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Build-up of toxic metals on the impervious surfaces of a commercial seaport

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Abstract
In the context of increasing threats to the sensitive marine ecosystem by toxic metals, this study investigated the metal build-up on impervious surfaces specific to commercial seaports. The knowledge generated in this study will contribute to managing toxic metal pollution of the marine ecosystem. The study found that inter-modal operations and main access roadway had the highest loads followed by container storage and vehicle marshalling sites, while the quay line and short term storage areas had the lowest. Additionally, it was found that Cr, Al, Pb, Cu and Zn were predominantly attached to solids, while significant amount of Cu, Pb and Zn were found as nutrient complexes. As such, treatment options based on solids retention can be effective for some metal species, while ineffective for other species. Furthermore, Cu and Zn are more likely to become bioavailable in seawater due to their strong association with nutrients. Mathematical models to replicate the metal build-up process were also developed using experimental design approach and partial least square regression. The models for Cr and Pb were found to be reliable, while those for Al, Zn and Cu were relatively less reliable, but could be employed for preliminary investigations.

Keywords: Marine ecosystem; Water quality modelling; Experimental Design; Stormwater pollutant processes; Stormwater quality

1. Introduction

The marine environment is a sensitive ecosystem that is home to a range of fauna and flora. Several studies have confirmed that marine ecosystems around the world are under serious threat due to pollution generated by various anthropogenic activities (Gao and Chen, 2012; Kucuksezgin et al., 2011). In particular, the presence of metals, which are toxic and persistent, can cause adverse impacts on the health of fauna and flora in the marine environment (Owen and Sandhu, 2000). Metals are contributed to the marine environment by diverse sources including the surrounding urban areas and seaports.

Anthropogenic activities associated with urban areas such as increased traffic activities can contribute a significant amount of metals to urban impervious surfaces, which are eventually transported to the marine environment by stormwater runoff. The characteristics of metal build-up on urban surfaces, particularly impervious surfaces along with the mathematical replication of the build-up process has been extensively investigated in research literature (for example Egodawatta et al., 2013; Gunawardena et al., 2014), contributing to the development of effective strategies to control metal contributions from urban areas to the aquatic environment.

However, only limited studies have investigated metal build-up on impervious surfaces specific to a commercial seaport (Goonetilleke et al., 2009), where a range of intense anthropogenic activities which are unique to this type of infrastructure such as container handling and heavy vehicle traffic activities occur. The limited knowledge currently available is a significant constraint to the design of effective management and treatment strategies to mitigate metal pollution originating from commercial seaports.

The primary aims of the study presented in this paper were to: (1) characterise the metal build-up on the impervious surfaces specific to a commercial port; (2) investigate the relationships of metals with other pollutants such as solids, organic carbon and nutrients, which influence metal behaviour in the build-up process and thereby provide essential knowledge for the design of effective treatment strategies; and (3) develop mathematical models to replicate the metal build-up process on impervious surfaces that are typical to a commercial port. The outcomes of the study can be extended to other commercial ports since the land uses investigated are typical to any commercial port.

2. Materials and methods

The study was conducted at the Port of Brisbane, Australia located adjacent to the Moreton Bay Marine Park, which has a high ecological and conservation value. The marine ecosystem consists of over 150 ha of mangroves, large seagrass areas, variety of fish species and resident and migratory shorebirds. The surrounding areas have experienced high urban growth, and coupled with a booming economy and intensive agricultural and tourist activities. These in turn have resulted in an increase in anthropogenic activities such as increased cargo handling at the Port (Goonetilleke et al., 2009).

Six study sites encompassing different land use activities specific to a commercial seaport were selected at the Port of Brisbane (Fig. 1). The sites included a vehicle marshalling area (site 1), a container storage facility (site 2), a container terminal (site 3), a quay line (site 4), an inter-modal operations area (site 5) and the main access roadway (site 6). The pollutant build-up samples were collected from 2.0 m × 1.5 m plot areas from the impervious surfaces of the selected study sites using a wet and dry vacuuming system. A detailed discussion on the build-up sampling protocol adopted can be found in Herngren et al. (2006). The samples were collected after a minimum of seven antecedent dry days as the total build-up asymptotes to an approximately constant value after this period of time (Egodowatta, 2007). The samples collected from the impervious surfaces were wet-sieved into different size fractions of <0.75 μm, 0.75-75 μm, 75-150 μm, 150-300 μm and >300 μm as the particle size plays a critical role in the adsorption of metals by particulates (Gunawardana et al., 2014).

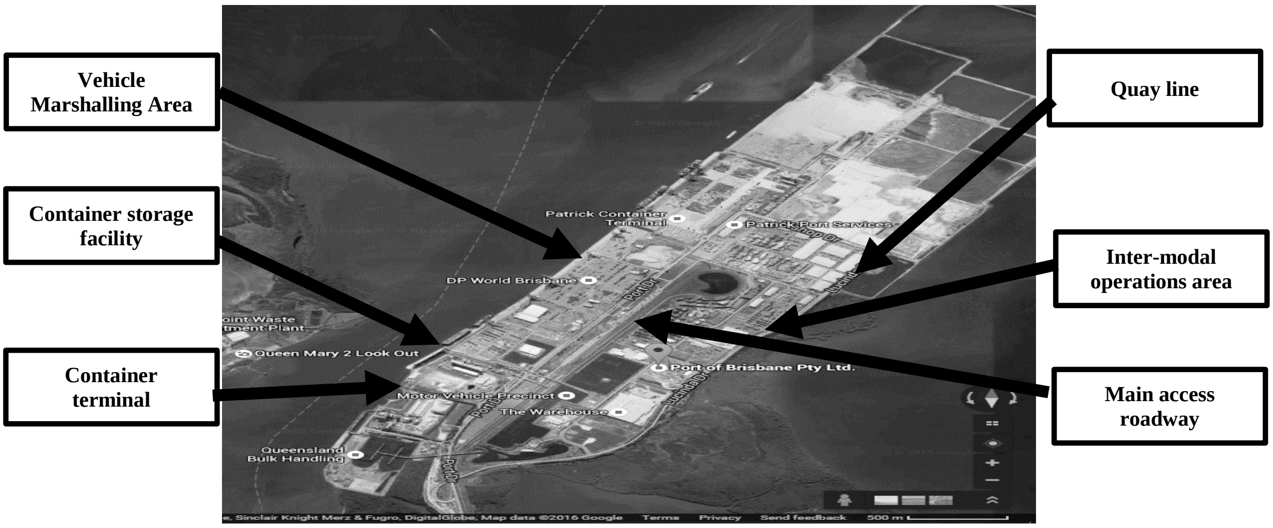

Fig. 1: Location of study sites

The study investigated total suspended solids (TSS), total organic carbon (TOC), total nitrogen (TN), total phosphorous (TP), aluminium (Al), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), arsenic (As), nickel (Ni), zinc (Zn) and mercury (Hg), which are common pollutants found in the environment (Gunawardena et al., 2013). The following methods were used for the laboratory analyses of pollutants: (1) TSS – 2540D and 2540C (APHA, 2005); (2) TOC – 5310C (APHA, 2005); (3) TN – 4500F and 4500B (APHA, 2005); (4) TP – 4500P (APHA, 2005); (5) Al, Pb, Cd, Cr, Cu, As, Ni and Zn – USEPA 200.7 (USEPA 2001) and 6010B (USEPA 1996); and (6) Hg – USEPA 7470A (USEPA 1994) and 3112B (APHA, 2005). The data analyses were performed using univariate and multivariate data analysis techniques. Mutlivariate analyses such as principal component analysis (PCA) and partial least squares regression (PLS) were conducted using MATLAB (Mathworks, 2013).

3. Results and Discussion

3.1 Metal build-up

The Hg load in the build-up was below the detection limit, while As, Cd and Ni loads were relatively very low. Consequently, these were excluded from further analysis. The average loads of other pollutants across the six study sites for the different particle size fractions are presented in Table 1(a) along with the corresponding standard deviation. As evident from Table 1(a), the pollutants were primarily present as fine particles <150 μm. The coarse particle fraction, i.e. >150 μm, was also present in significant amount. The predominant presence of finer particles is of concern since conventional sediment reduction approaches for stormwater treatment may not be effective in trapping finer particles.

In general, total solids load was found to be the highest followed by the total organic carbon load. Among metals, Al load was significantly higher than the rest. This can be attributed to the fact that Al is a major component in geogenic materials (Singh and Gilkes, 1992), and hence abundantly present in the environment. Though Zn, Cu, Pb and Cr are primarily contributed by the wear of vehicle components (Gunawardena et al., 2014), the Zn load was significantly higher than those of Pb, Cu and Cr, suggesting the presence of additional Zn sources such as container surfaces and roofs present at the study sites. However, their bioavailability is dependent on their association with other pollutants such as solids, organic carbon and nutrients as discussed in Section 3.2.

Table 1(b) gives the specific pollutant load in the total particulate build-up at the six study sites. Among the sites investigated in this study, sites 5 and 6 had relatively higher pollutant loads compared to the rest. Site 5 is the site of inter-modal operations and has inter-locking pavers, which can trap a relatively higher amount of pollutants in-between the pavers. On the other hand, site 6 is a roadway surrounded by unpaved areas and is used by heavy trucks. Consequently, a high amount of pollutants could have been contributed by geogenic sources and traffic activities. In contrast, sites 3 and 4 had the lowest amount of pollutants. Site 4 is the quay line, which has a smooth concrete pavement. Though appreciable traffic activities occur at site 4, its proximity to the shore could have resulted in the removal of a significant amount of pollutants from the smooth concrete surface by wind. Similarly, site 3 is used as a short term storage area, which could have limited the opportunity for the accumulation of a significant amount of pollutants. Sites 1 and 2, which are used for container storage and vehicle marshalling, respectively, had moderate amount of pollutants. It is worthy of note that similar trends were observed for other particle fractions investigated. Consequently, it is important that frequent street sweeping measures need to be undertaken in areas that were identified to have accumulated high pollutant loads, in order to reduce the pollutant contribution to the marine ecosystem.

Table 1: (a) Average pollutant loads for different particle sizes across the study sites (Average ± Standard deviation) and (b) Pollutant loads in total particulate sample

(a)

Size (µm)	^{a}Al	^{a}Cr	^{a}Cu	^{a}Zn	^{a}Pb	^{a}TP	^{a}TN	^{a}TOC	^{b}TS
< 150	339±433	2.7±3.1	6.9±5.8	99±111	4.8±4.4	36±65	128±203	296±119	22±21
150-300	78±99	0.6±0.6	1.8±1.4	43±45	1.8±1.6	7±15	23±19	64±62	6±5
> 300	50±77	0.5±0.6	2.3±3.4	76±142	1.3±2.2	15±34	34±56	82±103	4±7
Total particulate	257±223	2.3±2.0	5.4±4.7	128±127	5.1±4.1	52±62	102±113	246±196	26±22

(b)

Site	^{a}Al	^{a}Cr	^{a}Cu	^{a}Zn	^{a}Pb	^{a}TP	^{a}TN	^{a}TOC	^{b}TS
1	78	0.25	1.1	17	0.47	51	78	56	8.9
2	232	2.8	4.7	102	7.5	11	51	249	17
3	14	0.11	0.26	7.1	0.32	0.00	3.7	25	1.2
4	30	0.18	2.5	9.3	0.25	3.5	8.5	60	2.4
5	648	5.7	6.0	206	8.1	28	93	471	66
6	541	4.7	18	424	14	219	380	614	61

Notes:
a – unit is $mg/3m^2$; b - unit is $g/3m^2$ ($3m^2$ was the size of the sampling area)
Site identification: 1 – Vehicle marshalling area, 2 – Container storage facility, 3 – Container terminal, 4 – Quay line; 5 – Inter-modal operation area; 6 – Roadway.

3.2 Relationships of metals with other pollutants in build-up

Principal Component Analysis (PCA) was used to investigate the relationships of metal ions with other pollutants in build-up since this knowledge is essential for understanding the potential bioavailability of metal ions. PCA projects the objects and variables of a data matrix on the orthogonal principal components (PCs) in order to extract valuable information (Mostert et al., 2010). The first PC explains the highest variance in the data, while the rest is explained by the subsequent PCs in decreasing order. In general, the projection of objects and variables on the first two PCs are plotted as biplots, which facilitate the visual observation of patterns and relationships between objects and variables leading to increased understanding of a complex data set. An acute angle between the loading vectors in the biplot suggests that the corresponding variables have a strong positive correlation, while an obtuse angle indicates a negative correlation. The variables are independent if the related vectors are orthogonal.

The data matrix used in this study is presented in Table S1 in the Supplementary Information. It consisted of pollutant build-up loads for the different particle sizes. Since the outliers present in a data matrix can significantly affect the reliability and accuracy of the analysis outcomes, the outliers in the data matrix were identified using the box-whisker plots presented in Fig. 2. Consequently, samples 5a, 6a and 6b had outlier values for one or more pollutants. These outliers are attributed to sampling and/or testing errors or abnormal conditions prevailing during the sampling period and were excluded from further analysis.

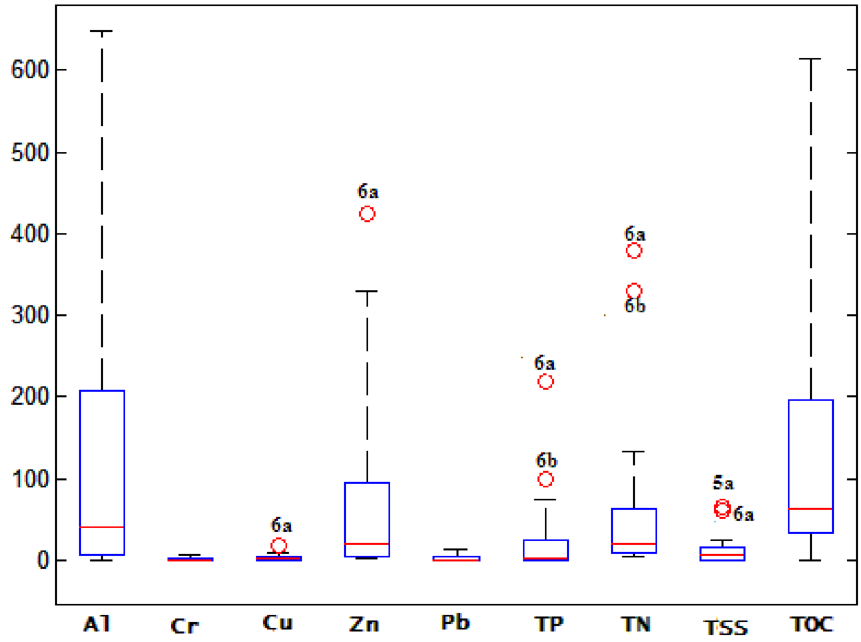

Fig. 2: Box-whisker plots for metals, nutrients, solids and organic carbon

The outlier-free data set was subjected to PCA to investigate the inter-relationships between the objects and variables. The data matrix consisted of the pollutant loads (variables) in the build-up for different particle sizes collected from the six port specific land uses (objects). The data matrix (25 objects and 9 variables) was first normalised (z-transformed) as a pre-treatment measure and then subjected to PCA. The resulting PCA biplot (Fig. 3) explains 78% of the total variance of the original data suggesting that the outcomes derived from PCA is reliable.

According to Fig. 3, samples from sites 5 and 6 generally have positive scores on PC1, while sites 3 and 4 have negative scores. This is in agreement with the pattern observed in the original data (Section 3.1), where the sites 5 and 6 had the highest pollutant loads and the sites 3 and 4 had the lowest loads. Therefore, PC1 discriminates the samples based on the level of pollution. In contrast, on PC2, most sampling sites are close to the origin suggesting that PC2 has less influence in discriminating the samples. There is no clear clustering of the samples based on the particle size fractions suggesting that the site specific characteristics play a significant role in the characteristics of pollutant build-up on the port impervious surfaces, compared to the influence of particle size.

The relationships between metals and other pollutants such as TSS, TOC and nutrients were investigated using the PCA biplot since these pollutants can adsorb and/or form complexes with metals (Weber et al., 1991). Consequently, they can influence metal characteristics such as mobility and bioavailability. In Fig. 3, the investigated metals have a strong positive correlation with TSS since the angles between their vectors are acute. This suggests that Cr, Al, Pb, Cu and Zn were predominantly attached to solids. Solids can desorb the metal ions depending on the characteristics of solids and media such as stormwater or sea water. Additionally, a treatment system to retain solids can be effective in reducing Cr, Al, Pb, Cu and Zn loads.

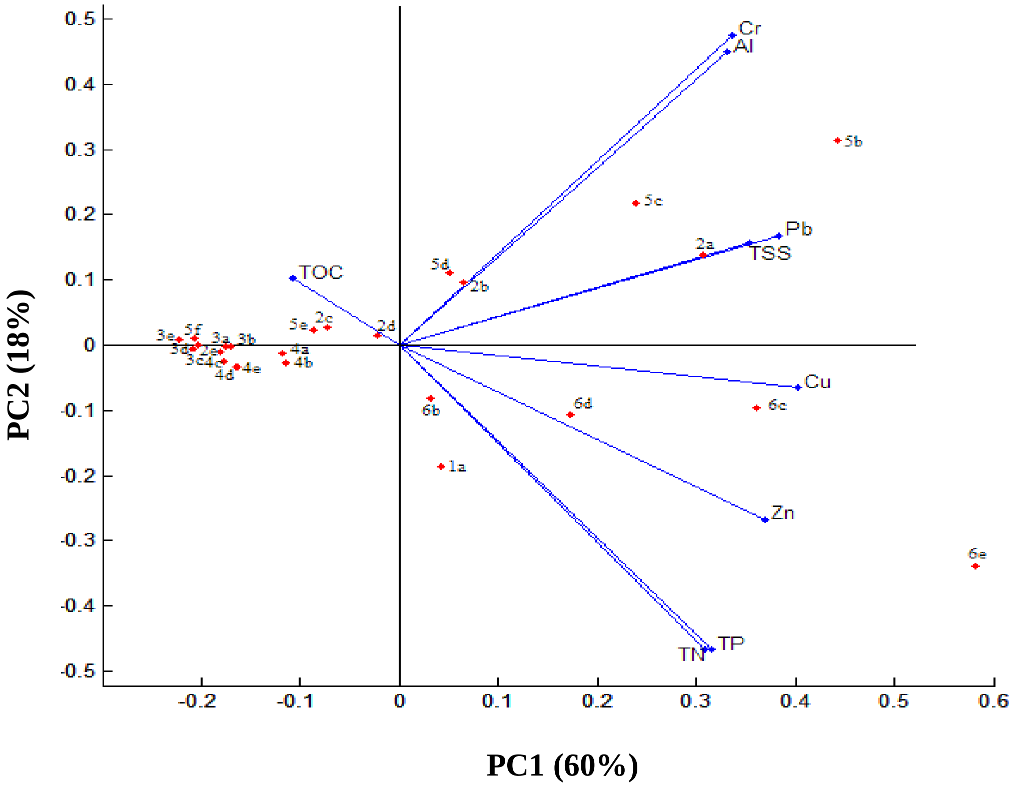

Fig. 3: PCA biplot

Similarly, Cu and Zn have a strong positive correlation with TN and TP, while Pb has a relatively weaker correlation. This can be attributed to the tendency of Cu and Zn to form stable complexes with ligands containing nitrogen and phosphorous (Ghasemi et al., 2013; Uchimiya et al., 2011). Since nutrient complexes are generally soluble or can be converted to soluble forms, there is a high potential that Cu and Zn can become bioavailable. Meanwhile, Cr and Al vectors are perpendicular to nutrient vectors suggesting Cr and Al loads are independent of nutrient loads. Therefore, it can be hypothesised that significant amount of Cr and Al were not present as nutrient complexes.

TOC vector has a negative correlation with Zn, Cu and Pb vectors and no correlation with Cr and Al vectors. This suggests that more favourable binding sites for metal ions were present in nutrients and TSS compared to TOC. Gunawardana et al. (2015) also suggested that solids such as clay forming minerals can out-compete TOC in forming complexes. Furthermore, the TOC vector has a strong negative correlation with nutrient vectors suggesting that nutrients are predominantly present in inorganic form (Wu et al., 2007).

3.3 Mathematical replication of metal loads

Mathematical replication of the build-up process was undertaken to enable the accurate prediction of metal loads present on impervious surfaces and to model stormwater quality. Such capabilities are essential for creating effective measures to mitigate the potential degradation of the marine ecosystem from pollutants transported by stormwater runoff. The models developed can be extended to other commercial ports since they incorporate land uses that are typical to any commercial port.

In this study, partial least squares regression (PLS) was employed to formulate the mathematical replication of the metal build-up process on impervious surfaces at the port. PLS is a multivariate regression technique that is used to simultaneously extract the underlying factors in both the independent and dependent variables. Consequently, it is a sophisticated extension of the conventional multiple linear regression (Ruiz et al., 2008). The calibration data matrix for PLS was selected using experimental design techniques.

3.3.1 Experimental design

Experimental design techniques facilitate strategic planning and execution of controlled experiments, where the independent variables or factors are varied systematically at different levels to investigate their influence on a response or predictor variable (Brereton, 2003). As such, experimental design techniques are useful in mathematically replicating a process such as the pollution build-up process. In this study, TSS, TN, TP and TOC loads were considered as the independent variables to replicate the build-up process as they are associated with the metal loads in build-up as discussed in Section 3.2. However, the strong correlation between TN, TP and TOC loads as evident from Fig. 3 can result in collinearity problem, which can lead to poor precision in the estimation of regression coefficients (Park et al., 2014). Therefore, TOC load was selected as the representative variable for TN and TP loads. Consequently, the independent variables were reduced to TSS and TOC loads. The metal loads were taken as the dependent variables.

In this study, Taguchi L_9 orthogonal array design (Table 2) was used for experimental design since this method requires a relatively reduced number of experiments compared to the conventional full factorial design (Zhou et al., 2000). In Taguchi L_9 orthogonal array design, three levels need to be assigned for each independent variable. Unlike laboratory based experiments, assigning precise levels to variables is a challenging task in field experiments because of the difficulty in controlling the variability in the independent variables (Ogunkunle et al., in press). For example, three values for pH of water in a laboratory experiment can be easily set as 4, 6 and 8, while stormwater pH in the field can vary depending on the catchment characteristics.

In the development of the prediction model for the volatile organic compounds on urban roads, in which the experimental design technique was used to select the calibration data matrix, Mahbub et al. (2011) randomly assigned the data points to ‘high’ and ‘low’ levels. In the present study, an alternative method is proposed for systematic allocation of levels in the experimental design for field based studies.

In the proposed method, levels are assigned as a range rather than as a precise value. As such, a range up to 33rd percentile was assigned as the first level of a variable, 33rd to 67th range was assigned as the second level and over 67th percentile was considered as the third level. A detailed explanation of the calculation involved with this method is provided in the Supplementary Information.

The ranges assigned for the first, second and third levels of TSS were 0.03 – 1.16, 1.17 – 10.2 and 10.3 – 25.6 g/3m^2, respectively. Similarly, 0.00 – 0.04, 0.05 – 0.08 and 0.09 – 0.37 g/3m^2 were used as the first, second and third levels of TOC, respectively. The resulting Taguchi design is given in Table 2.

Table 2: Results of Taguchi orthogonal array design

Taguchi Array		Independent variable load (g/3m^2)		Dependent variable load (g/3m^2)				
TS	**TOC**	**TSS**	**TOC**	**Al**	**Cr**	**Cu**	**Zn**	**Pb**
1	1	0.27	0.03	3.78	0.03	0.91	5.59	0.10
1	2	0.65	0.05	6.11	0.06	0.65	5.03	0.28
1	3	0.23	0.17	3.19	0.02	0.27	2.05	0.07
2	1	1.36	0.02	33.54	0.53	0.95	20.12	0.60
2	2	6.72	0.06	73.92	0.49	2.05	26.43	1.31
2	3	2.76	0.37	0.00	0.04	0.33	1.66	0.00
3	1	16.49	0.02	267.92	2.13	6.05	160.12	4.62
3	2	18.41	0.06	441.73	2.76	3.50	86.50	3.68
3	3	17.79	0.21	130.82	1.53	3.22	52.21	3.77

3.4.2 Model development

The data matrix developed using the Taguchi orthogonal array experimental design (Table 2) was subjected to PLS analysis to develop the mathematical replication of metal build-up. The mathematical models developed were validated using the Leave-One-Out Cross-Validation (LOOCV) method. The corresponding MATLAB codes developed for LOOCV is presented in the Supplementary Information. The Relative Prediction Error (RPE), Standard Error of Cross Validation (SECV) and Cross-Validated Coefficient of Determination (Q^2) were used to investigate the validity of the equations and the corresponding formulae are given in the Supplementary Information.

The outcomes of the analysis are presented in Table 3. The data variances explained by the mathematical models were over 75% indicating that the outcomes of PLS are reliable. The RPE values of 36% and 21% for Cr and Pb, respectively, are considered well within the error limits for complex natural systems as suggested by Egodawatta et al. (2013). Additionally, Cr and Pb had low SECV and high Q^2 values, which suggest that the developed models can replicate the build-up of these metals and can also be used for quantitative prediction of loads in the build-up on port impervious surfaces. Furthermore, it can be concluded that Cr and Pb loads in pollutant build-up are strongly dependent on the TSS and TOC loads.

In contrast, the equations for Al and Zn have relatively higher RPE values. Additionally, SECV values for Al and Zn are very high along with very low Q^2 indicating that the replication of Al and Zn based on TSS and TOC loads are less reliable. This suggests that traffic and anthropogenic factors such as average daily traffic volume can play an important role in Al and Zn build-up in addition to the characteristics of TSS and TOC. Though Cu has a high RPE value, it has relatively lower SECV and moderate Q^2 values. Therefore, the model for Cu can be used in preliminary investigations.

Table 3: PLS regression results

Metal	Regression parameters			Error values		Q^2	Variance Explained
	Constant	TS	TOC	SECV	RPE		
Al	24.3	16.2	-306.6	132	65	35	80
Cr	0.18	0.12	-1.8	0.5	36	78	92
Cu	1.0	0.21	-4.5	1.4	45	56	84
Zn	16.5	5.3	-131.4	50	69	22	75
Pb	0.26	0.22	-2.4	0.6	21	92	96

4. Conclusions

The primary conclusions from the investigation of pollutant build-up on the impervious surfaces of a commercial seaport are:

- The solids load in the build-up is the highest followed by organic carbon. Among metals, Al load is the highest followed by Zn load. Pb, Cu and Cr loads are moderate, while As, Cd, Ni and Hg are relatively very low.
- The inter-modal operations site and the access roadway have relatively higher pollutant loads followed by the container storage and vehicle marshalling sites. The quay line and short term storage areas have the lowest pollutant loads. The observed trend in pollutant loads are attributed to a range of site-specific characteristics such as the type of impervious surfaces and the nature of the anthropogenic activities.
- Cr, Al, Pb, Cu and Zn are predominantly attached to the solids and significant amount of Cu, Pb and Zn are found as nutrient complexes. Solids and nutrients out-compete organic carbon in forming complexes with metal ions in the build-up.
- Mathematical models developed to replicate the build-up process for Cr and Pb are more reliable because of the acceptable relative prediction errors, low standard error of cross-validation and high cross-validated coefficient of determination.
- In contrast, the models for Al and Zn have high relative prediction errors, high standard error of cross-validation and low cross-validated coefficient of determination suggesting that these are relatively less reliable. This is attributed to the fact that Al and Zn build-up is governed by traffic factors such as average traffic volume rather than the solids and organic carbon present in the build-up.
- The predictive model developed for Cu has a high relative prediction error. However, due to the fact that it has a relatively lower standard error of cross-validation and high cross-validated coefficient of determination, suggests that the model can be useful in preliminary investigations.

Acknowledgments

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Supplementary information

The Supplementary information provided include the data matrix used in the study, assignment of levels to each variable for statistical design of the field based experiments, ordering of the data matrix according to Taguchi design, results of Taguchi orthogonal array design and the Formulae used for error function and the Matlab codes used for PLS.

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SUPPLEMENTARY INFORMATION

Build-up of toxic metals on the impervious surfaces of a commercial seaport

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Table S1: Data matrix used in the study after removing mercury, arsenic, cadmium and nickel (The loads are in $mg/3m^2$ except for TSS, which is in $g/3m^2$)

[a]ID	Al	Cr	Cu	Zn	Pb	TP	TN	TSS	TOC
1a	78	0.25	1.1	17	0.47	51	78	8.9	56
2a	232	2.8	4.7	102	7.5	11	51	17	249
2b	142	1.6	3.6	36	3.6	5.2	22	10	235
2c	36	0.48	1.7	23	1.7	1.6	8.3	8.1	70
2d	44	0.54	2.2	38	2.2	1.7	20	10	64
2e	8.9	0.10	0.70	8.6	0.50	0.00	3.2	1.0	58
3a	14	0.11	0.26	7.1	0.32	0.00	3.7	1.2	25
3b	7.6	0.08	0.45	4.4	0.20	0.00	9.3	0.70	78
3c	3.1	0.02	0.39	2.0	0.06	0.00	6.2	0.11	171
3d	1.1	0.00	0.16	0.97	0.00	0.00	9.3	0.09	171
3e	0.93	0.00	0.09	0.86	0.00	0.00	6.2	0.03	265
4a	30	0.18	2.5	9.3	0.25	3.5	8.5	2.4	60
4b	17	0.11	2.7	4.8	0.18	0.00	23	3.0	76
4c	3.3	0.03	0.60	1.5	0.06	0.00	15	0.26	45
4d	3.2	0.03	0.88	1.5	0.20	0.00	20	0.45	30
4e	4.4	0.03	0.94	9.7	0.00	0.00	17	0.09	30
5a	648	5.7	6.0	206	8.1	28	93	66	471
5f	0.00	0.04	0.33	1.7	0.00	0.00	17	2.8	368
5b	607	4.8	5.4	76	4.8	20	26	25	0.00
5c	442	2.8	3.5	86	3.7	0.00	26	18	55
5d	239	1.4	2.0	66	3.1	0.00	11	7.7	37
5e	53	0.96	1.6	33	0.88	0.00	11	1.5	18
6a	541	4.7	18	424	14	219	380	61	614
6f	238	1.6	7.5	115	4.4	99	329	0.00	219
6b	18	0.22	1.3	18	0.18	5.5	91	26	146
6c	179	1.7	7.0	128	5.1	48	69	15	18
6d	102	0.90	3.7	108	3.3	35	57	11	18
6e	183	1.2	8.2	329	5.3	74	133	16	37

Note: [a] In the site ID, the number denotes the sites, while the small cap letter denotes the particle size; 1 – Vehicle marshalling area, 2 – Container storage facility, 3 – Container terminal, 4 – Quay line; 5 – Inter-modal operation area; 6 – Roadway; a – total particulates, f - particle size < 0.75 µm, b – particle size 0.75 – 75 µm, c - particle size 75 – 150 µm, d - particle size 150 – 300 µm, e - particle size > 300 µm.

Assigning levels to each variable in statistical design of field based experiments
The following steps were followed in assigning levels for variables in a field experimental design:
Step 01: Minimum, 33rd percentile, 67th percentile and maximum for TSS and TOC were calculated from the outlier free data matrix (Table S2).

Table S2: Descriptive statistics for TSS and TOC

Descriptive statistics	TSS ($g/3m^2$)	TOC ($g/3m^2$)
Minimum	0.03	0.00
33rd percentile	1.2	0.04
67th percentile	10	0.08
Maximum	26	0.37

Step 02: Three level Taguchi design was used in this study. The three levels were determined based on Table S2 and are presented in Table S3.

Table S3: TSS and TOC ranges assigned for levels

Level	Range	TSS range	TOC range
1	Minimum – 33rd percentile	0.03 – 1.2	0.00 – 0.04
2	slightly higher than 33rd percentile – 67th percentile	1.3 – 10	0.05 – 0.08
3	slightly higher than 67th percentile - Maximum	11 – 26	0.09 – 0.37

Step 03: Taguchi array corresponding to two factors with three levels were chosen and the data matrix was ordered according to the design as shown in Table S4.

Table S4: Ordering the data matrix according to Taguchi design (Similar colors indicate similar levels)

Taguchi Array		Experimental Data						
TSS	TOC	TS	TOC	Al	Cr	Cu	Zn	Pb
1	1	0.45	0.03	3.2	0.03	0.88	1.5	0.20
1	1	0.09	0.03	4.4	0.03	0.94	9.7	0.00
1	2	1.0	0.06	8.9	0.10	0.70	8.6	0.50
1	2	0.26	0.05	3.3	0.03	0.60	1.5	0.06
1	3	0.70	0.08	7.6	0.08	0.45	4.4	0.20
1	3	0.11	0.17	3.1	0.02	0.39	2.0	0.06
1	3	0.09	0.17	1.1	0.00	0.16	0.97	0.00
1	3	0.03	0.26	0.93	0.00	0.09	0.86	0.00
2	1	1.2	0.02	14	0.11	0.26	7.1	0.32
2	1	1.5	0.02	53	0.96	1.6	33	0.88
2	2	2.4	0.06	30	0.18	2.5	9.3	0.25
2	2	3.0	0.08	17	0.11	2.7	4.8	0.18
2	2	8.1	0.07	36	0.48	1.7	23	1.7
2	2	10	0.06	43	0.54	2.2	38	2.2
2	2	8.9	0.06	78	0.25	1.1	17	0.47
2	2	7.7	0.04	239	1.4	2.0	66	3.1
2	3	2.8	0.37	0.00	0.04	0.33	1.7	0.00
3	1	25	0.00	607	4.8	5.4	75	4.8
3	1	15	0.02	179	1.7	7.0	128	5.1
3	1	11	0.02	102	0.90	3.7	108	3.3
3	1	16	0.04	183	1.2	8.2	329	5.3
3	2	18	0.06	442	2.8	3.5	86	3.7
3	3	17	0.25	232	2.8	4.7	102	7.5
3	3	10	0.24	142	1.6	3.6	36	3.6
3	3	26	0.15	18	0.22	1.3	18	0.18

Step 04: The average of each experimental combination was calculated to develop the calibration matrix used for Partial Least Squares Regression as shown in Table S5 (Same as Table 2 in the manuscript).

Table S5: Results of Taguchi orthogonal array design

Taguchi Array		Independent variable load		Dependent variable load				
TS	TOC	TSS	TOC	Al	Cr	Cu	Zn	Pb
1	1	0.27	0.03	3.78	0.03	0.91	5.59	0.10
1	2	0.65	0.05	6.11	0.06	0.65	5.03	0.28
1	3	0.23	0.17	3.19	0.02	0.27	2.05	0.07
2	1	1.36	0.02	33.54	0.53	0.95	20.12	0.60
2	2	6.72	0.06	73.92	0.49	2.05	26.43	1.31
2	3	2.76	0.37	0.00	0.04	0.33	1.66	0.00
3	1	16.49	0.02	267.92	2.13	6.05	160.12	4.62
3	2	18.41	0.06	441.73	2.76	3.50	86.50	3.68
3	3	17.79	0.21	130.82	1.53	3.22	52.21	3.77

Formulae for error function and the Matlab codes used for PLS

Error functions

$$\text{RPE} = \sqrt{\frac{\sum\left(\text{Y}_{\text{predicted}} - \text{Y}_{\text{measured}}\right)^2}{\sum \text{Y}_{\text{measured}}^2}} \times 100\%$$

$$\text{SECV} = \sqrt{\frac{\sum\left(\text{Y}_{\text{predicted}} - \text{Y}_{\text{measured}}\right)^2}{\text{N}}}$$

$$\text{Q}^2 = \left[1 - \frac{\sum\left(\text{Y}_{\text{predicted}} - \text{Y}_{\text{measured}}\right)^2}{\sum(\overline{\text{Y}} - \text{Y}_{\text{measured}})^2}\right] \times 100\%$$

where N is the number of samples, $\text{Y}_{\text{predicted}}$ is the metal loads predicted using the developed models, $\text{Y}_{\text{measured}}$ is the metal loads measured from the experimental data and $\overline{\text{Y}}$ is the mean of $\text{Y}_{\text{measured.}}$

Matlab codes

```
function [b,RPE,SECV,Q2,VARI] = CVPLS (x,y)
%CVPLS returns Partial Least Squares regression coefficients (b) with %relative prediction error (RPE), standard error of cross-validation %(SECV) and cross-validated coefficient of determination (Q2). The %input y is the data matrix containing dependent variables and x is %the data matrix containing independent variables.

[XL,YL,XS,YS,b,VARI] = plsregress(x,y);
%Matlab built-in function that performs partial least squares %regression and returns the regression coefficients matrix, b. The %first element of matrix b is the constant followed by regression %coefficients.

PredictMatrix = [];

for n = 1:length(y)
%Data matrix for model development, consists of all data points except one
   TestIndex = n;
   TrainIndex = setdiff(1:length(y),TestIndex);
   X=x(TrainIndex,:);
   Y=y(TrainIndex,:);
   [XL1,YL1,XS1,YS1,b1,VARI1] = plsregress(X,Y);
%Prediction of Y using regression coefficient for the one left out %sample
   PredictedY = [1 x(TestIndex,:)]*b1;
%Data matrix consisting of measured and predicted values
   MeasuredVsPredict = [y(TestIndex,1), PredictedY];
   PredictMatrix = [PredictMatrix; MeasuredVsPredict];
end
```

```
[NSamples NVariables] = size(X);
MeasuredY  = PredictMatrix(:,1);
PredictedY = PredictMatrix(:,2);

%Relative error of prediction
RPE = 100*(sqrt (sumsqr (PredictedY-MeasuredY)/(sumsqr(MeasuredY))));

% Standard error of cross validation
SECV = sqrt(NSamples/(NSamples-1))*sqrt(sumsqr(MeasuredY-
PredictedY)/NSamples);

%Cross-validated R2
Q2 = 100*(1-(sumsqr (PredictedY-MeasuredY)/sumsqr(MeasuredY-
mean(MeasuredY))));
```