



Geochemical and Sedimentary flux Aspects in Amazon Continental Shelf

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Abstract

This study was conducted in Amazon Continental Shelf (47°52'W-4°19'N and 51°04'W-2°16'S) to evaluate the geochemical and sedimentary flux of C, N and P, and the metals Fe, Mn and Al all associated with bottom sediments. Sampling occurred between 1997 and 2007 always between May-June, the period considered of most discharge of Amazonas and Pará rivers. Chemical analyzes were conducted according to international standards and usual proceedings. Results showed there was a similarity between the data from the various sampling sites, which reinforces the argument that there is homogeneity of the study area due to mixture of the sedimentary discharge from rivers Amazonas and Pará by the oceanic currents action. A trend of transport and sedimentation were observed mainly in the inner shelf by the organic compounds and metals correlation.

Keywords: Bottom sediments, nitrogen, phosphorous, river discharge, Amazonian.

Introduction

The sediment dynamics in the Amazon Continental Shelf (ACS) is directly linked to the immense load of suspended sediments transported by the Amazon basin, which contributes an estimated volume of 11-13 10⁸ t/year of sediments^{1,2}. The events of sediment transport and deposition occurring in the coastal area near the estuary of Amazonas and Pará rivers are unique on the planet. No river in the world has the ability to influence both the coastal zone as the ocean, as does the Amazon River, which flow in the period of greatest change comes to the physical and chemical conditions of the waters of the Atlantic Ocean for over 200km from the Brazilian coast. As a result of that intense dynamics, coastal geomorphology is constantly remodeled by sedimentary processes.

Geochemical surveys were conducted on the ACS³, under Equatorial North Current (ENC) and North Brazil Current (NBC) influence, to understand the behavior various geochemical elements associated with bottom and suspended sediments, allowing greater understanding of the environmental conditions in this coastal ecosystem. This study aims to estimate geochemical and sedimentary flux aspects of the distribution of nutrients (C, N and P), and percentage of Fe, Mn and Al associated with sediments of the shelf.

Material and Methods

Study area: The North Brazil Current (NBC) extends from Orange Cape (OC figure-1), in the state of Amapá, to the São Marcos bay, in the state of Maranhão. The northern Brazilian continental margin is considered the type depositional, where

the continental shelf formation and slope are both related to depositional processes, restricting aspects erosive events to isolated locations. The depositional load that is discharge on the stretch of coast above and below of the mouth of the Amazon River is immense, and can be considered one of the largest areas of sediment dynamics in the world. The NBC can be subdivides into three parts: Guianiense coast, Amazon gulf and Eastern Amazon coast. The Guianiense coast extends from the Oiapoque River to the North Cape (NC – figure-1), and is formed by overlapping tertiary lands in the Precambrian crystalline basement. In this region develop extensive muddy tidal plains occupied by mangroves, which grow toward the interior of the continent to coastal wetlands. This is a typical region of coastal deposition, driven by tides that redistribute the Amazonian mud that the ENC pushes toward the North. The area of the Amazon gulf is occupied by a large estuarine-deltaic complex, while the Eastern Amazon coast extends into the São Marcos bay, and is marked by tertiary sediments presence of the Group Barriers, crossed by many rivers. The coastal dynamics has high influence on the geomorphology of the coastline in the study area. The north coast is influenced by waves generated by the trade winds of NE, producing a tidal range above four meters, reaching 8 to 12m^{4,5}.

The waters of the Amazon River emptying into the ocean to form a surface layer of variable thickness between 10-20m, under which there is a salt layer, which migrates toward the continent. Shape up this point a vertical stratification due to density difference, which extends the ACS of 60 to 185km wide, during the drought, and 80 to 230km during the floods⁶. The climate according to the Köppen classification is type tropical humid "Am" for the Marajó Bay (PA) and "Af" for the

Pará River, with high temperatures and rainfall. The trade winds are quite active on the ACS throughout the year. The variation of these winds is mainly associated to the oscillations of the Intertropical Convergence Zone (ZCIT).

Analytical proceeds: Twenty sampling sites between the isobaths 19 to 100m (figure-1), within a range that extends from 12 to 200 nautical miles offshore, were collected between 1997-2007, always between the months of May-June, period considered the largest discharges of the Amazon River basin. Sampling was carried out with the support of the Brazilian's Interministerial Commission for Sea Resources (CIRM) and Ministry of Environment.

Samples of bottom sediments were obtained with Van-Veen sampler, and packed in plastic bags in cold storage at -20°C . In the Laboratory of Chemistry of the Federal University of Pará samples were dried 45°C for 48h, homogenized, pulverized and sieved through 230 mesh (0.063mm) for later chemical analysis. For determining the organic carbon (OC) and total nitrogen (TN) samples were first treated with 10% HCl to convert the carbonate into CO_2 . The treated samples were brought to the heating plate at 80°C until the total elimination of hydrochloric

acid. We determined the levels of OC and TN in a LECO analyzer model CNS-2000. The concentrations of organic matter (OM) were obtained by multiplying the levels of OC by a reason of 1.72⁷. To find the levels of total phosphorus (TP) and metal oxides, the samples were subjected to acid extraction energy [$1\text{ HCl} + 1\text{ HNO}_3 + 1\text{ HF} + 1\text{ HClO}_4$] in the heater plate with temperature of 100°C . The last solutions were filtered through Whatman 44 filter and placed in 50ml flasks. The readings were performed by the technique of molecular absorption for TP and by ICP-AES for the metals, according to recommendations and general protocols^{7,8}. Iron, manganese and aluminum were determined in the bottom sediments by the atomic absorption spectrophotometer methods, with acid digestion⁸.

From the results of carbon and nitrogen we calculate the ratio C:N. Descriptive statistical analyses of central tendency were applied to the results, obtaining mean, maximum, minimum and standard deviation for the environmental variables studied. To find possible relationships between the sampling sites for the geochemical characteristics, we apply Correlation analysis and Cluster analysis to the results.

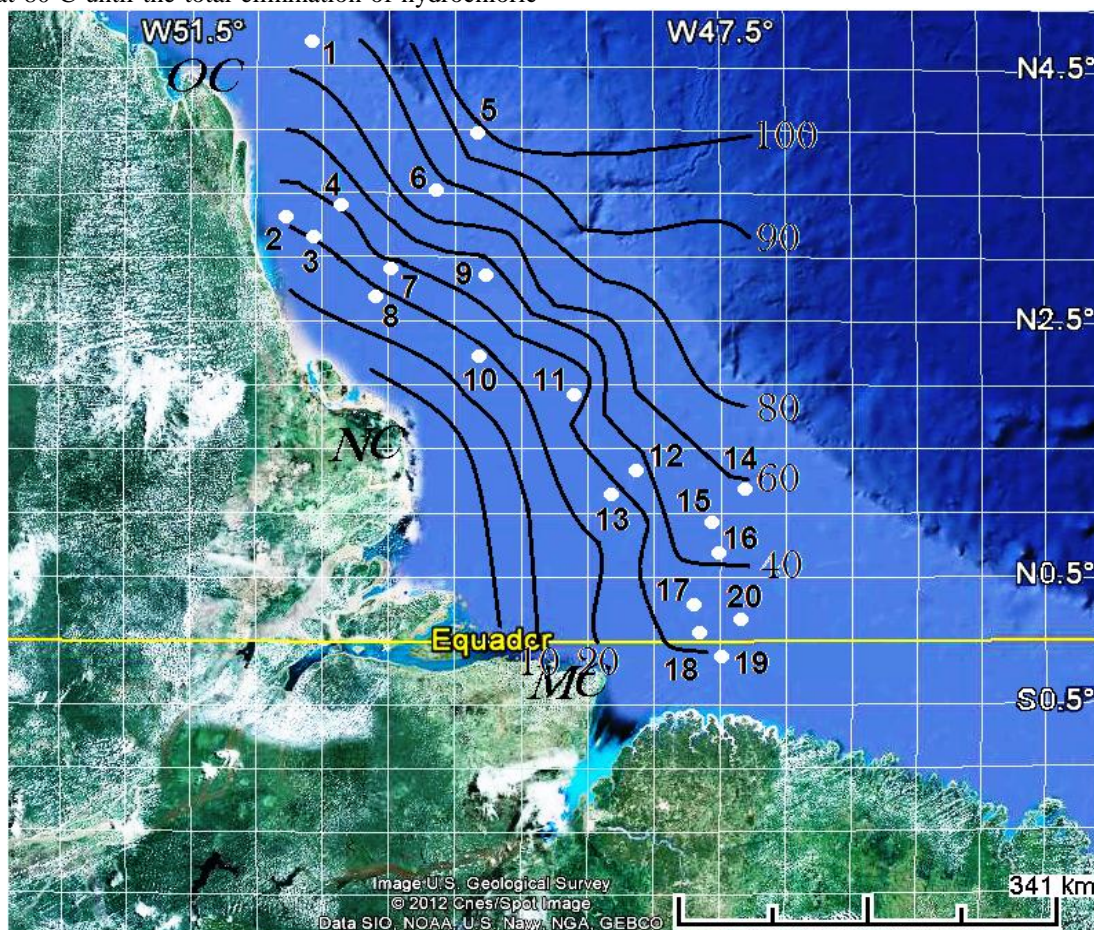


Figure-1

Map of the ACS with the place of the sampling sites and bathymetric curves for the region between the Orange Cape (OC) and Maguari Cape (MC) (Source: Google Earth, 2012 - modified)

Results and Discussion

We observed that in the mouth of the Amazon and Pará rivers the sediment dynamics follows the flow of fluvial waters, and the sediments were deposited in SE-NW direction (parallel to shore) across the inside area of the continental shelf, influenced by coastal current (figure-2). That pattern of current helps explain the distribution and concentration of organic and inorganic elements in the ACS. Table-1 shows the values of central tendency for TP, OC, TN, OM, C:N ratio, Fe₂O₃, MnO and Al₂O₃. In general, TP distribution in the sediments of the region was homogeneous. The sedimentation processes were favored throughout the ACS, providing high deposition of sediments transported by pelitic rivers discharges. It is possible that phosphate salts may be being transferred to the water system by leaching processes of soils along the Amazon River basin, with successive dissolution of the elements. We emphasize the processes of weathering and leaching of nutrients flow between compartments ground-water, especially in the study area, where rainfall average rainfall is greater than 2600mm/yr. Studies on flow and modeling of N and P in lake systems have shown that leaching is primarily responsible for the input of material allochthonous, especially nitrogen, to the lakes⁹⁻¹¹. The systematic phosphate in the diverse rivers systems of the Amazon was examined¹². The authors concluded that 50% of the phosphate released into the ocean from the Amazon

River is the result of suspended solids dissociation, with a balance between the dissolved and particulate phases.

The OC mean content determined in this study was 0.75±0.42%, where the sampling sites 1, 4, 14 and 20 had the highest concentrations as opposed to sampling sites 5, 10 and 16 that had the lowest levels (table-1). The mean value for OC was very close to the mean value of 0.74% determined by Ottmann¹³ for that region. There is much variation in organic compounds content in marine sediments, where the recent surface sediments usually contain 1 to 5% of OC¹⁴. The low values found for OC can be explained by high levels of suspended material of terrigenous source associated to discharges of the Amazon and Pará rivers. The suspended material may cause low transparency of the water column so, reducing the primary production process and discouraging organic material deposition. The mean of TN in the samples was 0.08±0.03%, ranging from 0.02 to 0.14% (table-1). We note that the highest levels of TN were determined at stations located inside area of the shelf, near the 20m isobath, and that the bottom sediments, composed especially for coarse sand, were those with lower nitrogen content, as described by Siqueira & Braga³. The content of nitrogen in organic form increases towards the coastal areas¹⁵. TN values determined in this study coincided with the values between 0.012 to 0.092%^{13,16} determined to ACS.

Table-1
Mean values of chemical and sedimentological parameters in bottom sediments of the ACS (n= 191 samples)

Station	Lat. N	Long. W	Depth* (m)	N	TP (%)	OC (%)	TN (%)	OM (%)	C:N	Fe ₂ O ₃ (%)	MnO (%)	Al ₂ O ₃ (%)
1	04°43.5'N	50°47.7'W	72	9	0.08	0.65	0.09	1.11	7.51	6.72	0.10	10.33
2	03°37.3'N	50°48.2'W	22	9	0.08	1.14	0.10	1.96	11.69	6.72	0.11	10.33
3	03°23.9'N	50°25.7'W	20	9	0.09	0.49	0.07	0.84	6.58	6.86	0.11	11.49
4	03°32.8'N	50°20.1'W	37	9	0.09	2.31	0.11	3.97	20.46	6.86	0.11	11.49
5	03°57.2'N	49°24.9'W	100	8	0.06	0.32	0.03	0.55	9.25	3.28	0.05	8.12
6	03°20.6'N	49°50.7'W	70	9	0.09	0.87	0.09	1.49	9.59	6.57	0.10	10.33
7	03°07.6'N	49°59.2'W	26	9	0.08	0.73	0.09	1.25	7.77	6.43	0.10	10.33
8	02°59.9'N	50°04.4'W	22	9	0.09	0.70	0.10	1.20	7.34	6.72	0.11	11.49
9	03°00.2'N	49°24.6'W	37	10	0.07	0.57	0.09	0.98	6.52	5.00	0.06	10.39
10	02°25.8'N	49°11.8'W	19	10	0.06	0.19	0.03	0.32	7.66	4.29	0.05	9.82
11	02°05.1'N	48°45.8'W	27	10	0.08	0.59	0.08	1.01	7.34	5.72	0.06	10.77
12	01°26.7'N	48°12.6'W	38	10	0.08	0.48	0.07	0.82	6.81	5.86	0.09	10.33
13	01°04.0'N	48°34.2'W	28	10	0.08	0.66	0.10	1.13	6.34	6.00	0.09	11.14
14	01°16.6'N	47°28.3'W	59	10	0.01	1.04	0.02	1.78	43.08	0.86	0.01	2.64
15	01°05.0'N	47°53.0'W	48	10	0.07	0.57	0.08	0.33	7.57	5.15	0.05	10.58
16	00°52.4'N	47°44.4'W	46	10	0.07	0.37	0.05	0.63	7.45	4.72	0.05	10.01
17	00°39.9'N	47°52.9'W	39	10	0.07	0.56	0.07	0.96	7.66	5.36	0.05	10.01
18	00°07.4'N	47°49.2'W	26	10	0.09	0.92	0.12	1.58	7.50	6.29	0.07	10.77
19	00°00.5'N	47°43.6'W	24	10	0.08	0.77	0.12	1.32	6.60	6.43	0.10	10.77
20	00°26.0'N	47°27.0'W	32	10	0.08	1.01	0.14	1.73	7.11	4.43	0.04	9.07
Mean	-	-	-	-	0.08	0.75	0.08	1.25	10.09	5.51	0.08	10.01
Min	-	-	-	-	0.01	0.19	0.02	0.32	6.34	6.89	0.11	11.49
Max	-	-	-	-	0.09	2.31	0.14	3.97	43.08	0.86	0.01	2.24
S.D.	-	-	-	-	0.02	0.42	0.03	0.77	8.15	1.45	0.03	1.89

* Depths obtained during the collections.

The values of OM ranged from 0.32-3.97% with mean $1.25 \pm 0.77\%$ for the all area studied, especially the sampling site 4 in the 34m isobath, which reached the highest level (3.97%). The contents of OM showed an increasing trend to the depths between 20 and 50m, then decreasing from that to the vicinity of 100m isobath. We believe that this pattern of distribution of OM is associated with the particle size and texture of sediment of the ACS, which from the mouth of the Amazon and Pará rivers to 50m isobath presents predominance of muddy sediments (silt plus clay); between 50-65m isobaths presents predominance of sandy-clay sediments, and from that point toward the ocean presents sandy sediments¹⁷ (figure-2). In principle, the main sources of OM to the compartment studied are terrigenous materials associated with planktonic organisms brought by the Amazon and Pará rivers. OM in this area is maintained in suspension by the NBC, thus hampered their sedimentation.

The terrestrial organic matter associated to sediments transported by the Amazon River is biologically refractory¹⁸. For the authors, the sedimentary particles after entering the continental shelf, mingle with labile organic matter and are deposited on the bottom, where a variety of geochemical reactions happen. The organic matter incorporated in sedimentary deposits can be split into two fractions: a fraction labile, which is recycled in the sediment; and a fraction refractory (residual), which is associated with the mineral phase of sediment¹⁹. Some studies show the relationship between the amount of organic material associated with the particles of minerals, especially silt plus clay, and the OM ability in to capture minerals and ionic elements on its surface^{10,17,20,21}. It is

suggested that more than 90% of OM preserved into marine bottom sediments is intimately associated with mineral surfaces, and the adsorption of organic matter to these surfaces have a stabilizing effect on component molecules, delaying much the remineralization process²⁰.

We observed a wide variation in the C:N of the samples, ranging from 6.34 to 43.08 with average 10.09 ± 8.15 . The sampling sites 2, 4 and 14, on isobaths 22, 37 and 59 meters respectively, were those with a higher C:N ratio in the layer of sediment deposition (table-1). These sampling sites suffer greater influence of terrigenous material originated from weathering, which is carried by the river system of Amazonas and Pará rivers. Other sampling sites showed a trend of marine deposits at these sites. We believe that the organic material deposited on the sedimentary matrix comes from various sources or processes of organic fragments: i. as terrigenous material from rivers Amazonas and Pará; ii. by the existence of a remineralization of organic nitrogen from the particulate organic material during its passage through the water column, so that when the material is deposited at the bottom has a more pronounced the C:N ratio, and iii. by the denitrification process that eventually may be occurring in bottom sediments, implying loss of nitrogen organic from compartment sediment. In one of the first studies in the ACS by Ottmann¹³, the author obtained mean ratio C:N of 23, very close to the highest value found in this study. Toward the ocean to the river mouth, the gradient of sedimentary region studied ranged from a sedimentary environment typically marine to sediments of continental sources.

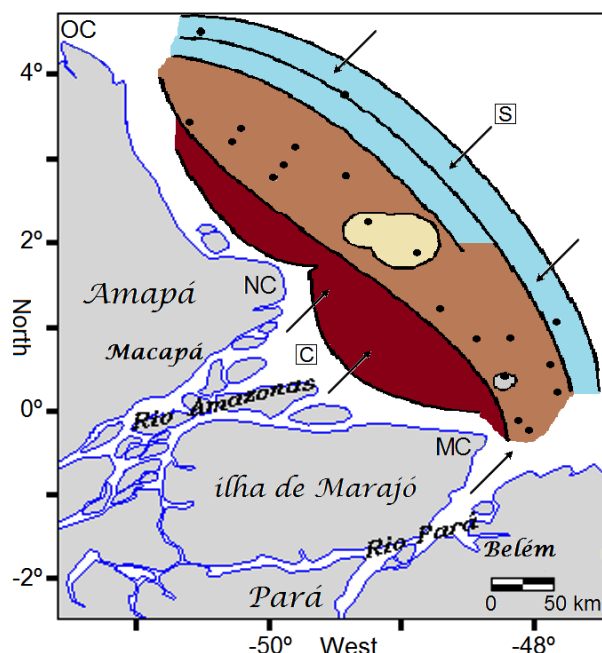


Figure-2

Flux of sediment transport inside the ACS. Legends: OC= Orange Cape; NC= North Cape; MC= Maguari Cape; [C]= silt plus clay "muddy" and [S]= sand

With respect to the oxides of the elements analyzed, Fe_2O_3 ranged from 0.86-6.89%, with mean $5.51 \pm 1.45\%$, and the sampling site 12 was highlighted by low concentrations of oxide (0.86%). The percentages obtained for MnO ranged from 0.01 to 0.11%, mean $0.08 \pm 0.03\%$. For MnO we see a tendency of clustering of the low values in the areas of discharges of both Amazon and Pará rivers. Already Al_2O_3 showed most variation between the sampling sites, the levels ranged from 2.24 to 11.49, with mean $10.01 \pm 1.89\%$. The Amazon basin suffers intense weathering process with laterites formation¹⁸. The lateritic process produces layers of oxides and hydroxides of Fe, Mn and Al as well as poor clays in cations in the Amazon basin (note of the authors). The Amazon River carries 82% of the total iron element from laterites in suspension, carrying many trace elements associated with iron¹⁸. The formation of large amounts of lateritic crust, as well as deposits of Mn in the basement of the Amazon region, were suggested to explain the large amount of Fe/Mn¹³, which forms a brown film on a certain amount of sand in bottom sediments collected in the region of the mouth of the Amazon River. In sediments of the ACS were found clay minerals group listed in order of abundance as: kaolinite> smectite> illite> montmorillonite> chlorite (dates unpublished of the authors).

The results showed a low correlation between the variables (table-2). Oxides showed a correlation factor " r_s " exceeding 0.93, indicating that their concentrations are directly proportional to each other. A good correlation between macroelements presumes a common source or both have been subject to similar mechanisms of enrichment²².

Cluster analysis was applied to evaluate the degree of aggregation between the twenty sampling sites under the variables studied influence (figure-3). The results showed three tiny distinct groups formation. The first group, with a distance matrix of less than 20 units, may be further divided into three subgroups (SG) formed by sampling sites $\text{SG}_{1A}=\{4, 6, 8 \text{ and } 9\}$, $\text{SG}_{1B}=\{11, 13, 14, 15, 16, 17 \text{ and } 20\}$ and $\text{SG}_{1C}=\{3, 7 \text{ and } 10\}$.

The first subgroup (SG_{1A}) is located in the north of the ACS, the second and largest subgroup (SG_{1B}) is distributed between the mouths of both Amazon and Pará rivers, and the third subgroup (SG_{1C}), with the sampling sites 3, 7 and 10 do not show a clear spatial pattern analysis, these being distributed from the upper part of the mouth of the Amazon River, in the direction north of the ACS. The analysis showed that the second group (G_2) is formed by sites {2, 12, 18 and 19}. All groups formed, the G_2 aggregation is the least present a spatial pattern, with the sites being fully dispersed from each other. The third group (G_3) is formed by the sites {1 and 5}, both located further north and further offshore, in the deeper regions. The results suggest that the pattern of homogenization that occurred in the study area is due to some geochemical and oceanographic phenomena, such as the strong discharge from both Amazon and Pará rivers, and the NBC interference associated to tidal currents. Pearson's analysis confirmed that there was a slight positive correlation between muddy sediments and the metallic oxides concentration, with $R^2= 0.5792$ (figure-4), result of the likeness of the metallic elements for small particles of silt plus clay and organic matter loaded negatively, as is explained by the Cation Exchange Capacity¹⁰.

Conclusion

The discharges of Amazon and Pará rivers play an important role in the transport of suspended and total solids from continent to the Amazon Continental Shelf. The sediment dynamic in the region plays a constructor, since it is constantly changing the landscape with transport and deposition of land at the mouth and in the coastal zone. Argillaceous sediments show great affinity for organic matter, so that the muddy bottom sediments of the inside part of the ACS are rich in organic compounds, while the sand sediments of the outside part of the ACS show low levels of nutrients. The results revealed that the ACS is an enormous system with geochemical characteristics resulting from the interaction fluvial and marine.

Table-2
Correlation analysis for the variables studied (n= 191 samples).

	Depth	TP	OC	TN	OM	C/N	Fe_2O_3	MnO	Al_2O_3
Depth	1.0000	-	-	-	-	-	-	-	-
TP	-0.3411	1.0000	-	-	-	-	-	-	-
OC	0.6156	-0.1866	1.0000	-	-	-	-	-	-
TN	-0.0221	-0.0824	-0.0073	1.0000	-	-	-	-	-
OM	0.6105	-0.2096	0.9987	-0.0012	1.0000	-	-	-	-
C/N	0.3009	-0.0895	0.4319	-0.8408	0.4240	1.0000	-	-	-
Fe_2O_3	-0.1977	0.1623	-0.0676	-0.3884	-0.0528	0.2065	1.0000	-	-
MnO	-0.3453	0.2770	-0.2671	-0.2996	-0.2567	0.0375	0.9524	1.0000	-
Al_2O_3	-0.2959	0.2187	-0.2013	-0.3947	-0.9300	0.1942	0.9344	0.9357	1.0000

Bold correlation ≥ 0.5

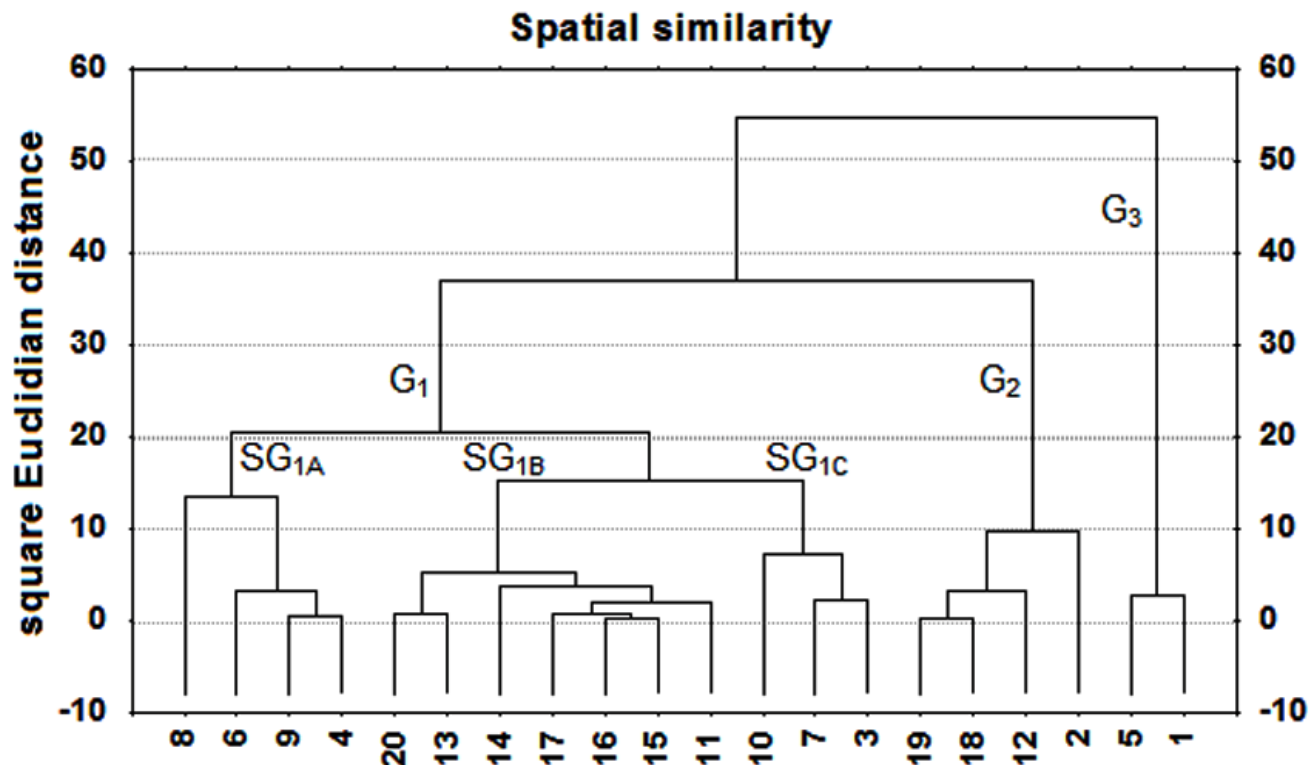


Figure-3
Cluster of the sampling sites in ACS (n= 191 samples)

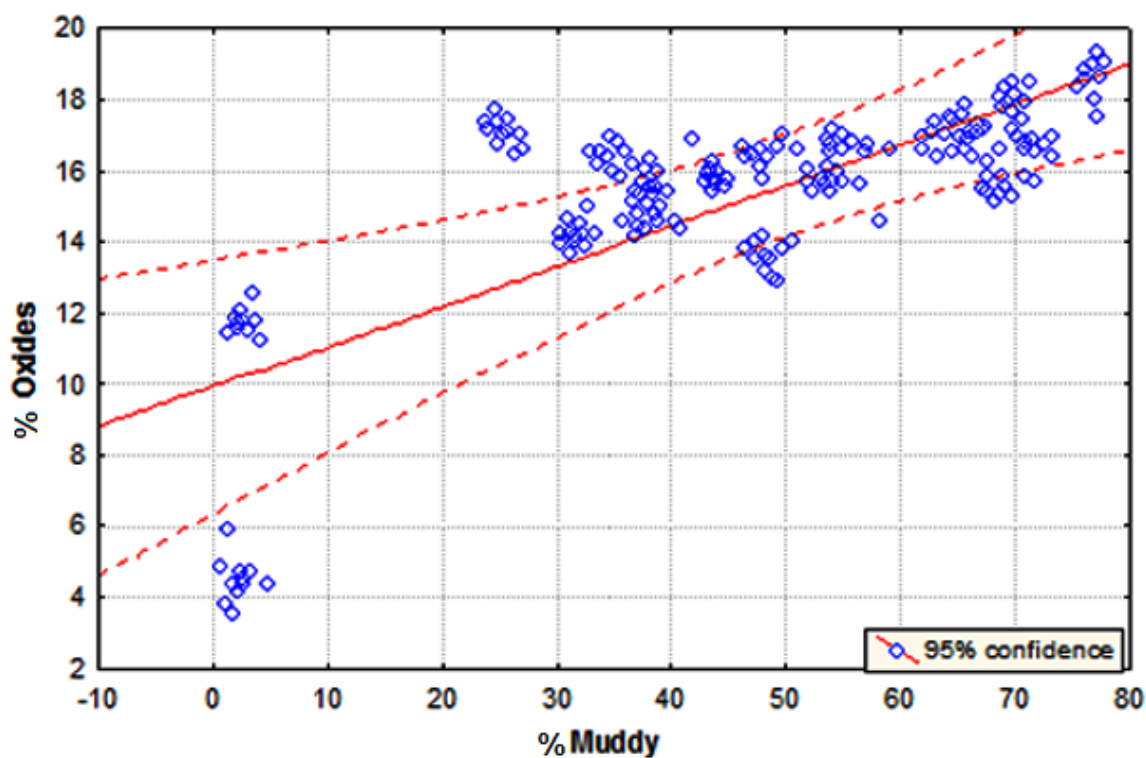


Figure-4
Scatterplot muddy vs. metallic oxides (Pearson's analysis) to casewise MD deletion. Oxides=9.9270+0.1132*muddy
[correlation: r=0.7611] (n= 191 samples)

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