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Carbon Matrix as a Surrogate Measure for Polycyclic Aromatic Hydrocarbon Pollution in Road Sediments

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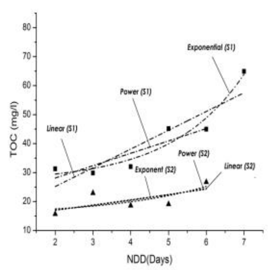
Graphical abstract



Abstract

The influence of road sediment on pollution prevalence was well documented. However, the accumulation rate of an organic matrix on impervious surfaces which could be used as a surrogate measure of polycyclic aromatic hydrocarbon (PAH) availability has not been given desired attention. This paper presents a first glimpse of the influence of consecutive dry days on the buildup of the organic matrix on a different road type, and how the most important measure of the organic matrix could be used as a precursor for the availability of PAH. The total organic carbon shows high variability between roads of different surface type and conditions. The role of road sweeping on inorganic and organic content of road deposits has also been discussed. The road deteriorating surface condition indicated a stronger correlation with carbon matrices deposit on road sediment, which is a vector for pollution courier on sealed surfaces.

Keywords: Build-up; inorganic carbon; total carbon; total organic carbon; PAH, sediments

1.0 INTRODUCTION

To ease prediction of pollution in metropolitan environment, it is astute to relate sediment build-up to easily quantifiable parameters of its physical characteristics that may give a primary insight into its hazard potential. Pollutants accumulate on impervious surfaces from diver's sources, such as atmospheric fallout, vehicle wear, anthropogenic activities, industrial spewing and abrasion of a parent urban sealed surface, thereby making it difficult to trace them to a particular origin. Buildup is a complex process that involves a number of multifaceted phenomena that influence the accumulation of pollutants in the environment, such as wind erosion and street cleaning. Among the urban sealed facades, road surfaces are the most widely investigated due to their strategic location in the metropolitan landscape. Road directly emptied its runoff to the adjacent drains; it covers wider proportion of urban impervious surfaces. This paper presents the modelling of a carbon matrix as a surrogate measure of polycyclic aromatic hydrocarbon presence in urban road sediments.

Understanding the relationship between Carbon matrices as a likely potential for a pollution buildup on road surfaces is critically important for predicting PAH-related pollution load from urban sealed surfaces. The potential to model buildup processes is still in contention[1]. However, a number of experieriential models exist that make it possible to use calibrated empirical formulae with input from the local data to estimate the future pollution load from impervious surfaces. The formulae could be linear (Equation 1 and 2), power (Equation 3), exponential (Equation 4) and other variants such as Michaelis-Menton (Equation 5). Hvitved-Jacobsen *et al.* suggested that Equation 1 could be used to predict pollutant's accumulation at any antecedent dry day(s) [1]:

$$B_t = B_0 + r_t A \Delta t \text{ ....(1)}$$

where B_t (g) is the weighted mass of the accumulated pollutants over surface area A (m^{-2}) during antecedent dry period Δt (d). r_t (g m^{-2} d^{-1})is the rate of pollutant builup and B_0 (g)is the initial mass of pollutant buildup at $\Delta t = 0$.

Huber concludes that pollutant build-up equations borders within the following Equations [2]:

$$B = \lambda t \text{ ....(2)}$$
$$B = \lambda t^{\gamma} \text{ ....(3)}$$
$$B = B_{limit}(1 - e^{-\gamma t}) \text{ ....(4)}$$
$$B = B_{limit}(\frac{t}{\lambda} + t) \text{ ....(5)}$$

B is the buildup mass (g), λ and γ are empirical parameters that are site specific.

Attempt to establish surrogates in predicting pollution has yielded different outcomes [3-9]. For instance Kobriger *et al.* found that a linear equation exists between Total Solis (TS) and Average Daily Traffic (ADT), while Kayhanian *et al.* found no correlation between event mean concentrations (EMC) of highway runoff pollutants with the Annual Average Daily Traffic (AADT) [5, 9]. This lack of consensus among researchers implies high variability of study sites and the need to further studies at a local scale. However, researchers have confirmed the influence of land use and number of dry days (NDD) in accumulating pollutants in urban areas [9, 10].

Total organic carbon (TOC) is the measure of available carbon chained to an organic compound. The amount of total organic carbon present in a water sample is one of the quantitative pointers to the water characteristic. TOC has been used as a tool for the measurement of possible organic contamination in waters and drinking water [11, 12]. The major sources of TOC in waters include both the synthetic and natural organic matter sources. Quantification of TOC often involves measurement of the Inorganic Carbon (IC), and the Total carbon (TC) contents. The IC is the content of carbonic acid and dissolved carbon dioxide present in the sample while the TC is the sum total of both the organic and inorganic carbon available in the sample. Therefore, TOC is a function of the other two matrices (IC and TC), and can be obtained by using the differential method. Because of the affinity of organic carbon to combine with other elements in the environment, its excess poses a threat to public health and the environment.

The persistence of PAHs in the environment is relative to the availability of TOC on carrying sediments [13, 14]. The presence of organic carbon in sediments can be a good source of food for fauna, but it’s over availability can also cause destruction of aquatic species [15]. Viguri *et al.* studied the relationships between the 16 priority PAHs, the amount of surface sediments and the organic carbon parameters, they reported that a linear relationship existed between the amount of sediments and the availability of organic matter, while the PAHs correlates exponentially with TOC [16]. However, Boitsov *et al.* found a strong linear relationship between the concentration of PAH and TOC [11]. These types of established relationships are vital for predicting PAH using measured physical parameters. Furthermore, Hinga found direct relationship between PAH degradation and the available TOC in marine sediments and posited that TOC provides useful knowledge in predicting biodegradation of different sediment's type [12].

Land use exhibits distinctive influence on the accumulation of street dust at different rates with a different build-up pattern. Sartor and Boyd identified ADT, Surrounding land use, road surface type and condition, season of the year and public work practices as the principal factors affecting street dust accumulation [10]. However, Pitt *et al.* found that the road surface texture plays a more important role in road sediment retention than land use [17]. Kayhanian *et al.* found elevated levels of pollutants in urban highway with higher AADT than non-urban highways with AADT <30,000 [9]. However, they found higher levels of Total suspended solids (TSS), Chemical Oxygen demand (COD), Total dissolved solids (TDS) Turbidity and ammonia in non urban highways.

2.0 EXPERIMENTAL

Skudai is located in Peninsular Malaysia between 6^0 45’ and 1 ^{0}20’ N latitudes and 99^0 40’and 104^0 20’ E longitudes it has moderate industrial activities, but its proximity to Singapore could aggravate its pollution level. It rains most of the days, hardly allowing for accumulation of pollutants. Three sites were chosen based on their differing characteristics as shown in Figure 1. Jalan Pertanian 29 (S2) was chosen to represent a newly constructed road. Yusop *et al.* described the Pertanian catchment housed 147 homes and was described as high density low cost area [18]. Jalan Pulai 62 (S1) was chosen to represent mid-aged road and a semi-urban main road serving two separate catchments in Pulai Utama; one catchment consisted of 165 and the other 327 houses of mixed single, double and triple stories. A car park (S3) was chosen inside Universiti Teknologi Malaysia (UTM) to represent an old road with heavy traffic parking and to represent Institutional and parking lot. Table 1 highlighted the general characteristics of these chosen roads.

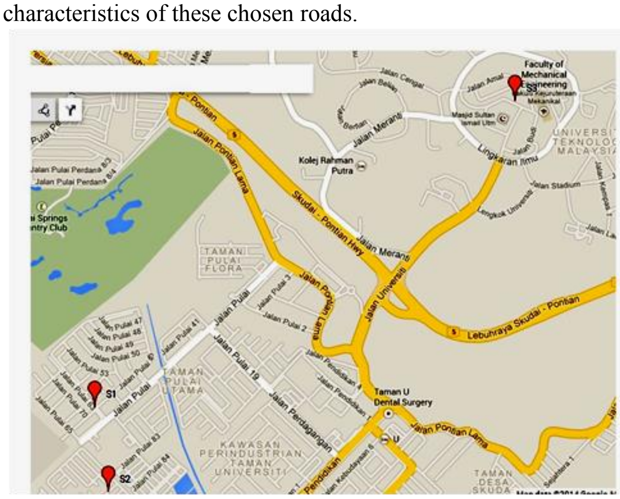


Figure 1 Site location map in Skudai, Johor Bahru, Malaysia

Table 1 Characteristics of chosen roads

Name	Road class	Traffic condition	Road surface condition	Remarks
S1	Residential road	Light	smooth	New <1 year
S2	Semi Urban Highway	Moderate	moderate	Mid-age; 15 years
S3	Parking	high	rough	Old > 15 years

The collection campaign starts in June 2013 after indications from the weather forecast for an anticipated dry period. The area received 8 mm of rainfall two days before the sample collection begins. A corridor of 3.8mx14.0m was cleared using soft and hard handheld brushes one day after the rain for all the sites. A vacuum cleaner of high suction power with 96% efficiency was used to collect the accumulated road dust for 2, 3, 4, 5, 6, and 7 days NDD. The NDD seven on S2 and S3 were not collected because of rain immediately after collecting NDD seven on S1. The NDDs were collected as the number of days progresses without rain. Samples were collected on a strip of 1m starting from the camber downwards to the shoulder of the road; this provides a good sample representation.

To ensure all samples were taken within the strips, the vacuum was repeated three times in both directions. Samples recovered from the vacuum cleaner were immediately taken to the laboratory and stored in accordance with EPA[19] before analysis. Subsequently, the samples were analysed for carbon matrices within 24hrs after collection as recommended by Duncan.[20] The Shimadzu auto sampler TOC analyser (Model TOC-VCSH) was used to measure the TC, IC and TOC in each sample. Before its use, the samples were trickled through a filter paper with 0.45 µm pore size to remove all sediments.

3.0 RESULTS AND DISCUSSION

Figure 2 shows the relationship between the concentration of inorganic carbon and the progressive number of dry days for S1, S2 and S3. There was street sweeping on NDD three in S3; this is indicated at the sharp drop of concentration, after this day there was progressive build up as shown on the figure. S1 and S2 show an appreciation of IC as the number of days progresses, but at different concentration.

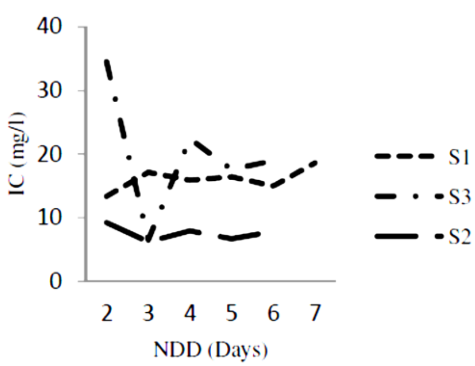


Figure 2 Inorganic carbon build-up for S1, S2, and S3

The carbon matrix parameters as seen in Figure 2, 3, and 4, increases with deteriorating road condition. This indicated that the road surface condition has a profound influence on the accumulation of IC, TC and TOC. Even though there was an evacuation of sediments on S3, which decreases the concentration of IC to a record low of 6. 5mg/l the concentration of IC surpasses the other two sites after subsequent days. The concentration of TC and TOC as presented in Figure 2 and 3 show a similar result except that the TC and TOC did not show appreciation until NDD five when they begin to appreciate. This can be explained by the effectiveness of the sweeping method (airstream blower) to have evacuated most of the inorganic carbon content leaving behind more residue of organic carbon content.

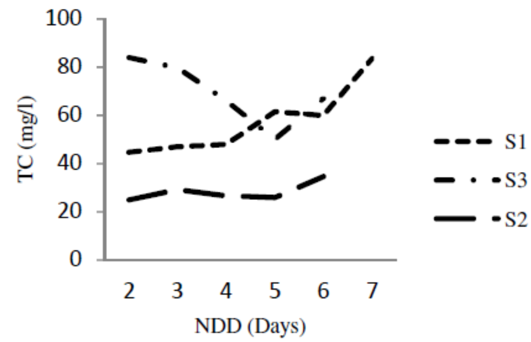


Figure 3 Total Carbon build-up for S1, S2, and S3

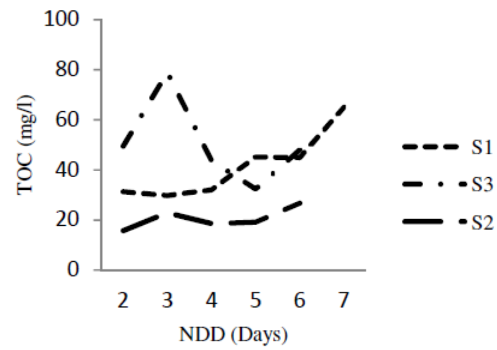


Figure 4 Total organic carbon build-up for S1, S2, and S3

The buildup rate of the inorganic carbon as indicated on Figure 2 is faster in the parking area than residential and urban highways. This could be attributed to the location of the parking area considered in this research. The parking area is located next to a very busy road linking most of the University faculties and the library; the frequent re-suspension of inorganic content on the adjacent road is likely to end up accumulated on the parking which has a rougher surface that could make their storage favourable. The highest recordable value of IC (34.40 mg/l) was on S3 during the NDD two, while the slightest was recorded on S2 (6.24 mg/l) during the NDD three. Similarly, TC was found at an elevated level of 84.0 mg/l and the slightest at 25.0 mg/l respectively for S3 and S2 for same NDDs. The trend for TOC peaks a different NDDs; S3 peak on NDD three with 79.0 mg/l, and the least peak at 16.0 mg/l on S2. Generally, S3 is more likely to contribute more concentration of PAH followed by S1 and then the least input of PAH in storm water pollution would be S2. This result demonstrated that pollution from parking positions should not be underrated to contribute PAH input to pollution, especially those with deteriorating road surface condition. New road indicated least pollution of PAH compared with the other roads considered in this research this may be due to its least capacity to retain pollutant's inputs, and its surface condition may enhance redistribution of accumulated pollutants.

The relationship of TOC to the number of dry days for S1 and S2 were modelled as shown in Figure 5. The resulting modelled equations are presented in Equations (6-8). Both sites show a good correlation between the TOC and the NDD, the regression best fit was tried for linear, exponential, and power equations. The exponential model shows a stronger correlation with R^2 of 0.92 for S1, 0.35 for S2. The power equations yielded R^2 of 0.85 and 0.30 respectively, while the linear equations result in R^2 of 0.80 and 0.25 correspondingly. The weaker correlation in S2 could be attributed to the lack of extended data beyond NDD five. Consecutive NDD of more than five days is rear in Malaysia because of persistent sequential days of rainfall.

$TOC = TOC_0 + Exp(R_t d)$ ....(6)
$TOC = kd^{ß}$ ....(7)
$TOC = TOC_0 + R_t d$..(8)

TOC_0 is the initial concentration of total organic carbon at d=0
R_t is the rate of sediment accumulation measured in a litre of water
d is the corresponding number of dry day(s)
ß and k are empirical constants that depends on the road conditions; these coefficients are defined in Table 2.

Table 2 S1 and S2 modelled parameter values

Location	R_t(Eq.6)	R_t(Eq.7)	k	ß
S1	0.5	4.27	18.40	1.19
S2	0.4	1.82	14.22	1.10

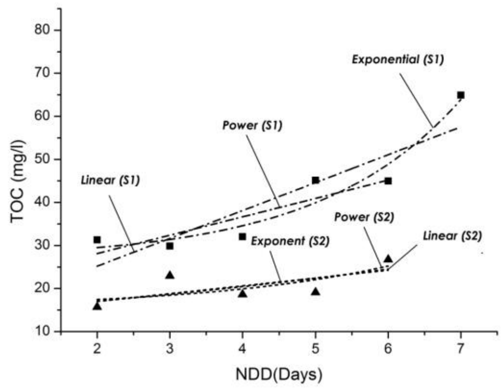


Figure 5 Modelled relationships between TOC and NDD for S1 and S2

■4.0 CONCLUSION

This paper demonstrated the importance of road type and its characteristics on the buildup of organic matrices. Surface condition was found to influence the buildup pattern and the concentration of carbon matrices on a road profoundly. The TOC as a constituent of IC and TC was modelled in this research as a precursor for availability of PAH on roads with unbroken build-ups. A good fit was obtained for exponential, linear and power equations. The linear equation can be conveniently used to predict the prevalence of PAH on roads using an established linear relationship of TOC and PAH. There is need for further study to establish the influence of other surrogates to measure PAH availability on road surfaces.

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