Water Research 202 (2021) 117386

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Water-sediment interactions and mobility of heavy metals in aquatic environments

Lorena S. Miranda [a], Buddhi Wijesiri [a], Godwin A. Ayoko [b,c], Prasanna Egodawatta [a,c], Ashantha Goonetilleke [a,c,*]

[a] Faculty of Engineering, Queensland University of Technology (QUT), GPO Box 2434, Brisbane, 4001, Queensland, Australia
[b] Faculty of Science, Queensland University of Technology (QUT), GPO Box 2434, Brisbane, 4001, Queensland, Australia
[c] Centre for the Environment, Queensland University of Technology (QUT), GPO Box 2434, Brisbane, 4001, Queensland, Australia

ARTICLE INFO

Keywords:
Heavy metals
Riverine sediment pollution
Estuarine sediment pollution
Sediment geochemistry
Metal bioavailability
Urban water pollution

ABSTRACT

The adsorption-desorption behaviour of heavy metals in aquatic environments is complex and the processes are regulated by the continuous interactions between water and sediments. This study provides a quantitative understanding of the effects of nutrients and key water and sediment properties on the adsorption-desorption behaviour of heavy metals in riverine and estuarine environments. The influence levels of the environmental factors were determined as conditional regression coefficients. The research outcomes indicate that the mineralogical composition of sediments, which influence other sediment properties, such as specific surface area and cation exchange capacity, play the most important role in the adsorption and desorption of heavy metals. It was found that particulate organic matter is the most influential nutrient in heavy metals adsorption in the riverine environment, while particulate phosphorus is more important under estuarine conditions. Dissolved nutrients do not exert a significant positive effect on the release of heavy metals in the riverine area, whilst dissolved phosphorus increases the transfer of specific metals from sediments to the overlying water under estuarine conditions. Furthermore, the positive interdependencies between marine-related ions and the release of most heavy metals in the riverine and estuarine environments indicate an increase in the mobility of heavy metals as a result of cation exchange reactions.

1. Introduction

The risks posed by heavy metals to aquatic environments are intrinsically related to their interactions with water and sediments. While adsorbed to sediments, heavy metals pose a relatively low toxicity risk (Machado et al., 2018; Peng et al., 2009). However, changes in the environmental conditions (e.g., pH, organic matter concentration) can enhance their exposure to living organisms and degrade water quality (Li et al., 2020; Thanh-Nho et al., 2019; Wijesiri et al., 2019a). The interactions of heavy metals with water and sediments are primarily in the form of adsorption and desorption reactions (Bradl, 2004; Duodu et al. 2016; Wijesiri et al., 2019b). These interactions are strongly influenced by the physico-chemical characteristics of water, including pH and salinity, and in the case of sediments, include mineralogy, specific surface area (SSA) and cation exchange capacity (CEC) (Ashayeri & Behnam, 2019; Keshavarzifard et al., 2019). Furthermore, nutrients commonly found in aquatic ecosystems, including phosphorus, nitrogen, and organic matter, have been reported to affect the geochemical behaviour of heavy metals (Liu et al., 2019a; Miranda et al., 2021). However, the selectivity of the various metals for the different binding sites in sediments depends on the ionic properties of the metal species, such as ionic radii, electronegativity, hydrolysis constant, and softness (Kinraide & Yermiyahu, 2007; McBride, 1989; Sposito, 2016).

The physico-chemical properties of water and sediments change widely along a waterway due to the nature of hydrodynamic process and the stream geomorphology (e.g., stream slope). These factors regulate the physical mixing of riverine and estuarine waters, as well as the transport and deposition of particles with different physico-chemical characteristics (Dey, 2014; Sun et al., 2018). Therefore, the geochemical behaviour of heavy metals, and thus, the associated toxicity risks, can vary depending on the type of aquatic ecosystem, including rivers and estuaries, as these environments present quite different

---

* Corresponding author.

E-mail addresses: l.miranda@qut.edu.au (L.S. Miranda), b.mahappukankanamalage@qut.edu.au (B. Wijesiri), g.ayoko@qut.edu.au (G.A. Ayoko), p.egodawatta@qut.edu.au (P. Egodawatta), a.goonetilleke@qut.edu.au (A. Goonetilleke).

https://doi.org/10.1016/j.watres.2021.117386
Received 6 February 2021; Received in revised form 21 June 2021; Accepted 22 June 2021

geochemistry.

Past studies have described the influence of water and sediment properties on the adsorption and desorption of heavy metals, separately (for example, Keshavarzifard et al., 2019; Liu et al., 2019a; Shen et al., 2020; Wang & Li, 2011). The mobility of heavy metals in aquatic ecosystems have also been investigated using the partitioning coefficient (ratio of metal concentrations between particulate and dissolved phases at equilibrium) (Thanh-Nho et al., 2018; Tomczak et al., 2019). However, this simplistic approach neglects the dynamic nature of flowing aquatic ecosystems (both vertical and horizontal processes), as the partitioning coefficient is generally estimated based on a stationary perspective, where the environmental characteristics are expected to remain constant over time.

A recent study carried out by Wijesiri et al. (2019b) in the Shenzhen River, China, proposed a novel approach for investigating the interactions of heavy metals with water and sediments using Bayesian Networks (BN). The variables included in their BN models were restricted to organic carbon in water and in sediments, pH in water and the mineralogical composition of the sediments. However, other properties that play a fundamental role in the adsorption and desorption behaviour of heavy metals, such as electrical conductivity, CEC and SSA (Keshavarzifard et al., 2019; Machado et al., 2018; Zhao et al., 2013), were not included in the study by Wijesiri et al. (2019b) due to the lack of available data. Furthermore, the binding competition between metals was not considered in their study. This is a critical aspect of adsorption-desorption behaviour, as the competition among heavy metals for negative sorption sites can dramatically influence their bioavailability in aquatic environments (Huang et al., 2018; Miranda et al., 2021). Given the complexity of aquatic ecosystems, the lack of available data and the neglect of the influence of the binding competition among heavy metals could be the reasons constraining the structure and reliable performance of the BN models developed by Wijesiri et al. (2019b) for some metals.

In addition to that, there are no reported studies that have applied the BN approach to quantitatively estimate water-sediment-heavy metals interactions in riverine and estuarine environments, separately. The substantial differences in the physico-chemical and biological characteristics of such environments result in changes in the geochemical behaviour of heavy metals. Thus, individual models comprising input data from different types of ecosystems (riverine and estuarine) are unable to provide robust estimations of metal mobility and bioavailability.

The current knowledge gaps constrain the evaluation of the potential bioavailability of heavy metals under different physico-chemical conditions inherent in riverine and estuarine environments. Moreover, it is also important to understand the role of sediments in relation to water pollution, as heavy metals may not be permanently attached to sediments, but can be released into the overlying water column in bioavailable form (Huang et al., 2020; Sun et al., 2020). Additionally, understanding the influence of particulate and dissolved nutrients, such as phosphorus and nitrogen, on the dynamic behaviour of heavy metals in different aquatic ecosystems is an urgent need given the increasing input of nutrients from anthropogenic activities to urban waterways.

This study addresses these limitations by investigating the continuous interactions of heavy metals with water and sediments influenced by a range of physico-chemical properties and nutrients in riverine and estuarine environments. The binding competition between heavy metals has been considered. The research outcomes are expected to be a step enhancement in knowledge to support the effective management of urban aquatic ecosystems by considering their physico-chemical characteristics and the dynamic behaviour of heavy metals.

2. Materials and methods

2.1. Study area and sampling design

Bulimba Creek is the second largest creek in Brisbane, Queensland State, Australia. The creek travels over 39 km down to the confluence with the Brisbane River Estuary, the longest urbanised waterway in South-East Queensland. The catchment area has a sub-tropical climate with wet summers and dry winters. The largest section of Bulimba Creek's main branch is primarily surrounded by residential developments, while commercial, industrial, rural, and natural land uses also exist.

Thirteen sampling sites were selected along the waterway spanning five land uses (residential, commercial, industrial, rural, and natural) and two different environmental conditions, classified as riverine (sites BC1- to BC-6) and estuarine (sites BC-7 to BC-13) (Fig. 1). The diversity of surrounding land uses contributed to the variability in the physico-chemical characteristics of the samples, which was a fundamental requirement for the modelling studies. The estuarine and riverine areas were classified based on the tidal influence exerted by the Brisbane River Estuary (Miranda et al., 2021). Four sampling episodes were carried out bi-monthly (from November/2018 to May/2019) during the wet season and were separated by rainfall events. This sampling design was adopted to ensure the occurrence of typical sediment movement, flushing of the streambed and associated variability in the physico-chemical characteristics of the samples collected from the same locations. Variability in sample characteristics was a fundamental requirement for the envisaged statistical analyses and, hence, to explain how changes in the influential factors account for changes in the concentrations of heavy metals. In total, 52 water samples and 52 sediments samples were collected. The geographic coordinates of the sampling sites, as well as the surrounding land uses are listed in Table S1 in the Supplementary Information. Detailed information on the spatial and temporal criteria adopted for the sampling design can be found elsewhere (Miranda et al., 2021).

2.2. Sample collection, storage, and preservation

At each location, sediment and water samples were collected from the middle of the creek by either wading into the stream (sites BC-1 to BC-9) or boating (sites BC-10 to BC-13), avoiding stream bed disturbance. The sediment samples were collected into polyethylene bags using a Van Veen stainless-steel grab sampler (AS/NZS, 1999). The water samples were collected into pre-cleaned high density polyethylene (HDPE) bottles by submerging them to about 10 cm below the water surface (AS/NZS, 1998). The water samples intended for the analysis of heavy metals were preserved with HNO_3 to reach pH <2, whilst no preservatives were added to the samples intended for the other chemical tests described in Section 2.3. The water and sediment samples were transported on ice to the laboratory and frozen at -20 °C until further analysis, except the water samples collected for the analysis of heavy metals, which were cooled to ≤ 6 °C (AS/NZS, 1998).

2.3. Physico-chemical characterisation of water and sediments

The electrical conductivity (EC) and pH of the water samples were measured *in situ*. In the laboratory, the water samples were filtered through a 0.45 μm pore-diameter membrane filter and tested for dissolved nutrients (dissolved organic carbon – DOC, dissolved nitrogen – DN, and dissolved phosphorus – DP), and six dissolved heavy metals typically associated with anthropogenic activities (Cd, Cu, Cr, Ni, Pb, and Zn) (Ma et al., 2021; Wijesiri et al., 2021).

The sediment samples were analysed for three crustal metals (Al, Fe and Mn), six heavy metals commonly originating from anthropogenic activities (Cd, Cu, Cr, Ni, Pb, and Zn), nutrients (total organic carbon – TOC, total nitrogen – TN, and total phosphorus – TP), specific surface area (SSA), cation exchange capacity (CEC), and mineralogical

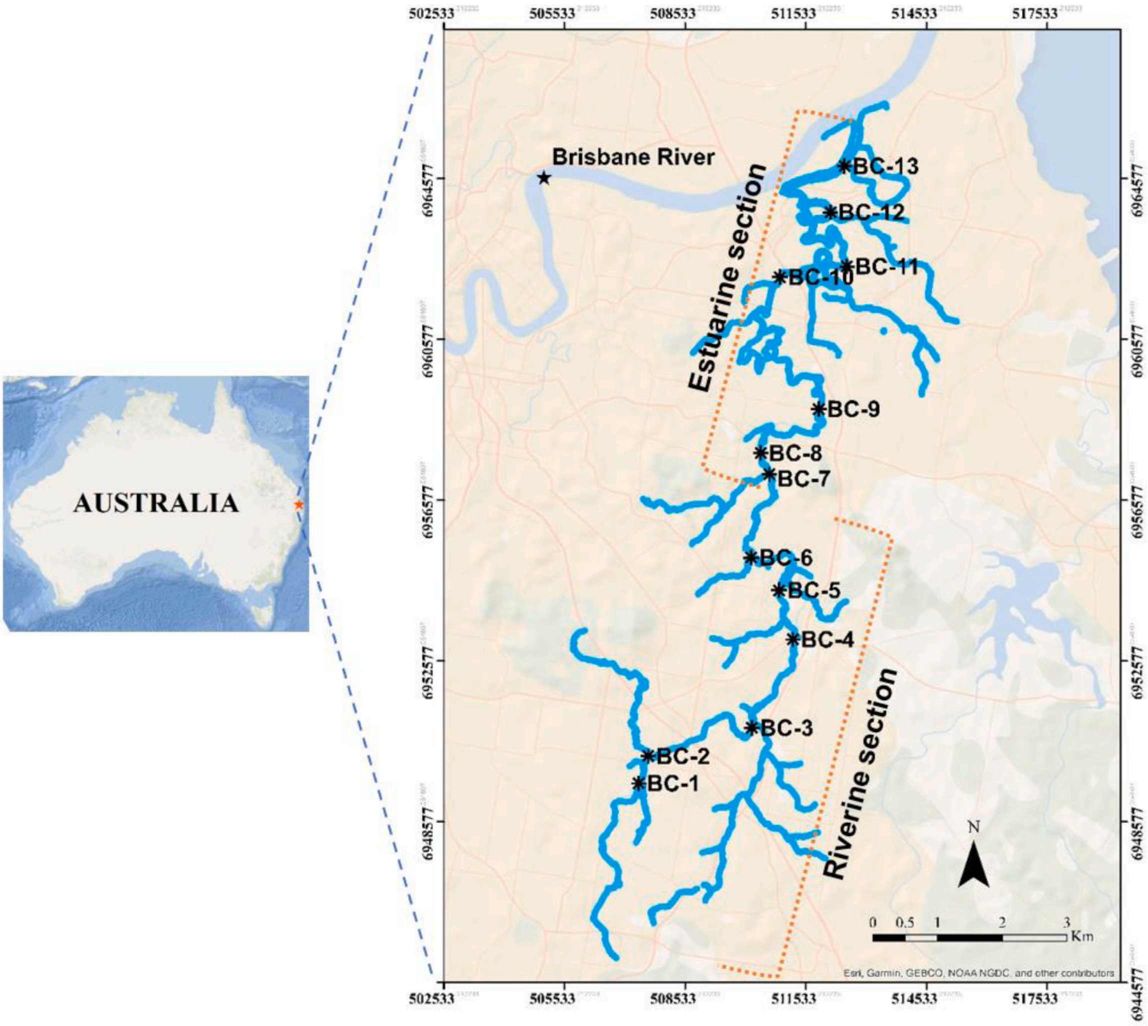

Fig. 1. Sampling sites along Bulimba Creek.

composition. The weak-acid extraction method (WE-method) described by Duodu et al. (2017) was employed for the analysis of heavy metals, as it focuses on the extraction of metals as the potentially bioavailable fraction, which is primarily involved in the interactions between water and sediments. Therefore, using the WE-method ensures that the relationships between heavy metals and the influential factors identified from the statistical analyses are primarily a result of water-sediment exchange instead of the geological setting of the study area. The analytical methods adopted for the analyses of the water and sediment samples are given in Table S2 in the Supplementary Information. Quality assurance (QA) and quality control (QC) protocols implemented to assess the precision and reproducibility of the analytical methods are also described in the Supplementary Information.

2.4. *Statistical data analysis*

Bayesian Networks (BN) model was employed to investigate the metal interactions between water and sediments. BN offers a unique opportunity for modelling complex environmental systems by encoding causal relationships to quantify the relative influence of individual variables describing the entire system (Wijesiri et al., 2019a; Witten et al., 2017). Unlike some widely used bivariate statistical techniques, such as correlation analysis, BN permits the inclusion of several predictors in a single model to simulate the response variable. Therefore, the use of BN is significantly more robust to investigate the complex interactions between heavy metals and the influential factors.

In this study, 24 × 16 (objects × variables) and 24 × 11 (objects × variables) data matrices were used for the riverine BN models, whilst 28 × 19 (objects × variables) and 28 × 11 (objects × variables) data matrices were used for the estuarine BN models. The objects were the samples collected during the four sampling episodes in the riverine (6 × 4) and estuarine (7 × 4) areas. In the riverine and estuarine models, the variables of the 24 × 11 or 28 × 11 data matrices were the same and include pH, EC, DP, DOC, six heavy metals in water, and the metal of interest in sediments. The variables of the 28 × 19 data matrices (estuarine models) were TP, TOC, CEC, SSA, five minerals, six heavy metals in sediments, three geogenic metals in sediments, and the metal of interest in water. The variables of the 24 × 16 data matrices (riverine models) were similar to those included in the estuarine models, with exception of the minerals, kaolinite, illite, and muscovite, as these were not detected in the riverine area. The statistical analyses were undertaken at 0.05, 0.01 and 0.001 significance levels. Detailed information on the BN method and its application in the present study is given in the Supplementary Information. RStudio statistical software suite was used to perform the analyses.

3. Results and discussion

3.1. *Structure and performance of the Bayesian Networks model*

The physico-chemical data obtained from the laboratory tests were used as input data in the BN models. The laboratory results are discussed in detail in the Supplementary Information. Before applying the BN algorithm, a model diagram was created for depicting the chain of causal relationships among variables (Fig. 2). In a BN model, the variables (nodes) are linked in a direct acyclic graph (DAG) (Scutari, 2010). For this reason, the exchange of heavy metals between water and sediments was investigated by developing two BN models to avoid a loop in the model structure. Model 1 described the adsorption of heavy metals (transfer from water to sediments), whilst model 2 described the desorption of heavy metals (transfer from sediments to water). The Markov Property of BN was used to estimate the conditional dependencies among the set of continuous variables (Witten et al., 2017).

As indicated by Wijesiri et al. (2019a), the BN structure relies on expert elicited knowledge. Therefore, the variables included in the model were selected based on the research literature due to their reported influence on the behaviour of heavy metals in aquatic environments (Keshavarzifard et al., 2019; Liu et al., 2019b; Thanh-Nho et al., 2018; Wijesiri et al., 2019b). To date, little is known about the relationships between nitrogen compounds and heavy metals (Kang et al., 2019; Miranda et al., 2021). Furthermore, Miranda et al. (2021) found strong positive correlation between TN and TOC ($r=0.98$, $p<0.001$) in the Bulimba Creek sediments. Therefore, in order to avoid large standard errors due to multicollinearity between independent variables (Curtis & Ghosh, 2011) and to comply with the prior knowledge criteria of BN, TN was considered a redundant predictor and was removed from the analysis. TOC was retained in the model as extensive knowledge exists on its influence in relation to the adsorption and desorption behaviour of heavy metals in various environmental compartments (Gao & Chen, 2012; Liang et al., 2017; Thanh-Nho et al., 2019). Furthermore, metals in water and in sediments were included in the models as parent variables to account for their binding competition.

The proposed models were fitted with observed data obtained from field and laboratory tests. The data for model 1 (adsorption) included TP, TOC, SSA, CEC, mineralogy, metals in water and metals in sediments (Al, Fe, Mn, Cd, Cr, Cu, Ni, Pb and Zn). The data for model 2 (desorption) included pH, EC, DOC, DP, metals in water and metals in sediments (Al, Fe, Mn, Cd, Cr, Cu, Ni, Pb and Zn). The adsorption and desorption BN models were run separately for the riverine and estuarine environments, as these environments possess very different physico-chemical characteristics that can significantly influence the geochemical behaviour of heavy metals (Miranda et al., 2021).

The BN outcomes for model 1 (adsorption) and model 2 (desorption) are expressed as conditional regression coefficients given in Tables 1 and 2, respectively. The prediction performances of the BN models were evaluated using the root mean squared error (RMSE). The observed vs predicted plots and residual plots are depicted in Fig. S6 to S9 in the Supplementary Information. Leave-one-out cross-validation method was performed for estimating the goodness of fit of the models. This method provides an accurate estimation of model performance for small datasets (Vehtari et al., 2017).

The RMSE values (Tables 1 and 2) show that the BN models performed satisfactorily for most metals in both models (adsorption and desorption). However, the lower RMSE and higher R^2 indicate a better

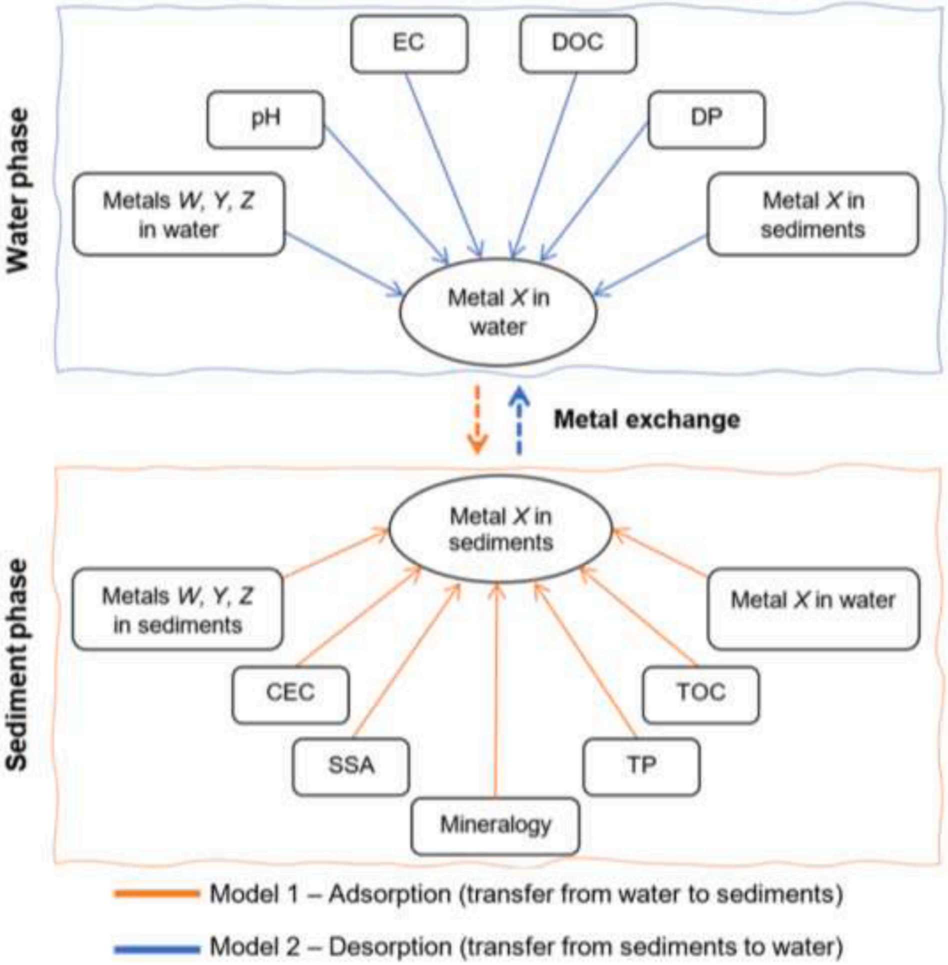

Fig. 2. Graphical structure of the BN models of metal interactions between water and sediments.
Note: Metal *X* corresponds to the target metal being modelled as the dependent variable, while metals *W, Y* and *Z* correspond to the other metals competing for charge sites (independent variables).

Table 1
Bayesian Networks outcomes for model 1 (adsorption – metal transfer from water to sediments)

Influential factors	Conditional regression coefficients (conditional Gaussian distribution, log transformed data)											
	Riverine environment (BC-1 - BC-6)						Estuarine environment (BC-7 - BC-13)					
	Cd_s	Cr_s	Cu_s	Ni_s	Pb_s	Zn_s	Cd_s	Cr_s	Cu_s	Ni_s	Pb_s	Zn_s
(Intercept)	16.16	17.91	4.03	20.89	-12.37	20.58	0.32	1.62	3.10	0.29	1.42	-2.01
TP_s	0.76	-0.04	-0.06	-0.15	0.11	0.22	0.47	0.40	-0.36	0.18	0.95	-0.19
TOC_s	-6.03	0.54*	0.72***	1.19	-0.42	0.03	0.89	0.25	-0.001	-0.04	-0.71	0.87
SSA	-4.59	1.06**	0.73**	1.22	-0.61	0.13	-0.28	0.18	-0.39	0.02	0.27	0.13*
CEC	0.47	-0.08	-0.10	-0.44	0.19	-0.18	0.52	0.08	0.15	0.05	-0.46	0.22
Quartz	**-1.53**	**-11.10***	**-2.78**	**-13.24**	**6.94**	**-10.26**	**0.73**	**-0.81**	**-0.46**	**-0.40**	**-0.41**	**0.79**
Illite							**-0.87**	**0.32**	**0.43**	**0.02**	**0.31**	**-0.70***
Kaolinite							**0.65**	**-0.65**	**-0.19**	**-0.05**	**-0.17**	**0.24**
Muscovite							**-0.28**	**0.007**	**0.11**	**-0.09**	**0.007**	**-0.05**
Amorphous	**-0.53**	**-0.18**	**0.04**	**0.05**	**0.01**	**-0.07**	**-0.24**	**-0.08**	**-0.22**	**-0.41**	**-0.27**	**0.4**
Al_s	**-5.47**	**1.09****	**0.59***	**1.74**	**-0.67**	**0.43**	**-2.30**	**-0.24**	**-0.41**	**-0.51**	**0.09**	**0.99**
Fe_s	**0.34**	**0.22**	**-0.09**	**0.08**	**0.19**	**-0.08**	**1.57**	**0.40**	**0.06**	**0.74**	**0.16**	**-0.95**
Mn_s	**1.31**	**-0.06**	**-0.14**	**-0.25**	**0.36**	**-0.31**	**-0.32**	**0.38**	**-0.39**	**0.24**	**0.21**	**0.01**
Cd_s		0.02	0.06	0.09	-0.02	-0.02		-0.01	0.27	-0.04	-0.01	-0.11
Cr_s	1.92		-0.26	-0.96	0.31	-0.11	-0.07		0.19	-0.27	-0.17	0.10
Cu_s	7.73	-0.61		-1.27	0.43	0.41	0.98	0.21		0.30	0.63	0.28**
Ni_s	1.29	-0.28*	-0.11		0.27	-0.25	-0.62	-1.10	0.39		-0.59	0.49
Pb_s	-0.78	0.02	0.13	0.48		0.66	-0.14	0.012	0.37	-0.15		0.47
Zn_s	-0.58	-0.07	0.06	-0.22	0.55		-0.14	0.10	0.37	0.14	0.25	
Cd_w	0.09						-0.20					
Cr_w		0.18*						0.12				
Cu_w			-0.004						-0.44			
Ni_w				0.60						-0.02		
Pb_w					-0.01						0.17	
Zn_w						0.05						0.19**
RMSE	0.29	0.03	0.03	0.06	0.05	0.06	0.13	0.08	0.06	0.04	0.08	0.04
R^2	0.75	0.99***	0.99***	0.91*	0.98***	0.98***	0.94**	0.96**	0.96***	0.98***	0.90*	0.99***
p-value	0.353	2.77e-05	6.58e-06	0.02	0.0002	0.0001	0.004	0.001	0.001	0.0001	0.027	2.17e-05

Notes: Conditional density: target Ms | TP: TOC: CEC: SSA: Qtz: Amp: Al: Fe: Mn: Ms: target Mw: competing metals in sediments
TP, total phosphorus; TOC, total organic carbon; CEC, cation exchange capacity; SSA, specific surface area; _w, metals in water; _s, metals in sediments
*, **, *** Significant at $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively (based on the cross-validation results)
Bold text indicates the mineral components, which accounted for the highest influence (negative or positive) in the transfer of heavy metals between water to sediments.

Table 2
Bayesian Networks outcomes for model 2 (desorption – metal transfer from sediments to water)

Influential factors	Conditional regression coefficients (conditional Gaussian distribution, log transformed data)											
	Riverine environment (BC-1–BC-6)						Estuarine environment (BC-7–BC-13)					
	Cd_w	Cr_w	Cu_w	Ni_w	Pb_w	Zn_w	Cd_w	Cr_w	Cu_w	Ni_w	Pb_w	Zn_w
(Intercept)	-4.75	1.98	-4.31	1.46	-20.41	-9.09	-9.64	-3.53	-2.31	2.29	0.88	2.42
pH	3.64	-0.24	3.60	-2.25	16.22	5.91	7.90	3.18	4.48*	-3.29***	1.31	0.31
EC	-1.73	-1.45***	1.81*	0.80*	0.67	6.19*	0.30	0.21	-0.34***	0.09	-0.69	0.17
DP	-0.67*	0.04	-0.01	0.09	-0.19	0.71	-0.25	0.07	0.25	-0.11	0.49	0.73
DOC	0.18	0.10	-0.20	0.06	-0.99	-0.89	-1.24	-0.32	-0.17	0.36**	-0.46	-1.69
Cd_w		-0.38***	0.60*	0.25**	-0.65	1.81*		0.11	0.00	0.05	-0.37	0.06
Cr_w	-1.70**		1.50**	0.77***	-1.47	4.94***	0.25		0.23	0.05	1.294*	-0.20
Cu_w	0.61*	0.38***		-0.18	0.71	-1.26	0.01	0.40		0.26**	-1.22	0.54
Ni_w	1.34	0.97**	-1.21		3.09	-4.22	2.25	0.78	1.206*		0.62	1.44
Pb_w	-0.18*	-0.04	0.15	0.06		0.01	-0.28	0.25*	-0.11	0.00		0.20
Zn_w	0.23	0.13***	-0.15	-0.09*	0.01		-0.02	0.00	0.06	0.02	0.12	
Cd_s	-0.08						-0.10					
Cr_s		0.31*						-0.07				
Cu_s			-0.42						0.153*			
Ni_s				-0.25*						-0.04		
Pb_s					0.04						0.65	
Zn_s						-0.53						-0.22
RMSE	0.14	0.06	0.13	0.04	0.32	0.37	0.24	0.12	0.08	0.04	0.29	0.35
R^2	0.80**	0.98***	0.85**	0.93***	0.60	0.64**	0.88***	0.88***	0.76**	0.89***	0.62*	0.64*
p-value	0.006	3.47e-08	0.001	1.54e-05	0.176	0.005	1.17e-05	1.53e-05	0.002	8.1e-06	0.044	0.03

Notes:
Conditional density: target Mw | pH: EC: DP:DOC: Mw: target Ms: competing metals in water
EC, electrical conductivity; DP, dissolved phosphorus; DOC, dissolved organic carbon; _s, metals in sediments; _w, metals in water
*, **, *** Significant at $p < 0.05$, $p < 0.01$, $p < 0.001$, respectively (based on the cross-validation results)

performance of model 1 (adsorption, Table 1) compared to model 2 (desorption, Table 2) in both, riverine and estuarine environments. This is evidenced by the plots of observed vs predicted values (Fig. S6 to S9/ Supplementary Information). These outcomes imply that the factors influencing the adsorption of metals to sediments are primarily related to the sediment properties included in model 1. However, predictor variables other than those included in model 2 can potentially influence the release of heavy metals from sediments and should be incorporated into the model structure as new knowledge becomes available.

Interestingly, the *p*-values calculated for the BN model 1 performed for Cd (riverine environment, Table 1) and for the BN model 2 performed for Pb (riverine environment, Table 2) were greater than 0.05, implying that the model outcomes are not statistically significant. This signifies that the adsorption of Cd and the desorption of Pb under riverine conditions are more complex compared to the other metals and cannot be properly explained by the model structure adopted in this study. Therefore, further investigation of the influential factors is necessary for describing the adsorption of Cd and the desorption of Pb under riverine conditions.

3.2. Influence of sediment and water properties on the exchange of heavy metals

3.2.1. Mineralogy

The conditional regression coefficients estimated for the mineral phases in the BN model 1 (adsorption, Table 1) show that the mineral components accounted for the highest influence in the transfer of heavy metals from water to sediments. Among all minerals, quartz exerted the strongest effect on the exchange behaviour of heavy metals in the riverine environment (highest conditional regression coefficients), whilst clays and oxides of Al, Fe and Mn were more important in the estuarine area. However, the relationships with mineral constituents were either negative or positive, depending on the metal ion.

Generally, quartz demonstrates a negative influence on the adsorption of heavy metals in both riverine and estuarine areas (Table 1) due to its physico-chemical inertia (Jayarathne et al., 2018a; Sparks, 2003). This implies that increasing concentrations of quartz are likely to hinder the immobilisation of heavy metals to the solid particles, increasing their potential bioavailability in the dissolved phase. This is evidenced by the substantially greater negative coefficients given for quartz in the BN model 1 for the riverine environment (Table 1), where higher percentages of this mineral were found, compared to the estuarine area (Fig. S4(a)/Supplementary Information).

Interestingly, the positive conditional regression coefficients modelled for the adsorption of Cd and Zn in the estuarine environment (Table 1) indicate that quartz can positively influence the adsorption of these metals. As pointed out by past researchers, Cd and Zn are relatively more soluble than other metals, signifying that they do not tend to form strong bonds with solid particles compared to other metals (Gao & Chen, 2012; Huo et al., 2013; Jayarathne et al., 2018b). Therefore, Cd and Zn are more vulnerable to the competition for sorption sites and tend to attach to less competitive binding positions present on the surfaces of quartz. As reported by Taqvi et al. (2007), the terminal oxygen atoms composing the structure of quartz are neutralised through hydration. Therefore, the greater hydration sphere shown by Cd and Zn compared to the other metals could be responsible for their preferential interactions with quartz. Furthermore, it is clear from Table 1 that under estuarine conditions, Cd and Zn have the highest affinity for Fe and Al oxides, respectively. This suggests that these metals can be retained on Fe and Al oxides coated on quartz or present as part of the tetrahedral mineral structure (Aşçı et al., 2010). Another reason for the positive influence shown by quartz on the adsorption of Cd and Zn in the estuarine area could be the input of marine carbonates associated with quartz. As demonstrated by Xie et al. (2019) and Zhang et al. (2017), Cd and Zn have a particular affinity to precipitate with carbonate minerals.

As shown in Table 1 (estuarine environment), heavy metals present a selectivity for specific clay minerals, signifying that the charge sites offered by certain clays are more propitious for the complexation of some metals over others. For example, Cr, Cu and Pb prefer to attach to the vacant charge sites present on the surfaces of illite (positive conditional regression coefficients), while only Cu has affinity for muscovite. On the other hand, Cd and Zn are more likely to attach to clay minerals of kaolinite (Table 1).

The differences in the affinity of heavy metals with illite and kaolinite would be attributed to the type of surface charge present in these clays, as permanent charge sites predominate in illite, while kaolinite is dominated by variable charges (Kamprath & Smyth, 2005). Therefore, more competition for adsorption sites is expected on the surfaces of illite due to the comparatively higher CEC, resulting in the association of Cd and Zn to the less competitive binding positions in kaolinite. The higher adsorption of Cd to kaolinite ($\beta= 0.65$) compared to Zn ($\beta = 0.24$) results from the larger ionic radius exhibited by Cd (Rieuwerts et al., 1998).

3.2.2. SSA and CEC

The high SSA of sediments is primarily contributed by clays, organic matter, and mineral oxides, which generally possess high CEC (Bergaya et al., 2018; Jayarathne et al., 2017). As shown in the BN model 1 (adsorption, Table 1), the conditional regression coefficients calculated for SSA are generally positive in both riverine and estuarine models. This signifies that the immobilisation of heavy metals in sediments tend to increase as SSA increases.

Under riverine conditions, SSA exerted the strongest influence on the adsorption of Ni ($\beta = 1.22$), followed by Cr ($\beta = 1.06$), Cu ($\beta = 0.72$), and Zn ($\beta = 0.13$) (Table 1). The positive order of coefficients exhibited by SSA is generally similar to the order of the negative coefficients calculated for quartz in relation to Ni, Cr, Cu and Zn, confirming the inverse relationship between quartz and SSA and the low ability of quartz to retain cations. Furthermore, negative conditional regression coefficients were estimated for CEC in the models developed for Ni, Cr, Cu and Zn in the riverine environment (Table 1). Considering that the influence of CEC is related to a two-way (reversible) interaction between water and sediments, it can be argued that the signals (positive or negative) given for each CEC coefficient indicate the likely transfer direction of the corresponding metal. For example, the negative CEC coefficients modelled for Cr ($\beta = -0.075$), Cu ($\beta = -0.098$), Ni ($\beta = -0.444$), and Zn ($\beta = -0.181$), indicate that the occurrence of cation exchange reactions in the riverine area are likely to result in the release (decreasing adsorption) of these metals from sediments to water.

On the other hand, the positive value estimated for CEC ($\beta = 0.189$) in relation to the adsorption of Pb in the riverine area (Table 1) signifies that cation exchange reactions result in the adsorption of Pb to sediments. However, the negative interdependence with SSA ($\beta = -0.614$) demonstrates that the adsorption of Pb through weak bonds tend to occur on the surfaces of large particles, such as quartz (positive conditional regression coefficient). This could be a result of the association with Mn and Fe oxides present as coatings on the surfaces of quartz in the riverine area, as these geogenic metals are positively correlated with Pb (Table 1).

Under estuarine conditions, increasing CEC generally favours the transfer of heavy metals from water to sediments (adsorption) (Table 1). This is attributed to the considerably greater concentrations of clays, mineral oxides, and nutrients resulting in higher SSA and CEC in the estuarine sites compared to the riverine area. Although the adsorption of Cd and Cu to estuarine sediments is positively influenced by CEC, this process is unlikely to occur on the surfaces of fine particles (high SSA), as indicated by the negative coefficients given for SSA in Table 1 ($\beta = -0.28$ for Cd and -0.39 for Cu). These findings reinforce the influence of mineral phases on the other properties of sediments and, consequently, in the adsorption and desorption behaviour of heavy metals in aquatic environments.

3.2.3. EC

The electrical conductivity of the aqueous media influences the concentrations of dissolved ions, including Ca^{2+}, Mg^{2+} and Na^{+}, which can be readily exchanged by heavy metals in the solid phase (Abdel-Satar et al., 2017; Prathumratana et al., 2008). It is clear from Table 2 (desorption) that most dissolved metals show positive interdependencies with EC, implying that an increase in the concentrations of marine-related ions is likely to enhance the transfer of heavy metals from sediments to the water phase. This corroborates with the findings of Machado et al. (2018) and Zhao et al. (2013), who reported higher remobilisation of heavy metals from sediments to water triggered by rising concentrations of marine-related ions.

Despite the higher concentrations of marine-related ions in the estuarine section of Bulimba Creek, the BN outcomes (Table 2) show that the magnitude (either positive or negative) of the conditional regression coefficients estimated for EC is greater in the riverine model than in the estuarine model. This indicates that heavy metals attached to the riverine sediments are more sensitive to changes in the ionic composition of the water phase compared to the metals attached to the estuarine sediments. The reason for such behaviour is primarily attributed to the low adsorption capacity of the riverine sediments due to the high loads of quartz and the limited amounts of nutrients and clays minerals. In this case, the weak bonds can be readily broken due to the action of exchangeable cations (e.g., Na^+, Mg^{2+} and Ca^{2+}), prompting the dissolution and, thus, potential bioavailability of heavy metals in the riverine environment.

The negative coefficients given for EC in relation to Cd (β = -1.73) and Cr (β = -1.45) in the riverine model (Table 2) imply that rising ionic concentrations tend to reduce the solubility of these metals. Therefore, the release of Cd and Cr is not primarily prompted by the exchange with marine-related metals, and other influential factors (e.g. DOC) would exert a more significant influence on their bioavailability under riverine conditions. Du Laing et al. (2008), for example, have reported that Cd has a strong affinity for sulphides, which can immobilise this metal in sediments under low salinity levels.

The negative relationships shown by EC with Cu (-0.34) and Pb (-0.69) under estuarine conditions (Table 2) could be attributed to the stronger affinity of Cu and Pb with some mineral components present in the estuarine sediments, which are responsible for limiting the release of these metals into the water column. This is confirmed by the conditional regression coefficients estimated for illite in the BN model 1 performed for these metals (Table 1), which are positive only for Cu and Pb. The studies carried out by Uddin (2017), and Gu and Evans (2007) indicate that illite has a comparatively higher adsorption capacity for Pb and Cu than for the other metals investigated in the present study. Once again, these findings confirm the prominent influence of sediments, particularly the mineralogical composition, in relation to the pollution of water by heavy metals.

3.2.4. pH

The positive effect of acidic pH in relation to the transfer of heavy metals from sediments to the overlying water has been widely documented in the research literature (Atkinson et al., 2007; Keshavarzifard et al., 2019; Thanh-Nho et al., 2019). This is due to the greater concentrations of hydrogen ions (low pH), which have a strong exchange capacity to displace heavy metals from negatively charged surfaces (Fairbrother et al., 2007). However, the outcomes of the BN model 2 in relation to predicting the desorption of heavy metals (Table 2) show positive relationships between pH and most dissolved metals under both, riverine and estuarine conditions. This suggests that increasing pH values (lower H^+ concentrations) would increase the transfer of heavy metals from sediments to water.

Bulimba Creek is being progressively influenced by anthropogenic activities from upstream to downstream in the riverine and estuarine sections of the creek (Miranda et al., 2021), whilst the pH levels increase in the same direction. This would result in relatively higher inputs of dissolved metals towards the downstream sections of both environments due to wash-off from surrounding land uses following rainfall events. Such high inputs of dissolved metals are particularly evident in the estuarine area (Fig. S5(b)/Supplementary Information), as it contains the majority of the industrial land use in the catchment. Furthermore, the increasing salinity from upstream to downstream of the riverine area and, more obviously, the estuarine area (Fig. S4(b)/Supplementary Information) can promote the dissolution of heavy metals, as discussed in Section 3.2.3. Therefore, it can be concluded that the effects of the salinity gradient and land use developments overshadow the influence of exchangeable H^+ in relation to the behaviour of heavy metals described by the BN models for the Bulimba Creek (Table 2). This is attributed to the low variability in the pH values measured in the study area (6.14 - 8.04). Past researchers (for example, Tomczak et al., 2019) have reported limitations in explaining the influence of pH on the behaviour of heavy metals in aquatic environments due to the low pH variability.

Interestingly, the negative conditional regression coefficients shown by Ni in the BN model 2 related to both, riverine and estuarine areas (Table 2), suggest that Ni is more sensitive to small variations in the concentrations of H^+ and can pose relatively high toxicity risks even at pH close to neutral. Further investigation comprising of a larger pH variability is required to obtain conclusive evidence in relation to its influence on the behaviour of heavy metals under riverine and estuarine conditions.

3.3. *Influence of nutrients on the exchange of heavy metals*

As shown in Table 1, the positive conditional regression coefficients estimated for TOC indicate that it is the primary nutrient inducing the adsorption of heavy metals, except Pb (β = -0.419), to the riverine sediments. On the other hand, the uptake of heavy metals by the estuarine sediments is mostly influenced by increasing TP loads, except for Cu (β = -0.359) and Zn (β = -0.193). The varying affinities of heavy metals to particulate nutrients depending on the type of ecosystem (riverine or estuarine) are attributed to the stability of the metal complexes formed with either, organic matter or phosphorus, and the availability of such nutrients in the environment.

While metal phosphates are insoluble even at neutral to slightly acidic pH levels (Olaniran et al., 2013), organic metal complexes are more sensitive to reductions in the pH due to the chemical structure of organic molecules, which are essentially formed by carbon and hydrogen ions (Klein, 2017). Therefore, the higher availability of phosphorus in the estuarine section enhances the opportunities for the formation of relatively more stable complexes (e.g., metal phosphates), though interactions with organic ligands also occur. The limited formation of metal phosphates in the riverine sites could be attributed to the low concentrations of phosphorus in the area, resulting in higher competition among heavy metals for binding positions in the phosphorus components.

Unlike the other metals, the transfer of Cd and Zn from water to sediments, and, thus, their immobilisation in the estuarine section of the creek, primarily increases due to the growing TOC concentrations (Table 1). As reported by Miranda et al. (2021), the preferred binding position for Zn is present in organic matter. However, when limited amounts of organic ligands exist, Zn tends to associate with other compounds, such as phosphorus. Therefore, the increased TOC concentrations in the estuarine section of the creek favour the complexation of Zn to its preferred charge site. This is enhanced by the greater amount of vacant charge sites in clays and mineral oxides in the estuarine area, reducing the competition with other metals for organic ligands. The lower binding competition with other metals would also increase the opportunities for Cd to complex with both, phosphorus and organic matter (β = 0.47 and 0.89, respectively).

Furthermore, Table 1 shows that the adsorption of Pb to sediments is positively influenced by TP regardless of the environment (riverine or estuarine) due to its particular ability to form strong interactions with phosphorus compounds, such as phosphates (Seshadri et al., 2017; Shen et al., 2020). The conditional regression coefficients estimated for the riverine and estuarine areas reveal a significantly stronger influence of TP on the adsorption of Pb under estuarine conditions (β = 0.95) compared to the riverine area (β = 0.11), as the latter has lower TP availability resulting in higher binding competition among metals.

According to Table 2, dissolved nutrients do not exert a significant positive effect on the release of most heavy metals in the riverine area. As discussed in Section 3.2.1, the riverine sediments of Bulimba Creek present very low adsorption capacity due to the high loads of quartz. This would be the primary reason for the release of heavy metals into the aqueous phase instead of complexation with chemical compounds, such as DOC and DP. On the other hand, Table 2 shows that increasing DP concentrations tend to increase the transfer of certain metals from sediments to the overlying water in the estuarine environment. For example, positive relationships with DP are shown by Zn, Pb, and Cu in the estuarine area (β = 0.73, 0.49, and 0.25, respectively). Despite the known stability of metal phosphates (Sposito, 2016), acidic pH conditions (as per the WE-method used for determining heavy metals in this study) would cause the dissociation and consequent release of phosphorus and heavy metals in the dissolved form.

It is important to highlight that the riverine and estuarine environments undergo different biogeochemical processes, which influence the concentrations of particulate and dissolved nutrients differently (Park et al., 2015; Sin et al., 2015). Therefore, biogeochemical aspects should be considered when investigating the relationships between nutrients and heavy metals.

4. Conclusions

This study provides a comprehensive analysis of the influence of the physico-chemical properties of water and sediments on the exchange behaviour of heavy metals under riverine and estuarine conditions. The research outcomes revealed that the mineralogical composition of the sediments is the most important factor governing both, the adsorption and desorption behaviour of heavy metals, as the mineral phases influence other important properties of sediments, such as CEC and SSA. Among the sediment properties, quartz exerted the strongest negative influence on the exchange of heavy metals and favoured their release from sediments to water in the riverine environment. Clays and mineral oxides were more important in the estuarine area and promoted the transfer of heavy metals from water to sediments. However, the various metals showed selectivity for different types of clays.

The behaviour of the various metals in relation to a particular nutrient was regulated by its predominant phase (e.g., particulate or dissolved) in the environment, which was in turn, affected by the type of aquatic ecosystem (riverine or estuarine). While TOC was the primary nutrient inducing the adsorption of heavy metals to the riverine sediments, the uptake of heavy metals by the estuarine sediments was mostly influenced by TP. On the other hand, dissolved nutrients did not play a key role in the release of heavy metals in the riverine area, whilst dissolved phosphorus was important for the desorption of heavy metals in the estuarine area. Additionally, the research outcomes indicated that increasing concentrations of marine-related metals generally promote the solubility and potential bioavailability of heavy metals in both, riverine and estuarine ecosystems. Therefore, despite the favourable physico-chemical characteristics of the estuarine environment for the immobilisation of heavy metals in sediments, seawater intrusion can increase the risks posed by heavy metals to human and ecosystem health. Therefore, special attention should be given to the estuarine areas in terms of pollution by heavy metals.

Study limitations include the lack of land use data in the Bayesian Networks models. Investigating land use classes and configuration patterns could provide further-in depth understanding of the exchange behaviour of heavy metals and, hence, improve the performance of the models. Therefore, it is recommended that future research efforts are made to include land use information in modelling approaches by considering the simultaneous interactions between water and sediments.

Declaration of Competing Interest

None

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2021.117386.

References

Abdel-Satar, A.M., Ali, M.H., Goher, M.E., 2017. Indices of water quality and metal pollution of Nile River, Egypt. Egyptian J. Aquatic Res. 43 (1), 21–29. https://doi.org/10.1016/j.ejar.2016.12.006.

AS/NZS. (1998). *Water quality - Sampling - Part 1: Guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples.*

AS/NZS. (1999). *Water quality - Sampling - Guidance on the sampling of bottom sediments.*

Aşçı, Y., Nurbaş, M., Açıkel, Y.S., 2010. Investigation of sorption/desorption equilibria of heavy metal ions on/from quartz using rhamnolipid biosurfactant. J. Environ. Manage. 91 (3), 724–731. https://doi.org/10.1016/j.jenvman.2009.09.036.

Ashayeri, N.Y., Behnam, K., 2019. Geochemical characteristics, partitioning, quantitative source apportionment, and ecological and health risk of heavy metals in sediments and water: A case study in Shadegan Wetland. Iran. Mar. Pollut. Bull. 149, 110495 https://doi.org/10.1016/j.marpolbul.2019.110495.

Atkinson, C.A., Jolley, D.F., Simpson, S.L., 2007. Effect of overlying water pH, dissolved oxygen, salinity and sediment disturbances on metal release and sequestration from metal contaminated marine sediments. Chemosphere 69 (9), 1428–1437. https://doi.org/10.1016/j.chemosphere.2007.04.068.

Bergaya, F., Schoonheydt, R., Johnston, C.T., 2018. Surface and interface chemistry of clay minerals. Elsevier, San Diego, United Kingdom.

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interface Sci. 277 (1), 1–18. https://doi.org/10.1016/j.jcis.2004.04.005.

Curtis, S.M., Ghosh, S.K., 2011. A Bayesian approach to multicollinearity and the simultaneous selection and clustering of predictors in linear regression. J. Stat. Theory Practice 5 (4), 715–735. https://doi.org/10.1080/15598608.2011.10483741.

Dey, S. (2014). *Fluvial hydrodynamics: Hydrodynamic and sediment transport phenomena. GeoPlanet: Earth and Planetary Sciences* (pp. 687). doi: https://doi.org/ 10.1007/978-3-642-19062-9.

Du Laing, G., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F.M.G., Verloo, M.G., 2008. Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. Estuarine Coastal Shelf Sci. 77 (4), 589–602. https://doi.org/10.1016/j.ecss.2007.10.017.

Duodu, G.O., Goonetilleke, A., Ayoko, G.A., 2016. Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. Environ. Pollut. 219, 1077–1091. https://doi.org/10.1016/j.envpol.2016.09.008.

Duodu, G.O., Goonetilleke, A., Ayoko, G.A., 2017. Potential bioavailability assessment, source apportionment and ecological risk of heavy metals in the sediment of Brisbane River estuary, Australia. Mar. Pollut. Bull. 117 (1-2), 523–531. https://doi.org/10.1016/j.marpolbul.2017.02.017.

Fairbrother, A., Wenstel, R., Sappington, K., Wood, W., 2007. Framework for metals risk assessment. Ecotoxicol. Environ. Saf. 68 (2), 145–227. https://doi.org/10.1016/j.ecoenv.2007.03.015.

Gao, X., Chen, C.A., 2012. Heavy metal pollution status in surface sediments of the coastal Bohai Bay. Water Res. 46 (6), 1901–1911. https://doi.org/10.1016/j.watres.2012.01.007.

Gu, X., Evans, L.J., 2007. Modelling the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn (II) onto Fithian illite. J. Colloid Interface Sci. 307 (2), 317–325. https://doi.org/10.1016/j.jcis.2006.11.022.

Huang, C.P., Chai, Z.Y., Yen, P., How, C.M., Yu, C., Chang, C., Liao, V.H., 2020. The bioavailability and potential ecological risk of copper and zinc in river sediment are affected by seasonal variation and spatial distribution. Aquatic. Toxicol. 227, 105604 https://doi.org/10.1016/j.aquatox.2020.105604.

Huang, L., Jin, Q., Tandon, P., Li, A., Shan, A., Du, J., 2018. High-resolution insight into the competitive adsorption of heavy metals on natural sediment by site energy distribution. Chemosphere 197, 411–419. https://doi.org/10.1016/j.chemosphere.2018.01.056.

Huo, S., Xi, B., Yu, X., Su, J., Zan, F., Zhao, G., 2013. Application of equilibrium partitioning approach to derive sediment quality criteria for heavy metals in a shallow eutrophic lake, Lake Chaohu, China. Environ. Earth Sci. 69 (7), 2275–2285. https://doi.org/10.1007/s12665-012-2056-6.

Jayarathne, A., Egodawatta, P., Ayoko, G.A., Goonetilleke, A., 2017. Geochemical phase and particle size relationships of metals in urban road dust. Environ. Pollut. 230, 218–226. https://doi.org/10.1016/j.envpol.2017.06.059.

Jayarathne, A., Egodawatta, P., Ayoko, G.A., Goonetilleke, A., 2018a. Intrinsic and extrinsic factors which influence metal adsorption to road dust. Sci. Total Environ. 618, 236–242. https://doi.org/10.1016/j.scitotenv.2017.11.047.

Jayarathne, A., Egodawatta, P., Ayoko, G.A., Goonetilleke, A., 2018b. Assessment of ecological and human health risks of metals in urban road dust based on geochemical fractionation and potential bioavailability. Sci. Total Environ. 618, 236–242. https://doi.org/10.1016/j.scitotenv.2018.04.098.

Kamprath, E. J., & Smyth, T. J. (2005). Liming. In D. Hillel (Ed.), *Encyclopedia of soils in the environment* (pp. 350-358). Oxford: Elsevier.

Kang, M., Tian, Y., Peng, S., Wang, M., 2019. Effect of dissolved oxygen and nutrient levels on heavy metal contents and fractions in river surface sediments. Sci. Total Environ. 648, 861–870. https://doi.org/10.1016/j.scitotenv.2018.08.201.

Keshavarzifard, M., Moore, F., Sharifi, R., 2019. The influence of physicochemical parameters on bioavailability and bioaccessibility of heavy metals in sediments of the intertidal zone of Asaluyeh region, Persian Gulf, Iran. Geochemistry 79 (1), 178–187. https://doi.org/10.1016/j.geoch.2018.12.007.

Kinraide, T.B., Yermiyahu, U., 2007. A scale of metal ion binding strengths correlating with ionic charge, Pauling electronegativity, toxicity, and other physiological effects. J. Inorg. Biochem. 101 (9), 1201–1213. https://doi.org/10.1016/j.jinorgbio.2007.06.003.

Klein, D.R., 2017. Organic chemistry, 3rd ed. Wiley, Hoboken, New Jersey.

Li, M., Zhang, Q., Sun, X., Karki, K., Zeng, C., Pandey, A., Rawat, B., Zhang, F., 2020. Heavy metals in surface sediments in the trans-Himalayan Koshi River catchment: Distribution, source identification and pollution assessment. Chemosphere 244, 125410. https://doi.org/10.1016/j.chemosphere.2019.125410.

Liang, G., Zhang, B., Lin, M., Wu, S., Hou, H., Zhang, J., Qian, G., Huang, X., Zhou, J., 2017. Evaluation of heavy metal mobilization in creek sediment: Influence of RAC values and ambient environmental factors. Sci. Total Environ. 607-608, 1339–1347. https://doi.org/10.1016/j.scitotenv.2017.06.238.

Liu, J., Diao, Z., Xu, X., Xie, Q., 2019a. Effects of dissolved oxygen, salinity, nitrogen and phosphorus on the release of heavy metals from coastal sediments. Sci. Total Environ. 666, 894–901. https://doi.org/10.1016/j.scitotenv.2019.02.288.

Liu, M., Chen, J., Sun, X., Hu, Z., Fan, D., 2019b. Accumulation and transformation of 9heavy metals in surface sediments from the Yangtze River estuary to the East China Sea shelf. Environ. Pollut. 245, 111–121. https://doi.org/10.1016/j.envpol.2018.10.128.

Ma, Y., Mummullage, S., Wijesiri, B., Egodawatta, P., McGree, J., Ayoko, G.A., Goonetilleke, A., 2021. Source quantification and risk assessment as a foundation for risk management of metals in urban road deposited solids. J. Hazard. Mater. 408, 124912 https://doi.org/10.1016/j.jhazmat.2020.124912.

Machado, A.A.S., Spencer, K.L., Zarfl, C., O'Shea, F.T., 2018. Unravelling metal mobility under complex contaminant signatures. Sci. Total Environ. 622-623, 373–384. https://doi.org/10.1016/j.scitotenv.2017.11.239.

McBride, M. B. (1989). Reactions controlling heavy metal solubility in soils. In B. A. Stewart (Ed.), *Advances in soil science* (Vol. 10, pp. 1-56). New York, NY: Springer New York.

Miranda, L.S., Ayoko, G.A., Egodawatta, P., Hu, W., Ghidan, O., Goonetilleke, A., 2021. Physico-chemical properties of sediments governing the bioavailability of heavy metals in urban waterways. Sci. Total Environ. 763, 142984 https://doi.org/10.1016/j.scitotenv.2020.142984.

Olaniran, A.O., Balgobind, A., Pillay, B., 2013. Bioavailability of heavy metals in soil: impact on microbial biodegradation of organic compounds and possible improvement strategies. Int. J. Mol. Sci. 14 (5), 10197–10228. https://doi.org/10.3390/ijms140510197.

Park, Y., Cho, K.H., Park, J., Cha, S.M., Kim, J.H., 2015. Development of early-warning protocol for predicting chlorophyll-a concentration using machine learning models in freshwater and estuarine reservoirs. Korea. Sci. Total Environ. 502, 31–41. https://doi.org/10.1016/j.scitotenv.2014.09.005.

Peng, J., Song, Y., Yuan, P., Cui, X., Qiu, G., 2009. The remediation of heavy metals contaminated sediment. J. Hazard. Mater. 161 (2), 633–640. https://doi.org/10.1016/j.jhazmat.2008.04.061.

Prathumratana, L., Sthiannopkao, S., Kim, K.W., 2008. The relationship of climatic and hydrological parameters to surface water quality in the lower Mekong River. Environ. Int. 34 (6), 860–866. https://doi.org/10.1016/j.envint.2007.10.011.

Rieuwerts, J.S., Thornton, I., Farago, M.E., Ashmore, M.R., 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. Chem. Speciation Bioavailability 10 (2), 61–75. https://doi.org/10.3184/095422998782775835.

Scutari, M., 2010. Learning Bayesian Networks with the bnlearn R package. *2010,* 35(3), 22. https://doi.org/ 10.18637/jss.v035.i03.

Seshadri, B., Bolan, N.S., Choppala, G., Kunhikrishnan, A., Sanderson, P., Wang, H., Currie, L.D., Tsang, D.C.W., Ok, Y.S., Kim, G., 2017. Potential value of phosphate compounds in enhancing immobilization and reducing bioavailability of mixed heavy metal contaminants in shooting range soil. Chemosphere 184, 197–206. https://doi.org/10.1016/j.chemosphere.2017.05.172.

Shen, T., Tang, Y., Li, Y.J., Liu, Y., Hu, H., 2020. An experimental study about the effects of phosphorus loading in river sediment on the transport of lead and cadmium at sediment-water interface. Sci. Total Environ. 720, 137535 https://doi.org/10.1016/j.scitotenv.2020.137535.

Sin, Y., Lee, E., Lee, Y., Shin, K., 2015. The river–estuarine continuum of nutrients and phytoplankton communities in an estuary physically divided by a sea dike. Estuarine Coastal Shelf Sci. 163, 279–289. https://doi.org/10.1016/j.ecss.2014.12.028.

Sparks, D.L., 2003. Environmental soil chemistry, 2nd ed. Academic Press, San Diego.

Sposito, G., 2016. The chemistry of soils. Oxford University Press, Oxford, United States. Incorporated.

Sun, X., Fan, D., Liu, M., Liao, H., Zheng, S., Tian, Y., 2020. Budget and fate of sedimentary trace metals in the Eastern China marginal seas. Water Res. 187, 116439 https://doi.org/10.1016/j.watres.2020.116439.

Sun, X., Fan, D., Liu, M., Tian, Y., Pang, Y., Liao, H., 2018. Source identification, geochemical normalization and influence factors of heavy metals in Yangtze River Estuary sediment. Environ. Pollut. 241, 938–949. https://doi.org/10.1016/j.envpol.2018.05.050.

Taqvi, S.I.H., Hasany, S.M., Bhanger, M.I., 2007. Sorption profile of Cd(II) ions onto beach sand from aqueous solutions. J. Hazard. Mater. 141 (1), 37–44. https://doi.org/10.1016/j.jhazmat.2006.06.080.

Thanh-Nho, N., Marchand, C., Strady, E., Vinh, T., Nhu-Trang, T., 2019. Metals geochemistry and ecological risk assessment in a tropical mangrove (Can Gio, Vietnam). Chemosphere 219, 365–382. https://doi.org/10.1016/j.chemosphere.2018.11.163.

Thanh-Nho, N., Strady, E., Nhu-Trang, T., David, F., Marchand, C., 2018. Trace metals partitioning between particulate and dissolved phases along a tropical mangrove estuary (Can Gio, Vietnam). Chemosphere 196, 311–322. https://doi.org/10.1016/j.chemosphere.2017.12.189.

Tomczak, W., Boyer, P., Krimissa, M., Radakovitch, O., 2019. Kd distributions in freshwater systems as a function of material type, mass-volume ratio, dissolved organic carbon and pH. Appl. Geochem. 105, 68–77. https://doi.org/10.1016/j.apgeochem.2019.04.003.

Uddin, M.K., 2017. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chem. Eng. J. 308, 438–462. https://doi.org/10.1016/j.cej.2016.09.029 https://doi.org/doi.org/.

Vehtari, A., Gelman, A., Gabry, J., 2017. Practical Bayesian model evaluation using leave-one-out cross-validation and WAIC. Stat. Comput. 27 (5), 1413–1432. https://doi.org/10.1007/s11222-016-9696-4.

Wang, X., Li, Y., 2011. Measurement of Cu and Zn adsorption onto surficial sediment components: New evidence for less importance of clay minerals. J. Hazard. Mater. 189 (3), 719–723. https://doi.org/10.1016/j.jhazmat.2011.03.045.

Wijesiri, B., Liu, A., Deilami, K., He, B., Hong, N., Yang, B., Zhao, X., Ayoko, G.A., Goonetilleke, A., 2019a. Nutrients and metals interactions between water and sediment phases: An urban river case study. Environ. Pollut. 251, 354–362. https://doi.org/10.1016/j.envpol.2019.05.018.

Wijesiri, B., Liu, A., He, B., Yang, B., Zhao, X., Ayoko, G.A., Goonetilleke, A., 2019b. Behaviour of metals in an urban river and the pollution of estuarine environment. Water Res. 164, 114911 https://doi.org/10.1016/j.watres.2019.114911.

Wijesiri, B., Liu, A., Jayarathne, A., Duodu, G.O., Ayoko, A., Chen, L., Goonetilleke, A., 2021. Influence of the hierarchical structure of land use on metals, nutrients and organochlorine pesticides in urban river sediments. Ecol. Eng. 159, 106123 https://doi.org/10.1016/j.ecoleng.2020.106123.

Witten, I. H., Frank, E., Hall, M. A., & Pal, C. J. (2017). Probabilistic methods. In I. H. Witten, E. Frank, M. A. Hall & C. J. Pal (Eds.), *Data Mining* (4th ed., pp. 335-416): Morgan Kaufmann.

Xie, M., Alsina, M.A., Yuen, J., Packman, A.I., Gaillard, J., 2019. Effects of resuspension on the mobility and chemical speciation of zinc in contaminated sediments. J. Hazard. Mater. 364, 300–308. https://doi.org/10.1016/j.jhazmat.2018.10.043.

Zhang, G., Bai, J., Xiao, R., Zhao, Q., Jia, J., Cui, B., Liu, X., 2017. Heavy metal fractions and ecological risk assessment in sediments from urban, rural and reclamation-affected rivers of the Pearl River Estuary. China. Chemosphere 184, 278–288. https://doi.org/10.1016/j.chemosphere.2017.05.155.

Zhao, S., Feng, C., Wang, D., Liu, Y., Shen, Z., 2013. Salinity increases the mobility of Cd, Cu, Mn, and Pb in the sediments of Yangtze Estuary: Relative role of sediments' properties and metal speciation. Chemosphere 91 (7), 977–984. https://doi.org/10.1016/j.chemosphere.2013.02.001.