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Distribution of Dissolved Trace Metals Around the Sacrificos Coral Reef Island, in the Southwestern Gulf of Mexico

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Abstract A reef system in the southwestern Gulf of Mexico is affected by anthropogenic activities, sourced by urban, fluvial, and sewage waters. Dissolved metals have higher concentrations during the rainy season. V and Pb, were derived from an industrial source and transported to the study area by rain water. On the other hand, Jamapa River is the main source for Cu and Ni, which carries dissolved elements from adjacent volcanic rocks. Principal Component Analysis shows a common source for dissolved nitrogen, phosphates, TOC, and suspended matters probably derived from a sewage treatment plant, which is situated near to the study area.

Keywords Trace elements · Contaminant sources · Urban · Fluvial

Sacrificios Island belongs to the "Sistema Arrecifal Veracruzano" (SAV, for Veracruz Reef System) is located in the coastal area of Veracruz, Gulf of Mexico (Fig. 1). Its close proximity to the coastline makes it vulnerable due to coastal and river discharges, as well as by port activities, which are situated very close to the island. In 1992, the SAV was declared as a National Park and now it is a protected natural area.

The SAV is affected by the discharges of several rivers such as: La Antigua, Jamapa, and Papaloapan, which are transporting important amounts of solids in suspension. Due to its location, the Jamapa River has a greater influence in the SAV. Data on the mean annual flow of the Jamapa River during 50 years (CNA 1999) shows that the highest discharge occurs on October.

In this study, we specifically established the distributions of dissolved trace metals (V, Pb, Cu, and Ni) in the Sacrificios Island coral reef during three different periods: June 2004, October 2004, and February 2005. The spatial and temporal variations of dissolved nutrients, suspended matters, and dissolved organic carbon in surface and bottom waters were evaluated in this study to learn the degree of contamination, to identify the sites with highest heavy metal and nutrient concentrations as well as their sources, which might be related to natural or anthropogenic activities.

Sacrificios Island and its surroundings are shown in Fig. 1, the location. In marine sampling stations the depth ranges from 8 to 15 m. During winter (November to March) storms bring northern winds and rains to the coastal area. The rainy season goes from July to October and from April to June the dry season is present in the continental area. Weather changes have produced two long lasting seasons (the rainy season and the stormy season), and a short dry one.

Materials and Methods

On oceanographic cruises that took place on June and October (2004) and February (2005), surface and bottom water samples were collected at twenty three sampling sites around Sacrificios Island. Three water samples were collected in the estuarine area of the Jamapa River, in order to know the concentration of metals and nutrients in the freshwater supplied by the river to the study area (Fluvial

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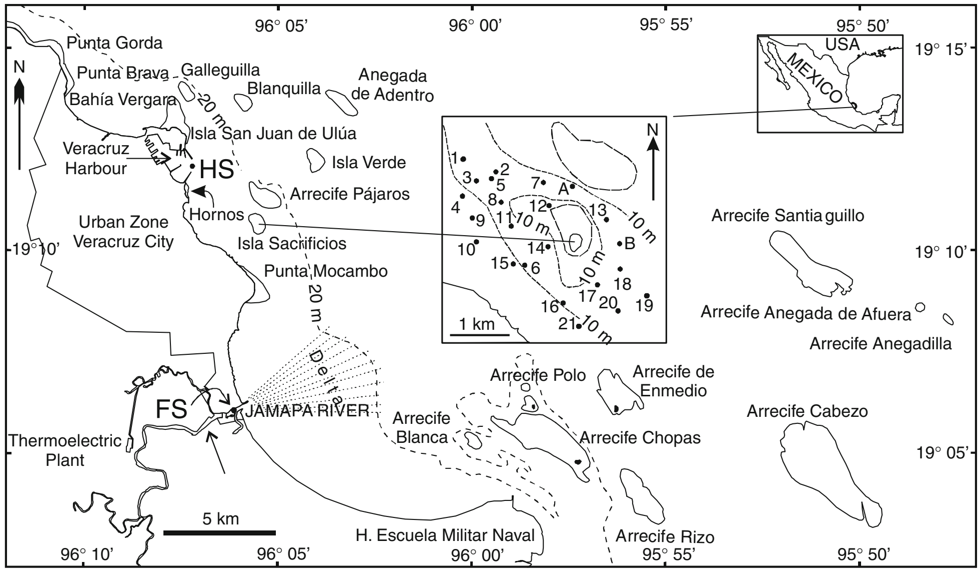

Fig. 1 Study area: Geographic distribution of SAV coral reefs with location of sampling stations (modified from Secretaria de Marina 2000)

Sample: FS), and three samples were collected between Veracruz Harbor and the study area (Harbor Sample: HS).

Salinity, temperature, pH, and total dissolved solids (TDS) were measured at each sampling site by a Hydrolab Data Sonde. Continuous temperature data was evaluated using HOBO thermistors with 0.02°C resolution. Water samples were collected at each site by a horizontal Niskin bottle. Water samples were kept under refrigeration in plastic bottles previous to laboratory work, where they were filtered through 0.45 µm weighted Millipore filters previously washed with 0.05 M HNO_3 for metal analysis. For nutrient analysis one drop of chloroform was added to minimize biological reactions in the samples. Filtered samples were kept under refrigeration until analysis. One liter of water was filtered through 0.45 µm weighted Millipore filters to evaluate the amount of suspended matter. An autoanalyzer Skalar San Plus System 1521 was used for nutrient analysis. The filtered sample used for metal analysis was adjusted to pH 2 with Suprapur HNO_3, and kept at 4°C before analysis. In the laboratory, samples were preconcentrated according to the method of Batterham and Parry (1996), metals were measured by AAS-GF, the percentage of metal recuperation using HPS Certified Seawater Reference material was Cu:101.61%, Ni:99.11%, Pb: 99.49% and V:97.6%. Total Organic Carbon (TOC) was measured in a Shimadzu model TOC-5000, by a non disperse combustion of carbon and measurement by IR. The coefficient of variation of the method was 5.17%. Oxygen values were measured by the Winkler method.

Principal Component Analysis was applied to all the 14 variables (Temperature, salinity, oxygen, TDS, TOC, pH, SM, PO_4, Tot N, Si, Cu, Ni, Pb, V) in order to identify the main parameters characterizing each season and the relationship among them.

Results and Discussion

Figure 1, shows bordering reefs and reef coralline islands, which constructed the SAV. In front of the Jamapa River discharge area, a submerged delta is observed according to the 20 m isobath (Secretaria de Marina 2000). No reefs are found in this delta region, due to the amount of terrigenous supplies that restrain reef formation. Waters surrounding the Sacrificos Island are influenced largely by the harbor (Veracruz Harbor), urban (Veracruz City), river (Jamapa and Papaloapan rivers) activities, and sewage discharges (treatment plant at Bahia de Vergara).

Mean salinity values are low (<33) at surface waters during the three seasons. However, slight spatial differences in salinity are more evident at bottom waters and low values are observed near the coast (Table 1). Low salinities detected throughout the year in the study area are due to the influence of urban discharges of Veracruz City, harbor effluents, sewage discharges from the treatment plant located in Bahía Vergara, but are mainly derived by the Jamapa River outflows. The homogenous salinity value observed in February 2004 is mainly due to the mixing of water by strong northern winds.

An analysis of 71 years of TS observations reported by CNA (1999) shows that higher temperatures are observed between June and September, whereas January and February are the coldest months. Satellite data for superficial temperatures at this time range from 20 to 23°C. The low influence of fresh water is observed in winter season and the surface area is relatively dominated by cold waters. Surface water temperature, where coral reefs are located was fairly constant about 29°C during June and October, and 21°C in February. The effect of wind in water temperature during a cold period shows that it drops 2°C in 24 h and it reaches a

Table 1 Dissolved trace metal concentration (µg/L) in surface and bottom waters around Sacrificios Island at different seasons and concentration from different coastal areas

	Cu (S)	Cu (B)	Ni (S)	Ni (B)	Pb (S)	Pb (B)	V (S)	V (B)
June								
Average	1.79	1.69	0.76	0.70	0.41	0.44	0.46	0.40
SD	0.66	0.91	0.68	0.40	0.22	0.16	0.30	0.33
Interval	0.67–3.56	03.36–4.34	0.29–3.45	0.18–2.03	0.05–0.89	0.26–0.87	0.01–1.19	0–04–1.11
Fluvial sample (FS)	2.99	3.44	0.85	1.61	0.89	0.87	1.19	1.05
Harbor sample (HS)	–	–	–	–	–	–	–	–
October								
Average	1.75	2.46	1.44	1.13	0.85	1.00	1.10	0.80
SD	1.33	4.49	1.58	0.43	0.36	0.38	0.64	0.61
Interval	1.15–5.29	0.07–16.98	0.55–7.62	0.51–1.98	0.32–1.35	0.62–1.60	0.41–2.57	0.22–2.19
Fluvial sample (FS)	3.45	5.76	3.83	1.81	1.47	3.49	2.09	1.74
Harbor sample (HS)	0.55	2.02	1.20	0.43	1.77	0.59	0.70	0.56
February								
Average	1.86	1.79	1.81	1.20	0.21	0.19	0.13	0.21
SD	1.29	1.41	1.61	1.07	0.20	0.20	0.14	0.19
Interval	0.0–4.36	0.0–4.74	0–0–5.10	0.0–4.20	0.0–0.69	0.0–0.77	0.0–0.47	0–0–0.61
Fluvial sample (FS)	4.22	3.94	4.72	3.35	0.69	0.77	0.98	0.64
Harbor sample (HS)	4.55	1.64	0.40	0.56	0.31	0.38	0.98	0.34
Other coastal areas								
Korean3[a]	0.4–1.23	–	–	–	0.03–0.09	–	–	–
Black sea[b]	7.6–28.8	–	0.65–1.03	–	0.003–0.13	–	–	–
English channel[c]	0.52	–	0.46	–	0.076	–	–	–
English coast[d]							0.95	
French coast[d]		–	–	–	–	–	1.1	–

S surface, *B* bottom

[a] Lee et al. 1998

[b] Tankéré 2001

[c] Chiffoleau et al.1999

[d] Auger et al.1999

minimum of 20.7°C within 36 h, due to the cold front lapse it increases again. The behavior was same up to 3 m depth from the surface. The influence of the weather on the hydrology of the area was evaluated by the use of Temperature/Salinity parameters, in June and a transition from October to February was observed. In October, shifts in the TS points, higher temperature, and more influence by the river discharges are also observed. It is identified due to the influence of Jamapa River, which carries larger yields of water (90 m^3/s) (CNA 1999), at this period. Winter time in the area is characterized by around 50 cold fronts in a year. The presence of slight thermal inversion (density in the water column was stable) was observed, which may be due to the fact that sampling was carried out immediately after the pass of a cold front and the water column was in the process of cooling during sampling.

In February, the high concentrations of oxygen (7 mg/L) are associated with low temperatures and both variables are apparently associated with the stormy season. In June, low oxygen values (2.87 mg/L) are associated with high TOC values (13.5 mg/L) in the northeastern part of the study area. The higher concentrations of suspended matters at these sites suggest that they are associated directly with the decomposition of organic matter.

High discharge of nutrients to the coastal zone increases the primary productivity, which produces an increase in organic matter concentration. However, the degradation consumes the dissolved oxygen from the water, which produced oxygen-deficient waters. The excess nutrient concentrations along the coastal zone reduces the water quality and have been associated with harmful algae blooms (Rabalais 2004).

The average total nitrogen concentration ($NH_4 + NO_2 + NO_3$) in the study area are higher in June (7.95 µM/L). The amount of total N supplied by the Jamapa River is also higher, with an average value of 120 µM/L. The distribution pattern of total dissolved inorganic nitrogen ($NO_2^- + NO_3^- + NH_4^+$) concentration from different sampling locations is similar. But, a slight enrichment in total dissolved inorganic nitrogen is noted in the northern part of the area under study.

Phosphate concentrations vary from 0.07 to 6.58 µM/L (Table 2). The highest average values both in the surface and at bottom waters, were observed during June (Table 2). The higher concentration of PO_4-P along the northern part of the study area is observed in June and February. This enrichment in PO_4-P may be associated with the sewage input derived from the treatment plant located at Bahia de Vergara. During October, the fluvial discharge is the main source for PO_4-P enrichment along the northern area. A statistical significant correlation study between phosphate concentration and suspended matter, TOC and Total nitrogen, thus suggesting they come from a common source.

Silica contents are quite variable and it range from 2.00 to 25 µM/L. The higher average values in surface water are observed in October (10.89 µM/L) and February (11.29 µM/L). Generally, the silica values are high in the northern part; however the samples collected from the area influenced by Jamapa River are also showing higher values. For example, sample number 19 located near to the river discharge area is high in silica (23.7 µM/L). Silica concentration is very high in the river water during the three sampling periods, which is due to the occurrence of volcanic rocks rich in silica along the Jamapa river basin. The vertical distribution reveals that the silica concentrations are higher in the surface than bottom waters, suggesting the influence of fluvial discharges by the River Jamapa. This interpretation is also supported by the significant negative correlation of silica with TOC, and salinity.

Table 2 Dissolved nutrient concentration (µmol/L) in at surface and bottom waters around Sacrificios Island during the three sampling periods

	Total N		PO_4		SiO_2	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
June						
Average	7.95	9.68	0.76	0.91	5.53	4.13
SD	2.63	4.94	0.85	1.14	4.83	3.11
Interval	4.22–13.26	4.02–22.88	0.11–2.58	0.07–4.54	2.0–25.00	2.55–18.38
Fluvial samples	120.00		2.29		455.00	
Harbor samples						
October						
Average	6.23	5.74	0.34	0.59	10.89	8.05
SD	1.95	2.57	0.24	1.46	1.95	2.29
Interval	3.19–10.10	2.57–11.10	0.12–1.00	0.08–6.58	7.45–14.10	5.17–14.84
Fluvial samples	93.50	35.80	2.50	4.70	488.00	168.70
Harbor samples	28.51	3.94	1.92	0.41	18.40	9.09
February						
Average	4.42	4.43	0.37	0.39	11.29	8.27
SD	2.31	1.79	0.14	0.12	4.61	1.65
Interval	1.52–10.10	2.55–9.83	0.18–0.81	0.14–0.59	7.16–23.70	5.11–11.99
Fluvial samples	6.40	7.70	4.65	2.45	784.84	215.40
Harbor samples	2.86	2.95	0.20	0.31	9.20	9.13
Other areas						
French coast[a]	7.8–23.0	–	0.4–0.85	–	3.0–13.0	–
England coast[a]	7.5–15.5	–	0.4–0.70	–	3.0–7.5	–
N Gulf of Mexico[b]	8.13	–	0.34	–	5.34	–
Guadiana R. coast september[c]	1.69 ND	–	0.06–0.1	–	1.8–3.2	–
Guadiana R. coast october[c]	0.29–11.36	–	0.29–0.79	–	3.2–3.9	–

ND non detected

[a] Bentley et al. (1999)

[b] Rabalais et al. (1996)

[c] Cravo et al. (2003)

The ocean is a dynamic system where the distribution pattern of their constituents is in constant movement. In the present work, an analysis of the distribution pattern of the metals at different periods of the year was carried out in order to evaluate the source for the dissolved metals.

Dissolved Cu concentration in the coastal area ranges from the detection limit to 16.98 μg/L; similar average values are obtained during June, October, and February. Using the data obtained in the present work, a representative distribution of each metal in different seasons with water levels are shown in Fig. 2.

The copper distribution pattern in surface water in all seasons shows a similar tendency. Figure 2a, shows distribution of Cu in surface water in February. Cu concentrations above average are noted along the NW and SE parts of the Sacrificios Island. This distribution pattern suggests the influence of three different sources to the study area: (1) possible urban influence, introduced through sampling points 4 and 9; urban storm water has been recognized as a substantial source of pollutants to the study area. Significant amount of metals, nutrients, and toxic organic substances can be derived by runoff from urbanized areas (Shirasuna et al. 2006), (2) the influence of fluvial discharges in the southern part can be observed by the higher concentration in sampling point 20, and, (3) the influence of harbor discharges can be observed by the increase in concentration towards east e.g., station 5. During June, the influence of fluvial and harbor discharges are lower (Table 1). However, in February the harbor influence seems to be higher. In February, the samples from sampling points 7 and A, are higher than average concentrations compare to the samples collected in October. The distribution pattern of Cu concentration in bottom water reflects only the influence of urban discharges in the area.

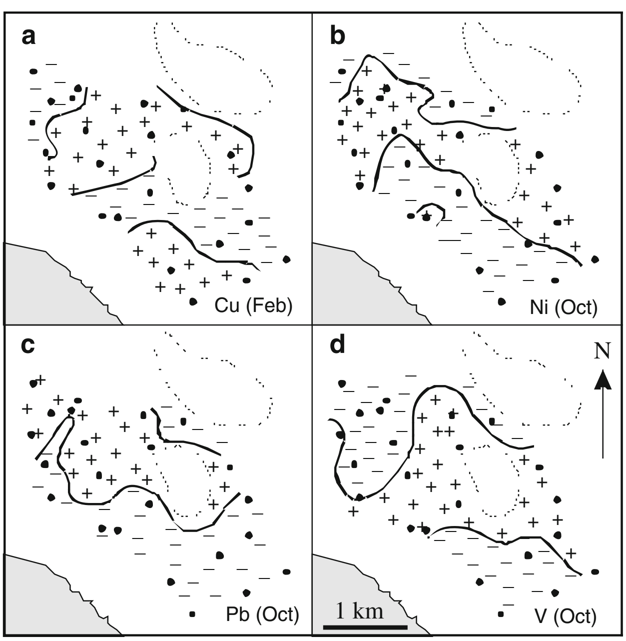

Fig. 2 Dissolved metal distribution in the study area. Values above the average are shown by (+) notation. **a** Cu concentration (μg/L) in surface water in February, average 2.0 μg/L. **b** Ni concentration (μg/) in surface water in October, average 1.0 μg/L. **c** Pb concentration (μg/L) in *bottom* water during February, average 0.2 μg/L. **d** V concentration in surface water in October, average 1.1 μg/L

Nickel concentration varies from the lower limit of detection to 7.62 μg/L and higher concentrations are observed in February. Ni distribution pattern in surface water suggests that this metal may introduced in to the study area only through urban discharges. Figure 2b, shows the distribution pattern observed for the surface water during October. Samples with Ni concentration above the average are located in the NW part of Sacrificios Island, which is apparently related to urban discharges located close to sampling points 4 and 9. A recent study on surface sediments by Rosales-Hoz et al. (2007) identified the higher concentration of Ni at sampling point 4, during October. The bottom water in June and October reveals a distribution pattern similar to that of the surface water. The negative correlation of Ni with salinity apparently supports that the introduction of Ni to the study area is by urban discharges through sampling points 4, 9, and 10.

Dissolved Pb concentrations from the detection limit to 1.6 μg/L are observed for the studied samples and higher values are noted in October in the coastal and harbor areas (Table 1). Anthropogenic Pb in the study area is mainly derived from gasoline, ferrous metal and iron/steel industries, which are very common along the Veracruz coastal area. Sadiq (1992) suggested that the major input pathway of Pb to marine environment is via atmospheric fallout. However, in this study the Pb concentrations in surface and bottom waters are very low in February, when the study area is affected by strong winds. Hence, it is identified that the distribution of Pb in surface and bottom waters are associated to harbor activities and not to atmospheric input, which is also supported by the higher concentration of Pb in the samples from the NE part of the Sacrificios Island. Pb in surface water during October (Fig. 2c) reflects a similar distribution.

Vanadium concentration in the coastal area is very different from one period to the other ($\sim$0.01 to 2.57 μg/L). V concentration is lower in February (0.13/0.21 μg/L, surface/bottom) than June (0.46/0.40 μg/L, surface/bottom) and October (1.10/0.80 μg/L, surface/bottom) and is due to the differences in temperature along the coastal area. Also the suspended matter transported by the river Jamapa at this time was lower. This is in good agreement with a study by Auger et al. (1999), which reports an inverse correlation between suspended matter and V concentration (Fig. 2d). Furthermore, a study of metal content in air particles from the highly industrialized area of Coatzacoalcos Harbor

(Rosales-Hoz et al. 2003) found that V was one of the main metals derived by wind.

The dissolved metal concentrations of this study are compared to values reported for other coastal areas (Table 1). This comparison points out that Cu and Ni concentrations are similar to the values reported from Campeche Bay, Gulf of Mexico (Vázquez-Botello et al. 2004) and Black sea (Tankéré et al. 2001). However, Pb concentration is significantly higher in this study than the values reported from the Black Sea. On the other hand, V concentration is similar to the values reported from the English and French Coasts.

The three axes examination on the PCA (48.45% of the total variability) summarizes the above mentioned results. The I–II plane shows the dry (June) and the cold (February) seasons in opposite position, and the rainy season (October) as a transition period (Fig. 3). February, negatively associated to the first axis was Characterized by the highest values of dissolved oxygen, whereas June, in the positive part of axis I, was characterized by the highest values of TOC, Total N, SM, and PO_4, suggesting their similar origin. The axis II separates bottom from surface stations, the former group associated to high salinity and TDS values, and the second to low temperatures. The I–III plane discriminates the rainy season (October) in the positive part of the third axis (Fig. 3). The trace metals Pb and V were also positively associated to this season, supporting the same origin for both of them (Fig. 3). The Cu placed in the central part of the planes and with low contributions to the axis formation, may represent different sources.

In conclusion, hydrographic characteristics of this study reveal the following points: (1) during the dry season the surface water (0–4 m) are with higher temperature and lower salinity. (2) In the rainy season, the water column presents a homogeneous distribution of temperature and salinity, which reflects more influence by fluvial discharges. (3) In the stormy season, a thermal inversion was observed in the area, with two well defined water masses in surface and bottom waters.

Cu concentration in the study area is similar through out the year, Cu distribution pattern suggests different sources related to urban, fluvial, and harbor discharges. Higher concentrations of Ni were observed in February. Pb and V concentrations are higher in October and their distribution pattern suggesting different sources. Ni and V are associated to urban discharges and Pb is related to harbor activities. Cu, Ni, and Pb concentrations are above the values reported for seawater, but resemble the values reported for coastal areas.

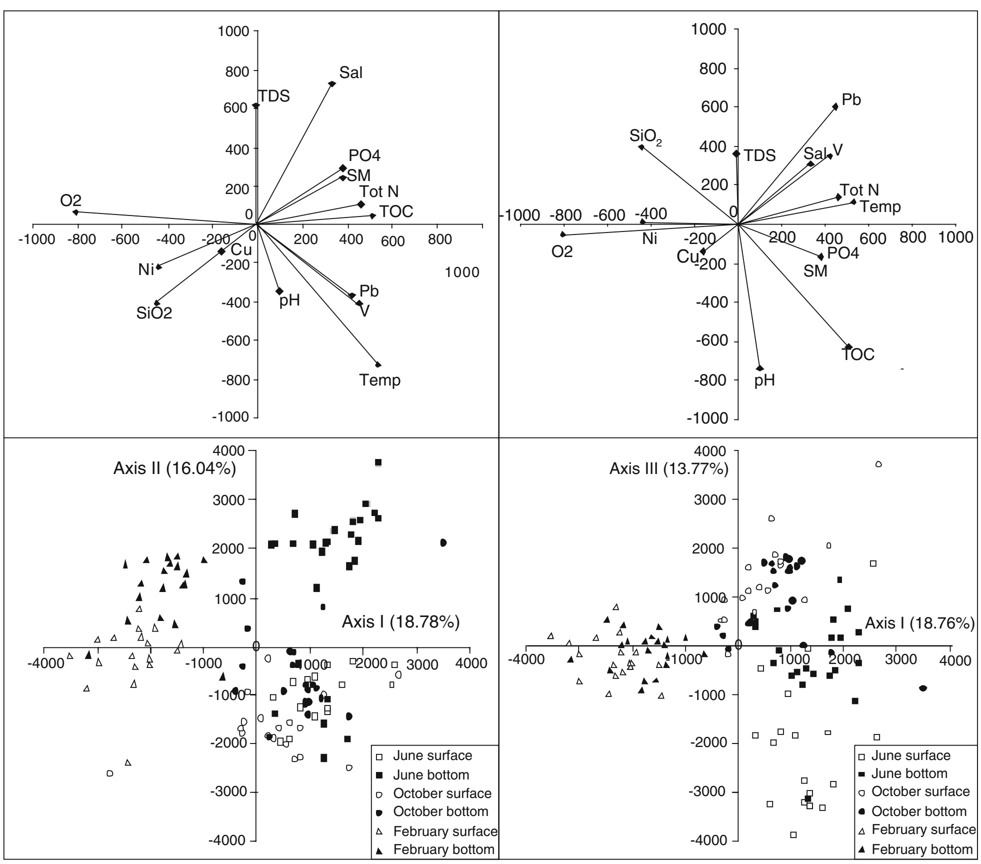

Fig. 3 Representation of variables and sampling stations in the I–II and I–III planes of the Principal Component Analysis

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