300 μm size range. Lastly, under combined traffic scenario, moderate traffic with average daily traffic ranging from 2300 to 5900 and average congestion of 0.47 were found to dominate SVOC and NVOC build-up on roads.

1. Introduction

Urban traffic activities are one of the predominant sources of stormwater pollutants that accumulate on urban roads and are eventually transported to receiving water bodies. In the context of traffic generated pollutants on urban roads, semi volatile organic compounds (SVOCs) are mainly associated with diesel, fuel oil 1–6 and kerosene, whilst the non volatile organic compounds (NVOCs) are mainly associated with motor oils and lubricants (Draper et al., 1996). In a broader sense, these pollutants are part of a larger family of hydrocarbons which are assessed as total petroleum hydrocarbon (Morrison and Boyd, 1992).

According to the criteria stipulated by the American Petroleum Institute (API), products such as diesel fuels, fuel oils 1–6 and heavier engine oils and lubricants are classified as diesel range organics (DROs) (API, 1994). These are the most widely used and distributed traffic related products. Homologous series of n-alkanes from decane to tetracontane are amongst the most common constituents of these products (Draper et al., 1996). In this context, particulate n-alkane concentrations on roads can also result from tyre abrasion and brake lining dust

* Corresponding author. Tel.: +61 7 3138 9945; fax: +61 7 3138 1170.
E-mail addresses: s.mahbub@qut.edu.au (P. Mahbub), g.ayoko@qut.edu.au (G.A. Ayoko), a.goonetilleke@qut.edu.au (A. Goonetilleke), p.egodawatta@qut.edu.au (P. Egodawatta).
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(Rogge et al., 1993). Brown et al. (1985) reported significant concentrations of vehicle generated SVOCs and NVOCs in urban runoff which may alter the quality of the receiving water, thus harming the endemic biological community. Whilst, both petrol and diesel engine vehicles emit gaseous and particulate hydrocarbons as a result of incomplete combustion (Neeft et al., 1996), Andreou and Rapsomanikis (2009) noted that past studies mainly characterised only one organic group (e.g., polycyclic aromatic hydrocarbons). As the characteristics of urban traffic in terms of traffic volume and congestion is rapidly changing with increased urbanisation throughout the world, an in-depth understanding of the impacts of traffic generated semi and non volatile organic compounds on the urban water environment is needed in order to develop appropriate mitigation measures.

The characterisation of the build-up of semi and non volatile organic compounds on urban roads due to changing traffic characteristics under rapid urbanisation is the key to the formulation of appropriate mitigation measures. In this context, the current state of knowledge on the build-up processes of semi and non volatile organic compounds on urban roads is limited. Brandenberger et al. (2005) in their investigation of the emissions of diesel fuels and lubricating oils under different driving conditions found that poor combustion, reduced conversion efficiency of the oxidation catalyst, and increased mean load of the vehicle driving cycle were the primary reasons for increased particulate emissions of lubricating oils and diesel fuels. However, while their results represented the effects of different driving cycles of the motor vehicles on the ambient concentrations of particulate pollutants, it is important to note that not all of the vehicular emissions are necessarily deposited on impervious surfaces. Ning et al. (2005) reported that the initial pollutant concentration at the exhaust pipe, exit velocity, exit angle, and crosswind intensity affect the pollutant dispersion pattern significantly even at the idle condition.

Traffic parameters such as, average daily traffic (ADT) and congestion on the road (volume to capacity ratio, V/C) along with pavement characteristics such as surface texture depth (STD) are reported to significantly influence pollutant build-up on urban roads (Mahbub et al., 2010a; Brown et al., 2004; Pitt et al., 1995). The dynamic variability of the traffic characteristics mentioned above poses a significant threat to urban water bodies through the accumulation of semi and non volatile organic compounds in the urban environment. In this study, the build-up processes of semi and non volatile organic pollutants have been characterised with respect to physico-chemical (e.g., particle size distribution), traffic and land use parameters, and pavement characteristics. The outcome of this study is expected to provide guidance for mitigating the impacts of semi and non volatile organic pollutants transported by urban stormwater runoff to receiving waters.

2. Materials and methods

2.1. Site selection

The site selection criteria were formulated using a suburb based approach. Two suburbs namely, Helensvale and Coomera in the Gold Coast region in Southeast Queensland, Australia were selected. The two selected suburbs also represent the transport infrastructure developed within the Gold Coast City region in the past decade. Eleven road sites (Table 1) located in three different land uses, namely, residential, commercial and industrial were selected for build-up sample collection. The selection of different land uses ensured a cross-section of traffic activities on road surfaces within the Gold Coast region.

2.2. Key study parameters

In the study, the key traffic parameter used was the Daily Traffic (ADT) instead of Average Annual Daily Traffic (AADT), as the former is predicted by a sophisticated transport model called ZENITH (GCCC, 2006) which is currently being used by the Gold Coast City Council. Gardiner and Armstrong (2007) have found that traffic levels measured as AADT are a poor proxy for stormwater runoff quality. Kayhanian et al. (2003) also reported that AADT itself does not have any direct correlation with pollutant build-up on road surfaces.

The Volume to Capacity ratio (V/C) of a roadway describes the traffic characteristics on the stretch of road during the peak hour (Ogden and Taylor, 1999). This parameter was found to vary quite significantly for the different sites that were selected for the study. Studies have shown that vehicle congestion due to increased traffic volumes in the urban areas had a direct influence on pollutant emission levels on roads (Smit et al., 2008). As such, Average Daily Traffic (ADT) and Volume to Capacity Ratio (V/C) were incorporated as the two principal traffic parameters that would influence the build-up of semi and non volatile organic compounds on urban roads.

The US Federal Highway Administration recommend specific pavement surface texture depths so that current and predicted traffic needs could be accommodated in a safe, durable, and cost effective manner (FHWA, 2005). The texture depth can influence pollutant build-up and wash-off from pavement surfaces (Pitt et al., 1995; Legret and Colandini, 1999). The road texture also affects the interactions between the vehicle tyres and the driving surface (Kreider et al., 2010). Hence, the surface texture depth of the pavement surfaces at the selected road sites was also incorporated into the study. Table 1 lists the selected sites with the identifiers adopted and the corresponding traffic and pavement characteristics.

2.3. Build-up sample collection

The pollutant build-up process was characterised as having four main functional forms such as, linear, power, exponential, and Michaelis–Menten (Huber, 1986). Amongst these, the non-linear asymptotic form proposed by Sartor et al. (1974) has been most often cited and also used in several stormwater quality models such as, DR3-QUAL, FHWA, SWMM (Huber, 1986). In this context, Egodawatta (2007) noted that pollutant build-up on road surfaces asymptote to an almost constant value after a seven-day antecedent dry period. Hence, in this study, seven dry days were allowed at each site prior to any sample collection. Samples were collected over a two-month period in April and May 2009. The weather was dry and the temperature during the sampling ranged between 22 °C and 25 °C. Three different time periods including 8–9 am in the morning, 12–1 pm at noon as well as 3–4 pm in the

Table 1 – Selected road sites with traffic and pavement parameters (partially adapted from Mahbub et al., 2010a).

Site Name Identifier	Land Use	Geo-Coordinates	Average Daily Traffic (ADT), vehicles/day	Volume to Capacity Ratio (V/C)	Surface Texture Depth (STD), mm	Age of the Road Section, (yrs)	Top Coat Material % of Aggregate Binder
Abraham Road CA	Commercial	27.865°S 153.307°E	13,028	1.11	0.6467	3	DG14[a] 5.1
Reserve Road RR	Residential	27.870°S 153.301°E	6339	0.45	0.7505	3	DG14[a] 5.1
Peanba Park Road RP	Residential	27.851°S 153.281°E	581	0.15	0.6844	4	DG10[b] 5.3
Billinghurst Cres RB	Residential	27.856°S 153.298°E	5936	0.74	0.7015	10	DG10[b] 5.3
Beattie Road IBT	Industrial	27.868°S 153.324°E	2670	0.24	0.7074	2	DG14[a] 5.1
Shipper Drive IS	Industrial	27.861°S 155.332°E	7530	0.55	0.6788	6	DG14[a] 5.1
Hope Island Road CH	Commercial	27.882°S 153.328°E	7534	0.57	0.7254	3	DG14[a] 5.1
Lindfield Road CL	Commercial	27.922°S 153.334°E	2312	0.33	0.9417	10	DG10[b] 5.3
Town Centre Drive CT	Commercial	27.929°S 153.337°E	24,506	0.62	0.6416	4	DG14[a] 5.1
Dalley Park Drive RD	Residential	27.887°S 153.346°E	3534	0.42	0.8342	10	DG10[b] 5.3
Discovery Drive RDS	Residential	27.899°S 153.327°E	9116	0.25	0.6957	2	DG14[a] 5.1

a Dense Grade Bitumen Asphalt with 5.1% aggregate binder.
b Dense Grade Bitumen Asphalt with 5.3% aggregate binder.

afternoon were chosen as sample collection time from the eleven sites to incorporate both rush hour and normal traffic.

A pilot study, reported in Mahbub et al. (2010b), was undertaken and 90% sample collection efficiency was achieved through a domestic vacuum cleaner with a water filtration system. This collection efficiency of the vacuum cleaner was for sand dust that passed 100% through 420 μm sieve and retained 100% on 0.7 μm Whatman® GF F glass fibre filter. The test was performed on the middle of the lanes of actual road surface subject to daily traffic. Three build-up plots of $2 \times 1.5\ m^2$ area were initially cleaned with deionised water and allowed to dry up for 1 h. It was assumed that the build-up of pollutants during 1 h was uniform for the three plots. Two of the plots were applied with 100 gm sand dust and the third plot was kept without applying any sand dust. The 'wet and dry vacuum' system (Mahbub et al., 2010b), which incorporates vacuuming of the build-up plot in dry and subsequently in wet condition was then applied at different combinations of pressure and time. The wet condition was created by a sprayer. The difference in the collected sand dust from the first two plots compared with the third plot at various combinations indicated that optimum pressure of 2 bar for 3 min was required to achieve to 90% collection efficiency. The total build-up sample was collected in 8 L deionised water.

2.4. *Sample preparation*

The collected samples were transported to the laboratory and 500 mL sub-samples were prepared using a churn splitter. 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 Whatman® GF B glass fibre filter was considered as the potential total dissolved fraction. In each case, 500 mL homogeneous sub-samples were prepared by mixing with deionised water, stored in 500 mL amber glass bottles with PTFE seals, preserved with 5 mL of 50% HCl at 4 °C in the laboratory and analysed within 40 days of collection.

2.5. *Sample testing*

The target SVOCs for the study were octane (OCT), decane (DEC), dodecane (DOD), tetradecane (TED), hexadecane (HXD), octadecane (OCD), Eicosane (EIC), docosane (DOC), tetracosane (TTC), hexacosane (HXC), and octacosane (OCC) having boiling points ranging from 125 °C to 432 °C. The target NVOCs were triacontane (TCT), dotriacontane (DTT), tetratriacontane (TRT), hexatriacontane (HXT), octatriacontane (OTT), and tetracontane (TTT) with boiling points ranging from 449 °C to 525 °C (Kudchadker and Zwolinski, 1966). The test methods adopted for the determination of SVOCs were USEPA 3510C, 8015, 8021, and 8260 (EPA, 2008). Draper et al. (1996) proposed modifications to the EPA methods to include the determination of motor oil with a carbon number up to C_{38} which was used as a guide to establish the Gas Chromatographic (GC) temperature programme in this study for the determination of both SVOC and NVOC simultaneously.

Calibration standards, internal standards, surrogate spikes and blanks were used in order to maintain quality control and quality assurance of the testing. Nine different calibration standards (17 component FTRPH calibration standards from Accustandard®) were prepared at 0.1, 0.5, 0.7, 1, 1.4, 7, 10, 28,

50 mg/L concentrations for each target analyte. The DRO internal standard (Sigma–Aldrich®) consisting of acenaphthene-d10, chrysene-d12, naphthalene-d8, perylene-d12, phenanthrene-d10, 1, 4-dichlorobenzene-d4 was added to each sample and standards at 5 mg/L concentration. Field blanks were used for each field sample collection episode and all results were blank corrected.

Three quality control standards (TPH Mix-1-DRO certified reference materials from Sigma–Aldrich®) at 1, 10 and 50 mg/L concentrations were prepared independently of the calibration standards and were included in each batch for comparison with the calibration standards. The sample batch was reanalysed if deviation of >10% from the certified value was observed for at least half of the target analytes in the quality control standards. One sample from each batch was spiked with another quality control standard at a concentration of 35 mg/L. Surrogate standards (Accustandard®) consisting of 10 mg/L of n-triacontane-d62 were added to seven randomly chosen samples. Seven field blanks were used to establish the limits of detection (LOD) for each analyte. Values less than LODs were replaced by half of the LOD values and values above the highest concentration limit of the calibration standard were discarded as outliers. Seven replicate sub-samples were prepared from randomly chosen samples from each of the eleven sites. The intra-site relative standard deviation was found within the range of 8–19% for each replicate. The inter-site relative standard deviation was found within the range of 15–21% for each analyte. This was within the range of the relative standard deviation suggested by Horwitz (1982) for ppm level concentrations. Table 2 shows the recoveries of the surrogates and the spikes. The test results for each of the five size fractions are provided as Supplementary Data available online with this study.

USEPA method 3510C (EPA, 2008) was used to extract SVOCs and NVOCs using the separatory funnel liquid–liquid extraction technique with 250 mL hexane as the exchange solvent. The samples were cleaned using standard column cleanup protocol with 5 cm silica gel and 5 cm pyrex® glass wool topped with 5 cm anhydrous Na_2SO_4 (EPA, 2008). Further concentration was carried out using the Kuderna-Danish apparatus followed by the nitrogen blowdown technique (EPA, 2008). The extractions and concentrations were carried out until a final extracted volume of 1 mL was achieved for Gas Chromatographic (GC) analyses.

A specially built HP5MS Agilent® capillary column of 30 m length, 0.32 mm internal diameter and 0.25 μm film thickness was used in the GC analyses. The column was temperature programmed to separate the analytes, which were then detected by a mass spectrometer interfaced to the GC. A splitless sample injection of 2 μL at an inlet temperature of 280 °C, inlet pressure of 35.58 kN/m^2 (5.16 psi) and a flowrate of 2.4 mL/min was used. The initial oven temperature was set at 40 °C, held at that temperature for 12 min, followed by an increase of 10 °C per min. until the oven temperature reached 300 °C and finally the temperature was held at 300 °C for 20 min. Hence, the total GC runtime was 58 min per sample. The identification of target analytes was performed by comparing their mass spectra with the electron impact spectra of authentic standards.

Other physico-chemical variables such as particle size distribution (PSD) of the sub-samples were determined using a Malvern Mastersizer S particle size analyser capable of

Table 2 – Percent recoveries of spikes applied at 35 mg/L and surrogate applied at 10 mg/L along with limits of detection for the target compounds.

Analytes		Limits of detection (LOD), mg/L	% recovery of spikes			% recovery of surrogate in randomly chosen samples						
			Batch 1	Batch 2	Batch 3	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Surrogate	n-triacontane-d62	–	–	–	–	76	79	104	88	81	96	113
Spiked SVOCs	Octane	0.54	128	110	101							
	Decane	0.32	80	82	83							
	Dodecane	0.44	131	124	97							
	Tetradecane	0.38	71	76	88							
	Hexadecane	0.85	75	88	84							
	Octadecane	0.71	72	79	91							
	Eicosane	0.34	90	86	104							
	Docosane	0.54	124	129	–							
	Tetracosane	0.05	110	91	92							
	Hexacosane	1.07	79	84	86							
	Octacosane	1.16	78	83	97							
Spiked NVOCs	Triacontane	1.02	84	70	71							
	Dotriacontane	1.32	69	79	75							
	Tetratriacontane	1.23	85	78	74							
	Hexatriacontane	1.06	98	84	65							
	Octatriacontane	0.60	–	82	71							
	Tetracontane	0.85	80	81	86							

analysing particle size between 0.05 and 900 μm diameter (Malvern, 1994). Total suspended solids (TSS) and total organic carbon (TOC) were analysed by methods 2540D and 5310B (APHA, 2005). The PSD of the sub-samples were compared with each other and used as a guide for homogeneity maintained in the sub-sampling process. The surface texture depths (STD) of the pavement surface at the selected road sites were determined according to method T250 (Main Roads, 2009). Additionally, the pH and electrical conductivity (EC) of each sample were measured using standard pH and EC probes in the laboratory according to methods 4500-H^+ B and 2510B respectively (APHA, 2005).

2.6. Data analyses

The data matrices consisted of 11 objects and 25 variables for each of the five particle size fractions noted above. The 11 road sites were considered as the 11 objects with identifiers listed in Table 1 with the prefixes C, I, or R for commercial, industrial, and residential land uses, respectively. Variables such as, ADT, *V/C*, STD, pH, EC, PSD, TSS, and TOC were considered as attributes of the objects responsible for the build-up of the target SVOCs and NVOCs, and hence considered as independent variables. After initial investigation of the probability distribution of the objects and variables in the data matrices, standardisation of the variables was performed as a pre-treatment measure so that each variable could be treated with equal importance in the data analysis.

Chemometric multivariate data analyses techniques such as, principal component analysis (PCA), preference ranking organisation method for enrichment evaluation (PROMETHEE) and geometric analysis for interactive aid (GAIA) were employed. Component extraction processes such as PCA and multicriteria decision-making processes such as PROMETHEE and GAIA have been used recently to characterise the incorporation of pollutants in stormwater runoff from urban roads (Jartun et al., 2008; Ayoko et al., 2007). A brief description of these techniques is discussed below.

2.6.1. PCA

The principal component analysis (PCA) is a data pattern recognition technique that extracts information from a data matrix by the projection of objects and variables to the principal components (PCs). The PCs are considered as the latent variables which are linear combinations of the original variables of the dataset. The PCA technique transforms the original variables to a new orthogonal set of PCs in such a way that they contain the data variance in a decreasing order, i.e., the first PC contains most of the data variance and the second PC contains the second largest variance and so on. 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'. More insight into the PCA technique can be found in Massart et al. (1997). In this study, SIRIUS2008 software (Sirius, 2008) was used to perform the PCA procedures.

2.6.2. PROMETHEE

PROMETHEE is an object ranking technique based on data criteria that uses some user defined preference functions to prioritise objects (Keller et al., 1991). The PROMETHEE method calculates the positive and negative outranking flows, ϕ^+ and ϕ^-, respectively based on the preference functions in order to rank the objects. The ϕ^+ value indicates how each object outranks all the others, whilst the ϕ^- value indicates how each object is outranked by all the others. This procedure is known as PROMETHEE I ranking. However, in some instances, two objects cannot be compared as they perform equally on different criteria. In these cases, the net outranking flow, ϕ which is the algebraic difference between ϕ^+ and ϕ^-, is calculated in order to facilitate the comparison. This procedure is known as PROMETHEE II ranking.

2.6.3. GAIA

GAIA is essentially a PCA biplot which facilitates a sensitivity analysis for multicriteria decision methods such as PROMETHEE (Keller et al., 1991). GAIA provides a graphical view of the objects and variables for net outranking flow ϕ in the form of a PCA biplot by decomposing the values from PROMETHEE II into unicriterion flows for each variable. The advantages of GAIA over a PCA biplot is that it produces a decision axis that takes into account the weights associated with the variables. These weights can be interactively adjusted for maximum achievable 'ϕ' net ranking values obtained by PROMETHEE II. This helps the decision-maker with an enriched understanding of the problem in terms of the detection of clusters of objects, conflicts in variables, inability to compare objects and so on. More details on the PROMETHEE and GAIA methods are discussed in Keller et al. (1991) and Ayoko et al. (2004). The DecisionLab 2000 software (Decision, 2000) was used to perform PROMETHEE and GAIA analysis.

3. Results and discussion

3.1. Trends in the original data

The bulk volume of the original data (presented as Supplementary Tables 1–5) makes it hard to discern any meaningful trends. Simple bi-variate correlations between the target variables at each of the five size fractions in Supplementary Tables 6–10 showed that the correlation of PSD, pH, EC, solids and organic carbon with the target SVOCs and NVOCs were very low, within a range of ±0.2 in the dissolved fraction of <1 μm. With the exception of EC, the correlations of PSD, pH, TSS and TOC with the target compounds started to increase from 1 μm to 300 μm size fractions. This suggested that the target compounds were mainly associated in non-ionic form with the particulate fraction 1–300 μm. More intrusive data analyses techniques such as, PCA, PROMETHEE and GAIA were employed to further investigate the trends noted in the original data matrices.

3.2. Exploratory PCA

Initially PCA was performed on the pre-treated data matrices starting with the total particulate fractions from 1 μm to >300 μm as well as the potential dissolved fraction of <1 μm taken together as shown in Fig. 1. All the physico-chemical,

traffic, pavement, and land use variables were included along with the target semi volatile and non volatile compounds.

The traffic parameters V/C and STD were found to be more strongly correlated with the target SVOCs and NVOCs than ADT in Fig. 1. This suggested that congestion on the road as well as the road texture conditions affected the build-up of SVOCs and NVOCs directly whilst ADT may have influenced the redistribution of particles on the road surface. Whilst the bulk of the free-flowing traffic was in the commercial and most of the residential areas, low traffic volumes were noted in the industrial areas. This explains the strong association of ADT with commercial and residential sites on PC1 in Fig. 1. The age and the grade of the top coat on the road as described in Table 1 was also found to be important as the STD in Fig. 1 positively correlates with most of the target variables.

In Fig. 1, only four objects (two residential and two industrial) were found to be associated with the target pollutants. This suggested that there is little or varying influence exerted by the land use parameters on the build-up of SVOCs and NVOCs. However, without detailed studies on the individual particle size fractions, these findings could not be validated. Fig. 2 shows biplots of the build-up of five individual size fractions from >300 μm to <1 μm.

In Fig. 2(a), the higher molecular weight NVOCs (422–562 g mol^{-1}) with boiling points ranging from 449 °C to 525 °C are strongly associated with the industrial sites whilst the comparatively lighter molecular weight SVOCs (114–394 g mol^{-1}) with boiling points ranging from 125 °C to 432 °C are mainly associated with the commercial sites for the >300 μm particulate fraction on PC1. There are some associations of residential sites (RDS, RP, RD, and RR) with octane (OCT) and tetradecane (TED) in Fig. 2(a). However, the association of residential sites with the build-up of either SVOCs or NOVCs was found to be generally negligible on both PCs for the >300 μm fraction.

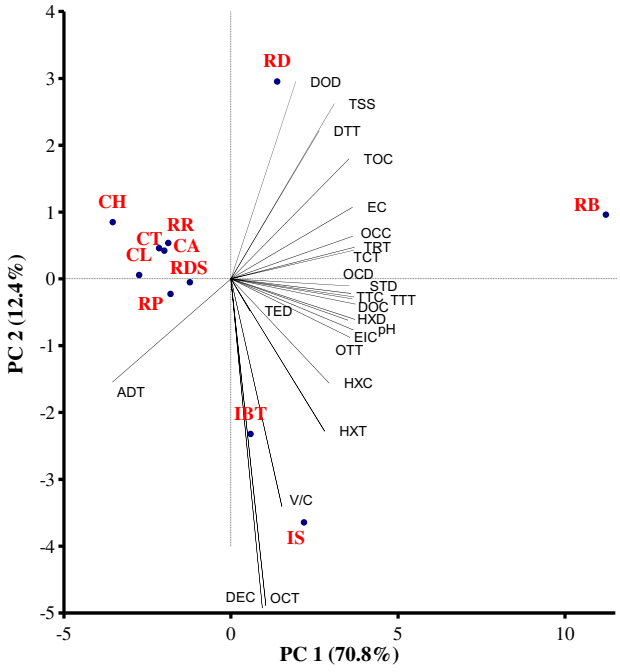

Fig. 1 – PCA biplot of total particulate fractions from <1 μm to >300 μm taken together.

In Fig. 2(b)–(d), similar findings suggested that the semi volatile components of petrol and diesel fuels are predominantly associated with the commercial areas whilst the non volatile heavier compounds were mainly associated with the industrial areas. The commercial areas in this study were close to carparks, shopping centres as well as service stations and the industrial areas mainly comprised of marine and light metal industries.

According to Table 1, the average congestion (0.66 ± 0.33) in the commercial areas was much higher than the average congestions (0.40 ± 0.22) in both the industrial and residential areas. The average volume of traffic in the commercial areas is almost twice the volumes for the residential and industrial areas. This suggested that slow moving traffic in the commercial areas were contributing significantly towards the build-up of SVOCs through exhaust and non-exhaust emissions, whereas, the strong correlations between NVOCs and the industrial sites observed in particulate fractions from >300 μm to 1 μm in Fig. 2 suggested that these NVOCs in the industrial areas may not necessarily originate from traffic alone. Usage of different types of motor oils and lubricants by machinery in the industrial areas may also contribute to the build-up of NVOCs in these areas. In either case, the contribution of residential areas to the build-up of such pollutants on urban roads is hardly noticeable. It is important to note that traffic generated SVOCs are prominently associated with particulate matter from 1 μm to >300 μm in the commercial areas in Fig. 2(a)–(d).

In Fig. 2(e), for the potential dissolved fraction of <1 μm, the three different land uses are not directly associated with the build-up of SVOCs and NVOCs as no clear separation of land use with target variables was identified in either of the PCs. There are some associations of residential objects (e.g., RB, RD, and RP) with the build-up of a few SVOCs and NVOCs in Fig. 2 (e). However, as the average volume of daily traffic in the residential study areas was quite similar (around 5100 vehicles per day) to the industrial areas, it is understandable that the traffic in the residential areas did not directly influence the build-up of SVOCs and NVOCs.

Patra et al. (2008) noted that coarser particles resuspend and redistribute faster than the finer particles due to vehicle induced turbulence and the reservoir of finer particles get replenished by grinding of the coarser particles under the vehicle wheels. The role of organic matter as a binding agent between solids and other pollutants has been discussed by Charlesworth and Lees (1999). They reported that organic matter acts as a predominant binder for particle sizes ranging from 63 μm to 2 mm during build-up. Hence, the 'land use independent' loadings of SVOCs and NVOCs in the potential dissolved fraction of <1 μm in Fig. 2(e) suggest that traffic may have caused the resuspension and redistribution of coarser particles generated elsewhere and replenished the fine particles of <1 μm size which has adsorbed the target organics which is independent of the land use. However, the extent of adsorption of target pollutants by the finer fraction of <1 μm may be very limited as the loading vectors of the target pollutants in the dissolved fraction of <1 μm are quite similar in magnitude to the particulate fractions in Fig. 2(a)–(d). This suggests that the variances of target pollutant concentrations in the dissolved

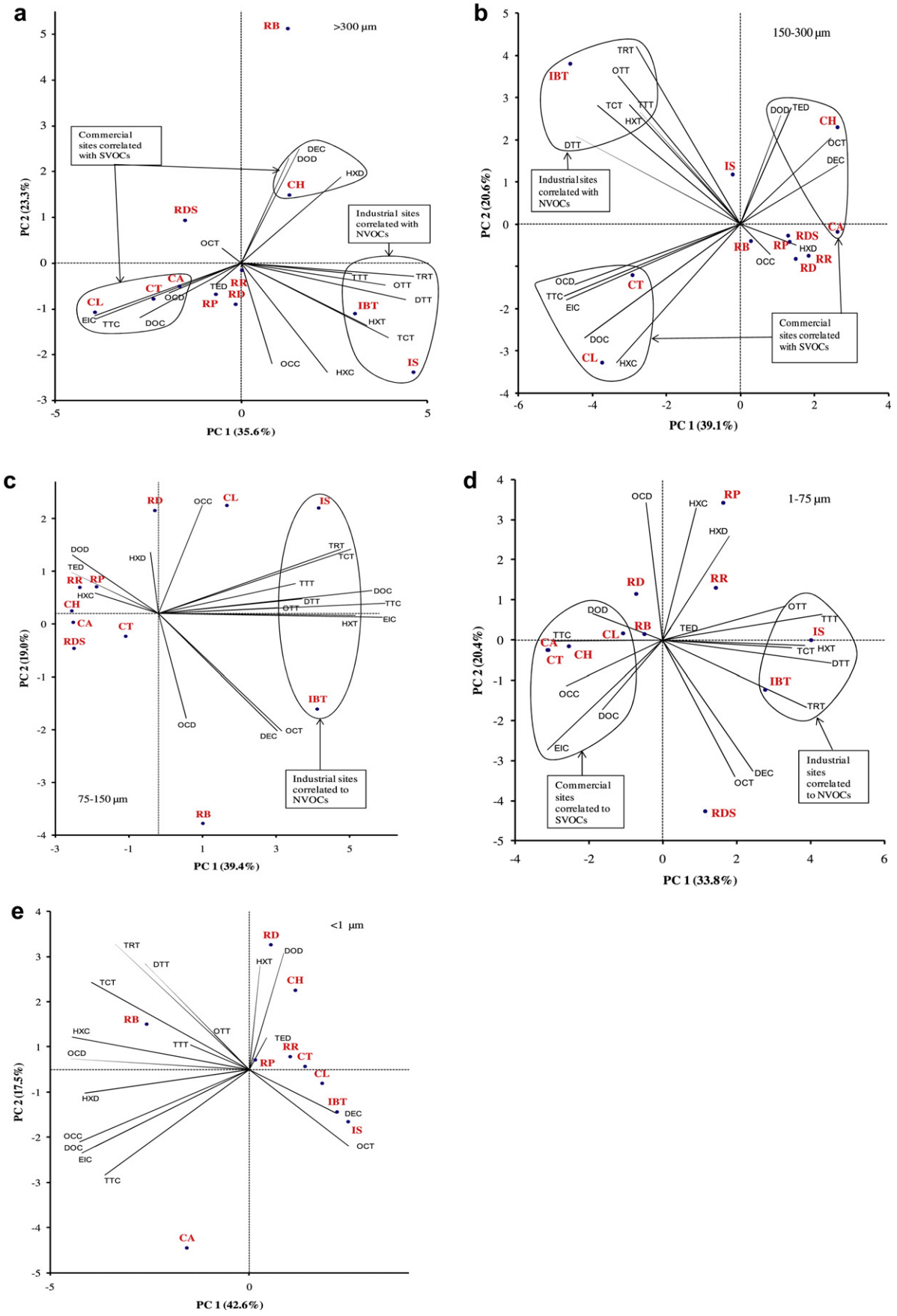

Fig. 2 – Individual PCA biplots for (a) >300 μm; (b) 150–300 μm; (c) 75–150 μm; (d) 1–75 μm; and (e) <1 μm size fractions.

fraction are quite similar to the particulate fractions. This is attributed to the fact that organic compounds have very limited solubility in most of the solvents which may cause the target pollutants to remain free without adsorbing to the fine particles and hence the potential dissolved fraction manifested similar variances as the particulate fractions.

The PCA analysis provides a fundamental characterisation of the build-up of traffic related SVOCs and NVOCs for different land uses. In order to characterise such build-up in terms of particle size fractions as well as the predominant urban traffic scenarios that influence build-up, PROMETHEE ranking and GAIA analysis were employed.

3.3. PROMETHEE

The preference ranking organisation method for enrichment evaluation (PROMETHEE) was applied to the same data matrices that were used for the PCA. In the context of ranking the study sites as urban traffic objects with variable traffic parameters, Mahbub et al. (2010a) proposed high, moderate, and low urban traffic scenarios based on a moderately soft fuzzy clustering technique that allows traffic attributes of different scenarios to intersect with each other. The high traffic scenario comprised of traffic volumes ranging from 9000 to 24,000 ADT with relatively high congestion; moderate traffic scenario comprised of ADT values ranging from 2300 to 5900 with moderate congestion whilst low traffic scenario was associated with low traffic volume ranging from 500 to 3500 ADT with low congestion.

This study adopted the same classification of urban traffic scenarios to interpret the PROMETHEE ranking. According to this urban traffic classification system, high traffic scenario comprised of objects IS, CT, CA, and RDS; moderate traffic scenario comprised of CH, CL, IBT, RB, and RR whilst low scenario comprised of RD and RP. Fig. 3 shows the 'ϕ' net outranking flows of the 11 traffic objects. The three different land use types and the five different size fractions were incorporated in the ranking. The Gaussian preferential function (Brans et al., 1986) with the threshold value set equal to the standard deviation of each criterion was used in the PROMETHEE model. This function was chosen according to the suggestion of Brans et al. (1986) who showed that the Gaussian function provided the least discontinuities and guaranteed the most stable results out of the six different preference functions in PROMETHEE.

In Fig. 3, all the objects with positive outranking flows are from commercial and residential sites. These along with the negatively ranked industrial sites suggest that traffic related build-up of SVOCs and NVOCs mainly occur in commercial and residential sites. However, the objects with negative outranking flows in Fig. 3 comprised of all three land uses (e.g., CA, RDS, IS, and CT). According to the above noted classification of traffic scenarios, most of the negatively ranked objects fall into the high traffic scenario. To the contrary, the top three objects (CL, CH, and RR) are from the moderate traffic cluster. Therefore, it is evident from the PROMETHEE ranking that the moderate traffic scenario with ADT values ranging from 2300 to 5900 with average congestion of 0.47 would dominate the SVOCs and NVOCs build-up.

The low traffic scenario (objects: RD and RP with very low positive outranking flow values) may have some impacts on such build-up through the resuspension and redistribution of coarse particles as both of them fall into residential land use. However, the high traffic scenario (objects: CA, CT, IS, and RDS) did not affect the build-up. Whilst the high traffic scenario had the highest average traffic volume and congestion, the role of texture depths may also play an important role in the SVOCs and NVOCs build-up. The average texture depths of the high traffic objects was 0.67 mm which was comparatively lower than the moderate and low traffic objects (0.77 mm). This difference could have led to weaker correlations between high traffic objects and the different particle size fractions investigated in the study. In order to facilitate the sensitivity of the findings derived through the PROMTHEE ranking, the geometric application for interactive aid (GAIA) was performed on the same data matrices used for PCA and PROMETHEE.

3.4. GAIA

The GAIA method provided a PCA biplot with a decision axis (pi) for all traffic scenarios and size fractions. The quality of the decision axis was tested for its stability by interactively changing the weights of the different variables in the data matrix for the maximum achievable 'ϕ' net ranking values and the optimised GAIA biplot is shown in Fig. 4.

The GAIA biplot in Fig. 4 isolates most of the moderate traffic objects from the high traffic objects. Additionally, the decision axis (pi) is strongly correlated with the higher particulate fractions of 75–300 μm fractions as well as the moderate traffic objects on both axes. This suggests that the target organic compounds are predominantly present in the 75–300 μm particulate fractions. The low traffic objects RD and RP as well as moderate objects IBT are also strongly correlated with the particulate fraction >300 μm, suggesting that the redistribution of particulate matter occurred in this

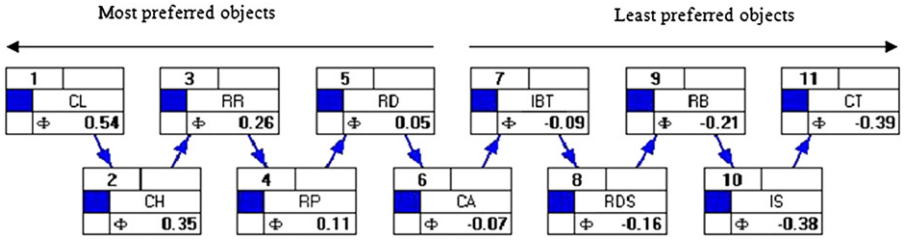

Fig. 3 – Combined PROMETHEE II net outranking flows of traffic objects showing commercial sites as predominant sources of SVOCs and NVOCs build-up.

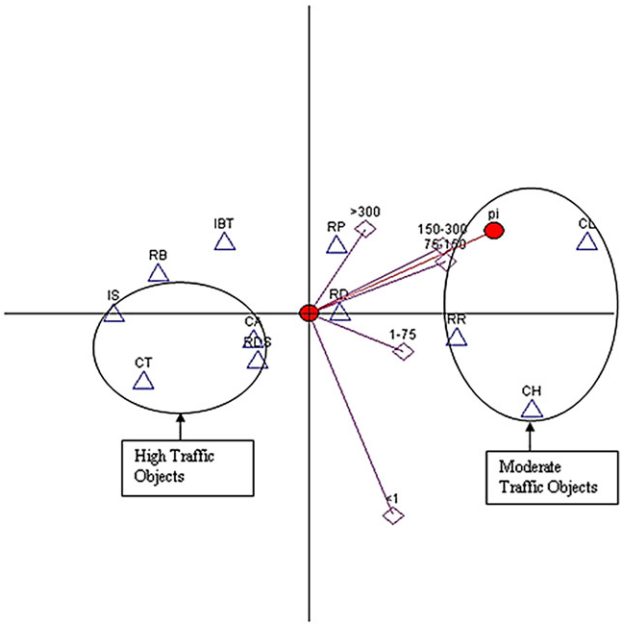

Fig. 4 – GAIA biplot for the build-up of SVOCs and NVOCs incorporating all size fractions as well as all traffic scenarios.

fraction. The potentially dissolved fraction <1 μm is not correlated with any of the traffic objects even though the magnitude of its loading vector is significant. This suggested that the presence of the fine fraction <1 μm did not contribute to the build-up of SVOCs or NVOCs and only the resuspension and the replenishment of the finer materials as described earlier are active in this fraction.

4. Conclusions

The build-up of traffic generated semi and non volatile organic compounds under combined traffic scenarios of low, moderate, and high has been characterised in this study. The key findings can be summarised as follows:

- The build-up of lighter semi volatile compounds is mainly associated with the commercial areas whilst non volatile lubricants and motor oil compounds are associated with the industrial areas. The residential areas do not significantly contribute to the build-up of such pollutants on urban roads. Congestion in the commercial areas appears to be the main source of build-up of SVOCs whilst industrial usage of lubricants and heavier oils may also contribute to the build-up of NVOCs in industrial areas.
- Moderate traffic scenario with ADT ranging from 2300 to 5900 and average congestion of 0.47 would predominate SVOCs and NVOCs build-up on urban roads under combined traffic scenarios. As a practical outcome of this finding, a moderate traffic scenario in any type of land use can be targeted as a significant source of such pollutants.
- Amongst the different size fractions, the particulate fraction 75–300 μm is the most predominant in associating with the SVOCs and NVOCs build-up. Particulate fraction > 300 μm primarily influences the redistribution of coarser particle due to vehicular activities. The potential dissolved fraction <1 μm is not associated with the build-up of SVOCs and NVOCs in any of the land uses investigated in the study. Therefore, mitigation measures for removal of SVOCs and NVOCs from build-up should target the 75–300 μm particulate fractions.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2011.02.033.

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