AES BIOFLUX

Advances in Environmental Sciences - International Journal of the Bioflux Society

Relative atomic variation (RAV) and correlation of elements: qualitative tools in the assessment of metal contamination in estuarine sediments

Hilario S. Taberna Jr.

Department of Chemistry, College of Arts and Sciences, University of the Philippines Visayas, 5023 Miagao, Iloilo, Philippines. Corresponding author: H. S. Taberna Jr., taberna_jr@yahoo.com

Abstract. Environmentally available Cr, Co, Cu, Ni, V, Li, Mn, Zn, Al, and Fe were determined in 60 surface sediments collected all along the Iloilo River Estuary in Central Philippines. The study area was divided into 3 sub-areas with 20 samples each representing the upper, middle, and mouth channels of the estuary. The average metal concentrations in the upper, middle, and mouth channels were: Cr (16.6, 19.0, and 18.4 µg g^{-1}, respectively), Co (8.19, 9.25, and 8.19 µg g^{-1}), Cu (18.7, 22.8, and 23.7 µg g^{-1}), Ni (28.1, 22.8, and 28.9 µg g^{-1}), V (44.7, 51.3 and 50.5 µg g^{-1}), Li (8.07, 9.44 and 10.3 µg g^{-1}), Mn (172, 164, and 143 µg g^{-1}), Zn (33.6, 41.9 and 47.3 µg g^{-1}), Al (1.48, 1.54 and 1.55 %) and Fe (1.68, 1.64, and 1.68 %). Results show that the metal levels in 3 different areas did not vary much from each other. Thus, it is difficult to identify the area of most concern with regards to heavy metal contamination. In order to address this problem, the indices of relative atomic variations (RAV) of metals in 3 different areas were determined. It was found out that RAV values determined for uncontaminated areas are in agreement with the reported metal/Al ratios of average continental rock and soils. Likewise, correlation coefficients were found useful in establishing the links between the metal and its carrier substances. It was demonstrated by this study that RAV and correlation coefficient were simple approaches to delineate metal contaminated areas in an estuary where meaningful cores for the determination of metal baseline concentration are difficult to acquire.
Key Words: heavy metals, grain-size effect, normalization, Iloilo river estuary.

Introduction. Although absolute concentration value of individual metal is useful in identifying contaminated sites, it has its own limitations. It is valid only if the concentration is really high and readily related to point sources. The reason for this is that grain size exercises a determining influence on the metal concentrations, both natural and anthropogenic, and variation in grain size in estuarine sediments is great even if they are from the same area (Förstner & Wittmann 1983). To compare metal data in estuarine sediments therefore, correction for grain-size effects is necessary. In addition, the influence of geologic, mineralogic, hydrologic, and biologic processes on element concentrations must be taken into account in the assessment of metal enrichment.

Allan & Brunskill (1977) had developed a sensitive qualitative tool, called the index of relative atomic variation (RAV), in the assessment of metal contamination in lake sediments. They defined RAV as the slope of the significant linear regression line for a particular element pair and similarity in RAV value implies similarity or possible homogeneity in a large number of processes in the geochemical cycle including weathering, transport, deposition, and diagenesis. It has been suggested that the RAV approach has a greater significance in the study of metal contamination in river sediments than the lake sediments because of the relative difficulty in obtaining meaningful cores of river sediments.

In this paper the amount of 10 elements (Cr, Co, Cu, Ni, V, Li, Mn, Zn, Al, and Fe) in 60 surface sediments collected all along the Iloilo River Estuary were reported. These metal values are considered to be environmentally available based on the analytical method used in the extraction of these metals. The metals Cr, Cu, Ni, Fe and Zn were considered in this study because these elements were the pollutants of primary concern in Iloilo River estuary (Taberna & Wenclawiak 2005) and the most common metals studied in port areas (Nasr et al 2006; Stakėnienė et al 2010; Ali et al 2011; Galkus et al 2012). Although the said elements, along with Co, V and Mn, were essential minerals and play important roles in biological systems, toxic effects could also manifest at high concentrations (Mukherjee et al 2004; Le et al 2009; Korbecki et al 2012; Nurnadia et al 2013). Aluminum has no known biological function and is a neurotoxic metal associated with the Alzheimer's disease (Tomljenovic 2011; Shaw et al 2014). However, Al together with Li and Fe were important in geochemical studies as normalizers to correct grain-size effect on metal concentrations (Loring 1990; Din 1992; Schiff & Weisberg 1999). Furthermore, correlation coefficients from the linear regression analyses provide clues to the possible association of metals in sediments. Determination of RAV values in surface sediments from the upper (agricultural-residential area), middle (residential-commercial area), and mouth (commercial-industrial area) of the estuary delimited the estuarine areas of most contaminated sediments.

Material and Method

Sampling procedure and site. Surface sediment samples (0-5 cm) were collected along the Iloilo River Estuary in December 2000. The study area was divided into 3 sub-areas with 20 samples each representing the upper, middle, and mouth channels of the estuary (Figure 1). The same sampling procedure and classification of samples were employed as reported by Taberna & Wenclawiak (2005).

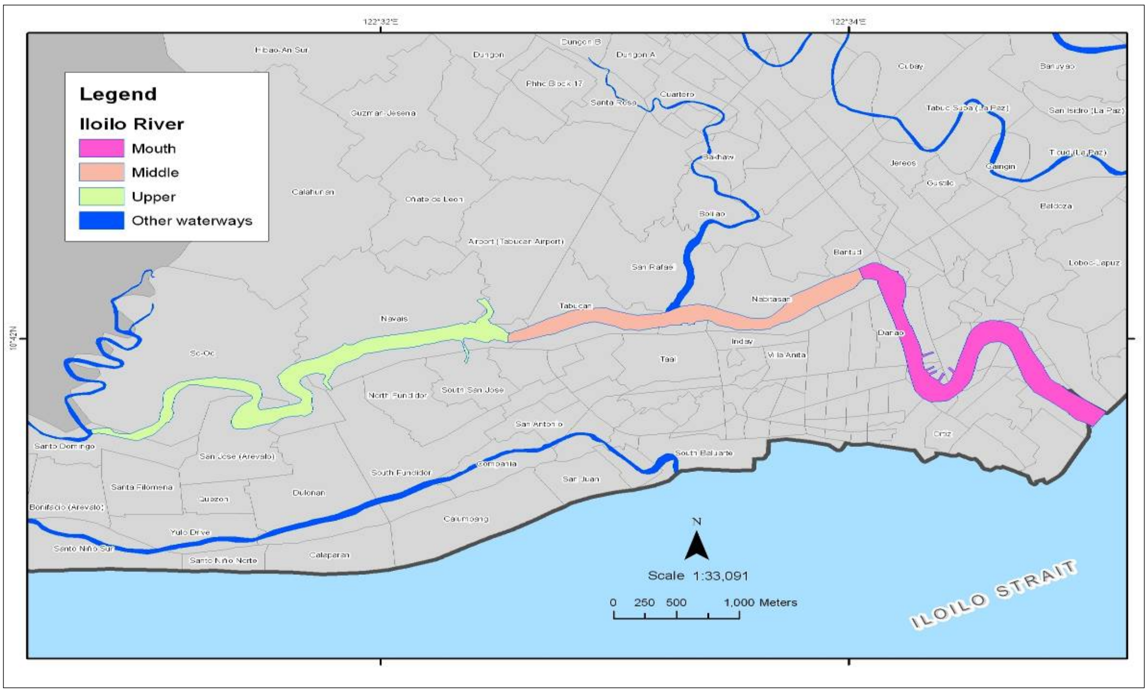


Figure 1. Map of Iloilo River estuary divided into 3 sub-areas: the upper, middle and mouth channels (Source: Moscoso (2014)).

Acid digestion. A representative wet sediment sample of 0.5 g was first digested in 20 mL 1:1 HNO_3 (p.a., ACROS ORGANICS) at 80±5^{o}C for about 1 hour using the open-beaker hot plate method. Then, 20 mL of deionized H_2O was added, washing the sides of the beaker to the sample, and digestion was continued until the sample solution was about 10 mL. After cooling, the acid digest was filtered in No. 595 Schleicher & Schleicher filter paper and diluted with deionized H_2O to 50 mL.

Metal determination. The metals Cr, Co, Cu, Ni, V, Li, Mn, Zn, Al, and Fe were measured by ICP-AES (LEEMANS, PS1000). Measurement conditions: power 1.0 kW, coolant 13 L min^{-1}, nebulizer 40 psi, auxiliary 0.3 L min^{-1}, pump rate 1.0 mL min^{-1}. The wavelengths (in nm) for these metals are: Cr - 267.720; Co - 228.616; Cu - 324.754; Ni - 231.604; V - 310.230; Li - 670.784; Mn - 257.610; Zn - 213.856; Al - 308.215; Fe - 259.940. The wavelength selection followed the instrument manufacturer's recommendation and in consonance with the US EPA Method 600/R-94/111 (US EPA 1994) that is by taking into consideration the freedom from spectral interferences and the different sensitivities and expected concentration of the metal in the sample.

Data analysis. Linear regression analyses were performed on the metal data from the three sites to determine the correlation coefficients for all possible pairs of elements. Then, the slopes of the linear regression, representing the index of the RAV, were calculated from the metal concentration (μmoles g^{-1}) of those metal pairs having significant correlations. All calculations and graphical presentations were carried out using SPSS v.16 program.

Results and Discussion. Environmentally available elements in surface sediments of the Iloilo River Estuary are listed in Tables 1, 2, 3. Metal contents of sediments from 3 different areas did not vary much from each other, thus, it is difficult to identify contaminated area using these data. Most of the samples are mud (80% are < 60 µm) and sandy mud (50-70% are < 60 µm).

Table 1

Metal concentrations (µg g^{-1} dry weight except for Al and Fe which were expressed in %) in surface sediments from the upper area (agricultural-residential area) of Iloilo River Estuary

Station no.	*Cr*	*Co*	*Cu*	*Ni*	*V*	*Li*	*Mn*	*Zn*	*Al*	*Fe*
SS1	11.0	11.4	9.19	18.7	34.5	3.59	215	21.5	1.28	1.35
SS2	14.1	9.05	9.04	24.1	36.1	4.78	213	30.1	1.21	1.47
SS3	16.6	11.1	16.3	22.4	43.0	7.20	184	29.7	1.44	1.68
SS4	21.5	10.7	17.6	35.0	57.1	11.6	207	33.4	1.71	2.15
SS5	15.3	6.38	16.6	21.6	37.2	6.73	139	28.0	1.34	1.50
SS6	15.3	8.63	17.8	23.2	38.5	7.10	228	30.7	1.46	1.66
SS7	13.3	7.61	15.4	37.5	43.1	7.78	190	32.0	1.63	1.72
SS8	16.5	6.86	17.4	23.6	44.1	6.73	159	34.9	1.73	1.90
SS9	24.5	11.3	30.7	26.1	49.6	11.2	260	45.6	1.53	1.90
SS10	15.2	9.96	21.2	41.7	47.2	6.79	181	31.7	1.47	1.56
SS11	22.1	9.79	26.1	27.2	52.9	9.26	152	40.6	1.51	1.76
SS12	15.3	8.09	16.7	20.2	36.3	8.24	154	29.3	1.41	1.59
SS13	12.7	6.08	16.6	19.5	43.7	3.76	121	27.5	1.27	1.23
SS14	19.2	7.85	21.1	23.2	43.6	9.77	159	37.7	1.62	1.77
SS15	19.1	10.1	7.81	34.9	49.8	10.8	181	38.4	1.39	1.84
SS16	20.5	9.73	16.5	33.8	52.3	13.1	145	41.2	1.65	2.01
SS17	21.2	7.76	23.6	21.2	44.4	11.8	160	47.8	1.71	1.97
SS18	13.0	6.54	13.9	31.1	39.1	9.41	101	31.1	1.42	1.39
SS19	15.3	8.82	29.9	37.6	58.1	6.06	161	34.1	1.71	1.72
SS20	11.3	7.94	30.6	39.6	43.5	5.71	129	26.1	1.16	1.42
Mean	16.6	8.19	18.7	28.1	44.7	8.07	172	33.6	1.48	1.68
Range	11.0-24.5	6.08-11.4	7.81-30.7	18.7-41.7	34.5-58.1	3.59-13.1	101-259	21.5-47.8	1.21-1.73	1.23-2.15

Table 2

Metal concentrations (μg g^{-1} dry weight except for Al and Fe which were expressed in %) in surface sediments from the middle area (residential-commercial area) of Iloilo River Estuary

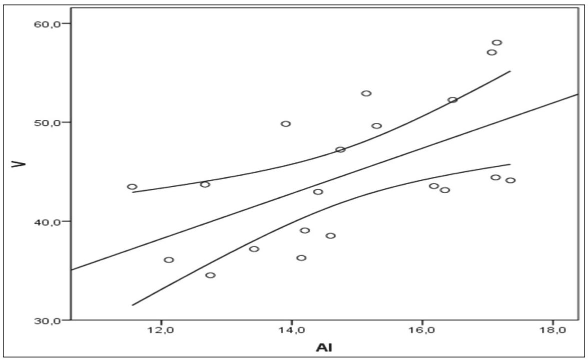
Station no.	Cr	Co	Cu	Ni	V	Li	Mn	Zn	Al	Fe
SMI1	19.6	8.63	21.4	24.4	61.5	5.98	124	34.0	1.60	1.68
SMI2	19.7	9.29	17.8	23.9	49.5	7.06	190	31.9	1.65	1.81
SMI3	19.0	12.2	24.9	35.3	57.6	7.36	165	30.9	1.69	1.75
SMI4	23.1	11.4	25.5	25.6	56.8	8.62	320	34.9	1.68	1.86
SMI5	12.8	9.82	6.1	20.4	33.0	5.92	336	24.0	1.02	1.07
SMI6	20.6	9.73	26.6	30.5	54.1	9.04	150	40.0	1.45	1.57
SMI7	20.6	10.4	28.6	32.6	55.3	9.58	152	40.0	1.48	1.62
SMI8	21.2	7.59	24.3	21.4	45.7	11.1	133	47.9	1.67	1.87
SMI9	23.2	9.21	21.8	23.5	63.4	11.6	170	40.4	1.58	1.60
SMI10	24.7	9.87	19.1	24.2	49.4	14.9	211	49.4	1.63	1.72
SMI11	15.7	9.23	22.1	36.8	48.5	8.08	131	34.4	1.52	1.55
SMI12	13.3	7.78	31.1	35.5	48.1	5.41	139	37.2	1.27	1.48
SMI13	24.6	9.14	25.1	23.1	45.5	12.8	180	53.0	1.63	1.77
SMI14	22.3	10.1	28.3	31.1	53.8	12.2	168	53.6	1.54	1.73
SMI15	15.5	8.79	22.7	37.5	46.5	8.53	95.4	39.4	1.37	1.47
SMI16	14.3	7.25	16.2	34.4	43.2	11.1	97.7	41.0	1.62	1.68
SMI17	19.1	8.6	23.1	21.7	45.6	13.1	131	45.8	1.51	1.51
SMI18	17.7	9.44	21.1	28.1	61.4	9.77	175	50.8	1.63	1.78
SMI19	14.6	6.74	19.5	23.6	54.5	5.84	107	55.7	1.64	1.59
SMI20	19.0	9.77	30.3	38.0	53.5	10.8	112	54.2	1.59	1.70
Mean	19.0	9.25	22.8	28.6	51.3	9.44	164	41.9	1.54	1.64
Range	12.8-24.7	6.74-12.2	6.12-31.1	20.4-37.5	34.8-58.4	5.41-14.9	95.3-335	24.0-55.7	1.02-1.69	1.07-1.87

Table 3

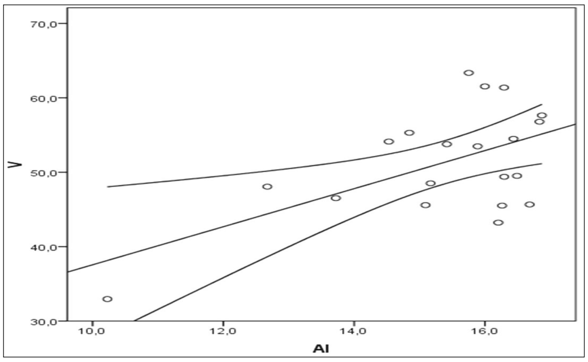
Metal concentrations (μg g^{-1} dry weight except for Al and Fe which were expressed in %) in surface sediments from the mouth area (commercial-industrial area) of Iloilo River Estuary

Station no.	Cr	Co	Cu	Ni	V	Li	Mn	Zn	Al	Fe
SMO1	14.9	7.14	17.4	20.5	38.1	11.0	96.3	33.4	1.23	1.12
SMO2	17.4	8.41	21.7	26.5	55.8	9.51	144	56.6	1.64	1.74
SMO3	23.6	10.6	29.1	30.6	58.4	13.7	176	57.5	1.70	1.83
SMO4	27.6	10.1	30.8	24.2	70.1	11.7	141	58.6	1.74	1.98
SMO5	14.9	7.25	20.3	21.2	34.8	10.3	128	44.3	1.15	1.19
SMO6	23.3	7.75	22.8	23.2	57.5	9.59	98.9	45.5	1.46	1.50
SMO7	21.5	9.74	28.6	23.7	47.4	12.3	148	64.5	1.53	1.73
SMO8	21.6	8.69	33.0	25.6	58.9	10.2	117	54.8	1.42	1.62
SMO9	15.5	7.51	32.5	35.7	54.9	7.58	114	52.5	1.57	1.68
SMO10	15.8	8.03	26.1	36.1	47.1	6.75	121	44.0	1.41	1.44
SMO11	13.1	7.32	29.9	36.9	51.1	5.14	116	40.3	1.53	1.53
SMO12	21.5	8.28	24.2	23.4	42.8	11.8	170	63.1	1.45	1.53
SMO13	25.4	8.47	33.2	25.0	66.0	10.9	167	75.2	1.60	1.93
SMO14	19.4	6.71	26.0	18.1	39.9	10.6	152	49.5	1.38	1.48
SMO15	16.3	6.70	19.9	28.4	46.8	11.0	141	45.0	1.74	1.91
SMO16	12.2	6.65	13.9	36.0	41.0	9.02	120	31.3	1.60	1.59
SMO17	20.6	9.14	20.6	28.8	53.6	11.8	214	40.1	1.56	2.15
SMO18	15.9	7.85	16.2	34.9	48.5	11.7	166	33.2	1.73	1.83
SMO19	16.5	8.71	16.7	37.0	52.4	11.9	166	30.9	1.87	1.97
SMO20	11.7	8.66	11.1	42.4	45.2	8.62	173	25.4	1.69	1.86
Mean	18.4	8.19	23.7	28.9	50.5	10.3	143	47.3	1.55	1.68
Range	11.7-27.6	6.65-10.6	11.1-33.2	18.1-42.4	34.8-58.4	5.14-13.7	96.3-214	25.4-75.2	1.14-1.87	1.12-2.15

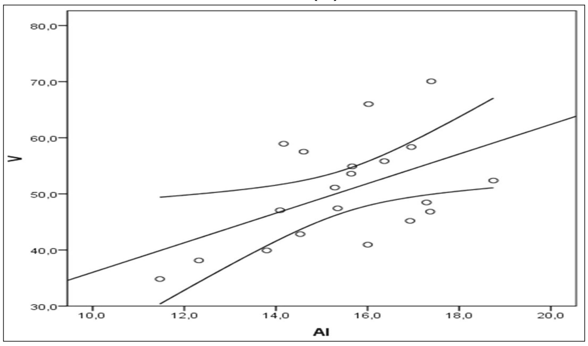
The use of correlation analysis in untangling the links between the metals and carrier substances has been reported in literatures (Jaquet et al 1982; Förstner & Wittmann 1983; Yu et al 2001; Heimbürger et al 2012). Figures 2 and 3 show the scatter-plot for V vs. Al and V vs. Fe in 3 areas of the estuary, respectively. V is significantly correlated with Al and Fe in the upper, middle, and mouth of the estuary with r^2 values of 0.35 and 0.42, 0.32 and 0.28, and 0.27 and 0.39, respectively. Significant correlations between V/Al and V/Fe indicate an allogenic relationship and that adsorption plays the vital role in removing V from water (Windom et al 1989).



(a)

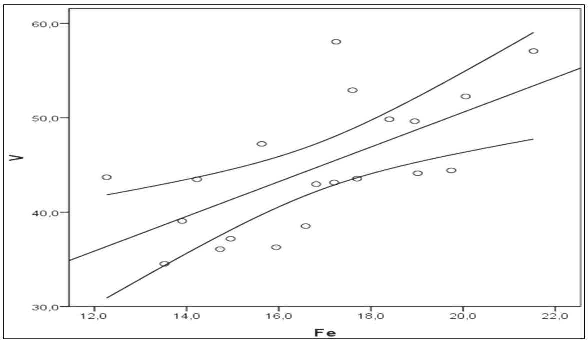


(b)

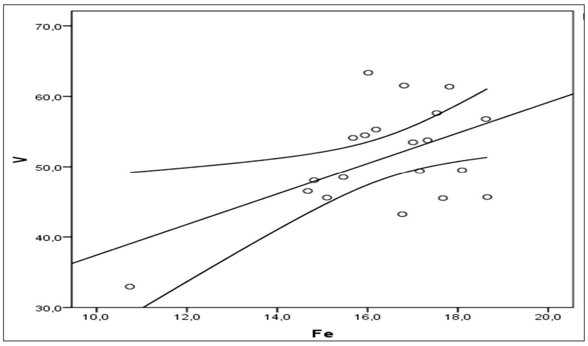


(c)

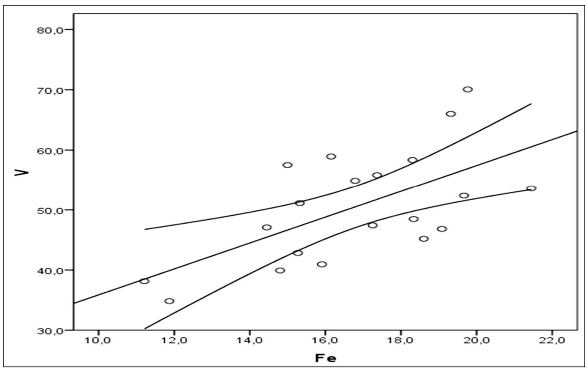
Figure 2. Scatter-plot for V/Al in the sediments from the (a) upper, (b) middle and (c) mouth areas of Iloilo River estuary.



(a)



(b)



(c)

Figure 3. Scatter-plot for V/Fe in the sediments from the (a) upper, (b) middle and (c) mouth areas of Iloilo River estuary.

Significant correlations also exist in all areas for Cr vs. Li (r^2 = 0.67, 0.43, and 0.32 for upper, middle and mouth, respectively) and Cr vs. V (r^2 = 0.37, 0.17, and 0.48, respectively). For Cr vs. Al (Figure 4) and Cr vs. Fe, significant covariations exist only in the upper (r^2 = 0.34 and 0.68, respectively) and middle (r^2 = 0.31 and 0.39, respectively) areas of the estuary. A great alteration in the strength of relationship occurs in the mouth. The loss of geochemical proportions between the two elements over a range of concentration changes indicates cultural contamination and natural anomalies (Allan & Brunskill 1977).

Like Cr, Zn covaries significantly with Al (Figure 4) and Fe only in the upper (r^2 = 0.41 and 0.56, respectively) and middle (r^2 = 0.19 and 0.17, respectively) areas. Correlation disappears for Zn vs. Al (0.00) and a great change occurs for Zn vs. Fe (0.01) in the mouth. The same relationship was observed for Zn vs. Li with r^2 values of 0.65, 0.35, and 0.08 in the upper, middle, and mouth areas, respectively. For Zn vs. V, significant correlations occur in the upper (0.31) and mouth (0.25) areas. A significant decrease in correlation occurs in the middle area (0.04).

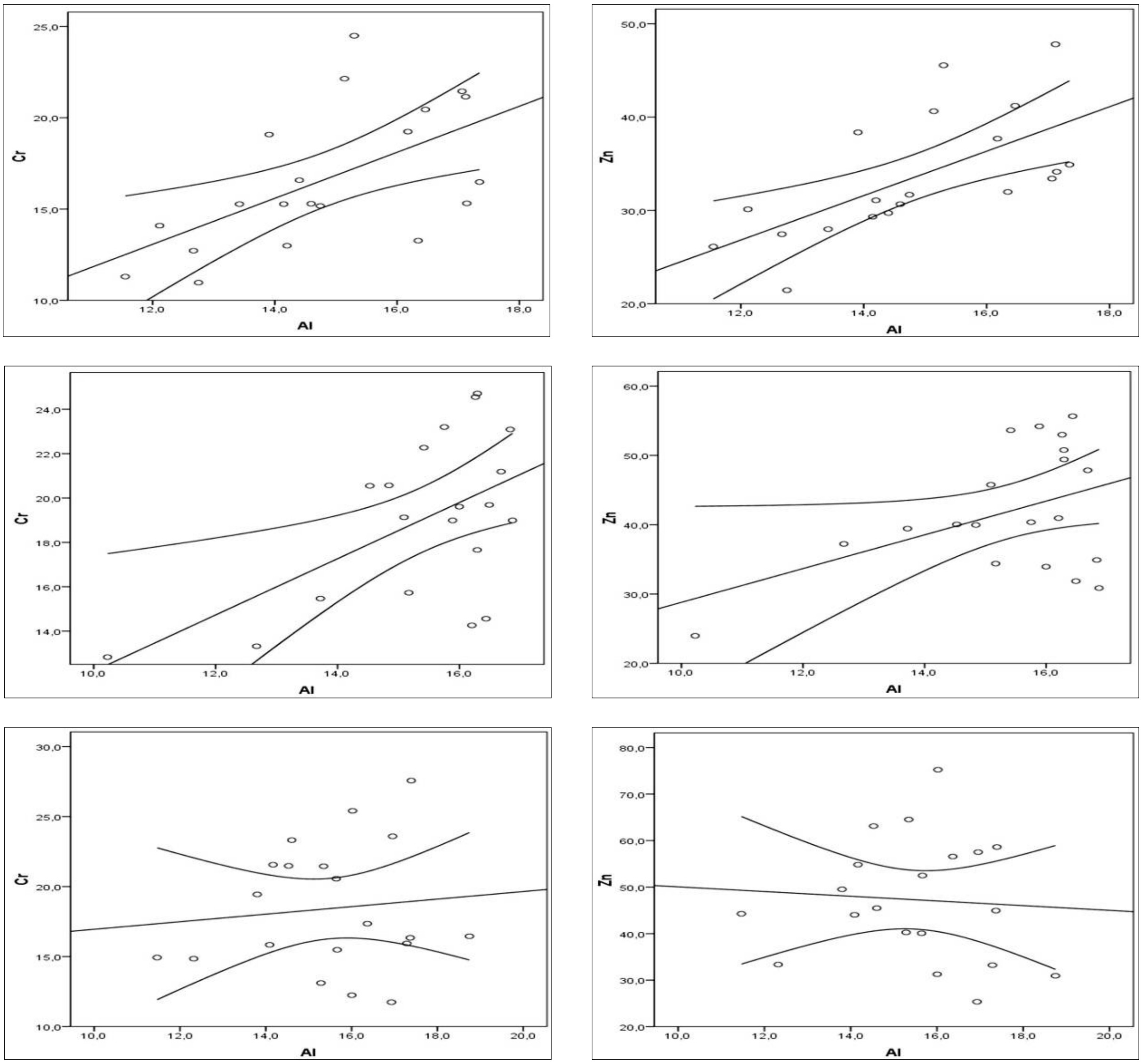


Figure 4. Scatter-plot for Cr/Al (left) and Zn/Al (right) in the sediments from the upper, middle and mouth areas of Iloilo River estuary.

Co shows positive correlation with Al, Fe, Li, and V. However, significant correlations occur only in the mouth area. Coefficient of determination for Al, Fe, Li, and V are 0.16, 0.29, 0.25, and 0.38, respectively. On the other hand, Co covaries significantly with Mn in all areas of the estuary. The strength of relationship reduces from upper to mouth. The r^2 values for upper, middle, and mouth areas are 0.48, 0.29, and 0.25, respectively.

Only Ni among the elements studied does not covary significantly with other elements in at least two areas of the estuary. Significant negative correlation exists for Ni against Zn, Li, and Cr in the mouth area with r^2 values of 0.28, 0.20, and 0.31, respectively. Ni vs. Mn shows significant negative (0.21) relationship in the middle area. Furthermore, significant positive correlation exists with Ni vs. Al (0.31) and Ni vs. V (0.34) in the mouth and upper areas, respectively. Ni covaries positively with Fe in the upper (0.04) and mouth (0.13) areas; however, the strength of relationship is weak. The unique relationship of Ni with the other elements may indicate that its chemistry is governed by different parameters, probably pyrite acts as the dominant host for this metal. The correlation coefficients between metals in 3 different areas of the estuary were presented in Table 4.

Table 4

Correlation coefficients of metals in sediments from the upper, middle and mouth areas of Iloilo River estuary; bold values means significant at p = 0.05 level

	Cu	*Cr*	*Ni*	*Zn*	*Li*	*Co*	*Mn*	*Fe*	*Al*	*V*
Fe	0.213	**0.823**	0.213	**0.751**	**0.803**	0.349	0.317		**0.814**	**0.648**
	0.457	**0.624**	-0.012	0.414	0.351	0.144	-0.194		**0.919**	**0.532**
	0.038	0.337	0.357	0.122	0.342	**0.541**	**0.710**		**0.858**	**0.622**
Al	0.280	**0.584**	0.181	**0.639**	**0.593**	0.042	0.092	**0.814**		**0.592**
	0.300	**0.560**	-0.070	0.439	0.363	0.064	-0.278	**0.919**		**0.568**
	-0.125	0.108	**0.556**	-0.069	0.221	0.396	**0.471**	**0.858**		**0.516**
V	**0.486**	**0.610**	**0.577**	**0.553**	**0.502**	0.334	0.033	**0.648**	**0.592**	
	0.467	0.409	0.111	0.189	-0.027	0.285	-0.195	**0.532**	**0.568**	
	0.583	0.691	0.046	0.500	0.123	0.617	0.150	0.622	0.516	
Cu		0.334	0.270	0.388	0.158	0.004	-0.048	0.213	0.280	**0.486**
		0.349	**0.480**	0.395	0.176	0.171	-0.408	**0.460**	0.300	**0.467**
		0.618	-0.310	0.799	-0.067	0.330	-0.150	0.038	-0.125	0.583
Cr	0.334		-0.011	**0.877**	**0.817**	0.394	0.302	**0.823**	**0.584**	**0.610**
	0.349		-0.344	0.327	**0.654**	0.431	0.201	**0.624**	**0.560**	0.409
	0.618		-0.562	0.761	0.562	0.627	0.249	0.337	0.108	0.691
Ni	0.270	-0.011		0.081	0.213	0.153	-0.079	0.213	0.181	**0.577**
	0.480	-0.344		-0.040	-0.153	0.164	**-0.460**	-0.012	-0.070	0.111
	-0.310	-0.562		-0.535	-0.451	0.022	0.132	0.357	0.556	0.046
Zn	0.388	**0.877**	0.081		**0.806**	0.152	0.132	**0.751**	**0.639**	**0.553**
	0.395	0.327	-0.040		**0.591**	-0.321	-0.415	0.414	0.439	0.189
	0.799	0.761	-0.535		0.278	0.406	0.099	0.122	-0.069	0.500
Li	0.158	**0.817**	0.213	**0.806**		0.219	0.047	**0.803**	**0.593**	**0.502**
	0.176	**0.654**	-0.153	**0.591**		0.073	-0.077	0.351	0.363	-0.027
	-0.067	0.562	-0.451	0.278		0.503	0.533	0.342	0.221	0.123
Co	0.004	0.394	0.153	0.152	0.219		**0.691**	0.349	0.042	0.334
	0.171	0.431	0.164	-0.321	0.073		**0.537**	0.144	0.064	0.285
	0.330	0.627	0.022	0.406	0.503		0.499	0.541	0.396	0.617
Mn	-0.048	0.302	-0.079	0.132	0.047	**0.691**		0.317	0.092	0.033
	-0.408	0.201	**-0.460**	-0.415	-0.077	**0.537**		-0.194	-0.278	-0.195
	-0.150	0.249	0.132	0.099	0.533	0.499		0.710	0.471	0.150

The relationship of the elements with organic C and total N were also determined. Linear regression analyses were applied to the metal/Al data vs organic C, total N, and available P data obtained on the same sediments (Tizon, unpublished data). Cu, V, Zn, and Cr are significantly correlated with organic C and total N in the commercial-industrial area with r^2 values of 0.54 and 0.61, 0.38 and 0.37, 0.37 and 0.66, and 0.45 and 0.55, respectively. However, in the residential-agricultural area, only Cu covaries significantly with organic C with r^2 value of 0.35 and no element is significantly correlated with total N. Cr is significantly correlated with total C. Ni, on the other hand, shows significant negative correlation with organic C and total N in the commercial-industrial area with r^2 values of 0.38 and 0.46, respectively and an almost zero correlation for both nutrients in the residential-agricultural area. No metal is correlated with available P in both areas of the estuary.

Determination of the RAV of elements in 3 different areas of the Iloilo River Estuary delimited the areas of most contaminated sediments. The sensitivity of the RAV value in detecting element proportions depends on the metal pairs selected for correlation (Allan & Brunskill 1977). Based from the linear regression analyses made to the metal data, Al, Fe, and Li were found to be sensitive predictors of Cr and Zn; Al and Fe for V; V for Cu and also for Cr and Zn; and Mn for Co. Al, Fe, and Li were commonly used as geochemical normalizers in the study of metal contamination in sediments (Windom et al 1989; Kersten & Smedes 2002; Acevedo-Figueroa et al 2006; Tavakoly Sany et al 2011; Heimbürger et al 2012; Ho et al 2013; Yuan et al 2013; Wiklund et al 2014).

The RAV values of elements in Iloilo River Estuary surface sediments are presented in Table 5.

Table 5

Relative atomic variation (RAV) of elements in Iloilo River Estuary surface sediments

Elements	*N*	*r^2*			*RAV*		
		End	*Middle*	*Mouth*	*End*	*Middle*	*Mouth*
V/Al	20	0.35	0.32	0.27	12	14	14
V/Fe	20	0.42	0.28	0.39	20	24	24
Cr/Al	20	0.34	0.31	ns	7	7	-
Cr/Fe	20	0.68	0.39	ns	14	14	-
Cr/Li	20	0.67	0.43	0.32	1533	1177	1645
Zn/Al	20	0.41	0.19	ns	10	10	-
Zn/Fe	20	0.56	0.17	ns	18	18	-
Zn/Li	20	0.65	0.35	ns	2076	2071	-
Cu/V	20	0.31	0.22	0.34	3963	2882	3412
Cr/V	20	0.37	0.17	0.48	3334	2018	3328
Zn/V	20	0.31	ns	0.25	4151	-	5579
Co/Mn	20	0.48	0.29	0.25	277	103	174

N – number of samples; ns - not significant at the 95% confidence level; all RAV values is in $x10^{-4}$.

V is relatively enriched in the middle and mouth areas relative to Al and Fe. Cr and Zn contaminations occur in the mouth area as indicated by the great alteration in magnitude of their respective RAV values. It is interesting to note that the slopes of Cr/Al, Cr/Fe, Zn/Al, Zn/Fe, and Zn/Li relationships in the upper and middle areas are the same despite of the variation of Cr (0.32 and 0.37 µmoles g^{-1}, respectively) and Zn (0.51 and 0.64 µmoles g^{-1}) concentrations. A geochemical balance of these elements is therefore maintained at the two stated sites. Cu and Cr are enriched in the upper and mouth areas relative to V. Cu/V and Cr/V RAV values are somehow similar on these two areas. Zn in relative to V is relatively enriched in the mouth than in the upper area and a geochemical imbalance exists between the two elements in the middle area. The higher inputs of Cu, Cr, and Zn in sediments relative to V could be attributed to the agricultural wastes in the upper area and from commercial and industrial wastes in the mouth. Cu, Cr, and Zn have stronger affinity to the organic C than V as confirmed by their respective correlation coefficient values. Co enrichment is observed in the upper area relative to Mn, despite of high Mn concentration. The higher input of Co could be attributed to the fish culture and piggery activities on this area. Fish and swine feeds are usually added with Co as supplement (Abdullah Alkhalaf et al 2010; Bokoye et al 2011).

Table 6 shows the comparisons between the RAV values in Iloilo River surface sediments and the metal/Al ratios for average continental crustal rocks and for average continental soils as reported by Windom et al (1989). Only RAV values of metal/Al pairs with significant correlation, except for Cu, were considered. The metal compositions of areas identified by the RAV approach as uncontaminated are similar to expected continental sources. Ni is somehow enriched in the mouth area, probably due to industrial input and Mn is depleted.

Table 6

Comparison of RAV[a] values to natural abundances

Metal	*End*		*Middle*		*Mouth*		*Metal/Al*[b]	
	r^2	*RAV*	r^2	*RAV*	r^2	*RAV*	*Crustal rock*	*Soil*
Cr	0.34	7	0.31	7	ns	-	10	9.8
Zn	0.41	10	0.19	10	ns	-	18	13
Cu	0.08[ns]	4.5	0.09 [ns]	4.4	ns	-	4.6	4.8
V	0.35	12	0.32	14	0.27	14		
Ni	ns	-	ns	-	0.31	9.8	7.1	7.0
Co	ns	-	ns	-	0.16	1.1	1.9	1.1
Fe	0.66	0.54	0.85	0.49	0.74	0.61	0.56	0.52
Li	0.35	35	ns	-	ns	-		
Mn	ns	-	ns	-	0.22	39	104	140

[a] all RAV values is in $x10^{-4}$ except for Fe; [b] metal/Al ratio as reported by Windom et al (1989);
ns – not significant at the 95% confidence level.

Conclusions. Metal concentrations alone are insufficient to identify anomalies or contamination in the surface sediments of Iloilo River Estuary because metal values in 3 study areas did not vary much from each other. The determination of relative atomic variation (RAV) of elements in surface sediments from 3 areas of the estuary delimited areas of most contaminated sediments. Cr, Cu, Zn, Ni, and V enrichments were identified to occur in the commercial-industrial area while that of Co was identified in the agricultural-residential area. Simple correlation analysis proves to be useful in untangling the links between the metal and carrier substances. Environmentally available elements bind in surface sediments of Iloilo River Estuary either by sorption, coprecipitation with hydrous Fe/Mn oxides, and complexation and flocculation with organic matter or by combination of 2 or all of these processes. The RAV values determined in areas considered to be uncontaminated are in agreement with the reported metal/Al ratios for the average continental rocks and soils. This study has demonstrated that the RAV approach is an effective tool in identifying metal contamination in estuarine sediments where meaningful cores for the metal background concentration determinations are relatively difficult to obtain.

Acknowledgements. The author would like to thank Prof. Dr. Bernd Wenclawiak of University of Siegen, Germany for hosting the research work and to the German Academic Exchange Service (DAAD) for the grant and to Mr. Allan Dino Moscoso for the preparation of site map.

References

Abdullah Alkhalaf N., Khaled Osman A., Ahmed Salama K., 2010 Monitoring of aflatoxins and heavy metals in some poultry feeds. African Journal of Food Science 4(4):192-199.

Acevedo-Figueroa D., Jiménez B. D., Rodríguez-Sierra C. J., 2006 Trace metals in sediments of two estuarine lagoons from Puerto Rico. Environmental Pollution 141:336-342.

Ali A. A., Elazein E. M., Alian M. A., 2011 Determination of heavy metals in four common fish, water and sediment collected from Red Sea coast at Jeddah Islamic Port. Journal of Applied Environmental and Biological Sciences 1(10):453-459.
Allan R. J., Brunskill G. J., 1977 Relative atomic variation (RAV) of elements in lake sediments: Lake Winnipeg and other Canadian lakes. In: Interactions between sediments and freshwater: Proceedings of an International Symposium, Amsterdam, September 6–10, 1976. Golterman H. L. (ed), The Hague: Junk & Wageningen, PUDOC, pp. 108–120.
Bokoye C. O., Ibeto C. N., Ihedioha J. N., 2011 Assessment of heavy metals in chicken feeds sold in south eastern, Nigeria. Advances in Applied Science Research 2(3):63-68.
Din Z., 1992 Use of aluminum to normalize heavy metal data from estuarine and coastal sediments of Strait of Melaka. Marine Pollution Bulletin 24:484-491.
Forstner U., Wittmann G. T. W., 1983 Metal pollution in the aquatic environment. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 486 pp.
Galkus A., Joksas K., Stakeniene R., Lagunaviciene L., 2012 Heavy metal contamination of harbour bottom sediments. Pol J Environ Stud 21(6):1583-1594.
Heimbürger L. E., Cossa D., Thibodeau B., Khripounoff A., Mas V., Chiffoleau J. F., Schmidt S., Migon C., 2012 Natural and anthropogenic trace metals in sediments of the Ligurian Sea (Northwestern Mediterranean). Chemical Geology 291:141–151.
Ho H. H., Swennen R., Cappuyns V., Vassilieva E., Neyens G., Rajabali M., Tran T. V., 2013 Assessment on pollution by heavy metals and arsenic based on surficial and core sediments in the Cam River Mouth, Haiphong Province, Vietnam. Soil and Sediment Contamination 22:415–432.
Jaquet J. M., Davaud E., Rapin F., Vernet J. P., 1982 Basic concepts and associated statistical methodology in the geochemical study of lake sediments. Hydrobiologia 91:139-146.
Kersten M., Smedes F., 2002 Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. Journal of Environmental Monitoring 4:109-115
Korbecki J., Baranowska-Bosiacka I., Gutowska I., Chlubek D., 2012 Biochemical and medical importance of vanadium compounds. Acta Biochimica Polonica 59(2):195–200.
Le Q. D., Shirai K., Nguyen D. C., Miyazaki N., Arai T., 2009 Heavy metals in a tropical eel *Anguilla marmorata* from the central part of Vietnam. Water Air Soil Pollut 204: 69–78.
Loring D. H., Naes K., Dahle S., Matishov G. G., Illin G., 1995 Arsenic, trace metals, and organic micro contaminants in sediments from the Pechora Sea, Russia. Marine Geology 128:153-167.
Mukherjee B., Patra B., Mahapatra S., Banerjee P., Tiwari A., Chatterjee M., 2004 Vanadium - an element of atypical biological significance. Toxicology Letters 150:135–143.
Nasr S. M., Okbah M. A., Kasem S. M., 2006 Environmental assessment of heavy metal pollution in bottom sediments of Aden Port, Yemen. International Journal of Oceans and Oceanography 1(1):99-109.
Nurnadia A. A., Azrina A., Amin I., Mohd Yunus A. S., Mohd Izuan Effendi H., 2013 Mineral contents of selected marine fish and shellfish from the west coast of Peninsular Malaysia. International Food Research Journal 20(1):431-437.
Schiff K. C., Weisberg S. B., 1999 Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. Marine Environmental Research 48:161-176.
Shaw C. A., Seneff S., Kette S. D., Tomljenovic L., Oller J. W. Jr., Davidson R. M., 2014 Aluminum-induced entropy in biological systems: implications for neurological disease. Journal of Toxicology, Article ID 491316, 27 pp., http://dx.doi.org/10.1155/2014/491316.

Stakėnienė R., Jokšas K., Galkus A., Lagunavičienė L., 2010 Pollution of bottom sediments in Šventoji Port. Environmental Research, Engineering and Management 1(47):13-23.
Taberna H. S., Wenclawiak B. W., 2005 Assessment of heavy metal contamination in surficial sediments of Iloilo River estuary. UPV Journal of Natural Sciences 2:166-180.
Tavakoly Sany B., Salleh A., Sulaiman A. H., Mehdinia A., Monazami G. H., 2011 Geochemical assessment of heavy metals concentration in surface sediment of West Port, Malaysia. International Journal of Biological, Veterinary, Agricultural and Food Engineering 5(8):58-62.
Tomljenovic L., 2011 Aluminum and Alzheimer's disease: after a century of controversy, is there a plausible link? Journal of Alzheimers Disease 23(4):567-598.
US EPA (United States Environmental Protection Agency), 1994 Method 600/R-94/111 Methods for the determination of metals in environmental samples. Available at: http://nepis.epa.gov/Exe/ZyPDF.cgi/300036HL.PDF?Dockey=300036HL.PDF. Accessed: November 2001.
Wiklund J. A., Hall R. I., Wolfe B. B., Edwards T. W. D., Farwell A. J., Dixon D. G., 2014 Use of pre-industrial floodplain lake sediments to establish baseline river metal concentrations downstream of Alberta oil sands: a new approach for detecting pollution of rivers. Environmental Research Letters 9 (2014) 124019 (9 pp.), doi:10.1088/1748-9326/9/12/124019.
Windom H. L., Schropp S. J., Calder F. D., Ryan J. D., Smith R. G., Burney L. C., Lewis F. G., Rawlinson C. H., 1989 Natural trace metal concentrations in estuarine and coastal marine sediments of the Southern United States. Environmental Science and Technology 23:314-320.
Yu K. C., Tsai L. J., Chen S. H., Ho S. T., 2001 Correlation analyses on binding behaviors of heavy metals with sediment matrices. Water Research 35(10):2417-2428.
Yuan X., Li T., Li J., Ye H., Ge M., 2013 Origin and risk assessment of potentially harmful elements in river sediments of urban, suburban, and rural areas. Polish Journal of Environmental Studies 22(2):599-610.

Received: 26 November 2014. Accepted: 28 January 2015. Published online: 01 February 2015.
Author:
Hilario S. Taberna Jr., Department of Chemistry, College of Arts and Sciences, University of the Philippines Visayas, 5023 Miagao, Iloilo, Philippines, e-mail: taberna_jr@yahoo.com

How to cite this article:
Taberna Jr. H. S., 2015 Relative atomic variation (RAV) and correlation of elements: qualitative tools in the assessment of metal contamination in estuarine sediments. AES Bioflux 7(1):41-51.