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RESEARCH ARTICLE

Trends of labile trace metals in tropical urban water under highly contrasted weather conditions

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Abstract The spatio-temporal trend of trace metals (Cd, Co, Cr, Cu, Ni, Pb, and Zn) in a tropical urban estuary under the influence of monsoon was determined using diffusive gradient in thin films (DGT) in situ samplers. Three different climatic periods were observed: period 1, dry with dredging activity; period 2, intermediate meaning from dry to wet event; and period 3, wet having continuous rainfall. Conforming to monsoon regimes, these periods correspond to the following: transition from winter to summer, winter, and summer monsoons, respectively. The distinction of each period is defined by their specific hydrological and physico-chemical conditions. Substantial concentrations of the trace metals were detected. The distribution and trend of the trace metals under the challenge of a tropical climate were able to follow using DGT as a sensitive in situ sampler. In order to identify the differences among periods, statistical analyses were performed. This allowed discriminating period 2 (oxic water) as significantly different compared to other periods. The spatio-temporal analysis was then applied in order to distinguish the trend of the trace metals. Results showed that the trend of trace metals can be described according to their response to (i) seasonal variations (Cd and Cr), (ii) spatio-temporal conditions (Co, Cu, Ni, and Pb), and (iii) neither (*i*) nor (*ii*) meaning exhibiting no response or having constant change (Zn). The correlation of the trace metals and the physico-chemical parameters reveals that Cd, Co, Cu, and Cr are proportional to the dissolved oxygen (DO), Cd and Ni are correlated pH, and Zn lightly influenced by salinity.

Keywords Labile trace metal · Urban water · Tropical climate · Monsoon · Statistics · DGT

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Introduction

Tropical waters are dynamic environments. There are loads of factors that influence these aqueous systems such as different activities like estuarine mixing, tidal currents, sediment remobilization, and fine grain sediments transport (Kuehl et al. 1996 and Breckel et al. 2005). Moreover, seasonal timescales (*e.g.*, monsoonal climate) induced by precipitation and other weather conditions affect the hydrological cycle (Chakraborty et al. 2010). Under monsoon regime, seasonal differences are pronounced and mostly distinguished by the absence and presence of precipitation (Takahashi 2013). This type of climate is challenging as uptight circumstances are at hand. Alterations in the hydro-climatic scheme can be experienced (Hestir et al. 2013). For instance, incident of disruptions of the ocean-atmosphere interactions can occur (Shirasago-Germán et al. 2015). These are principal sources of disturbance in water basins.

Nowadays, the increasing apprehensions on the tropical waters not only rest in the hydro-climatic conditions but also on the water quality as well. Particular interests are on the trace metals in terms of contamination and environmental risks. These are important environmental issues. Studies aim to know the possible effects of metals in urban runoff (Herngren et al. 2005) and pollution discharges (Ki et al. 2011) in the aquatic system and the biota.

Trace metals are ubiquitous, easily transported to water (Chen et al. 2014). The behavior of the trace metals in estuaries varies greatly due to environmental factors like hydrodynamic residence time, mixing patterns of transport processes, and reservoir management (Hatje et al. 2003; Masson et al. 2006; Masson et al. 2011). Another factor is the water chemistry that changes from freshwater to saltwater that influences their occurrence (Jiann and Wen 2009). The trend differs according to seasonal changes and suspended sediments concentrations (Park et al. 2011). Precipitation, for example, can play as an atmospheric wash out that delivers trace metals to aquatic ecosystem through deposition mechanism (Özsoy and Örnektekin 2009). To deduce, in tropical waters, trace metals can be perceived as active components in the environment and, at the same time, reactive elements in the aqueous systems. These directed toward serious intentions and efforts to assess the water quality of tropical waters including estuaries specially those who are situated in highly urbanized zones.

Labile trace metals are vital in examining the state of these tropical waters. This fraction can eventually help in assessing toxicity and associated risks (Pinheiro and Domingos 2005). However, measuring these specific forms requires collecting voluminous water which is tedious and time consuming (Graveline et al. 2010). Alternatively, in situ sampling technique can be employed. It can provide data over longer periods of time and reduces some of the drawbacks of grab sampling (INAP 2002).

For this reason, diffusive gradient in thin films (DGT) is used to monitor trace metals in aquatic system. This device has the ability to perform measurements (Davison and Zhang 1999) at a lower cost. It is an in situ method that can sequester labile fractions (Naylor et al. 2004; Li et al. 2005; Søndergaard et al. 2008; Vystavna et al. 2012a, b) even at very low concentrations (Zhang et al. 1995). This technique for measuring trace metal and monitoring water bodies is long-established and delivers valuable results with lesser sampling activities needed (Alfaro-De la Torre et al. 2000; Clarisse et al. 2009; Gao et al. 2010; Wu et al. 2011; Villanueva et al. 2013).

The purpose of this research is mainly to determine the labile trace metals response to differing climatic and physico-chemical conditions in a dynamic estuarine system in a tropical setting. The Pasig River in Manila, Philippines was chosen due to the distinct water dynamics (as this is an estuary in nature) and climate background. The seasonal changes are pronounced and contrasting because of the influence of the monsoon and precipitation anomalies over tropical regions (Villafuerte et al. 2014). These variations are caused by surface reverse directions and local winds (Han et al. 2009).

This study would like establish the trend of labile trace metals in a tropical water facing monsoon seasons. The focus is on determining the importance of the episodic events on the trace metal loads and availability of the labile fractions in highly industrialized and urbanized tropical water. The specific objectives are (1) to describe the trend of the labile trace metal (Cd, Co, Cr, Cu, Ni, Pb, and Zn), (2) to distinguish the effect of seasonal changes under monsoon regime in a tropical aquatic system in terms of hydrochemistry and physico-chemical conditions, and (3) to determine which among labile trace metals are more vulnerable to spatio-temporal changes.

Three local seasons were considered: dry, transition from dry to wet (intermediate), and wet. The difference in the seasonal pattern can lead to a premise that the trace metals trend will also be significantly distinct from each period. To assess if this premise holds, statistics were performed. Hydrochemistry and physical conditions were utilized as parameters. Spatio-temporal analysis was applied to better explain the labile trace metal trends.

Materials and methods

Site description

The Pasig River is an estuary of about 27 km long and approximately 80 m wide. The catchment is composed of 4 main tributaries (San Juan River, Marikina River, Napindan River, and Pateros-Taguig River) and 43 minor tributaries. It is located in the heart of Manila, Philippines (Fig. 1) and connects Laguna Lake (east), the biggest freshwater lake in the

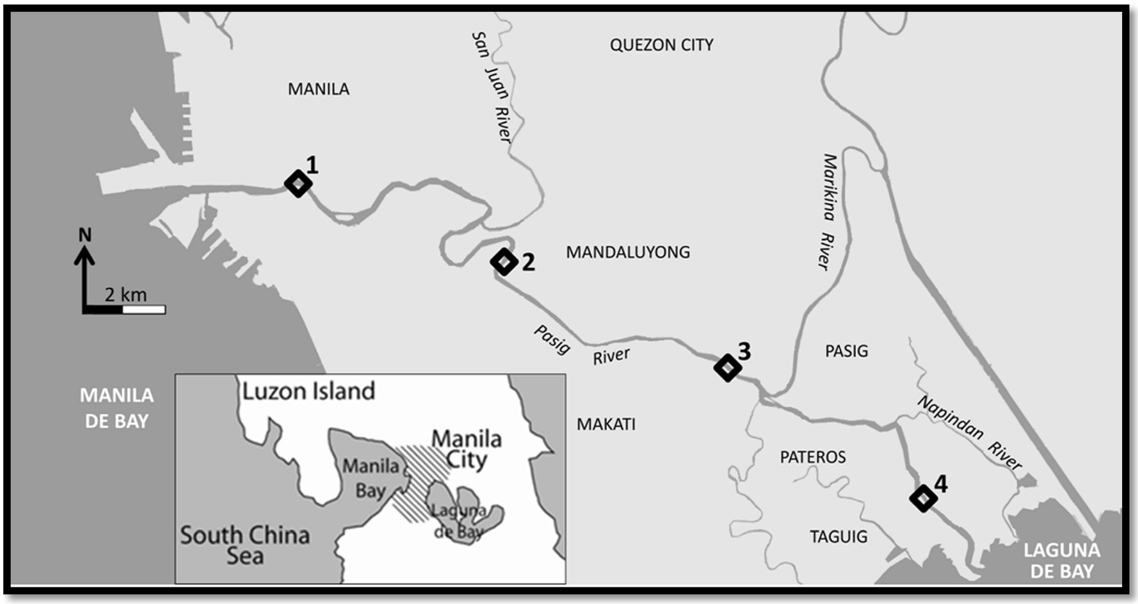


Fig. 1 The Pasig River map and sampling sites (point 1: moth of the Manila Bay; point 2: near the convergence of the San Juan River, point 3: near the confluence of the Marikina River; and point 4: near the Laguna Lake)

Philippines and the Manila Bay (west). The salinity intrusion from the bay can reach toward the whole stretch of the Pasig River to the mouth of the lake.

Manila Bay mostly serves as a shipyard. Laguna Lake has many functions that include aquaculture and fishery (open fishing), irrigation, power generation, and navigational lane. This site is situated in a highly industrialized and urbanized area with a rough estimated population of 11,500,000 plus fluxes of informal settlers which are about 30 % of the total Metro Manila region (Aiga and Umenai 2002). This water body normally receives non point sources of effluent wastes of different forms. Poor solid waste management is in addition a challenge in the area.

Sampling design

The sampling design followed seasonal patterns in the study area. Sampling campaigns were conducted that corresponded to period 1, dry with an ongoing dredging activity (April to May 2010); period 2, intermediate: from dry to wet season (January 2011); and period 3, wet season (May to June 2011). The rainfall behavior during the sampling campaigns is presented in Table 1. Following these differing precipitation rates, the hydrology of the Pasig catchment varied strongly in between periods.

Four sites (Fig. 1) were chosen representing the upstream (point 1: mouth of the Manila Bay), midstream (points 2 and 3 which are near the San Juan and Marikina River, respectively), and downstream (point 4: mouth of the Laguna Lake), with an approximate distance of 7 km in each site. Point 4 signals freshwater interference in the river. In each site, DGT in duplicates were fully immersed for 18 days. DGT field blank was provided per sampling campaign. Strict protocols of DGT deployment (Villanueva 2013) were followed for all sampling campaigns. Immediately, after the retrieval, the DGT probes were rinsed with deionized water and placed in pre-cleaned properly marked resealable plastic containers. A cooling compartment was prepared to transport the probes directly to the laboratory. DGTs were put in the refrigerator before the extraction of the trace metals.

During each sampling campaign, physical parameters such as dissolved oxygen (DO), water temperature, salinity, conductivity, and pH were measured in situ using YSI 6600 V2 data probe at a depth of approximately 1 m below the water surface. The range of values is presented in Table 2. According to the study of Materum 2010 and Villanueva 2013, total organic carbon (TOC) of the Pasig River ranged from 3.4 to 4.5 mg/L during May 2010 and 3.5 to 7.4 mg/L for January 2011.

Table 1 Rainfall rate during the sampling campaigns

Rainfall (mm)	Period 1	Period 2	Period 3
Days before sampling*			
10	0.8	5.4	19.6
20	0.8	14.4	125.2
Accumulated within the sampling period	6	79	79.8

*Days before DGT installation

Provided by Manila Observatory (unpublished data 2012)

Table 2 Physico-chemical parameters' range of values

Period	Water temperature (°C)	DO (mg/L)	pH	Salinity	Conductivity (ms/cm)
1	31	0.45–1.05	7.89–8.35	0.55–3.60	6.00–22.00
2	26–27	5.90–8.20	7.31–7.73	0.39–0.40	0.81–0.84
3	31–32	1.55–2.26	6.80–7.03	0.39–8.44	1.00–16.00

Determination of trace metals concentration

Standard solution Chelex-100 DGT probes were purchased from DGT Research Ltd., Lancaster, UK. DGT field blanks were extracted and analyzed using the same procedure for the DGTs immersed in the water. Laboratory procedural blanks were prepared. The detection limits were determined following the already established procedure (Pettke et al. 2012). In the laboratory, the membrane filter and the diffusive gel were carefully removed from the piston using Teflon tweezers. The gel was separated and placed into a clean *polypropylene* micro centrifuge tube. One milliliter of 1 M of HNO_3 (Fisher Scientific Analar grade) was added. After 24 h, dilution was performed. The trace metals were determined using inductively coupled plasma-mass spectrometry (Thermo Scientific*ELEMENT2*ICP-MS). From the elution solution, the accumulated mass of the trace metals then the concentrations were calculated. The detailed laboratory procedures (Dunn et al. 2007; Nyein Aung et al. 2008) and calculations (DGT Research 2002) can be found elsewhere (INAP 2002).

Trend analysis approach

Two approaches were applied: statistical and spatio-temporal analyses. The statistical analyses permit discriminating the periodical differences. This can also describe the relationship in between parameters: hydro- and physico-chemical variables and trace metal concentrations. The spatio-temporal analysis is valuable in determining the trends of the trace metals by evaluating their response in each seasonal or temporal variation and inspecting the increase or decrease of the concentration in a spatial sense.

Statistical tests

In order to determine the significance among periods using the concentrations of the pool of labile metals, series of statistical tests were utilized. Student *t* test was considered as it is appropriate for small data sets (population samples). This test is normally applied for the comparison of two means (Fritz and Berger 2015). Hence, allowing comparing a period to another using the concentration of the trace metals as data sets. Two-tailed *t* test was employed pairing each period's data sets (trace metals concentrations). The significance level was determined using the value $\alpha=0.05$. To validate and illustrate the difference, hierarchical cluster analysis was performed.

Correlation analysis was applied to determine the potential relationship of the physico-chemical parameters (DO, water temperature, pH, salinity, and conductivity) and how each can influence one another. Subsequently, the correlation of the physico-chemical parameters to the labile trace metals was carried out.

Spatio-temporal analysis

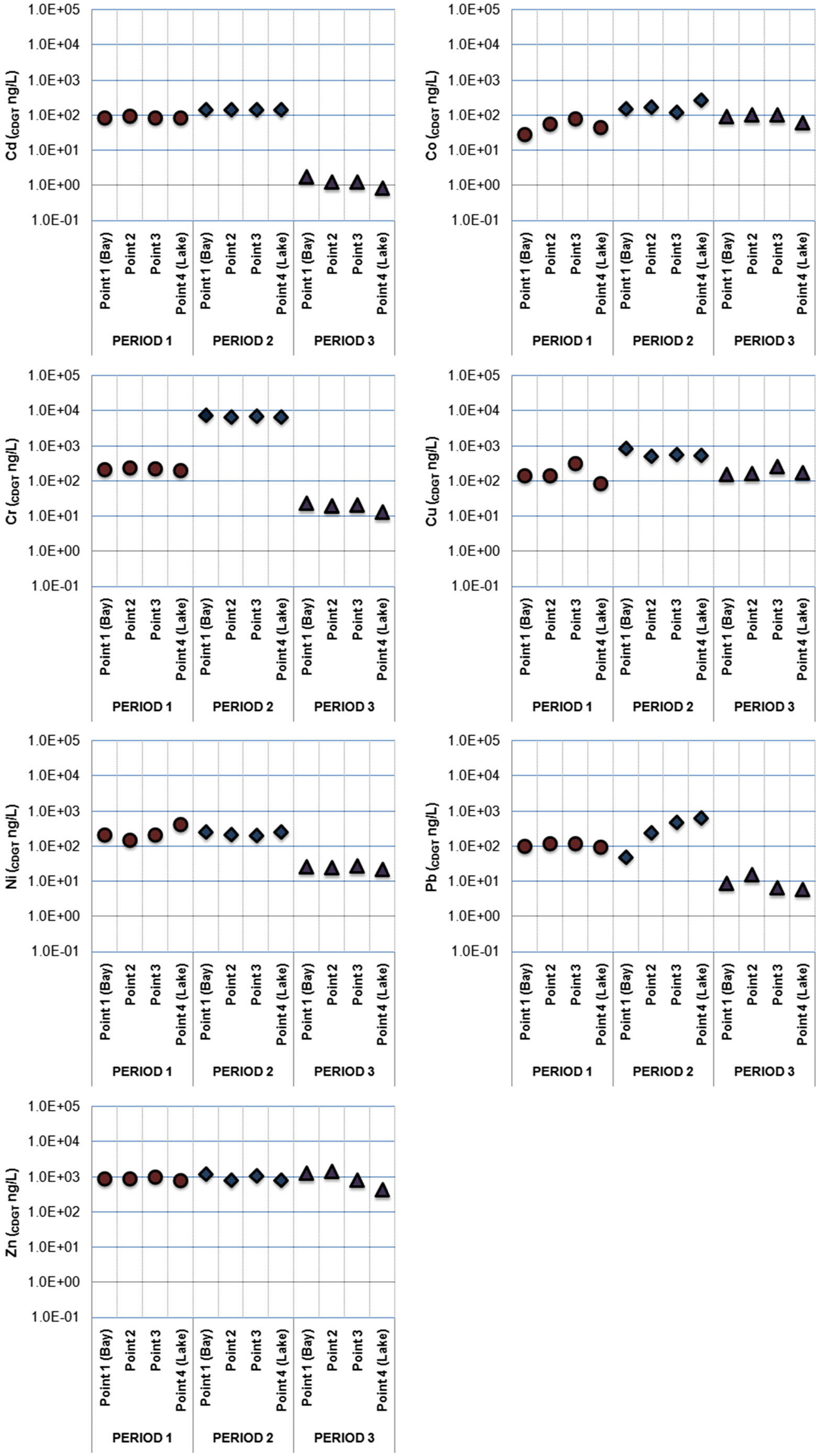
The spatio-temporal analysis can discriminate the trend of each labile trace metals by examining the tendency of concentrations. The variation can be sorted according to the inclination of each trace metal. This approach aids in determining which trace metals are susceptible to (i) seasonal or climatic conditions changes, (ii) spatial or local variations, (iii) both spatial and seasonal disparities, and (iv) neither spatial nor local situation (absence of changes). The first can be related to temporal events, while the second can be associated to anthropogenic activities and/or instantaneous contamination. The last can be described as having a conservative or constant trend.

Results

Environmental background and physico-chemical parameters

The physico-chemical characteristics of the water were recorded during each sampling period (Table 2). Period 1 combines two episodic events: dry season and dredging activity. The area experienced shortage on rainfall. Periods 2 and 3, on the other hand, both experienced pronounced rainfall (~79 mm). Period 2 showed the lowest record for water temperature, salinity, and conductivity. This period has the highest DO level. The periods were best described by the DO as the oxygen levels greatly varied through periods. DO range from 0.45 to 1.05 mg/L on period 1, 5.9 to 8.2 mg/L on period 2, and 1.55 to 2.26 mg/L on period 3. Only period 2 passed the Department Administrative Order (DAO 34) of the Philippine government. The DO requirement is >5 mg/L. The salinity was pronounced on period 3 (0.39 to 8.44 psu) which also indicated water mixing. In period 2, salinity was almost constant along the Pasig River stretch. Compared to DO, salinity and conductivity, pH did not exhibit strong variations.

Fig. 2 DGT-labile trace metals' concentrations (ng/L)



Labile trace metals in the Pasig River

The general trend observed was that most of labile trace metals concentrations increased during period 2 then decreased during period 3 (Figs. 2 and 3 and Tables 3 and 4). However, throughout the period, Zn seemed stable. During period 1, the only DGT-trace metals (at maximum) found at the river end is Ni located near the mouth of the bay (point 1). Minimum Ni was detected at the confluence of San Juan River (point 2) while Co has the least at the mouth of the bay (point 1). Maximum concentrations were mostly near the confluence of San Juan River (point 2: Cr, Cd, and Pb) and convergence of Marikina River (point 3: Co, Cu, and Zn).

The minimum concentrations of Cr, Cu, Zn, Cd, and Pb were found near the mouth of the lake area (point 4). In this period, at the river ends (points 1 and 4), lower values of Cr, Co, Cu, Cd, and Pb were found. In contrast, Ni has the lower values in the midstream (points 2 and 3). Zn concentration spatially varies. In period 2, minimum value of Pb is found near the mouth of the bay (point 1); Cr, Cu, and Zn were at the confluence of San Juan River (point 2); Co and Ni near Marikina River area (point 3); and Cd near the mouth of the lake (point 4). Maximum values of Cr, Cu, Zn, and Cd were found near the mouth of the bay (point 1), while, Co, Ni, and Pb at the mouth of the lake (point 4). At this period, the maximum values are all found at the river ends (points 1 and 4).

For period 3, Cu has the least concentration at the mouth of the bay (point 1). Maximum values were traced in the sampling points except near the lake: Cr and Cd were found near the bay area; at the confluence of San Juan River (point 2: Co, Zn, and Pb) and near at the Marikina River (point 3: Ni and Cu). Most of the minimum values were at the mouth of the lake (point 4: Cr, Co, Ni, Zn, Cd, and Pb).

Labile trace metal concentrations and statistical difference among periods

The Student *t* test was performed by pairing the data (period 1 vs. period 2; period 1 vs. period 3; and period 2 vs. period 3). The result of the statistical test is shown in Table 5. Significant difference were found in between periods 1 and 2 (α=0.05; p=0.022) and periods 2 and 3 (α=0.05; p=0.016) but not for period 1 and period 3 (α=0.05; p=0.437).

To illustrate, the hierarchical cluster analysis was performed generating a dendrogram (Fig. 4a). The dissimilarity between the periods agreed to the statistical analysis performed where period 2 was isolated (left). Observations on the spatial patterns of periods 1 and 3 showed that for both periods, most of the maximum concentrations of each trace element are found at the midstream (points 2 or 3), while most of the minimum concentrations of each trace element are at the endstream (points 1 or 4). Another dendrogram (Fig. 4b) was generated considering only periods 1 and 3. The result demonstrated that period 1 is grouped together, whereas period 3 is clustered into three groups.

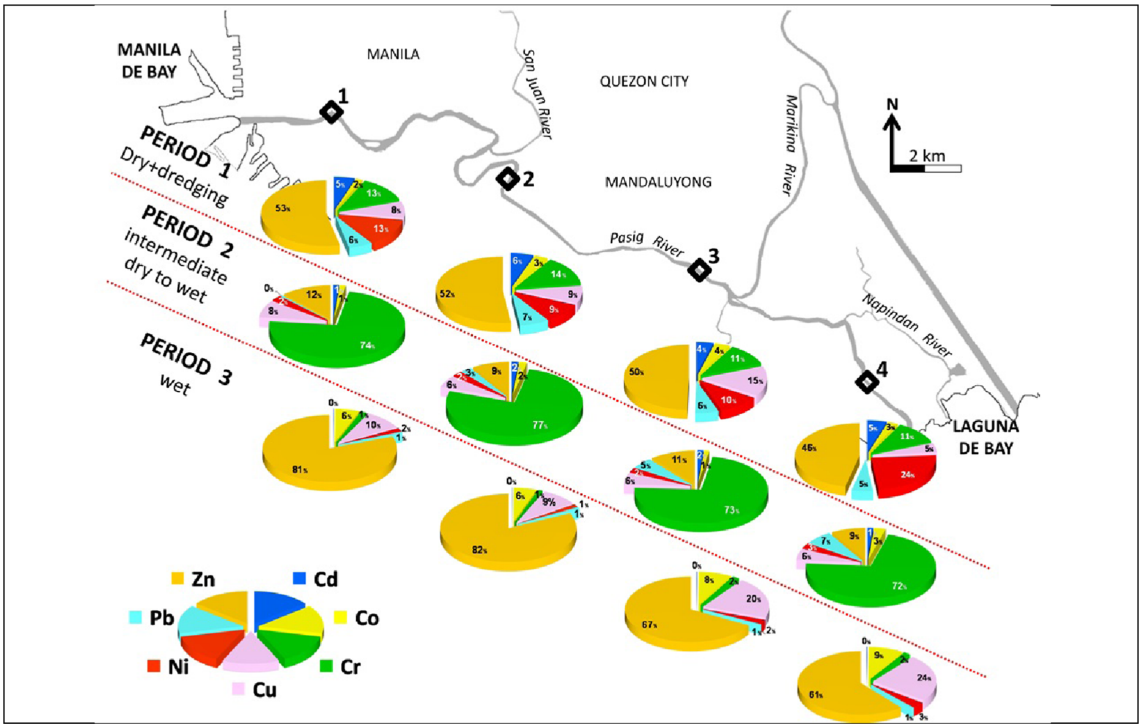


Fig. 3 Spatio-temporal variation of the trace metals among period

Table 3 Concentration range of detected labile trace metals in the Pasig River (ng/L)

Trace metals	Concentration ranges			RSD			Detection limit
	Period 1	Period 2	Period 3	Period 1	Period 2	Period 3	
Cd	87–94	141–146	0.9–1.8	1.75	1.04	0.19	0.21
Co	28–82	119–277	62–100	11.24	34.27	9.09	6.44
Cr	205–236	6841–7632	13–23	6.82	184.50	2.15	10.86
Cu	88–314	506–867	149–251	48.93	82.92	23.17	7.63
Ni	154–434	206–255	22–27	61.33	12.57	1.09	2.94
Pb	95–122	50–643	7–16	6.95	131.25	2.18	1.21
Zn	827–1027	793–1236	431–1468	42.34	103.60	232.11	100.00

Correlation among parameters

The correlation among physico-chemical parameters is shown in Table 6. DO has an inverse relationship to other physico-chemical parameters. This inverse relationship is more pronounced with respect to the water temperature ($\alpha=0.05$; $p=-0.91$). In terms of salinity, periods 1 and 3 showed evident water mixing. Although, the salinity values are lower in period 1, water mixing was also observed. There is also a weak confirmation of the inverse relationship of DO to salinity ($\alpha=0.05$; $p=-0.42$). Water temperature and salinity are positively correlated to conductivity, whereas DO showed negative correlation.

Table 4 Anthropogenic activities surrounding the Pasig River and the major trace metals concern

Site	Important activities	Major metals concern
Site 1	Shipyard	Ni
	Ceramic factory	Co, Cr ,Pb
	Electric company	Cu
	Textile and clothing	Cr, Zn
	Thermal power plant	Cd, Ni, Pb, Zn
	Food company	Pb, Cu
	Gasoline stations	Cd, Co, Cr, Cu, Ni, Pb, Zn
	Oil refinery	Cd, Cr, Pb
	Navigational lane	Cd, Co, Cr, Cu, Ni, Pb, Zn
Site 2	Oil refinery	Cd, Cr, Pb
	Steel	Cr
	Oil and petroleum company	Cd, Co, Pb, Zn
	Wood	Cu
	Electricity (electrical industry)	Cu
	Cigarettes	Cd
	Metal castings	Co, Cr, Ni, Zn
	Agroindustry	Cd, Cu, Pb
	Steels	Cr, Ni
Site 3	Navigational lane	Cd, Co, Cr, Cu, Ni, Pb, Zn
	Aquaculture	Cd, Co, Cr, Cu, Ni, Pb, Zn
Site 4	Fishing, irrigation	Cd, Zn
	Power generation	Cd, Pb
	Navigational lane	Cd, Co, Cr, Cu, Ni, Pb, Zn

Among trace metals (Table 7), Zn demonstrated weak correlation to other trace metals. Direct relationship was present in between the following trace metals: Co-Cd ($r=0.80$), Co-Cr ($r=0.77$), Cu-Cd ($r=0.71$), Cu-Co ($r=0.69$), Cu-Cr ($r=0.92$), and Ni-Cd ($r=0.75$). In between the physico-chemical parameters and the trace metals, DO followed the Cd, Co, Cu, and Cr, and pH is correlated to Cd and Ni. Potential relationship in between salinity and Zn was traced.

Discussion

Environmental background

The Philippines is within the regime of monsoon seasons of Southeast Asia (Loo et al. 2014). This type of climate system is dynamic as it is characterized by wet spell having periodic heavy rains and dry spell with seasonal changes driven by the wind directions (Stephens et al. 2008). The active factors coming from the interaction of the oceans and atmosphere could lead to droughts and wet episodes (Buckley et al. 2014). It has significant impacts on the environment including water systems (Cook and Jones 2012; Varis et al. 2012). Monsoon climate dictates the variability of the temperature of the water catchments (Meybeck 2009) and hydrodynamics (Fuchs et al. 2012). It can also affect the quality of the water resource (Wilkerson et al. 2002; Hestir et al. 2013). For these reasons, under this climate regime, it is noteworthy to know how the hydrochemistry of the Pasig River responds.

Monsoonal Climate Regime

Seasonality of monsoon can be categorized according to months. Cruz et al. 2012 explains that the main monsoon regimes are the Northeast monsoon and the Southwest monsoon. Northeast monsoon or the winter monsoon can be expected on November to March. Southwest monsoon or summer monsoon starts May and ends on September. On October,

Table 5 Student *t* test result

	Groups	*t*	df	Sig. (two-tailed)	Mean difference	Std. error difference
Period	Dry (1) vs. intermediate (2)					
	°°	−2.43	27.77	0.022*	−1109.41	455.75
	Dry (1) vs. Wet (3)					
	°	0.78	54.00	0.437	69.74	89.09
	Intermediate (2) vs. wet (3)					
	°°	2.57	28.32	0.016*	1179.15	458.05

*For 5 % level of significance, there is difference on the mean response of dry vs. intermediate, and intermediate vs. wet as showed in the *p* values (sig.<0.05)

° Equal variances assumed; °° equal variances not assumed

the transition from Southwest monsoon to Northeast monsoon occurs. Adhering to the monsoon regime, period 1 fell under the transition from Northeast to Southwest monsoon (in between winter and summer monsoon); period 2 experienced Northeast/winter monsoon; and period 3 encountered Southwest/summer monsoon.

Hydro-physico-chemical variation

The variation of DO followed by the water mixing express the differences among periods. Through periods there is a shift from almost anoxic to oxic then hypoxic waters. In terms of incidence of water mixing, the trend is as follows: Period 3> Period 1>Period 2. The conductivity follows the trend of the salinity, Period 2 having least values. The water temperature is almost the same for Periods 1; and 3 and lowest during Period 2. For pH, Period 1 was more basic than Period 2 and Period 3 played slightly acid to neutral water.

Spatio-temporal analysis on trace metals

Period 1 as stated was under a dry weather. Twenty days prior to the sampling campaign, there was only 0.8 mm of rainfall. A total of 6 mm of rainfall was accumulated within this sampling period which implied river low flow. At this period, there was an ongoing dredging activity. Dredging is an ecological disturbance that can affect the sediment structure (Mackie et al. 2007; Je et al. 2007). Both particulate forms (Nayar et al. 2004) and bioavailability (Lewis et al. 2001) of trace metals in the water column could increase (Cabrita 2014) due to resuspension (Fathollahzade et al. 2015). Studies showed that the release of the dissolved trace metals can be attributed to the binding mechanism to the solid phase or on the mechanisms involving sorptive phases (van den Berg et al. 2001). Also the changes in the water chemistry like pH and ionic strength can affect the release of the dissolved trace metals (i.e., lower pH increase the solubility of the trace metals).

In wet seasons, atmospheric deposition, surface runoff (Witt et al. 2010), and atmospheric precipitation (Migliavacca et al. 2005; Vuai and Tokuyama 2011) contribute to trace metals delivered to the receiving body (Dunn et al. 2007) such as rivers (Nyein Aung et al. 2008). Periods 2 and 3 both received almost the same amount of precipitation throughout the sampling campaign. However, 20 days before the sampling activity in period 3, the accumulated rainfall amount was only 125.2 mm already, whereas period 2 received only 14.4 mm. These periods displayed different hydro-chemical characteristics. The hydro-chemical condition illustrates the distinction of this period being least in salinity, water temperature, and conductivity at the same time highest in DO values. Period 3 has the highest recorded water temperature, salinity, and conductivity. Knowing the hydro-chemical background, the interesting issue is on what can be the response of each of these differing conditions to the labile trace metal concentrations.

Trace metal variation

The ranges of the trace metal concentrations are summarized in Table 3, while the variations are presented in Fig. 2. Period 2 is discriminated as significantly different to periods 1 and 3. In Table 4, the anthropogenic activities surrounding the river with the trace metals concern are identified. To illustrate the distribution of the different labile trace metals per period and site, pie charts were drawn in Fig. 3. These pie charts represent relative percentage of the concentrations of trace metals. Zn has the largest portion during periods 1 and 3. In period 2, Cr has the leading share. The second biggest part among periods is as follows: period 1: mostly Cd followed by Cr; period 2: Zn followed by Cu; and period 3: Cu then Co.

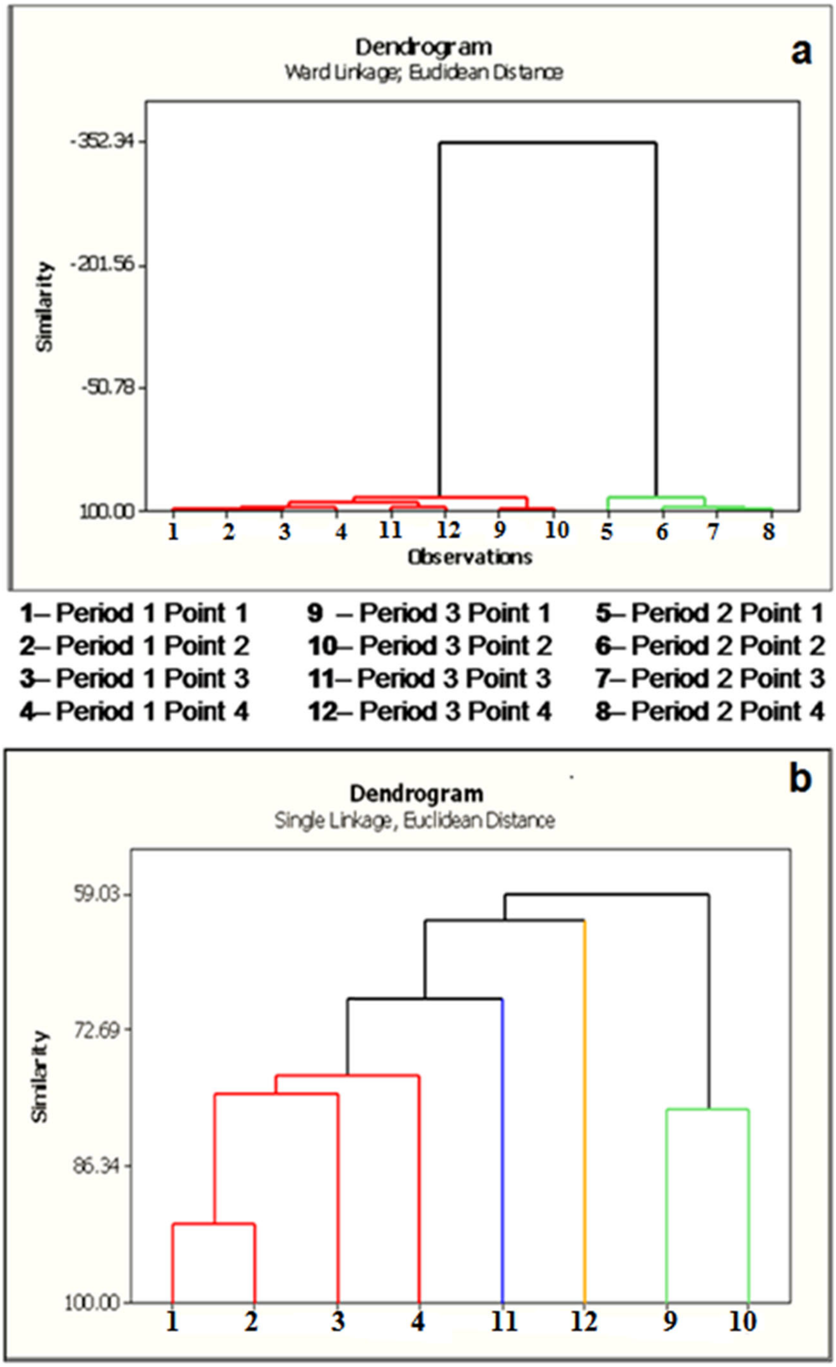


Fig. 4 Generated dendrogram. *Numbers* indicate sampling regime (Period) and points. **a** all The periods and **b** periods 1 and 3 (legend is provided in the middle)

Table 6 Correlation (*r*) among physico-chemical parameters

	Salinity	Dissolved oxygen	Water temp	pH	Conductivity
Salinity	1.00				
Dissolved oxygen	−0.42	1.00			
Water Temp	0.36	−0.92	1.00		
pH	−0.40	−0.25	0.09	1.00	
Conductivity	0.69	−0.70	0.52	0.26	1.00

Table 7 Correlation (r): among labile trace metals and labile trace metals to the physico-chemical parameters

	Cd	Co	Cr	Cu	Ni	Pb	Zn
Cd	1.00						
Co	0.48	1.00					
Cr	0.80	0.77	1.00				
Cu	0.71	0.69	0.92	1.00			
Ni	0.75	0.12	0.38	0.28	1.00		
Pb	0.68	0.71	0.69	0.47	0.40	1.00	
Zn	−0.04	0.06	0.06	0.16	−0.12	−0.14	1.00
pH	0.52	−0.25	−0.06	−0.04	0.75	0.08	−0.13
Salinity	−0.59	−0.28	−0.48	−0.48	−0.52	−0.41	0.53
DO	0.65	0.88	0.95	0.84	0.24	0.76	−0.02
Water temp	−0.78	−0.77	−0.98	−0.91	−0.28	−0.67	−0.18
Conductivity	−0.29	−0.60	−0.63	−0.63	−0.12	−0.38	0.25

Spatio-temporal variation of trace metals

As a point of observation, the variation of each trace metals follows three trends. The trace metals can be grouped according to their response in a spatio-temporal approach. First, the trace metals that exhibited seasonal (temporal) variation or changes of the concentrations differ between periods. Second, trace metals that are sensitive spatially and temporally, indicating variations in each site and in each period (season). Third, a trace metal that is constant through time. Seasonal variation is observed in labile trace metals Cd and Cr. The spatial and temporal sensitive trace metals are depicted by Co and Cu and mainly by Ni and Pb. Among the trace metals, Zn has a different trend by appearing constant through time.

Cr and Zn: the trend and origin

Significant concentrations of trace metals were detected in the Pasig River in varying amount. There is an interesting aspect in terms of anthropogenic and geogenic origins. In Fig. 3, the largest portions are Cr and Zn. Among the trace metals, Cr showed the most considerable trend in between periods. The results showed how the dissolved Cr in the Pasig River is sensitive to seasonal and hydrochemistry changes. There is a notable point in Cr being the highest during period 2. Table 4 provided probable sources of emissions situated at the riverbank. Cr could also be associated to atmospheric fallout or rainfall and surface runoffs (Neal et al. 1996). During period 3, a series of rainfall served as a wash out of Cr that is why lesser concentration was detected.

As the spatio-temporal analysis revealed, unlike Cr, Zn is neither affected by dilution nor the variation of physico-chemical parameters. Zn is normally abundant in urban water runoff. It is interesting to look at its geogenic origin. The interaction of Zn with Cd and the distribution in estuaries can be studied (Audry et al. 2004; Dudka et al. 1994).

The fractionation of Zn/Cd can explain the trace element pattern as a response to the geochemical phases. Its concentration ratio changes according to different geochemical phases occurring in geochemical path such as in streams, rivers, estuaries, coastal seas, and open oceans (Gerringa et al. 2001). The result of this study showed that Zn has a significant relationship to Cd (r=0.61). Zn/Cd ratio can give clear estimates on the relative geochemical behavior (Mazeina et al. 1999) and can trace their sources. The Zn/Cd ratio obtained ranges 9.32–11.65 for period 1; 5.88–8.48 for period 2; and 502.72–1174.83 for period 3. The ratio that ranges from 5–10 can be attributed for oceanic waters (Gerringa et al. 2001). In the world record, the ratio 7.5 is said to be carried by riverine suspended sediments to the oceans in dissolved phase (Viers et al. 2009). Higher ratio (>500), like in period 3, can be traced in ore elements from basaltic, igneous rocks, and sediments (Gerringa et al. 2001; Nolting et al. 1999; Gottesmann and Kampe 2007). Thus, there is an indication that most of Zn came from runoff.

Importance of the physico-chemical parameters on the labile trace metals

Physico-chemical environmental parameters are very essential in explaining the chemical spatial distribution of the trace metals. DO plays an important role which is highly influenced by seasonal changes (Sokolowski et al. 2001). As a main point, DO give inverse relationship to other physico-chemical parameters. This inverse relationship is more distinct with respect to the water temperature followed by conductivity. There is a weak proportional relationship in between DO and salinity. Although, the results confirmed the direct relationship in between conductivity and salinity, two tendencies were noticed. Period 1 showed higher slopes than period 3. Although salinity is lesser in period 1, conductivity is higher. pH displayed weak inverse correlation to salinity and conductivity.

Positive correlations (r>0.60) in between most of the trace metals were observed. Weak correlations (r<0.50) are found in between Cd-Co, Ni-Co-, Ni-Cr, and Ni-Cu. Zn portrayed no correlation with other trace metals. The relationships of the concentrations of physico-chemical parameters and labile trace metals among periods are presented in Fig. 5 and Table 7.

DO Pasig River showed that trace metals (Cd, Co, Cr, Cu, and Pb) are directly proportional to DO except for Ni and Zn. Oxic water favors dissolved metals (Buffle and van Leeuwen 1993). The oxic levels of each period are distinguished accordingly: period 1 is near anoxia, period 2 shows oxic water, and period 3 is hypoxic water (Table 2). Using the

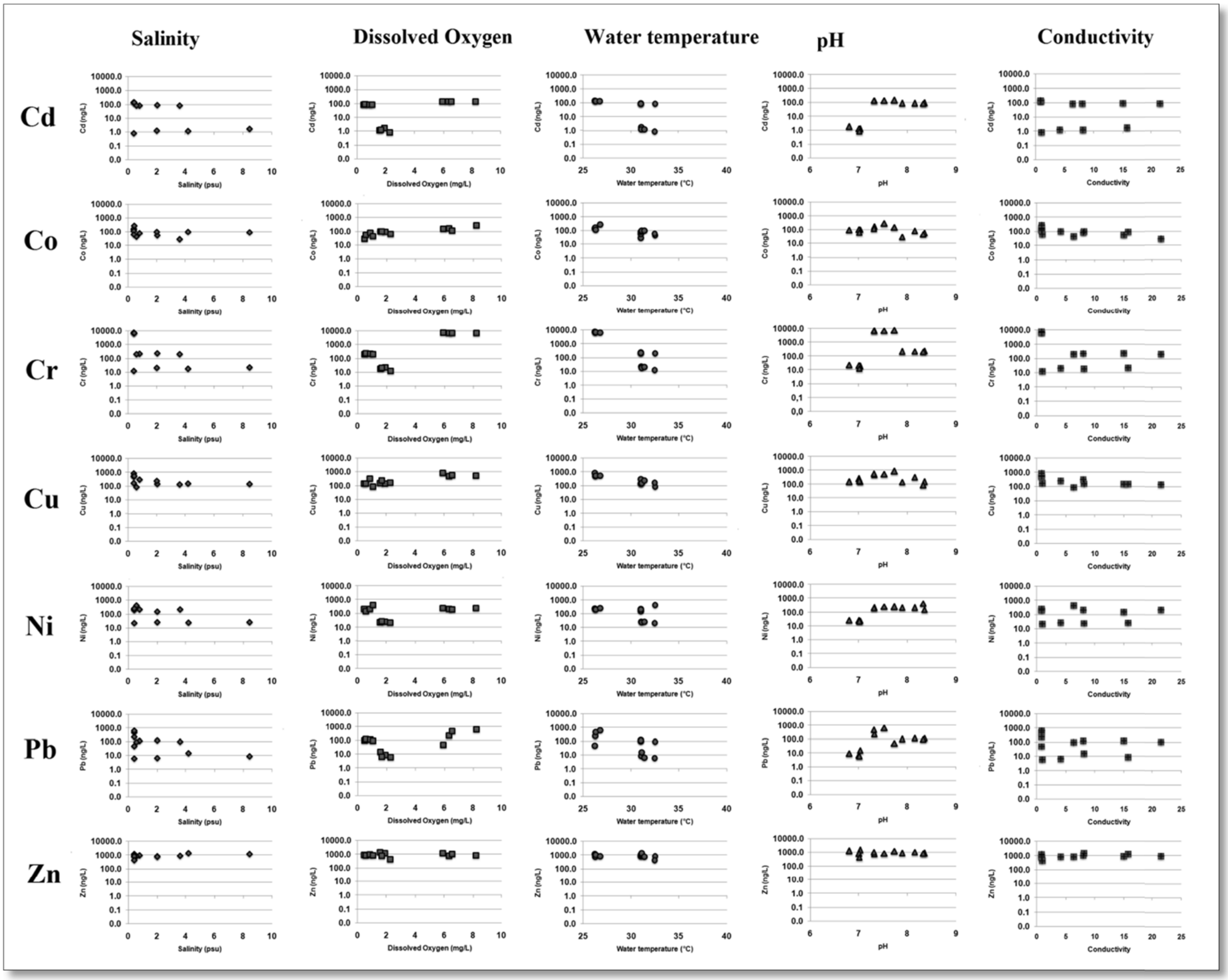


Fig. 5 Relationship of the physico-chemical parameters to the labile trace metal concentrations

abovementioned parameters and their relationships to the dissolved oxygen, period 2 should have the highest trace metal concentration followed by period 3. Period 1 will give the least concentrations. This is true for the actual case of period 2 only but not for periods 1 and 3. During period 3, continuous rainfall led to lesser concentrations of the trace metals. Figure 5 shows that from hypoxic toward oxic level, the concentrations of most of the trace metals (Cd, Co, Cr, Cu, Ni, and Pb) increased. In oxic water, trace metals are mostly driven by sorption reaction while trace metals are controlled by sulfide precipitation in anoxic water (Buffle and van Leeuwen 1992). Sulfides are strong reducing agents. Low concentration of trace metals in the anoxic water is due to metal sulfide precipitation (Zwolsman and Van Eck 1993).

pH Water pH influences the evolution of the concentration of Cd and Ni. The pH of the Pasig River is as follows: period 1, alkaline water; period 2 ~ neutral water; and period 3, near acidic and neutral water. Following the trace metal and pH relationship, period 1 should have the highest concentration while period 3 the least. This is true for the case for period 3. However, period 1 ranked the second in terms of labile trace metal concentration even if the water is alkaline. Period 2 is in the first order because of sorption. In Fig. 5, it presents that the concentrations of the trace metals are lower at pH ~7 then there is increase of concentrations after the neutral level until ph~ 7.5. The trace metals distribution is affected by the pH through acid-base reaction (vanLoon W and Duffy 2000). Trace metals sorption has proportional relationship with increasing pH (Munk et al. 2002). The adsorption of metal cations are more likely to happen when pH increases at the water column, as the latter increases the particle surface negative charge (Gurumurthy et al. 2013). This can also mean that desorption can be experienced predominantly in the acidic water. Water at high pH promotes insolubility of the trace metals.

Salinity and conductivity Most of the dissolved trace metals in periods 1 and 3 have the least concentration near the lake.

These periods showed decreasing salinity and conductivity from the bay to the lake. Flocculation of trace metals can be experienced in the area where the lowest salinity was found (Gerringa et al. 2001; Biati et al. 2010). This observation explains why least trace metal concentrations were found during this period at the mouth of Laguna Lake (except for Cu and Pb, *r*=0.47). Zn has consistent trend having the least concentration near the bay. Zn is mainly influenced by salinity (Boughriet et al. 1992). In this study, a probable relationship between Zn and salinity is observed (*r*=0.53). Like salinity, most of the trace elements have inverse proportion to conductivity. Negative correlations are mostly found for Co, Cr, and Cu.

Water quality threshold

The Pasig River is a highly urbanized water resource. Several industries and companies surround this river. Table 4 shows potential industrial sources of metals. The Philippines would like to comply with the United Nation's AGENDA 21 on the protection of the quality, supply, and potential source of water. In the past, Pasig River is an important water source for domestic consumptions of the local inhabitants. Progressively, water quality degradation sank in, manifested by high turbidity and foul smell. Rehabilitation programs are in place to bring back Pasig River to its previous state. Therefore, the concern on the state of the water quality is important.

If the occurrence of the trace metals in drinking water set by the World Health Organization (WHO 2008) will be followed, the following trace metals exceeded the value; Cr of period 2 which is above 2 μg/L; Cu which is above the minimum value of 0.005 μg/L; and Ni which is above 0.02 μg/L. Cd and Pb is less than the normal occurrence in drinking water (<1 and <5 μg/L, respectively). The Zn occurrence in the freshwater exceeded the WHO consideration as it is more than the range of 0.01–0.5 μg/L. Co is less than the norm. The Canadian Environmental Protection Act, 1999 of the Federal Environmental Quality Guidelines stated that worldwide, Co concentrations is less than 1 μg/L in surface freshwater and 0.3–1.7 μg/L in rainwater. This insinuates that the trace metal concentrations measured in the Pasig River are not negligible.

Comparison of results to other DGT studies

The measured concentrations in this study are compared to other studies that employed DGT in estuaries and coastal waters influenced by anthropogenic activities. For instance, there is an interesting study in the Basque-French estuaries (Montero et al. 2012) situated in an industrial and mining area. The measured concentrations in the Pasig River during periods 1 and 2 are within the range of the values obtained in this study: Cd (2–1570 ng/L) and Ni (30–3650 ng/L). For Cu (66–515 ng/L), the Pasig River has wider range and higher value. The coastal sites of Sardinia in Italy (Schintu et al. 2010) located in a mining and lead-zinc smelting area showed higher Cu concentration range (1.45–2.23 μg/L). The minimum value of Cd concentration in this site is the maximum value obtained in the Pasig River (0.9 μg/L). Patos Lagoon in Brazil (Costa and Wallner-Kersanach 2013), serves as marina, port, and shipyard, has lower Cu concentration (0.11–0.45 μg/L) than the Pasig River. Zn maximum concentration of the Pasig River is the minimum value in this site (0.8 μg/L). Baijao site of the Jiulong River in China is characterized as a highly multi-metal contaminated estuary (Weng and Wang 2014). Pasig River has higher Cd, Cr, and Pb concentration and wider range compared to this river. Jiulong River has ranges of 0.04–0.12, 1.59–7.72, 0.05–0.39 μg/L, respectively. The Co concentration of the Pasig River is within the range of the Jiulong River (0.15–0.95 μg/L). The study in the Tama River of Japan considered contrasted weather condition (Nyein Aung et al. 2008). In this study, Cu was not detected. Compared to the Pasig River, Tama River Ni, Pb, and Zn concentrations (72 h deployment: 0.8, 0.39, and 3.6 μg/L, respectively) have higher value than the Pasig River.

As a whole, measured concentrations in the Pasig River correspond to the results of the studies that have shown

Table 8 Detected sites which have highest and lowest labile trace metal concentrations

Trace metals	Site of highest concentration			Site of lowest concentration		
	Period 1	Period 2	Period 3	Period 1	Period 2	Period 3
Cd	2	1	1	4	4	4
Co	3	4	2	1	3	4
Cr	2	1	1	4	2	4
Cu	3	1	3	4	2	1
Ni	4	4	3	2	3	4
Pb	2	4	2	4	1	4
Zn	3	3	2	4	2	4

Site 1: near Manila Bay; Sites 2 and 3: midstream; Site 4: near Laguna Lake

evident contamination. Although these past studies are relevant, comparing is not easy. True enough that these sites are similar aquatic systems and DGTs were utilized; however, the conditions were not the same. Case in point is the duration of DGT deployment. DGT samplers in this study were immersed for more than 2 weeks, whereas most of the studies are done in shorter periods: Basque-French estuaries: 10 days; Patos Lagoon, Brazil: 72 h; Sardinia, Italy: 3 days; Tama River, Japan: 46, 48, and 72 h; and Jiulong River estuary, China: 48 to 72 h. Besides, not all considered highly seasonal contrasted conditions. Another important issue is that dredging activity was not a component of the reported studies.

Implication on water resources management

Labile trace metals are composed of inorganic and weak complexes species (Gourlay-Francé et al. 2011). These species can dissociate and/or has tendency for chemical changes. Serious ecological concerns are arising as these can be dangerous for the microorganisms like phytoplanktons (Baeyens et al. 2011) at a high concentration (Sigg 2014). Hence, it is recommended to measure the labile trace metals to better assess the water quality of the surface water.

The highest trace metal concentration varies according to season (Table 8). Spatial analysis indicates sources of the labile trace metals. For instance, Cd and Cr were highest near the bay area (site 2 during period 1 and site 1 for periods 2 and 3) and Ni was highest close to the lake (site 4 for periods 1 and 2 and site 2 for period 3). In terms of the lowest concentrations, Cd has lowest value always near the mouth of the lake. In this area also during period 3, least concentrations (Cd, Co, Cr, Ni, Pb, and Zn) were observed.

The Pasig River is in continuous water quality surveillance. The results provide information that trace metal contributes mostly to the natural water system (e.g., Cr and Zn) and needs more monitoring. From this study, water quality measurements can be done according to the susceptibility of the labile trace metals to the spatio-temporal trend. This can give an idea in determining the frequency of sampling campaigns. Labile trace metals that demonstrated spatio-temporal variation (i.e., Co, Cu, Ni, and Pb) need more sampling frequency. These are more exposed to changes in terms of concentration. Those who are sensitive to seasonal/temporal changes (i.e., Cd and Cr) can entail for lesser sampling campaigns. This is as the former are more vulnerable to labile trace metal contributors or sources. While, the one that exhibited constant change (Zn) does not require high sampling frequency. This means that the order of sampling frequency is as follows: spatio-temporally inclined>seasonally/temporally sensitive>unvarying or constant. These recommendations hold unless unanticipated instantaneous contamination is present (e.g., oil leaks).

Conclusion

The study determined the labile trace metals trend in tropical water (estuarine) under episodic event and differing climatic conditions (period 1: dry and simultaneous dredging; period 2: intermediate or in between dry and wet; period 3: wet). If the monsoon regime will be followed, period 1 was under the transition of winter to summer monsoon, period 2 was in an event of winter monsoon, and period 3 encountered summer monsoon.

The periods imply also different physico and hydrochemical characteristics. This discriminates the trend of trace metals. Considerable amount of trace metals were detected that can be a point of environmental concern especially during period 2. The general trend found in trace metal concentrations is as follows: period 2 present the higher one followed by the period 1 and period 3 having the lowest concentrations. The trend presented correlations in between the trace metals and physico-chemical parameters. The statistical tests showed that only period 2 is significantly different from periods 1 and 3.

The sensitivity of DGT as an in situ water sampler is established. This is as DGTs were able to follow the trend of the trace metals under contrasted climate conditions and episodic event. Evaluation based from the water quality threshold and other DGT studies proves that substantial trace metals contamination is present in the Pasig River. Furthermore, from the results, (1) highest trace metals that contribute to the Pasig River were determined (Cr and Zn); (2) three trends of trace metals were identified, such as (i) spatio-temporally inclined, (ii) seasonally or temporally sensitive, and (iii) constant or unvarying; and (3) can latter facilitate in deciding the frequency of sampling or monitoring. The precedence is of this order: spatio-temporally inclined (i.e., Co, Cu, Ni, and Pb)>seasonally/temporally sensitive (i.e., Cd and Cr)>unvarying or constant (i.e., Zn).

This study provides sound baseline information on the state of the water quality and its response to seasonal changes and environmental disturbance. It proves that the Pasig River is susceptible to these changes and disturbance as depicted by the variation of the values obtained from physico-chemical parameters and labile trace metal concentrations. Furthermore, major results presented that on the one hand, intermediate season (from dry to wet) can bring higher concentration of trace metals than the environmental disturbance (dredging). On the other hand, continues rainfall can cause washing effect through dilution (as the concentration of the labile trace metals notably diminished except for Zn).

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