



HAL
open science

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

J.D. Villanueva, Philippe Le Coustumer, A Denis, A Abuyan, Frederic Huneau, Mikael Motelica-Heino, Nicolas Peyraube, Hélène Celle-Jeanton, T.R. Perez, M.V.O Espaldon

► **To cite this version:**

J.D. Villanueva, Philippe Le Coustumer, A Denis, A Abuyan, Frederic Huneau, et al.. Trends of labile trace metals in tropical urban water under highly contrasted weather conditions. *Environmental Science and Pollution Research*, 2015, 22 (18), pp.13842-13857. 10.1007/s11356-015-4835-6 . insu-01165174

HAL Id: insu-01165174

<https://insu.hal.science/insu-01165174>

Submitted on 18 Jun 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

J. D. Villanueva^{1,2,3}, P. Le Coustumer¹, A. Denis², R. Abuyan⁴, F. Huneau^{5,6}, M. Motelica-Heino⁷, N. Peyraube², H. Celle-Jeanton^{8,9,10}, T.R. Perez¹¹, M.V.O. Espaldon³

¹Université de Bordeaux, EA 4592 Géoressources & Environnement, ENSEGID, 1 allée F. Daguin, F-33607 Pessac, France

²Université de Bordeaux, I2M-GCE, B18 Avenue des facultés, 33405 Talence, France

³University of the Philippines, Los Baños, School of Science and Environmental Management, College, Laguna 4031, Philippines

⁴Southern Luzon State University, Mathematics Department, Lucban 4328, Quezon, Philippines

⁵Université de Corse Pascal Paoli, Faculté des Sciences et Techniques, Laboratoire d'Hydrogéologie, Campus Grimaldi, BP 52, F-20250 Corte, France

⁶CNRS, UMR 6134, SPE, F-20250 Corte, France

⁷Université d'Orléans, UMR CNRS 7327, ISTO, Campus Géosciences, 1A rue de la Férellerie, F-45071 Orléans Cedex 2, France

⁸Clermont Université, Université Blaise Pascal, Laboratoire Magmas et Volcans, BP 10448, 63038 Clermont-Ferrand, France

⁹CNRS, UMR 6524, LMV, 63038 Clermont-Ferrand, France

¹⁰IRD, R 163, LMV, 63038 Clermont-Ferrand, France

¹¹Ateneo de Manila University, Department of Environmental Science, Loyola Height, Quezon City 1108, Philippines

Contact author: Philippe Le Coustumer

E-mail: plc@lnet.fr

1 **Abstract**

2
3
4 3 The spatio-temporal trend of trace metals (Cd, Co, Cr, Cu, Ni, Pb, and Zn) in a tropical urban
5 4 estuary under the influence of monsoon was determined using Diffusive Gradient in Thin
6 5 Films (DGT) *in situ* samplers. Three (3) different climatic periods were observed: Period 1-
7 6 dry with dredging activity; Period 2- intermediate meaning from dry to wet event; and Period
8 7 3- wet having continuous rainfall. Conforming to monsoon regimes, these periods correspond
9 8 to the following: transition from winter to summer; winter; and summer monsoons,
10 9 respectively. The distinction of each period is defined by their specific hydrological and
11 10 physico-chemical conditions.

12 11 Substantial concentrations of the trace metals were detected. The distribution and trend
13 12 of the trace metals under the challenge of a tropical climate were able to follow using DGT as
14 13 a sensitive *in situ* sampler. In order to identify the differences among periods statistical
15 14 analyses were performed. This allowed discriminating Period 2 (oxic water) as significantly
16 15 different compared to other periods. The spatio-temporal analysis was then applied in order to
17 16 distinguish the trend of the trace metals. Results showed that the trend of trace metals can be
18 17 described according to their response to: (i) seasonal variations (Cd and Cr); (ii) spatio-
19 18 temporal conditions (Co, Cu, Ni, and Pb); and (iii) neither (i) nor (ii) meaning exhibiting no
20 19 response or having constant change (Zn). The correlation of the trace metals and the physico-
21 20 chemical parameters reveals that Cd, Co, Cu, and Cr are proportional to the dissolved oxygen
22 21 (DO); Cd and Ni are correlated pH; and Zn lightly influenced by salinity.

23 **Keywords:** labile trace metal, urban water, tropical climate, monsoon, statistics, DGT
24

1 Introduction

2
3
4 3 Tropical waters are dynamic environments. There are loads of factors that influence these
5 4 aqueous systems such as different activities like estuarine mixing, tidal currents, sediment
6 5 remobilization, and fine grain sediments transport (Kuehl *et al.* 1996 and Breckel *et al.* 2005).
7 6 Moreover, seasonal timescales (*e.g.* monsoonal climate) induced by precipitation and other
8 7 weather conditions affect the hydrological cycle (Chakraborty *et al.* 2010). Under monsoon
9 8 regime, seasonal differences are pronounced and mostly distinguished by the absence and
10 9 presence of precipitation (Takahashi 2013). This type of climate is challenging as uptight
11 10 circumstances are at hand. Alterations in the hydro-climatic scheme can be experienced
12 11 (Hestir *et al.* 2013). For instance, incident of disruptions of the ocean-atmosphere interactions
13 12 can occur (Shirasago-Germán *et al.* 2015). These are principal sources of disturbance in water
14 13 basins.

15 14 Nowadays, the increasing apprehensions on the tropical waters not only rest in the
16 15 hydro-climatic conditions but on the water quality as well. Particular interests are on the trace
17 16 metals in terms of contamination and environmental risks. These are important environmental
18 17 issues. Studies aim to know the possible effects of metals in urban runoff (Herngren *et al.*
19 18 2005) and pollution discharges (Ki *et al.* 2011) in the aquatic system and the biota.

20 19 Trace metals are ubiquitous, easily transported to water (Chen *et al.* 2014). The
21 20 behavior of the trace metals in estuaries varies greatly due to environmental factors like
22 21 hydrodynamic residence time, mixing patterns of transport processes and reservoir
23 22 management (Hatje *et al.* 2003; Masson *et al.* 2006; Masson *et al.* 2011). Another factor is the
24 23 water chemistry that changes from freshwater to saltwater that influences their occurrence
25 24 (Jian and Wen 2009). The trend differs according to seasonal changes and suspended
26 25 sediments concentrations (Park *et al.* 2011). Precipitation, for example, can play as an
27 26 atmospheric wash out that delivers trace metals to aquatic ecosystem through deposition
28 27 mechanism (Özsoy and Örnektekin 2009). To deduce, in tropical waters, trace metals can be
29 28 perceived as active components in the environment and, at the same time, reactive elements in
30 29 the aqueous systems. These directed towards serious intentions and efforts to assess the water
31 30 quality of tropical waters including estuaries specially those who are situated in highly
32 31 urbanized zones.

32 32 Labile trace metals are vital in examining the state of these tropical waters. This
33 33 fraction can eventually help in assessing toxicity and associated risks (Pinhero and Domingo

1 2005). However, measuring these specific forms requires collecting voluminous water which
2 is tedious and time consuming (Graveline *et al.* 2010). Alternatively, *in situ* sampling
3 technique can be employed. It can provide data over longer periods of time and reduces some
4 of the drawbacks of grab sampling (INAP 2002).

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

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

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

28 Three (3) local seasons were considered: dry, transition from dry to wet (intermediate),
29 and wet. The difference in the seasonal pattern can lead to a premise that the trace metals
30 trend will also be significantly distinct from each period. To assess if this premise holds,
31 statistics were performed. Hydrochemistry and physical conditions were utilized as
32 parameters. Spatio-temporal analysis was applied to better explain the labile trace metal
33 trends.

1 **Materials and Methods**

3 **Site description**

5 The Pasig River is an estuary of about 27 km long and approximately 80 m wide. The
6 catchment is composed of 4 main tributaries (San Juan River, Marikina River, Napindan
7 River, and Pateros-Taguig River) and 43 minor tributaries. It is located in the heart of Manila,
8 Philippines (Fig. 1) and connects Laguna Lake (east), the biggest freshwater lake in the
9 Philippines and the Manila Bay (west). The salinity intrusion from the bay can reach towards
10 the whole stretch of the Pasig River to the mouth of the lake.

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

19 **Sampling Design**

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

27 Four sites (Fig. 1) were chosen representing the upstream (point 1: mouth of the
28 Manila Bay), midstream (points 2 and 3 which are near the San Juan and Marikina River,
29 respectively); and downstream (point 4: mouth of the Laguna Lake), with an approximate
30 distance of 7 km in each site. Point 4 signals freshwater interference in the river. In each site,
31 DGT in duplicates were fully immersed for 18 days. DGT field blank was provided per
32 sampling campaign. Strict protocols of DGT deployment (Villanueva 2013) were followed for
33 all sampling campaigns. Immediately, after the retrieval, the DGT probes were rinsed with de-

1 ionized water and placed in pre-cleaned properly marked resealable plastic containers. A
2 cooling compartment was prepared to transport the probes directly to the laboratory. DGTs
3 were put in the refrigerator before the extraction of the trace metals.

4 During each sampling campaign, physical parameters such as dissolved oxygen (DO),
5 water temperature, salinity, conductivity and pH were measured *in situ* using YSI 6600 V2
6 data probe at a depth of approximately 1m below the water surface. The range of values is
7 presented in [Table 2](#). According to the study of [Materum 2010 and Villanueva 2013](#), total
8 organic carbon (TOC) of the Pasig River ranged from 3.4 to 4.5 mg/L during May 2010 and
9 3.5 to 7.4 mg/L for January 2011.

11 **Determination of trace metals concentration**

12
13 Standard solution Chelex-100 DGT probes were purchased from DGT Research Ltd,
14 Lancaster, UK. DGT field blanks were extracted and analyzed using the same procedure for
15 the DGTs immersed in the water. Laboratory procedural blanks were prepared. The detection
16 limits were determined following the already established procedure ([Pettke et al.2012](#)). In the
17 laboratory, the membrane filter and the diffusive gel were carefully removed from the piston
18 using Teflon tweezers. The gel was separated and placed into a clean *polypropylene* micro
19 centrifuge tube. 1 ml of 1M of HNO₃ (Fisher Scientific Analar grade) was added. After 24
20 hours, dilution was performed. The trace metals were determined using inductively coupled
21 plasma-mass spectrometry (Thermo Scientific*ELEMENT2*ICP-MS). From the elution
22 solution, the accumulated mass of the trace metals then the concentrations were calculated.
23 The detailed laboratory procedures ([Dunn et al. 2007; Aung et al. 2008](#)) and calculations
24 ([DGT Research 2002](#)) can be found elsewhere ([INAP 2002](#)).

26 **Trend Analysis approach**

27
28 Two (2) approaches were applied: statistical and spatio-temporal analyses. The statistical
29 analyses permit discriminating the periodical differences. This can also describe the
30 relationship in between parameters: hydro and physico-chemical variables and trace metal
31 concentrations. The spatio-temporal analysis is valuable in determining the trends of the trace
32 metals by evaluating their response in each seasonal or temporal variation and inspecting the
33 increase or decrease of the concentration in a spatial sense.

1 **Statistical tests**

2
3 In order to determine the significance among periods using the concentrations of the pool of
4 labile metals, series of statistical tests were utilized. Student *t*-test was considered as it is
5 appropriate for small data sets (population samples). This test is normally applied for the
6 comparison of two means (Fritz and Berger 2015). Hence, allowing comparing a period to
7 another using the concentration of the trace metals as data sets. Two-tailed *t*-test was
8 employed pairing each period's data sets (trace metals concentrations). The significance level
9 was determined using the value $\alpha=0.05$. To validate and illustrate the difference, hierarchical
10 cluster analysis was performed.

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

16 **Spatio-temporal analysis**

17
18 The spatio-temporal analysis can discriminate the trend of each labile trace metals by
19 examining the tendency of concentrations. The variation can be sorted according to the
20 inclination of each trace metal. This approach aids in determining which trace metals are
21 susceptible to: (i) seasonal or climatic conditions changes; (ii) spatial or local variations; (iii)
22 both spatial and seasonal disparities; and (iv) neither spatial nor local situation (absence of
23 changes). The first can be related to temporal events, while, the second can be associated to
24 anthropogenic activities and/or instantaneous contamination. The last can be described as
25 having a conservative or constant trend.

1 Results

3 Environmental background and Physico-chemical parameters

5 The physico-chemical characteristics of the water were recorded during each sampling period
6 (Table 2). Period 1 combines two (2) episodic events: dry season and dredging activity. The
7 area experienced shortage on rainfall. Periods 2 and 3, on the other hand, both experienced
8 pronounced rainfall (~79 mm). Period 2 showed the lowest record for water temperature,
9 salinity, and conductivity. This period has the highest DO level. The periods were best
10 described by the DO as the oxygen levels greatly varied through periods. DO range from 0.45
11 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.
12 Only Period 2 passed the Department Administrative Order (DAO 34) of the Philippine
13 government. The DO requirement is >5 mg/L. The salinity was pronounced on Period 3 (0.39
14 to 8.44 psu) which also indicated water mixing. In Period 2, salinity was almost constant
15 along the Pasig River stretch. Compared to DO, salinity and conductivity, pH did not exhibit
16 strong variations.

18 Labile Trace Metals in the Pasig River

20 The general trend observed was that most of labile trace metals concentrations increased
21 during Period 2 then decreased during Period 3 (Fig. 2 and Table 3). However, throughout the
22 period, Zn seemed stable. During Period 1, the only DGT-trace metals (at maximum) found at
23 the river end is Ni located near the mouth of the bay (Point 1). Minimum Ni was detected at
24 the confluence of San Juan River (Point 2) while Co has the least at the mouth of the bay
25 (Point 1). Maximum concentrations were mostly near the confluence of San Juan River (Point
26 2: Cr, Cd and Pb) and convergence of Marikina River (Point 3: Co, Cu and Zn).

27 The minimum concentrations of Cr, Cu, Zn, Cd and Pb were found near the mouth of
28 the lake area (Point 4). In this period, at the river ends (Points 1 and 4), lower values of Cr,
29 Co, Cu, Cd and Pb were found. In contrast, Ni has the lower values in the midstream (Points 2
30 and 3). Zn concentration spatially varies. In Period 2, minimum value of Pb is found near the
31 mouth of the bay (Point 1); Cr, Cu and Zn were at the confluence of San Juan River (Point 2);
32 Co and Ni near Marikina River area (Point 3); and Cd near the mouth of the lake (Point 4).
33 Maximum values of Cr, Cu, Zn and Cd were found near the mouth of the bay (Point 1), while,

1 Co, Ni and Pb at the mouth of the lake (Point 4). At this period, the maximum values are all
2 found at the river ends (Point 1 and 4).

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

9 **Labile trace metal concentrations and statistical difference among periods**

10
11 The Student *t*-test was performed by pairing the data (Period 1 vs. Period 2; Period 1 vs.
12 Period 3; and Period 2 vs. Period 3). The result of the statistical test is shown in **Table 5**.
13 Significant difference were found in between Period 1 and 2 ($\alpha=0.05$; $p= 0.022$) and Period 2
14 and 3 ($\alpha=0.05$; $p= 0.016$) but not for Period 1 and Period 3 ($\alpha=0.05$; $p= 0.437$).

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

24 **Correlation among parameters**

25
26 The correlation among physico-chemical parameters is shown in **Table 6**. DO has an inverse
27 relationship to other physico-chemical parameters. This inverse relationship is more
28 pronounced with respect to the water temperature ($\alpha=0.05$; $p= -0.91$). In terms of salinity,
29 Periods 1 and 3 showed evident water mixing. Although, the salinity values are lower in
30 Period 1, water mixing was also observed. There is also a weak confirmation of the inverse
31 relationship of DO to salinity ($\alpha=0.05$; $p= -0.42$). Water temperature and salinity are
32 positively correlated to conductivity, whereas, DO showed negative correlation.

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

7 8 9 **Discussion**

10 11 **Environmental background**

12
13 The Philippines is within the regime of monsoon seasons of Southeast Asia (Loo *et al.* 2014).
14 This type of climate system is dynamic as it is characterized by wet spell having periodic
15 heavy rains and dry spell with seasonal changes driven by the wind directions (Stephens *et al.*
16 2008). The active factors coming from the interaction of the oceans and atmosphere could
17 lead to droughts and wet episodes (Buckley *et al.* 2014). It has significant impacts on the
18 environment including water systems (Cook and Jones 2012; Varis *et al.* 2012). Monsoon
19 climate dictates the variability of the temperature of the water catchments (Meybeck 2009)
20 and hydrodynamics (Fuchs *et al.* 2012). It can also affect the quality of the water resource
21 (Wilkerson *et al.* 2002; Hestir *et al.* 2013). For these reasons, under this climate regime, it is
22 noteworthy to know how the hydrochemistry of the Pasig River responds.

23 24 *Monsoonal Climate Regime*

25
26 Seasonality of monsoon can be categorized according to months. Cruz *et al.* 2012 explains
27 that the main monsoon regimes are the Northeast monsoon and the Southwest monsoon.
28 Northeast monsoon or the winter monsoon can be expected on November to March.
29 Southwest monsoon or summer monsoon starts May and ends on September. On October, the
30 transition from Southwest monsoon to Northeast monsoon occurs. Adhering to the monsoon
31 regime, Period 1 fell under the transition from Northeast to Southwest monsoon (in between

1 winter and summer monsoon); Period 2 experienced Northeast/winter monsoon; and Period 3
2 encountered Southwest/summer monsoon.

3 4 *Hydro-physico-chemical variation*

5
6 The variation of DO followed by the water mixing express the differences among periods.
7 Through periods there is a shift from almost anoxic to oxalic then hypoxic waters. In terms of
8 incidence of water mixing, the trend is as follows: Period 3>Period 1>Period 2. The
9 conductivity follows the trend of the salinity, Period 2 having least values. The water
10 temperature is almost the same for Periods 1; and 3 and lowest during Period 2. For pH,
11 Period 1 was more basic than Period 2 and Period 3 played slightly acid to neutral water.

12 13 **Spatio-temporal analysis on trace metals**

14
15 Period 1 as stated was under a dry weather. Twenty (20) days prior to the sampling campaign,
16 there was only 0.8 mm of rainfall. A total of 6 mm of rainfall was accumulated within this
17 sampling period which implied river low flow. At this period, there was an on-going dredging
18 activity. Dredging is an ecological disturbance that can affect the sediment structure (Mackie
19 *et al. 2007*; Je *et al. 2007*). Both particulate forms (Nayar *et al. 2004*) and bioavailability
20 (Lewis *et al. 2001*) of trace metals in the water column could increase (Cabrita 2014) due to
21 resuspension (Fathollahzadeh *et al. 2015*). Studies showed that the release of the dissolved
22 trace metals can be attributed to the binding mechanism to the solid phase or on the
23 mechanisms involving sorptive phases (van den Berg *et al. 2001*). Also the changes in the
24 water chemistry like pH and ionic strength can affect the release of the dissolved trace metals
25 (*i.e.* lower pH increase the solubility of the trace metals).

26 In wet seasons, atmospheric deposition, surface run-off (Witt *et al. 2010*), and
27 atmospheric precipitation (Migliavacca *et al. 2005*; Vuai *et al. 2011*) contribute to trace
28 metals delivered to the receiving body (Dunn *et al. 2007*) such as rivers (Aung *et al. 2008*).
29 Periods 2 and 3 both received almost the same amount of precipitation throughout the
30 sampling campaign. However, twenty days before the sampling activity in Period 3, the
31 accumulated rainfall amount was only 125.2 mm already, whereas, Period 2 received only
32 14.4 mm. These periods displayed different hydro-chemical characteristics. The hydro-
33 chemical condition illustrates the distinction of this period being least in salinity, water

1 temperature, and conductivity at the same time highest in DO values. Period 3 has the highest
2 recorded water temperature, salinity, and conductivity. Knowing the hydro-chemical
3 background, the interesting issue is on what can be the response of each of these differing
4 conditions to the labile trace metal concentrations.

6 *Trace metal variation*

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

17 *Spatio-temporal variation of trace metals*

19 As a point of observation, the variation of each trace metals follows three (3) trends. The trace
20 metals can be group according to their response in a spatio-temporal approach. First, the trace
21 metals that exhibited seasonal (temporal) variation or changes of the concentrations differ
22 between periods. Second, trace metals that are sensitive spatially and temporally, indicating
23 variations in each site and in each period (season). Third, a trace metal that is constant
24 through time. Seasonal variation is observed in labile trace metals Cd, and Cr. The spatial and
25 temporal sensitive trace metals are depicted by Co and Cu and mainly by Ni and Pb. Among
26 the trace metals, Zn has a different trend by appearing constant through time.

28 *Cr and. Zn: The trend and origin*

30 Significant concentrations of trace metals were detected in the Pasig River in varying amount.
31 There is an interesting aspect in terms of anthropogenic and geogenic origins. In **Fig. 3**, the
32 largest portions are Cr and Zn. Among the trace metals, Cr showed the most considerable
33 trend in between periods. The results showed how the dissolved Cr in the Pasig River is
34 sensitive to seasonal and hydrochemistry changes. There is a notable point in Cr being the

1 highest during Period 2. **Table 4** provided probable sources of emissions situated at the
2 riverbank. Cr could also be associated to atmospheric fallout or rainfall and surface runoffs
3 (**Neal et al. 1996**). During Period 3 series of rainfall served as a wash out of Cr that is why
4 lesser concentration was detected.

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

9 The fractionation of Zn/Cd can explain the trace element pattern as a response to the
10 geochemical phases. Its concentration ratio changes according to different geochemical
11 phases occurring in geochemical path such as in streams, rivers, estuaries, coastal seas and
12 open oceans (**Gerringa et al. 2001**). The result of this study showed that Zn has a significant
13 relationship to Cd ($r=0.61$). Zn/Cd ratio can give clear estimates on the relative geochemical
14 behavior (**Mazeina et al. 1999**) and can trace their sources. The Zn/Cd ratio obtained ranges
15 9.32-11.65 for Period 1; 5.88-8.48 for Period 2; and 502.72-1174.83 for Period 3. The ratio
16 that ranges from 5–10 can be attributed for oceanic waters (**Gerringa et al. 2001**). In the world
17 record, the ratio 7.5 is said to be carried by riverine suspended sediments to the oceans in
18 dissolved phase (**Viers et al. 2009**). Higher ratio (>500), like in Period 3 can be traced in ore
19 elements from basaltic, igneous rocks and sediments (**Gerringa et al. 2001; Nolting et al.**
20 **1999; Gottesman and Kampe 2007**). Thus, there is an indication that most of Zn came from
21 runoff.

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

23 Physico-chemical environmental parameters are very essential in explaining the
24 chemical spatial distribution of the trace metals. DO plays an important role which is highly
25 influenced by seasonal changes (**Sokolowski et al. 2001**). As a main point, DO give inverse
26 relationship to other physico-chemical parameters. This inverse relationship is more distinct
27 with respect to the water temperature followed by conductivity. There is a weak proportional
28 relationship in between DO and salinity. Although, the results confirmed the direct
29 relationship in between conductivity and salinity, two (2) tendencies were noticed. Period 1
30 showed higher slopes than Period 3. Although salinity is lesser in Period 1, conductivity is
31 higher. pH displayed weak inverse correlation to salinity and conductivity.

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

6 **DO.** Pasig River showed that trace metals (Cd, Co, Cr, Cu, and Pb) are directly
7 proportional to DO except for Ni and Zn. Oxidic water favors dissolved metals (Buffle and van
8 Leeuwen 1993). The oxidic levels of each period are distinguished accordingly: Period 1 is near
9 anoxia; Period 2 shows oxidic water; and Period 3 is hypoxic water (Table 2). Using the
10 abovementioned parameters and their relationships to the dissolved oxygen, Period 2 should
11 have the highest trace metal concentration followed by Period 3. Period 1 will give the least
12 concentrations. This is true for the actual case of Period 2 only but not for Periods 1 and 3.
13 During Period 3, continuous rainfall led to lesser concentrations of the trace metals. Fig. 5
14 shows that from hypoxic towards oxidic level the concentrations of most of the trace metals
15 (Cd, Co, Cr, Cu, Ni, and Pb) increased. In oxidic water, trace metals are mostly driven by
16 sorption reaction; while, trace metals are controlled by sulfide precipitation in anoxic water
17 (Buffle and van Leeuwen 1992). Sulfides are strong reducing agents. Low concentration of
18 trace metals in the anoxic water is due to metal sulfide precipitation (Zwolsman and Van Eck
19 1993).

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

1 **Salinity and Conductivity.** Most of the dissolved trace metals in Periods 1 and 3 have
2 the least concentration near the lake. These periods showed decreasing salinity and
3 conductivity from the bay to the lake. Flocculation of trace metals can be experienced in the
4 area where the lowest salinity was found (Gerringa *et al.* 2001; Biati *et al.* 2010). This
5 observation explains why least trace metal concentrations were found during this period at the
6 mouth of Laguna Lake (except for Cu and Pb, $r= 0.47$). Zn has consistent trend having the
7 least concentration near the bay. Zn is mainly influenced by salinity (Boughriet *et al.* 1992).
8 In this study a probable relationship between Zn and salinity is observed ($r=0.53$). Like
9 salinity, most of the trace elements have inverse proportion to conductivity. Negative
10 correlations are mostly found for Co, Cr, and Cu.

11 **Water Quality Threshold**

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

20 If the occurrence of the trace metals in drinking water set by the World Health
21 Organization (WHO 2008) will be followed, the following trace metals exceeded the value;
22 Cr of Period 2 which is above 2 $\mu\text{g/L}$; Cu which is above the minimum value of 0.005 $\mu\text{g/L}$;
23 and Ni which is above 0.02 $\mu\text{g/L}$. Cd and Pb is less than the normal occurrence in drinking
24 water ($<1 \mu\text{g/L}$ and $<5\mu\text{g/L}$, respectively). The Zn occurrence in the freshwater exceeded the
25 WHO consideration as it is more than the range of 0.01-0.5 $\mu\text{g/L}$. Co is less than the norm.
26 The Canadian Environmental Protection Act, 1999 of the Federal Environmental Quality
27 Guidelines stated that worldwide, Co concentrations is less than 1 $\mu\text{g/L}$ in surface freshwater
28 and 0.3-1.7 $\mu\text{g/L}$ in rainwater. This insinuates that the trace metal concentrations measured in
29 the Pasig River are not negligible.

1 Comparison of results to other DGT studies

2
3 The measured concentrations in this study are compared to other studies that employed DGT
4 in estuaries and coastal waters influenced by anthropogenic activities. For instance, there is
5 an interesting study in the Basque-French estuaries (Montero *et al.* 2012) situated in an
6 industrial and mining area. The measured concentrations in the Pasig River during Periods 1
7 and 2 are within the range of the values obtained in this study: Cd (2-1570 ng/L) and Ni (30-
8 3650 ng/L). For Cu (66-515 ng/L), the Pasig River has wider range and higher value. The
9 coastal sites of Sardinia in Italy (Schintu *et al.* 2010) located in a mining and lead-zinc
10 smelting area showed higher Cu concentration range (1.45-2.23 µg/L). The minimum value of
11 Cd concentration in this site is the maximum value obtained in the Pasig River (0.9 µg/L).
12 Patos Lagoon in Brazil (Costa and Wallner-Kersanach 2013), serves as marina, port and
13 shipyard, has lower Cu concentration (0.11-0.45 µg/L) than the Pasig River. Zn maximum
14 concentration of the Pasig River is the minimum value in this site (0.8 µg/L). Baijao site of
15 the Jiulong River in China is characterized as a highly multi-metal contaminated estuary
16 (Weng and Wang 2014). Pasig River has higher Cd, Cr, and Pb concentration and wider range
17 compared to this river. Jiulong River has ranges of 0.04-0.12 µg/L, 1.59-7.72 µg/L, 0.05-0.39
18 µg/L, respectively. The Co concentration of the Pasig River is within the range of the Jiulong
19 River (0.15-0.95 µg/L). The study in the Tama River of Japan considered contrasted weather
20 condition (Aung *et al.* 2007). In this study, Cu was not detected. Compared to the Pasig River,
21 Tama River Ni, Pb, and Zn concentrations (72 hours deployment: 0.8 µg/L, 0.39 µg/L, 3.6
22 µg/L, respectively) have higher value than the Pasig River.

23 As a whole, measured concentrations in the Pasig River correspond to the results of
24 the studies that have shown evident contamination. Although these past studies are relevant,
25 comparing is not easy. True enough that these sites are similar aquatic systems and DGTs
26 were utilized however the conditions were not the same. Case in point is the duration of DGT
27 deployment. DGT samplers in this study were immersed for more than two weeks, whereas,
28 most of the studies are done in shorter periods: Basque-French estuaries: 10 days; Patos
29 Lagoon, Brazil: 72 hours; Sardinia, Italy: 3 days; Tama River, Japan: 46, 48, and 72 hours;
30 and Jiulong River estuary, China: 48 to 72 hours. Besides, not all considered highly seasonal
31 contrasted conditions. Another important issue is that dredging activity was not a component
32 of the reported studies.

1 **Implication on water resources management**

2
3 Labile trace metals are composed of inorganic and weak complexes species (Gourlay-Francé
4 *et al.* 2011). These species can dissociate and/or has tendency for chemical changes. Serious
5 ecological concerns are arising as these can be dangerous for the microorganisms like
6 phytoplanktons (Baeyens *et al.* 2011) at a high concentration (Sigg 2014). Hence, it is
7 recommended to measure the labile trace metals to better assess the water quality of the
8 surface water.

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

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

1 Conclusion

2
3
4 3 The study determined the labile trace metals trend in tropical water (estuarine) under episodic
5 4 event and differing climatic conditions (Period 1: dry and simultaneous dredging; Period 2:
6 5 intermediate or in between dry and wet; Period 3: wet). If the monsoon regime will be
7 6 followed: Period 1 was under the transition of winter to summer monsoon; Period 2 was in an
8 7 event of winter monsoon; and Period 3 encountered summer monsoon.

9 8 The periods imply also different physico and hydro-chemical characteristics. This
10 9 discriminates the trend of trace metals. Considerable amount of trace metals were detected
11 10 that can be a point of environmental concern especially during Period 2. The general trend
12 11 found in trace metal concentrations is as follows: Period 2 present the higher one followed by
13 12 the Period 1 and Period 3 having the lowest concentrations. The trend presented correlations
14 13 in between the trace metals and physico-chemical parameters. The statistical tests showed that
15 14 only Period 2 is significantly different from Periods 1 and 3.

16 15 The sensitivity of DGT as an *in-situ* water sampler is established. This is as DGTs
17 16 were able to follow the trend of the trace metals under contrasted climate conditions and
18 17 episodic event. Evaluation based from the water quality threshold and other DGT studies
19 18 proves that substantial trace metals contamination is present in the Pasig River. Furthermore,
20 19 from the results: 1. highest trace metals that contribute to the Pasig River were determined (Cr
21 20 and Zn); 2. three (3) trends of trace metals were identified: (i) spatio-temporally inclined; (ii)
22 21 seasonally or temporally sensitive; (iii) constant or unvarying; and 3. the can latter facilitate in
23 22 deciding the frequency of sampling or monitoring. The precedence is of this order: spatio-
24 23 temporally inclined (*i.e.* Co, Cu, Ni and Pb)>seasonally/temporally sensitive (*i.e.* Cd and Cr)>
25 24 unvarying or constant (*i.e.* Zn).

26 25 This study provides sound baseline information on the state of the water quality and its
27 26 response to seasonal changes and environmental disturbance. It proves that the Pasig River is
28 27 susceptible to these changes and disturbance as depicted by the variation of the values
29 28 obtained from physico-chemical parameters and labile trace metal concentrations.
30 29 Furthermore, major results presented that on one hand, intermediate season (from dry to wet)
31 30 can bring higher concentration of trace metals than the environmental disturbance (dredging).
32 31 On the other hand, continues rainfall can cause washing effect through dilution (as the
33 32 concentration of the labile trace metals notably diminished except for Zn).

1 **Acknowledgement**

2
3 This research was funded by the Lyonnaise des Eaux Company, Bordeaux, France and was done with
4 the help of the Pasig River Rehabilitation Commission (PRRC), LCDR Christopher Meniado of the Philippine
5 Coast Guards (PCG) and his staff, the Department of Natural Resources and Environment-Environmental
6 Management Bureau (DENR-EMB) and Dr. Gemma Narisma, Genie Lorenzo and James Simpas of the Manila
7 Observatory. The authors are also grateful to the French Embassy in the Philippines for giving financial
8 assistance for field mobility, the European Union ERASMUS MUNDUS External Cooperation Window (ECW)
9 Lot 12/13 and the Bourse Eiffel Excellence (Programme 2012-2013) from the French Ministry of Foreign
10 Affairs for providing the academic grant and to Prof. Jorg Schäfer, Dr. Farah Homsy and Mr. Patrick Sin for all
11 their technical inputs and support; and M. Jean Bernard Delmas for his encouragements.
12
13

1 **References**

- 2 Aiga H, Umenai T (2002) Impact of improvement of water supply on household economy in a
3 squatter area of Manila. *Soc. Sci. Med.* 55:627-641. DOI:10.1007/BF02932265. PMID:
4 PMC2723519.
- 5 Alfaro-De la Torre MC, Beaulieu PY, Tessier A (2000) *In situ* measurement of trace metals in
6 lakewater using the dialysis and DGT techniques. *Anal. Chim. Act.* 418:53-68.
7 DOI:10.1016/S0003-2670(00)00946-6.
- 8 Atkinson CA, Jolley DF, Simpson SL (2007) Effect of overlying water pH, dissolved oxygen,
9 salinity and sediment disturbances on metal release and sequestration from metal
10 contaminated marine sediments. *Chemosphere.* 69:1428-1437. DOI: 10.1021/es4009272.
- 11 Audry S, Jörg S, Blanc G, Bossy C, Lavaux G (2004) Anthropogenic components of heavy
12 metal (Cd, Zn, Cu, Pb) budgets in the Lot-Garonne fluvial system (France). *Appl Geochem*
13 19:769-786. DOI: 10.1016/j.apgeochem.2003.10.002
- 14 Aung NN, Nakajima F, Furumai H (2008) Trace metal speciation during dry and wet weather
15 flows in the Tama River, Japan, by using diffusive gradients in thin films (DGT). *J.*
16 *Environ. Manage.* 10:219-230. DOI: 10.1016/0165-9936(81)80014-3.
- 17 Baeyen W, Bowie AR, Buesseler K, Elskens M, Gao Y, Lamborg C, Leermakers M, Remenyi
18 T, Zhang H (2011) Size-fractionated labile trace elements in the Northwest Pacific and
19 Southern Oceans. *Marine Chemistry* 126:108-113. DOI:10.1016/j.marchem.2011.04.004
- 20 Biati A, Karbassi AR, Hassani AH, Monavari SM, Moattar F (2010) Role of metal species in
21 flocculation rate during estuarine mixing. *International Journal of Science and Technology*
22 2:327-336. ISSN: 1735-1742. DOI: 10.1007/BF03326142.
- 23 Boughriet A, Oudane B, Fisher JC, Wartel FM, Leman G (1992) Variability of Dissolved Mn
24 and Zn in the Seine Estuary and chemical speciation of these metals in suspended matter.
25 *Wat. Res.* 26:10,1359-1378. DOI: 10.1016/0043-1354(92)90130-V
- 26 Breckel EJ, Emerson S, Balistrieri LS (2005) Authigenesis of trace metals in energetic tropical
27 shelf environments. *Cont. Shelf. Res.* 25:1321-1337. DOI: 10.1016/j.csr.2005.02.001.
- 28 Buckly BM, Fletcher R, Wang S-Y S, Zottoli B, Pottier C (2014) Monsoon extremes and
29 society over the past millennium on mainland Southeast Asia. *Quat. Sci. Rev.* 95:1-19.
30 <http://dx.doi.org/10.1016/j.quascirev.2014.04.022>.
- 31 Buffle J, van Leeuwen HP (1992) *Environmental Particles. Environmental and physical*
32 *chemistry series. Volume 1, Lewis Publishers, Inc.*
- 33 Buffle J, van Leeuwen HP (1993) *Environmental Particles. Environmental Analytical and*
34 *Physical Chemistry Ser. CRC Press ISBN-13.9780873718950*
- 35 Cabrita MT (2014) Phytoplankton community indicators of changes associated with dredging
36 in the Tagus estuary (Portugal). *Environ. Pollut.* 191:17-24.
37 DOI:10.1016/j.envpol.2014.04.001.
- 38 Chakraborty P, Babu PVR, Acharyya T, Bandyopadhyay D (2010) Stress and toxicity of
39 biologically important transition metals (Co, Ni, Cu and Zn) on phytoplankton in a tropical
40 freshwater system: An investigation with pigments analysis by HPLC. *Chemosphere*
41 80:548-553. DOI: 10.1016/j.chemosphere.2010.04.039.

- 1 Chen J, Zhang R, Wang H, Li J, Hong M, Li X (2014) Decadal modes of seas surface salinity
2 and the water cycle in the tropical Pacific Ocean: The anomalous late 1990. Deep-Sea Res.
3 PT I 84:38-49. DOI:10.1016/j.dsr.2013.10.005.
- 4 Clarisse O, Foucher D, Hintelmann H (2009) Methylmercury speciation in the dissolved phase
5 of a stratified lake using the diffusive gradient in thin film technique. Environ.
6 Pollut. 157:987-993. DOI:10.1016/j.envpol.2008.10.012.
- 7 Cook CG, Jones RT (2012) Paleoclimatic dynamics in continental Southeast Asia over the last
8 ~30,000 Cal yrs BP. Palaeogeogr. Palaeoclimatol. Palaeoecol. 339-341:1-11.
9 DOI:10.1016/j.palaeo.2012.03.025.
- 10 Costa LD, Wallner-Kersanach M (2013) Assessment of the labile fractions of copper and zinc
11 in marinas and port areas in Southern Brazil. Environ. Assess. 185:6767-6781.
12 DOI: 10.1007/s10661-013-3063-0.
- 13 Cruz FT, Narisma TG, Villafuerte II MQ Cheng-Chua KU, Olaguera LM (2012) A
14 climatological analysis of the southwest monsoon rainfall in the Philippines. Atmos. Res.
15 122:609-616. DOI: 10.1016/j.atmosres.2012.06.010
- 16 Davison W, Zhang H (1999) Diffusional characteristics of hydrogel used in DGT and DET
17 techniques. Anal.Chim.Acta 398:329-340. DOI:10.1007/s10661-013-3063-0
- 18 DGT Research (2002) DGT-for measurements in water, soils and sediments. DGT Research
19 Ltd., Lancaster.
- 20 Dudka S, Piotrowska M, Chlopecka A (1994) Effect of elevated concentrations of Cd and Zn in
21 soil on spring wheat yield and the metal contents of the plants. Water Air Soil.
22 Pollut. 76:333-341. DOI:10.1007/BF00482710.
- 23 Dunn RJK, Teasdale PR, Warnken J, Jordan MA, Arthur JM (2007) Evaluation of the *in situ*,
24 time-integrated DGT technique by monitoring changes in heavy metal concentrations in
25 estuarine waters. Environ. Pollut. 148:213-220. DOI:10.1016/j.envpol.2006.10.027.
- 26 Fathollahzade H, Kaczala F, Bhatnagar A, Hogland W (2015) Significance of environmental
27 dredging on metal mobility from contaminated sediments in the Oskarshamn Harbor,
28 Sweden. Chemosphere 119:445-451. DOI:10.1016/j.chemosphere.2014.07.008.
- 29 Fritz M, Berger PD (2015) Comparing two designs (or anything else!) using paired sample T-
30 Tests. Improving the User Experience Through Practical Data Analytics. Chapter 3 :71-89.
31 DOI: 10.1016/B978-0-12-800635-1.00003-3
- 32 Fuchs R, Dupouy C, Douillet P, Caillaud M, Mangin A, Pinazo C (2012). Modelling the impact
33 of a La Niña event on a South West Pacific Lagoon. Marine Poll. Bull. 64:1596-1613.
34 <http://dx.doi.org/10.1016/j.marpolbul.2012.05.016>.
- 35 Gao Y, Baeyens W, De Galan S, Poffijn A, Leermakers M (2010) Mobility of radium and trace
36 metals in sediments of the Winterbeek: Application of sequential extraction and the DGT
37 techniques. Environ. Pollut. 158:2439-2445. DOI:10.1016/j.envpol.2010.03.022.
- 38 Gerringa LJA, de Baar HJW, Nolting RF, Paucot H (2001) The influence of the salinity on the
39 solubility of Zn and Cd sulphides in the Scheldt estuary. J. of Sea Res. 46:201-211.
40 DOI:10.1016/S1385-1101(01)00081-8.
- 41 Gourlay-Francé C, Bressy A, Uher E, Lorgeoux C (2011) Labile, dissolved and particulate
42 PAHs and trace metals in wastewater passive sampling, occurrence, partitioning in treatment
43 plants. Water. Sci. Technol. 63:7:1327-33. DOI:10.2166/wst.2011.127. DOI:
44 10.2166/wst.2011.127.

- 1 Gottesmann W, Kampe A (2007) Zn/Cd ratios in calcsilicate-hosted sphalerite ores at
2 Tumurtijn-ovoo, Mongolia. *Chemie der Erde* 67:323-328.
3 DOI:10.1016/j.chemer.2007.01.002
- 4 Graveline N, Maton L, Luckge H, Rouillard J, Strosser P, Palkaniete K, Rinaudo J-D, Taverne
5 D, Interwies E (2010) An operational perspective on potential uses and constraints of
6 emerging tools for monitoring water quality. *TrAC* 29:5. DOI: 10.1016/j.trac.2010.02.006
- 7 Gurusurthy GP, Balakrishna K, Tripti M, Audry S, Riotte J, Braun JJ, Udaya Shankar HN
8 (2013) Geochemical behavior of dissolved trace elements in a monsoon-dominated tropical
9 river basin, Southwestern India. *Environ. Sci. Pollut. Res.* DOI:10.1007/s11356-013-2462-7
- 10 Han W, Moore AM, Levin J, Zhang B, Arango HG, Curchitser E, Di Lorenzo E, Gordon AL,
11 Lin J (2009) Seasonal surface ocean circulation and dynamics in the Philippine Archipelago
12 region during 2004-2008. *Dynam. Atmos. Oceans* 47:114-137.
13 DOI:10.1016/j.dynatmoce.2008.10.007
- 14 Hatje V, Apte SC, Hales LT, Birch GF (2003) Dissolved trace metal distribution in Port
15 Jackson estuary (Sydney Harbour), Australia. *Mar. Pollut. Bull.* 46:719-730.
16 DOI:10.1016/S0025-326X(03)00061-4
- 17 Herngren L, Goonetilleke A, Ayoko GA (2005) Understanding heavy metal and suspended
18 solids relationships in urban stormwater using simulated rainfall. *J. Environ. Manage.*
19 76:149-158. DOI:10.1016/j.jenvman.2005.01.013.
- 20 Hestir EL, Schoellhamer DH, Morgan-King T, Ustin SL (2013) A step decrease in sediment
21 concentration in a highly modified tidal river delta following the 1983 El Niño floods. *Mar.*
22 *Geol.* 345:304-313. <http://dx.doi.org/10.1016/j.margeo.2013.05.008>
- 23 INAP (2002) Diffusive Gradients in Thin-Films. A technique for Determining Bioavailable
24 Metal Concentrations. Theory and Application Literature
25 Survey [http://www.inap.com.au/public_downloads/Research_Projects/Diffusive_Gradients_i](http://www.inap.com.au/public_downloads/Research_Projects/Diffusive_Gradients_in_Thin-films.pdf)
26 [n_Thin-films.pdf](http://www.inap.com.au/public_downloads/Research_Projects/Diffusive_Gradients_in_Thin-films.pdf)
- 27 Je C, Hayes DF, Kim KS (2007) Simulation of resuspended sediments resulting from dredging
28 operations by a numerical flocculent transport model. *Chemosphere* 70:187-195.
29 DOI:10.1016/j.chemosphere.2007.06.033
- 30 Jiann KT, Wen LS (2009) Intra-annual variability of distribution patterns and fluxes of
31 dissolved trace metals in a subtropical estuary (Danshuei River, Taiwan). *J. Mar. Syst.*
32 75:87-99. DOI:10.1016/j.jmarsys.2008.08.002.
- 33 Kuehl SA, Nittrouer CA, Allison MA, Faria LEC, Dukat DA, Jaeger JM, Pacioni TD,
34 Figueiredo AG, Underkoffler EC (1996) Sediment deposition, accumulation, and seabed
35 dynamics in an energetic fine-grained coastal environment. *Cont. Shelf Res.* 5/6:787-
36 815. DOI:10.1016/0278-4343(95)00047-X.
- 37 Lewis MA, Weber DE, Stanley RS, Moore JC (2001) Dredging impact on an urbanized Florida
38 bayou: effects on benthos and algal-periphyton. *Environ. Pollut.* 115:161-171.
39 DOI:10.1016/S0269-7491(01)00118-X.
- 40 Li W, Zhao H, Teasdale PR, Wang F (2005) Trace metal speciation measurements in waters by
41 the liquid binding phase DGT device. *Talanta* 67:3:571-578.
42 DOI:10.1016/j.talanta.2005.03.018.

- 1 Loo YY, Billa L, Singh A (2014) Effect of climate change on seasonal monsoon in Asia and its
2 impact on the variability of monsoon rainfall in Southeast Asia. GSF xxx:1-7.
3 DOI:10.1016/j.gsf.2014.02.009
- 4 Mackie JA, Natali SM, Levinton JS, Sanudo-Wilhelmy SA (2007) Declining metal levels at
5 Foundry Cove (Hudson River, New York): Response to localized dredging of contaminated
6 sediments. Environ. Pollut. 149:141-148. DOI:10.1016/j.envpol.2007.01.010.
- 7 Masson M, Blanc G, Schäfer J (2006) Geochemical signals and source contributions to heavy
8 metal (Cd, Zn, Pb, Cu) fluxes into the Gironde Estuary via its major tributaries. Sci. Total.
9 Environ. 370:133-146. DOI: 10.1016/j.scitotenv.2006.06.011.
- 10 Masson M, Blanc G, Schäfer J, Parlanti E, Le Coustumer P (2011) Copper addition by organic
11 matter degradation in the freshwater reaches of a turbid estuary. Sci. Total Environ.
12 409:8:1539-1549. DOI:10.1016/j.scitotenv.2011.01.022.
- 13 Materum R (2010) Physicochemical and particulate characterization of selected urban-
14 impacted aquatic systems in Manila (The Philippines) and Bordeaux (France). Rapport de
15 Stage. FDEA. Université Bordeaux 1
- 16 Mazeina LP, Bessonov DU, Bortnikova SB (1999) Zinc and Cadmium behaviour in tailings.
17 Geochemistry of the Earth's Surface, Armannsson (ed.) Balkerna, Rotterdam, ISBN 90 5809
18 073 6
- 19 Meybeck M (2009) Asia-Monsoon Asia. Rivers and Streams.– Gems Water program UNEP,
20 global river water quality data. <http://www.gemsstat.org/descstats.aspx>
- 21 Migliavacca D, Teixeira EC, Wiegand F, Machado ACM, Sanchez J (2005) Atmospheric
22 precipitation and chemical composition of an urban site, Guaíba hydrographic basin, Brazil.
23 Atmos. Environ. 39:1829–1844. DOI:10.1016/j.atmosenv.2004.12.005.
- 24 Montero N, Belzunce-Segarra MJ, Gonzalez JL, Larreta J, Franco J (2012) Evaluation of
25 diffusive gradient in thin films (DGT) as a monitoring tool for the assessment of the
26 chemical status of transitional waters within the Water Framework Directive. Mar. Poll.
27 Bull. 64:31-39. DOI: 10.1016/j.marpolbul.2011.10.028.
- 28 Munk LA, Faure G, Pride DE, Bigham JM (2002) Sorption of trace metals to an aluminum
29 precipitate in a stream receiving acid rock-drainage; Snake River, Summit County,
30 Colorado. Appl. Geochem. 17:421-430. DOI:10.1016/S0883-2927(01)00098-1.
- 31 Nayar S, Goh BPL, Chou LM (2004) Environmental impact of heavy metals from dredged and
32 resuspended sediments on phytoplankton and bacteria assessed in *in situ* mesocosms.
33 Ecotox. Environ. Safe 59:349-369. DOI:10.1016/j.ecoenv.2003.08.015
- 34 Naylor C, Davison W, Motelica-Heino M, Van den Berg GA, Van Der Heidjt LM (2004)
35 Simultaneous release of sulfide with Fe, Mn, Ni and Zn in marine harbor sediment measured
36 using a combined metal/sulfide DGT probe. Sci. Total Environ. 328:275-
37 286. DOI: 10.1016/j.scitotenv.2004.02.008.
- 38 Neal C, Smith CJ, Jeffrey HA, Harrow M, Neal M (1996) Dissolved chromium pollution in
39 rainfall and surface waters in mid-Wales during the mid-1980s. Sci. Total Environ. 188:2-3,
40 127-138. DOI:10.1016/0048-9697(96)05180-7.
- 41 Nolting RF, de Baar HJW, Timmermans KR, Bakker K (1999) Chemical fractionation of zinc
42 versus cadmium among other metals nickel, copper and lead in the northern North Sea. Mar
43 Chem 67:267-287. DOI: 10.1016/S0304-4203(99)00076-6

- 1 Özsoy T, Örnektekin S (2009) Trace elements in urban and suburban rainfall, Mersin,
2 Northeastern Mediterranean. Atmos. Res. 94:203-219. DOI:10.1016/j.atmosres.2009.05.017.
- 3 Park JH, Inam E, Abdullah MH, Agustiyani D, Duan L, Thuong Hoang T, Kim KW, Kim SD,
4 Nguyen MN, Pekthong T, Sao V, Sariya A, Savathvong S, Sthiannopkao S, Syers JK,
5 Wirojanad W (2011) Implications of rainfall variability for seasonal and climate-induced
6 risks concerning surface water quality in East Asia. J. Hydrol. 400:323-332.
7 DOI: 10.1016/j.jhydrol.2011.01.050.
- 8 Pettke T, Oberli F, Audétat A, Guillong M, Simon A, Hanley J, Klemm L (2012) Recent
9 developments in element concentration and isotope ratio analysis of individual fluid
10 inclusion by laser ablation, single and multiple collector ICP-MS. Ore Geol. Rev. 44:10-38.
11 DOI: 10.1016/j.oregeorev.2011.11.001.
- 12 Pinheiro JP, Domingos RF (2005) Impact of spherical diffusion on labile trace metals
13 speciation by electrochemical stripping techniques. J. Electroanal. Chem. 581:167-175.
14 DOI:10.1016/j.jelechem.2004.12.024
- 15 Schintu M, Marras B, Durante L, Meloni P, Contu A (2010) Macroalgae and DGT as indicators
16 of available trace metals in marine coastal waters near a lead-zinc smelter. Environ. Monit.
17 Assess. 167:653-661. DOI 10.1007/s10661-009-1081-8
- 18 Shirasago-Germán B, Pérez-Lezama EL, Chávez EA (2015) Influence of El Niño-Southern
19 Oscillation on the population structure of a sea lion breeding colony in the Gulf of
20 California. Estuar. Coast. Shelf. S. 154:69-76. <http://dx.doi.org/10.1016/j.ecss.2014.12.024>
- 21 Sigg L (2014) 4.15-Metals as water quality parameters-Role of speciation and Bioavailability.
22 Reference Module in Earth Systems and Environmental Sciences. Comprehensive Water
23 Quality and Purification. 4:315-328. DOI:10.1016/B978-0-12-382182-9.00090-6
- 24 Sokolowski A, Wolowicz M, Hummel H (2001) Distribution of dissolved and labile particulate
25 trace metals in the Overlying bottom water in the Vistula River Plume (Southern Baltic Sea).
26 Mar. Pollut. Bulletin 42:10:967-980. PII: S0025-326X(01)00069-8. DOI:10.1016/S0025-
27 326X(01)00069-8
- 28 Søndergaard J, Elberling B, Asmund G (2008) Metal speciation and bioavailability in acid
29 mine drainage from a high Arctic coal mine waste rock pile: Temporal variations assessed
30 through high-resolution water sampling, geochemical modeling and DGT. Cold Reg. Sci.
31 Technol 54:89-96. DOI:10.1016/j.coldregions.2008.01.003.
- 32 Stephens M, Matthey D, Gilbertson DD, Murray-Wallace CV (2008) Shell-gathering from
33 mangroves and seasonality of the Southeast Asian Monsoon (*Geloina erosa*) from the Great
34 Cave of Niah, Sarawak: methods and reconnaissance of mollusks of early Holocene and
35 modern times. J. Archaeol. Sci. 35:2686-2697. DOI:10.1016/j.jas.2008.04.025
- 36 Sokolowski A, Wolowicz M, Hummel H (2001) Distribution of dissolved and labile particulate
37 trace metals in the Overlying bottom water in the Vistula River Plume (Southern Baltic Sea),
38 Mar.Pollut. Bull. 42(10): 967-980. [http://dx.doi.org/10.1016/S0025-326X\(01\)00069-8](http://dx.doi.org/10.1016/S0025-326X(01)00069-8)
- 39 Takahashi, HG (2013) Orographic low-level clouds of Southeast Asia during the cold surges of
40 the winter monsoon. Atmos. Res. 131:22-33. DOI:10.1016/j.atmosres.2012.07.005
- 41 van den Berg GA, Meijers GG, van der Heijdt LM, Zwolsman JJ (2001) Dredging-related
42 mobilisation of trace metals: a case study in The Netherlands. Water Res. 35:8:1979-86.
43 DOI:10.1016/S0043-1354(00)00452-8

- 1 vanLoon W, Duffy SJ (2000) Environmental Chemistry: A Global Perspectives. Oxford
2 University Press Incorporated. ISBN 0198564406, 9780198564409
- 3 Varis O, Kumm M, Salmivaara A (2012) Ten major rivers in monsoon Asia-Pacific: An
4 assessment of vulnerability. Appl. Geogr. 32:441-454. DOI:10.1016/j.apgeog.2011.05.003.
- 5 Viers J, Dupré B, Gaillardet J (2009) Chemical composition of suspended sediments in World
6 Rivers: New insights from a new database. Sci. Total. Environ. 407:853-868.
7 DOI:10.1016/j.scitotenv.2008.09.053.
- 8 Villafuerte II MQ, Matsumoto J, Akasaka I, Takahashi HG, Kubota H, Cinco TA (2014) Long-
9 term trends and variability of rainfall extremes in the Philippines. Atmos. Res. 137:1-13.
10 DOI: 10.1016/j.atmosres.2013.09.021.
- 11 Villanueva JD (2013) Suivi par capteurs passifs des polluants émergents dans les eaux de
12 surface en contexte urbain (Monitoring emerging pollutants in surface waters using *in situ*
13 sampling devices in an urban context), Ph. D. thesis, Université Bordeaux, France
- 14 Villanueva JD, Le Coustumer P, Huneau F, Motellica-Heino M, Perez TR, Materum R,
15 Espaldon MVO, Stoll, S (2013) Assessment of trace metals during episodic events using
16 DGT passive sampler: A proposal for water management enhancement. Water Resour.
17 Manag. 27:12:4163-4181. DOI: 10.1007/s11269-013-0401-5.
- 18 Vystavna Y, Huneau F, Motellica-Heino M, Le Coustumer P, Vergeles Y, Stolberg F (2012a)
19 Monitoring and flux determination of trace metals in rivers of the Seversky Donets basin
20 (Ukraine) using DGT passive samplers. Environ. Earth. Sci. 65:1715-1725.
21 DOI: 10.1007/s12665-011-1151-4.
- 22 Vystavna Y, Huneau F, Schäfer J, Motellica-Heino M, Blanc G, Larrose A, Vergeles Y,
23 Dyadin D, Le Coustumer P (2012b) Distribution of trace elements in waters and sediments
24 of the Seversky Donets transboundary watershed (Kharkiv region, Eastern Ukraine). Appl.
25 Geochem. 27:2077-2087. DOI: 10.1016/j.apgeochem.2012.05.006.
- 26 Weng N, Wang WX (2014) Variations of trace metals in two estuarine environments with
27 contrasting pollution histories. Sci. Total. Environ. 485-486:604-614.
28 DOI:10.1016/j.scitotenv.2014.03.110.
- 29 Wilkerson FP, Dugdale RC, Marchi A, Collins CA (2002) Hydrography, nutrients and
30 chlorophyll during El Niño and La Niña 1997-99 winters in the Gulf of the Farallones,
31 California. Progr. Oceanogr. 54:293-310; DOI: 10.1016/S0079-6611(02)00055-1.
- 32 Witt MLI, Mather TA, Baker AR, De Hoog JCM, Pyle DM (2010) Atmospheric trace metals
33 over the south-west Indian Ocean: Total gaseous mercury, aerosol trace metal concentrations
34 and lead isotope ratios. Mar. Chem. 121:2-16. DOI: 10.1016/j.marchem.2010.02.005
- 35 Vuai SAH, Tokuyama A (2011) Trend of trace metals in precipitation around Okinawa Island,
36 Japan, Atmos. Res. 99:80-84. DOI: 10.1016/j.atmosres.2010.09.010
- 37 World Health Organization (2008) Guidelines for drinking-water quality. Vol. 1 3rd Ed., ISBN
38 978 92 4 154761 1
- 39 Wu Z, He M, Lin C (2011) *In situ* measurements of concentrations of Cd, Co, Fe and Mn in
40 estuarine porewater using DGT. Environ. Pollut. 159:1123-1128.
41 DOI:0.1016/j.envpol.2011.02.015.
- 42 Zhang H, Davison W, Miller S, Tych, W (1995) *In situ* high resolution measurements of fluxes
43 of Ni, Cu, Fe, and Mn and concentrations of Zn and Cd in porewaters by DGT. Geochim.
44 Cosmochim. Ac. 59:20:4181-4192. DOI:10.1016/0016-7037(95)00293-9

1 Zwolsman JJG, Van Eck GTM (1993) Dissolved and particulate trace metal geochemistry in
2 the Scheldt estuary, S.W. Netherlands (water column and sediments). *Neth. J. Aquat. Ecol.*
3 2:4:287-300. DOI: 10.1007/BF02334792.

4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 **List of Tables**

2 **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

3 *Days before DGT installation

4 Provided by Manila Observatory (unpublished data 2012)

5
6
7 **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

8
9 **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

1 **Table 4** Anthropogenic activities surrounding the Pasig River and the major trace metals
 2 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
	oil refinery	Cd, Cr, Pb
	steel	Cr
oil and petroleum company	Cd, Co, Pb, Zn	
Site 2	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

3

4

Table 5 Student t-test result. *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)

Groups		t	df	sig. (2 tailed)	MeanDifferenc e	Std. ErrorDifferenc e
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

°Equal variances assumed °°Equal variances not assumed

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

1 **Table 7** Correlation (*r*): among labile trace metals and labile trace metals to the physico-
 2 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

4 **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

1 **Figures**

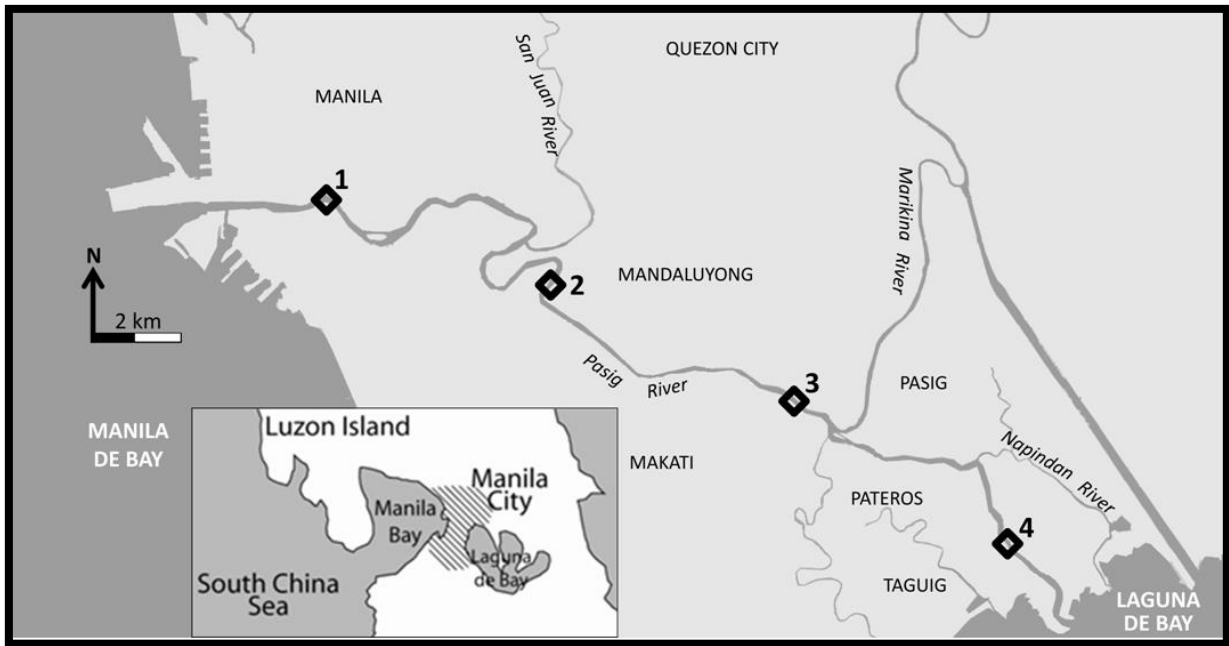


Fig. 1 The Pasig River map and sampling sites (Point 1: moth of the Manila Bay; Point 2: near the convergence of the San Juan River, Point 3: near the confluence of the Marikina River; and Point 4: near the Laguna Lake)

2

3

4

5

6

7

8

9

10

11

12

13

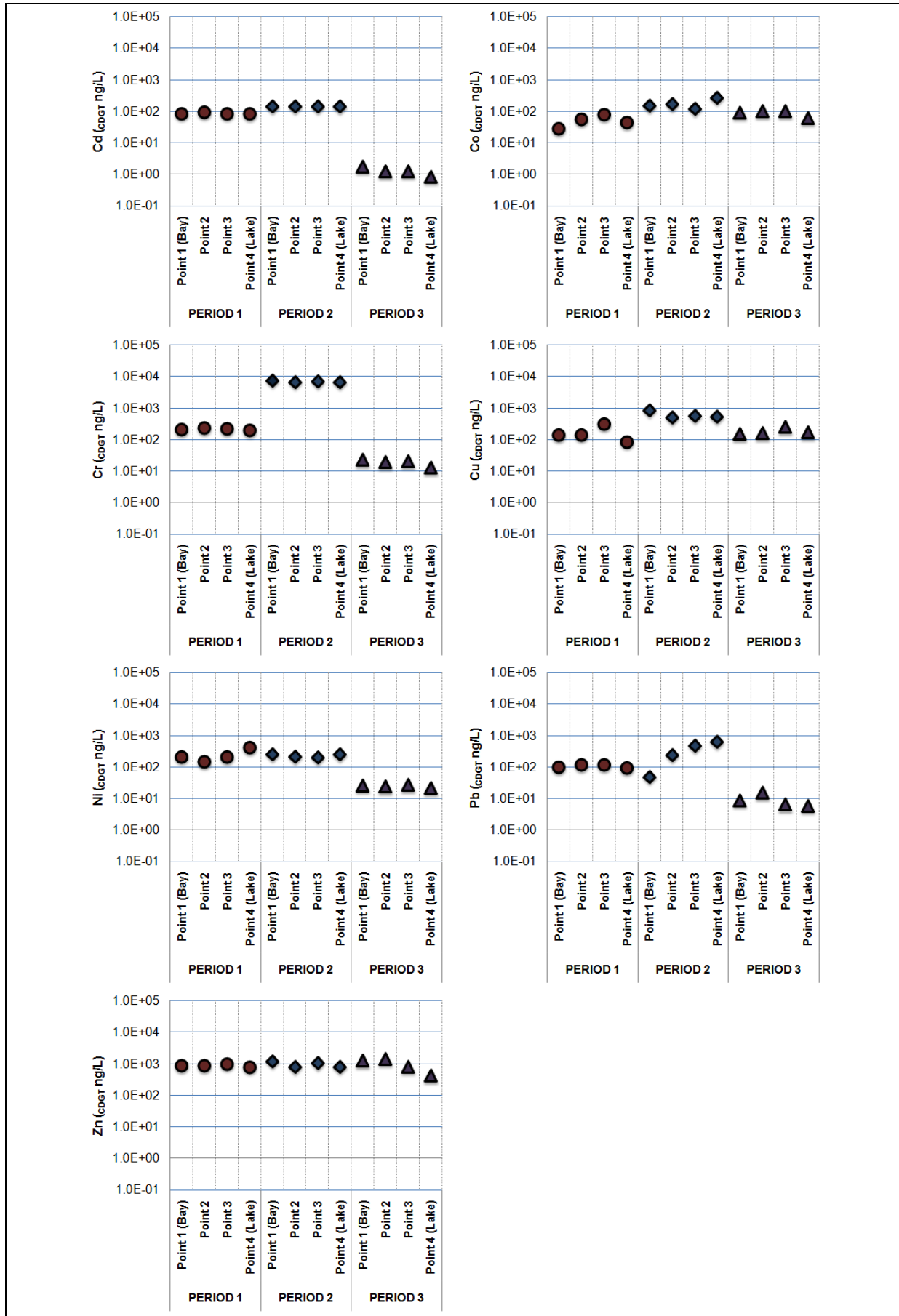


Fig. 2 DGT-labile trace metals' concentrations (ng/L)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49

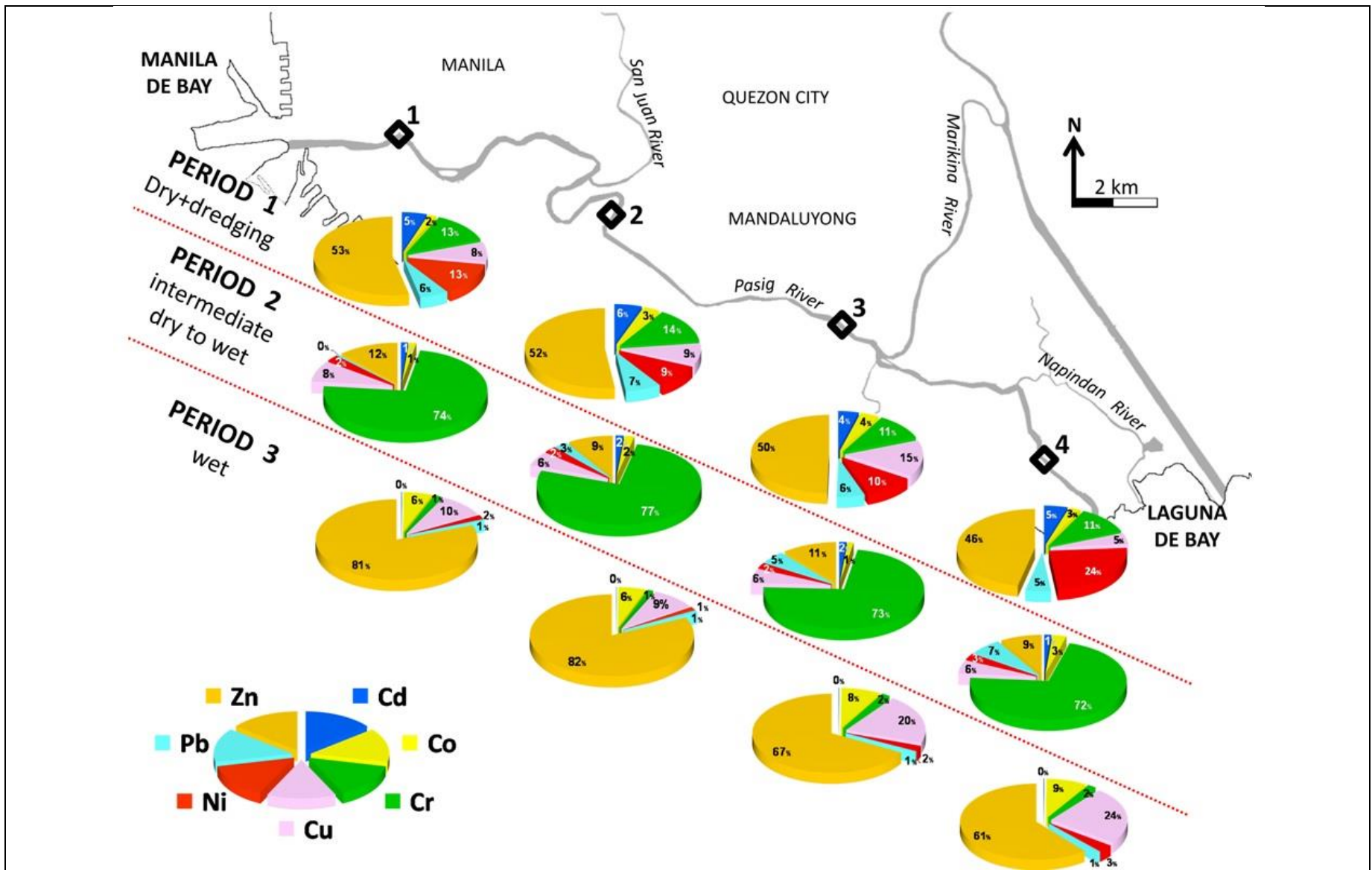
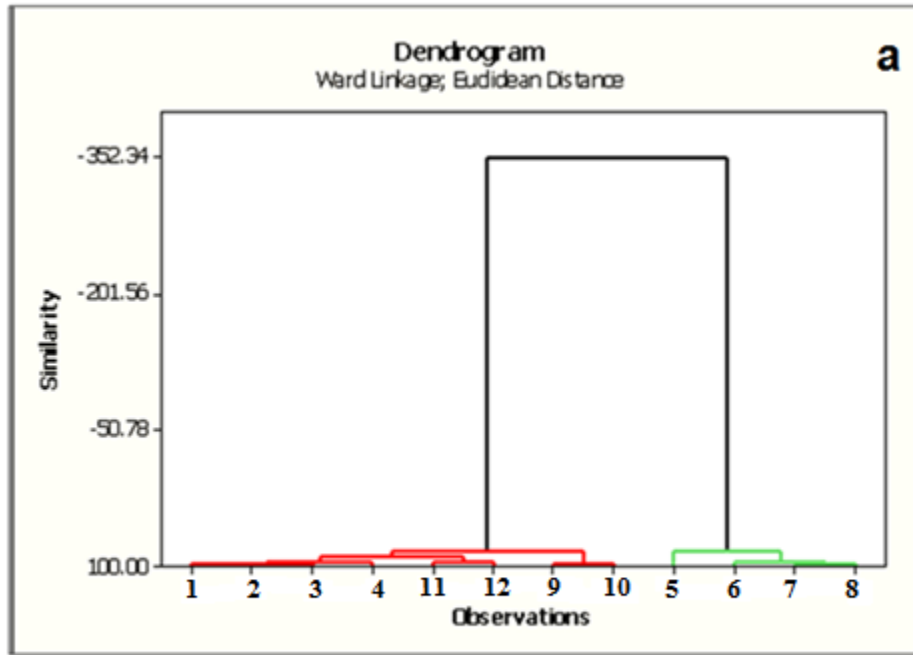


Fig. 3 Spatio-temporal variation of the trace metals among period



1– Period 1 Point 1 9 – Period 3 Point 1 5– Period 2 Point 1
2– Period 1 Point 2 10– Period 3 Point 2 6– Period 2 Point 2
3– Period 1 Point 3 11– Period 3 Point 3 7– Period 2 Point 3
4– Period 1 Point 4 12– Period 3 Point 4 8– Period 2 Point 4

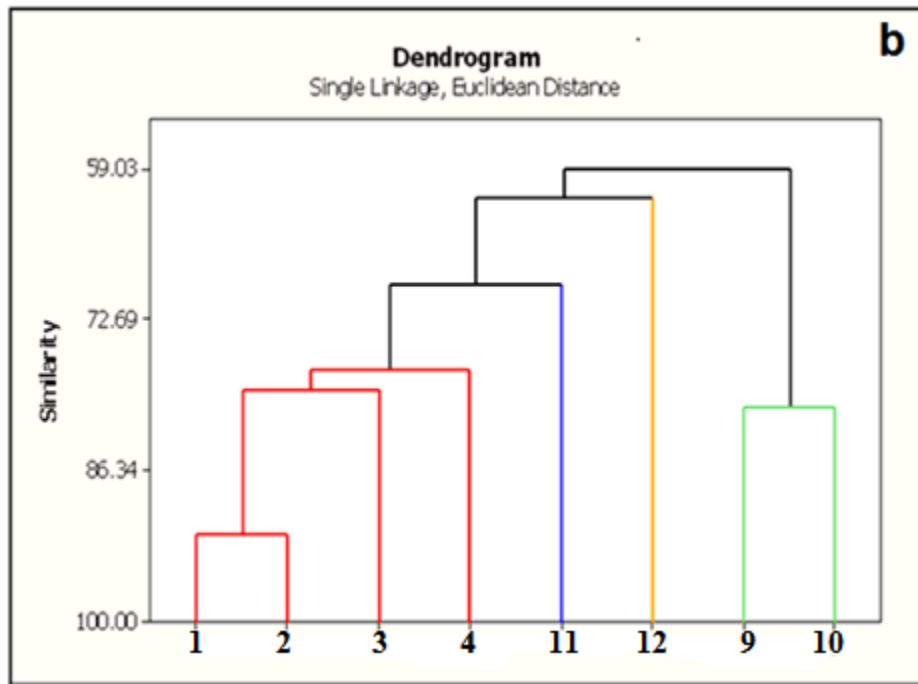


Fig. 4 Generated dendrogram. Numbers indicate sampling regime (Period) and points. a: all the Periods and b: Periods 1 and 3 (Legend is provided in the middle)

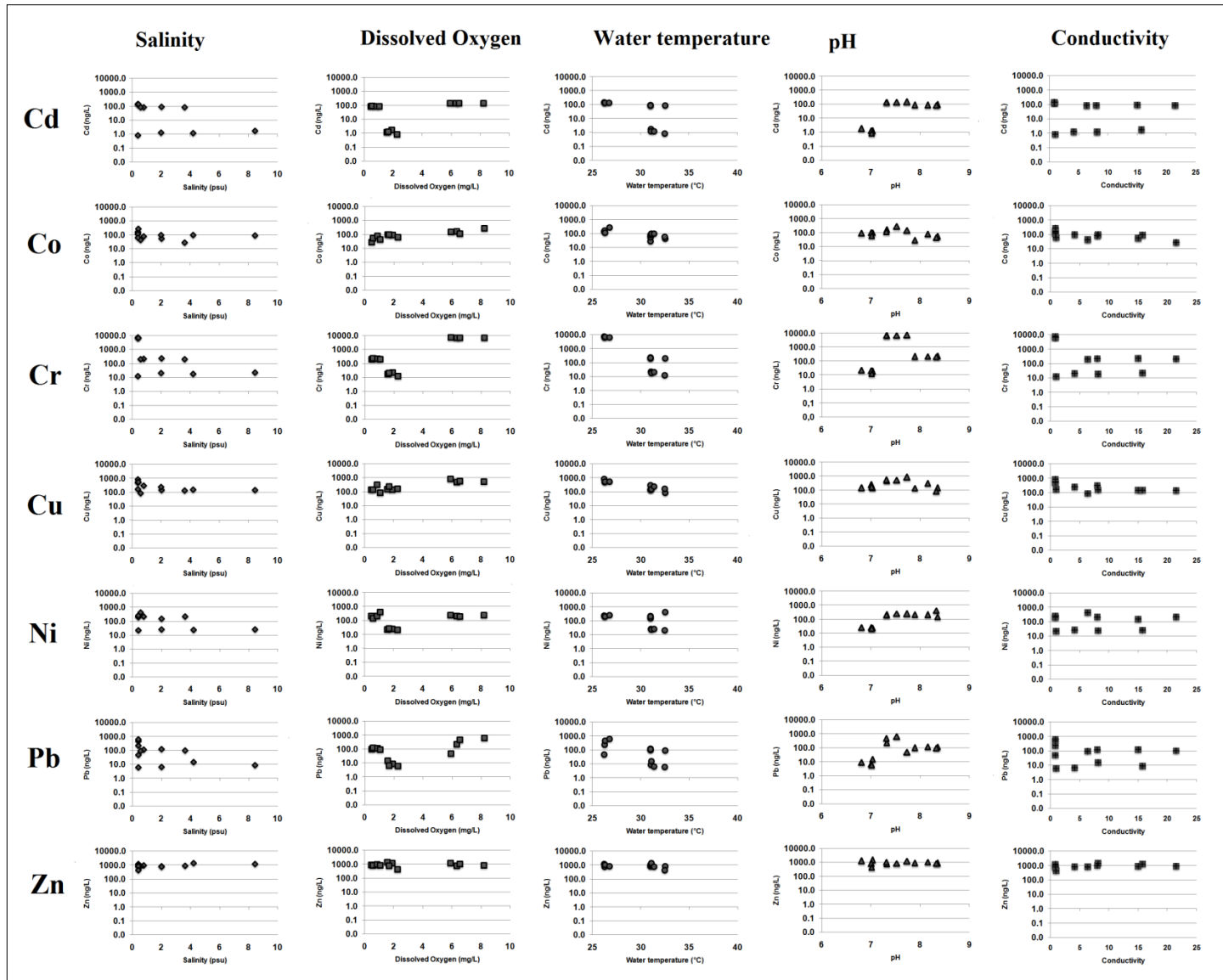


Fig. 5 Relationship of the physico-chemical parameters to the labile trace metal concentrations

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65