Heavy metals in road-deposited and water sediments at Kogarah bay, Sydney: Enrichment, sources, and fractionation

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Abstract

Road deposited sediment samples from highway and the industrial area of Kogarah, Sydney, the largest city of Australia, were analyzed for metal pollution (Cu, Cr, Pb, Ni, Cd, Zn, Fe, Mn and As). Hakanson's method was used to determine the Risk Index (RI) and ecological risks. Of the 10 heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, and Zn) investigated, the ratios of concentrations of Zn, Cu, V, Cr, and Sb in RDS to those in the adjacent natural soils (NS) were greater than 5. The metals concentrations in water sediments in the catchment area were same or only marginally higher than in NS. Metals concentrations in the mobile fraction (exchangeable) of RDS were: Fe > Mn, Zn > Cu, Pb > Cr, Ni, V, Cd, Sb, but the mobile fraction concentration percentage of total concentration was highest for Cd and lowest for Fe, Cr, Ni, V. Correlation, cluster and principal component analyses identified probable natural and anthropogenic sources of contaminants. The dust had elevated concentrations of As, Hg, Pb, Cd, Cu, Cr, Ni, Zn, Fe, Mn and PAHs. Enrichment factors of Cu, Pb, Cd and Zn showed that the dust is extremely enriched in these metals. The overall decreasing metal concentration order was: Pb > Mn > Fe > Zn > Cu > Cr > Ni > Cd. Significantly positive correlation was only found between Cu and Pb (R^2 = 0.980). Multivariate statistical analyses revealed that Cu, Pb, Zn, Fe *and PAHs and, to a lesser extent, Cr and Ni have common anthropogenic sources. While Mn and Fe were identified to have natural sources, Cd may have different anthropogenic origins. Traffic and related activities, petrogenic and pyrogenic sources are likely to be the main anthropogenic sources of heavy metals in Sydney. All samples demonstrated relatively low-medium ecological risk.*

Key words

Heavy metals, road-deposited sediments, water sediments, heavy metals fractionation

1. Introduction

Road dust often contains elevated concentrations of heavy metals and can influence on human health. Therefore, a study on the characteristics of heavy metals in road dust was carried out in Sydney, Australia. Numerous studies have been conducted on heavy metals accumulation in RDS (Loganathan et al. 2013). However, very few studies have been reported on the comparison of metal concentrations between RDS, water sediments (WS), and natural soils (NS) within a catchment area (Birch 2011). Such a study is important in assessing the heavy metals contributions from RDS and natural soils to the local water bodies, so that control measures can be adopted, if necessary, to reduce pollution of the water bodies from RDS.

Road dust makes a significant contribution to the pollution in the urban environments, especially in big cities. Interest in the levels of contaminants associated with road dust has risen in the recent years. Many studies on street dust throughout the world have focused on elemental concentrations and source identification. Road dusts in urban area are indicators of heavy metals contamination from atmospheric deposition, vehicle emissions, urbanization and industrialization, etc. [6].

Concentrations of heavy metals in such road dust are extremely variable [5]. Environmental and health effects of heavy metal pollutants in road dust are dependent on the mobility and availability of the elements. The mobility and availability of the metal elements in the environment is significantly affected by their chemical speciation and partitioning within or on dust matrices [1]. The sequential extraction procedures have been applied most commonly for studying the chemical association of contaminants such as heavy metals in soil, sediment and road dust.

Escalating rate of vehicle usage as a result of the rapid growth of urban population causes increasing amounts of road-deposited sediments (RDS) in many parts of the world. RDS contain high concentration of inorganic and organic pollutants, of them heavy metals are a major component. Heavy metals, at elevated concentrations, have harmful effects on humans and aquatic environment. The sources of the metals in RDS are vehicle parts and exhaust emission, road surface, and lithology of the area

(Loganathan et al. 2013). The mobile fraction of heavy metals in RDS consisting of exchangeable forms (Mohammed et al. 2012) has the potential of transportation into neighbouring water bodies by stormwater to cause environmental degradation of the water.

The aims of the study were to determine heavy metals (1) distributions in RDS, WS, and NS, (2) enrichments in RDS and WS by comparing concentrations in RDS and WS with those in NS, (3) potential mobility, and (4) possible sources.

2. Experimental methods

Sample collection

Eleven samples of RDS, 7 samples of NS, and 11 samples of WS were collected in and around Kogarah bay, Sydney and analysed for heavy metals, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, and Zn. Road dust sampling was carried out in March, 2006. Road dust was obtained inside the vaccum filter attached in the vacuum cleaner operated by an electrical generator. Road deposited sediments was taken from 200m along the left and right side of the road. 600g of road dust was collected with 100m^2 of area. Then this sample was transferred to a plastic bag.

Sample preparation for analysis

In the laboratory, the collected sample was dried at room temperature for seven days. The road dust which has a diameter of above 2000um was removed by using a 2mm stainless steel sieve. Then the remained road dust was sieved through the laboratory test sieves as follows: 850ptm, 180ptm, and 75ptm in order to separate the sample into four different size-fractions: < 75ptm, 75 - 180ptm, 180 - 850ptm, and 850 – 2000ptm. After that, the sieved samples were homogenize and stored in desiccator until extraction.

Pseudo-total metal concentrations were determined by aqua regia digestion followed by analysis of the diluted digests using ICP-OES and ICP-MS. International and Australian reference standard samples analysed in parallel with the unknown samples gave 85-108% recovery of metals. Fractionation of the metals was conducted according to the Standards, Measurements and Testing Program of the European Union (Kartal et al. 2006). Metals concentrations in the fractions were measured using ICP-OES and ICP-MS.

The analytical methods

The heavy metals in road dust were extracted by aqua regia extraction method. 3g of sample was extracted with 14.4ml of aqua regia, HNO_3 : HCl (1: 3 v/v), and 15.6ml of deionized water. Then the mixture was boiled at 70^0C for lhr in the water bath. The extracted solution was filtered by using the filter

The chemical association of heavy metals in road dust was determined by the sequential extraction methods including a BCR procedure (first stage) and Tessier et al. procedure (first stage and second stage). Then the concentrations of 15 heavy metals were analyzed by atomic absorption spectrometry.

3. Discussion

Concentrations of all heavy metals were higher in RDS than in NS (Fig. 1), indicating that vehicle activity and road surface have contributed to the accumulation of heavy metals in RDS. The mean of pollution index (PI), the ratio of metal concentration in RDS to that in NS, was more than 5 for Zn, Cu, V, Cr, and Sb. This suggests that vehicle brakes and tyre wear were the possible sources for Zn, Cu, Cr, and Sb in RDS and road surface for V (Loganathan et al. 2013). The metals concentrations in WS were same or marginally higher than in NS (PI lower than 5 for all metals), probably because WS originated from both RDS and NS with greater contribution from the latter.

Fractionation data for RDS showed that the concentration of the most mobile of the four fractions, the exchangeable metal fraction (Fraction 1), decreased in the order Fe

> Mn, Zn > Cu, Pb > Cr, Ni, V, Cd, Sb (Fig. 2). The mobile fraction as a percentage of total concentration was, however, lowest for Fe and highest for Cd, because of the high total concentration of Fe and low total concentration of Cd. Therefore Fe, Mn, Zn, Cu, and Pb from RDS were expected to have been transported more than the other metals to the neighbouring water bodies by stormwaters. However, no major difference in total concentration between WS and NS was noticed for these or other metals probably because of low amounts of metals transported from RDS compared to the amounts already present in WS and the wider distribution of the transported metals in the large volume of water in the bay.

The method of determining ecological risks of heavy metals orginally introduced by Hakanson et al., 1980 where RI<150: low ecological risk, 150<RI<300: moderate ecological risk, 300<RI<600: high ecological risk.

From these results and the criteria presented in Table 1, all sampling locations show very low-moderate ecological risks. Some RDS samples show the maximum RI value and ecological risk of the dust samples. The lowest ecological risk is for the sample from the water sediment. The concentrations of heavy metals were presented in the Figure

4. Conclusions

The ratio of metal concentration in RDS to that in NS, was more than 5 for Zn, Cu, V, Cr, and Sb, suggesting that vehicle brakes and tyre wear would have probably caused the enrichment of Zn, Cu, Cr, and Sb in RDS and road surface for V. Metals fractionation data showed that the potential mobility of the metals, an indication of the metals transportation by stormwater, decreased in the order Fe > Mn, Zn > Cu, Pb > Cr, Ni, V, Cd, Sb.

Table 1. Comparison of measured metal concentrations (mg/kg) obtained using HNO_3/HCl solution digestion and certified values on the Australian reference standard (stream sediment, AGAL-10)

	AGAL-10			NSC DC 73309			
	Measured values** (mg/kg)	Certified values* (mg/kg)	Recovery (%)	Measured values** (mg/kg)	Certified values* (mg/kg)	Recovery (%)	Recovery (spiking)
Sb	5.9	6.4	92	7.2	14.9	-	93
As	17.0	17.2	99	180	188	96	111
Cd	10.1	9.33	108	1.8	2.3	78	104
Cr	87	82	106	22	40	-	98
Cu	23.6	23.2	102	76	79	96	104
Fe	18880	19950	95	28400	30700	93	98
Pb	41.4	40.4	102	640	636	101	97
Mn	230	241	96	2120	2490	85	97
Hg	10.7	11.6	92	<0.1	0.07	-	98
Ni	18.3	17.8	103	13	14.3	97	98
V	25.1	25.3	99	23	47	-	99
Zn	61	57	107	360	373	97	107

Recovery = (measured value/certified value) x 100

*: Report the method used

**: Report the direct values that obtained

* CRM NSC 73390 Sediment,

* Australian Certified materials (sediment) AGAL-10

Table 2. Range of heavy metals in RDS, sediment and natural soil in Kogarah, Sydney (2012) (Unit:mg/kg)

Metals	RDS			Sediment			Natural soil		
	Mean (N=11)	S.E	Range	Mean (N=11)	S.E	Range	Mean (N=7)	S.E	Range
As	3.43	0.50	2.0-8.5	7.3	1.4	1.7-14.0	4.24	2.01	1.2-17
Hg	0.19	0.06	0.1-0.66	0.1	0.0	0.1-0.28	0.11	0.01	0.1-0.17
Sb	6.45	0.77	2.7-10	0.2	0.0	0.1-0.4	0.71	0.10	0.36-1.1
Fe	19645	1281	13100-25100	11392	1725	3990-20600	5972	1894	2420-10400
V	74.36	7.66	41-130	23.0	2.5	11.0-37.0	8.39	1.83	3.4-17
Pt	0.17	0.03	0.1-0.48	0.1	0.0	<0.1	<0.1	-	<0.1
Pd	0.34	0.05	0.16-0.63	0.1	0.0	<0.1	<0.1	-	<0.1
Rh	0.1	0.0	<0.1	0.1	0.0	<0.1	<0.1	-	<0.1
Cd	0.19	0.01	0.1-0.26	0.2	0.0	0.1-0.5	0.19	0.03	0.1-0.29
Cr	42.00	3.13	28-64	12.9	2.0	4.1-20.0	4.39	0.90	2.4-9.8
Cu	263.45	44.35	73-540	47.8	13.1	11.0-160.0	19.21	3.90	6.5-34
Ni	13.99	1.66	5.4-25	6.5	0.7	2.2-11	3.17	1.05	1.1-9.7
Mn	540.91	49.78	300-840	72.1	6.6	47.0-120.0	108.14	25.51	24-200
Pb	164.64	31.37	54-370	45.2	5.3	19.0-77.0	54.29	10.94	23-100
Zn	543.64	63.01	210-890	116.5	11.7	51.0-170.0	74.29	22.19	28-210

Table 3. The potential ecological risk indices (RI) of RDS and sediment from different sampling site in Kogarah, Sydney (2012)

Sampling site	Mean value of Er					RI	Ecological risk
	Cr	Pb	Cu	Cd	Zn		
	12.8	5.0	28.6	15.7	3.8	65.8	
	18.7	5.3	33.8	28.2	2.8	88.8	
	22.3	12.0	96.3	17.2	5.7	153.5	Moderate risk
	20.5	8.5	19.0	15.7	4.7	68.4	
	16.4	6.3	24.7	26.6	6.7	80.8	
RDS	26.0	24.9	140.5	36.0	6.3	233.8	Moderate risk
	17.3	16.6	65.1	29.8	10.1	138.8	
	16.4	34.1	75.5	40.7	12.0	178.7	Moderate risk
	15.0	29.5	85.9	36.0	9.7	176.1	Moderate risk
	29.2	12.0	119.7	28.2	9.4	198.5	Moderate risk
	16.0	12.9	65.1	31.3	9.3	134.5	
Ave.						**138.0**	**Low-moderate risk**
	1.9	1.8	2.9	15.7	0.7	22.9	
	3.6	3.3	6.2	15.7	1.2	30.0	
	4.2	1.9	41.6	15.7	0.7	64.2	
	2.2	2.3	5.7	15.7	1.5	27.4	
	5.9	4.0	7.5	36.0	1.6	55.1	
WS	12.8	5.2	28.6	31.3	2.3	80.2	
	4.4	4.1	6.8	18.8	1.3	35.4	
	8.2	5.3	9.1	23.5	2.0	48.1	
	9.1	5.5	12.2	18.8	2.2	47.8	
	6.4	5.3	7.5	29.8	1.8	50.8	
	5.9	7.1	8.6	72.1	2.0	95.7	
Ave.						**46.6**	**Low risk**

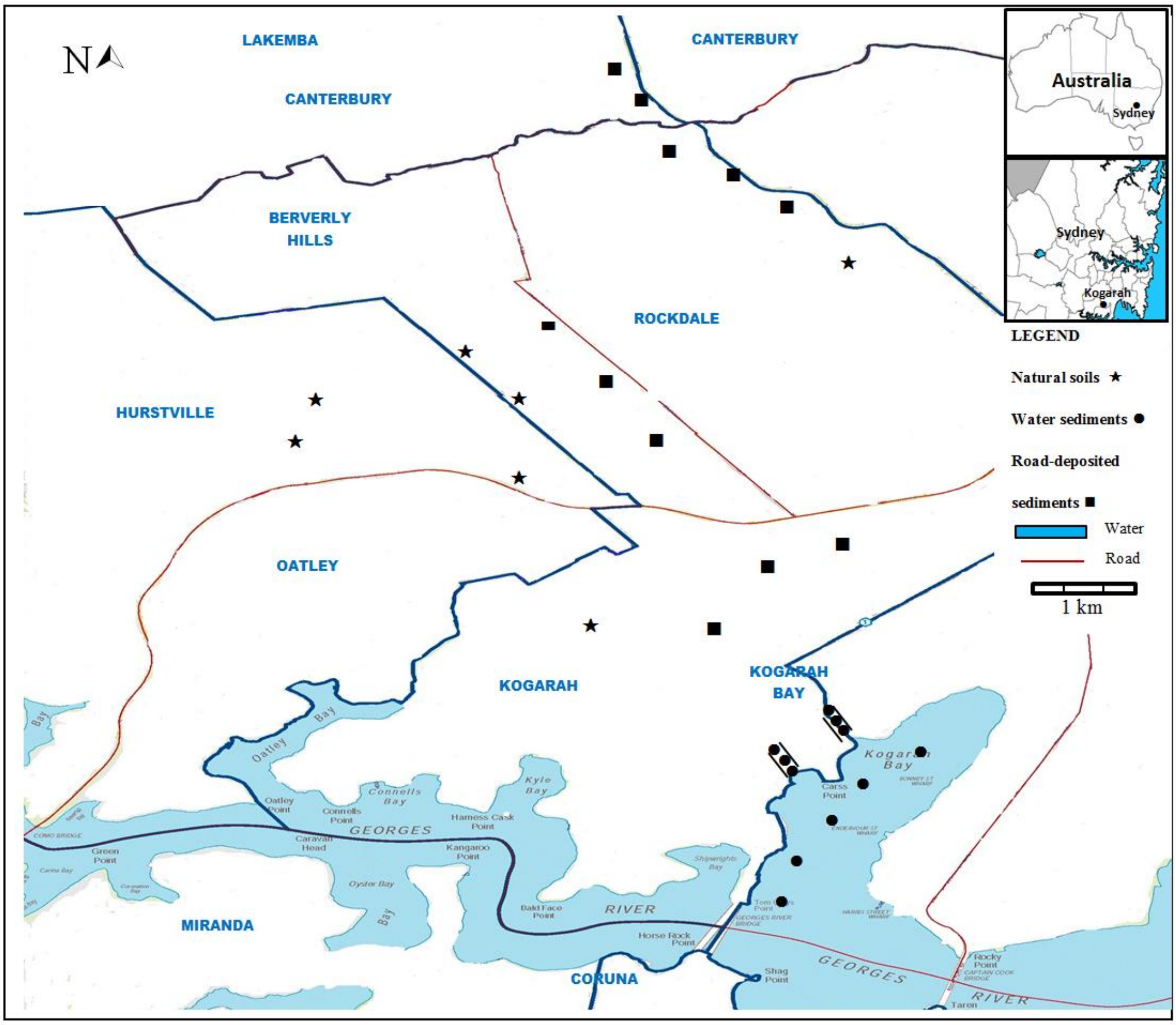


Figure 1. Sampling sites in Kogarah, Sydney (2012)

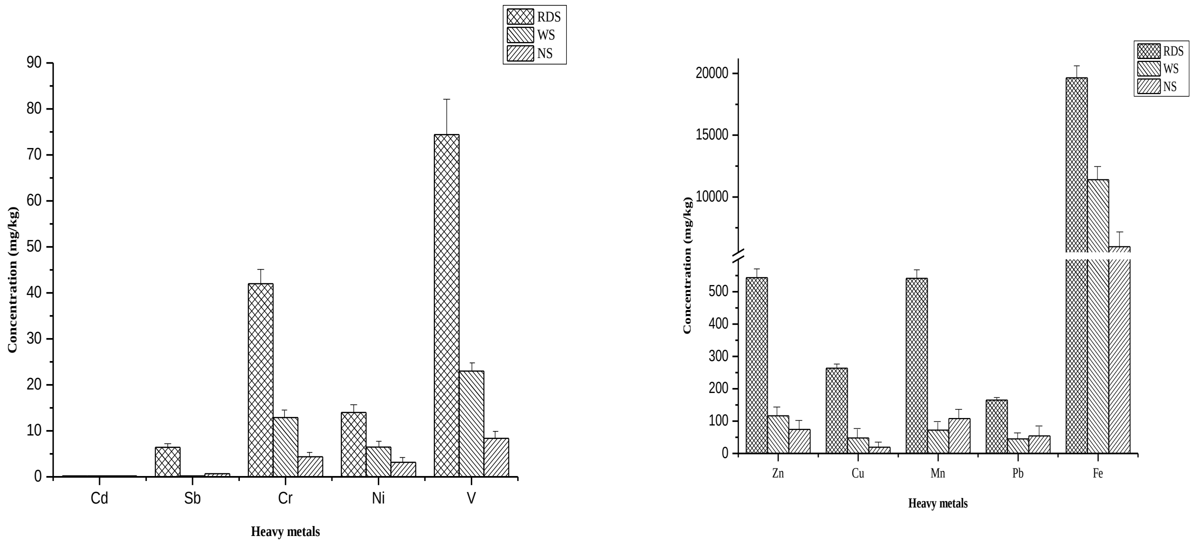


Figure. 1. Mean heavy metal concentrations (vertical lines on top of bars = standard errors)

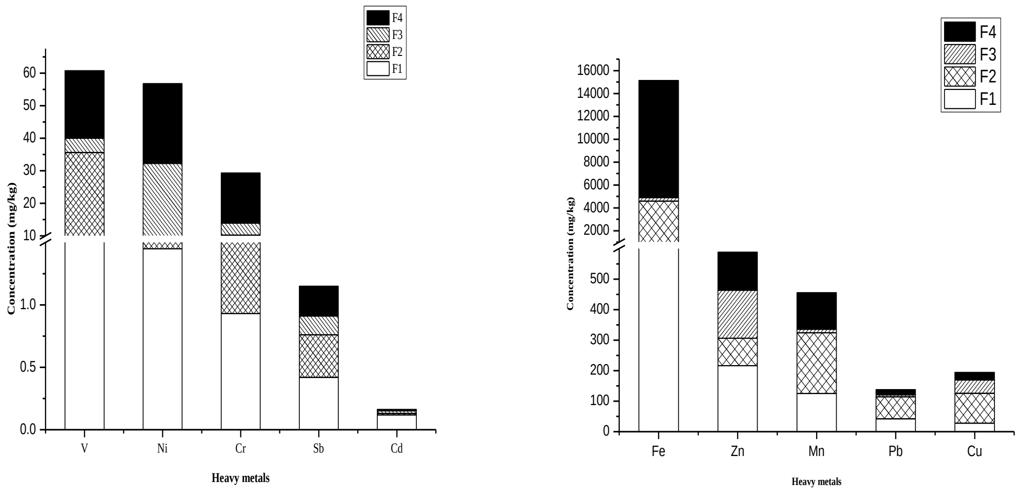
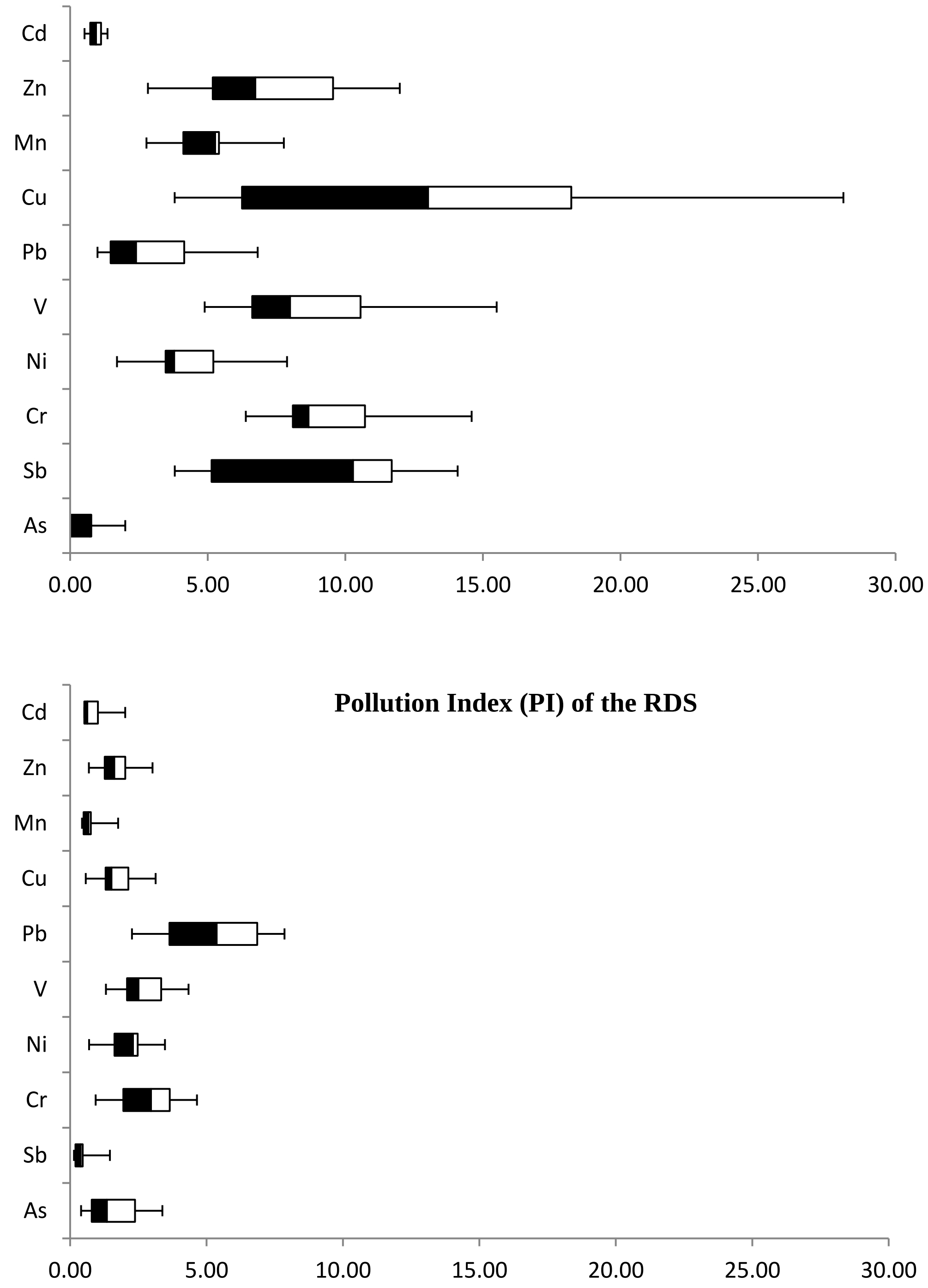


Figure. 2. Concentrations of metal fractions in RDS (F1, exchangeable + water and acid soluble; F2, reducible; F3, oxidisable; F4, residual)



Pollution Index (PI) of the RDS

Pollution Index (PI) of the WS

Figure 3. Pollution Index values of RDS and WS

(The line separating the dark and light shaded area inside the box represents the median; the boxes mark the 25th and 75th percentiles; the horizontal line outside the box, the whisker, denotes the maximum and minimum values)

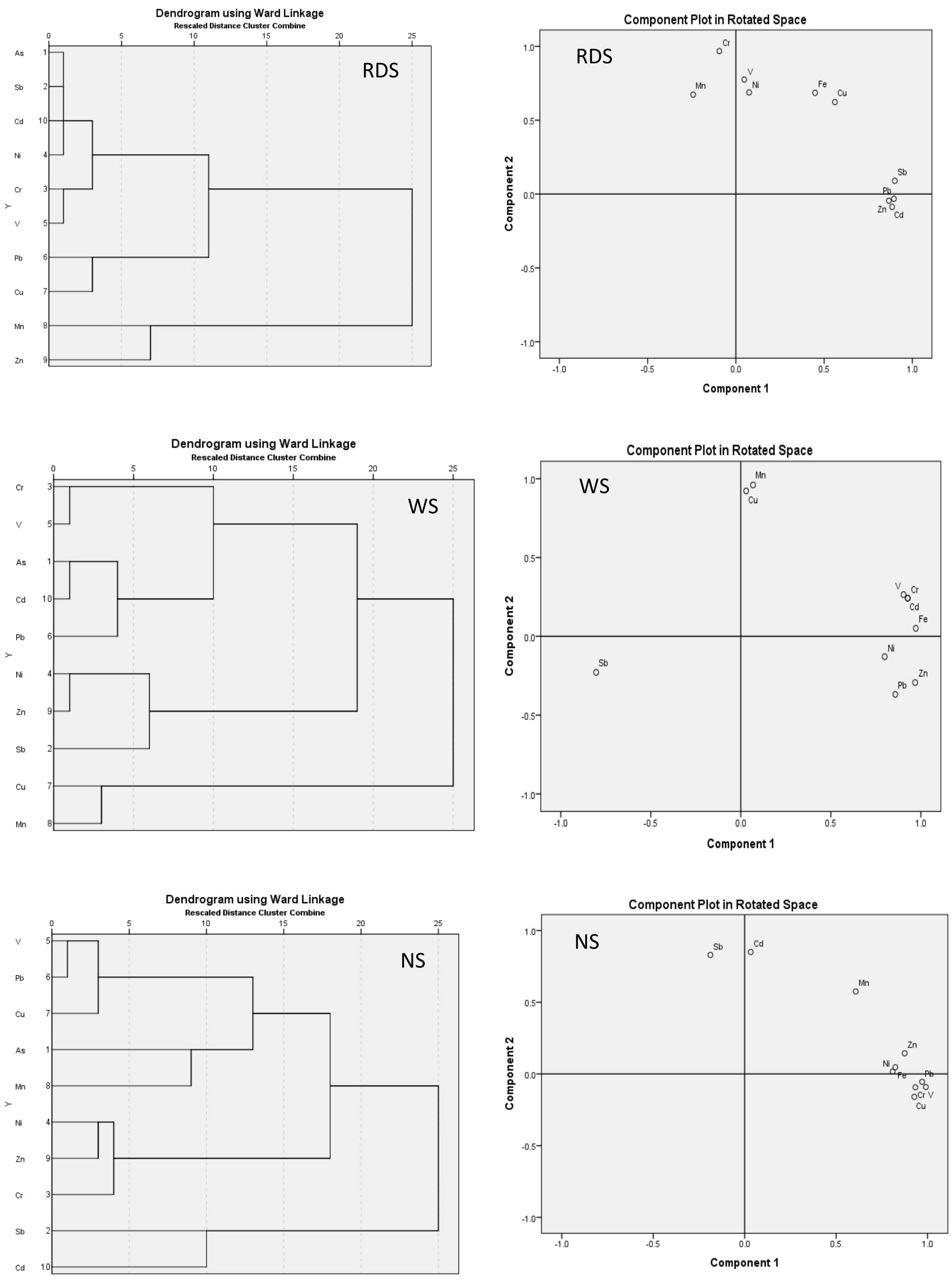


Figure 4. Hierachical dendograms and principal component analysis for 10 metals in RDS, WS and NS

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