



Physicochemical characterization of sediments from the coastal wetland of Samborombón Bay, Argentina

Eleonora S. Carol^a, Eduardo E. Kruse^a, Eduardo L. Tavani^{b,*}

^a Consejo Nacional de Investigaciones Científicas y Técnicas, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Calle 64 N° 3 (entre 119 y 120), (B1904AMA) La Plata, Argentina

^b Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC), Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Camino Centenario y 506, C.C. 49, (B1897ZCA) M.B. Gonnet, Argentina

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ABSTRACT

An exhaustive physicochemical characterization of sediments collected in the southern part of the coastal wetland of Samborombón Bay, Buenos Aires province, Argentina, was carried out to determine if the nitrogen and the phosphorus found derive from the organic matter. Samples were extracted from different geological environments: coastal plain, sand sheets, intertidal plain and water courses. Aspects analyzed involved the identification of mineralogical species present in sediments, distribution of grain size and specific surface. Major components were quartz and feldspars, while in some samples traces of calcite, hematite or kaolinite were found. As a novel fact, it is important to highlight that the ignition of sediments for organic matter valuation by weight loss was made between 200 and 500 °C. In this way, the thermal breakdown and the exclusion of the released hydration water were assured. Likewise, it was established that specific surface is an aspect conditioned by the hydrology of the system. Standard techniques were used for the chemical analysis of organic carbon, nitrogen and phosphorus. The most abundant element was organic carbon (0.279–2.840% w/w), with nitrogen (0.200–0.522% w/w) and phosphorus (0.028–0.185% w/w) following in descending order. The results obtained show a different source for each of the two macronutrients studied: organic matter for nitrogen and inorganic substances for phosphorus. Finally, it was determined by means of the C:N ratio that the organic matter is of marine origin.

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1. Introduction

Coastal wetlands are interface areas between terrestrial and aquatic environments. Some of their distinctive functions are the protection and stabilization of coasts, flood control and nutrient retention (Reddy and Delaune, 2008). Phosphorus and nitrogen are the macronutrients that plants use more abundantly for their growth (Harrison, 1999). A possible source of both nutrients is organic matter, being the carbon its main elemental component (Bohn et al., 1993).

Biogeochemical processes and matter transport are regulated by the hydrologic and geomorphologic properties of wetlands (Johnston et al., 2001). In these environments, runoff and groundwater flow are slow. Consequently, the sedimentation of the material in suspension and the interaction of the components

dissolved in water with the wetland substratum are favored. Due to such characteristics, as well as to their functions of accumulation and recycling of nutrients, wetlands are considered of great importance (Mitsch and Gosselink, 2007).

Nitrogen and phosphorus can be found in wetland as dissolved ions, particulate material or substances associated to sediments. The presence of both elements is the result of physicochemical processes (sedimentation, adsorption, precipitation, flocculation) and biological mechanisms (liberation by microorganisms). Substances retained can be inorganic, organic or a combination of them. In turn, certain features of each sedimentary environment determine the process type that characterises the association between nutrients and sediments (Bruland and DeMent, 2009; Dunne et al., 2006; Novak and Watts, 2006; Reina et al., 2006; Ferguson et al., 2004; Pant and Reddy, 2001; Howarth et al., 2000; Sundareshwar and Morris, 1999; Collender and Hammond, 1982).

Sediments have frequently been described by means of a classification that takes into account the content of sand, silt and clay

* Corresponding author. Tel.: +54 221 4840247; fax: +54 221 4750075.
E-mail address: etavani@netverk.com.ar (E.L. Tavani).

(Almeida et al., 2010; Connell-Madore and Katsube, 2008; Seiderer and Newell, 1999; Alam et al., 1998). When the adsorption is evaluated, clays are the most active inorganic constituents. Organic matter modifies such a behavior due to two main reasons, it has high adsorption capacity and it can block the access of dissolved ions to the reactive sites of clays (Harrison, 1999). Consequently, analyses of this substance and of organic carbon are also necessary to understand the dynamics of the system.

The organic matter of sediments is constituted by residues of vegetal origin (plants, roots, leaves, grass, etc.), residues of animal origin (insects, microorganisms, etc.) and the products of their respective decompositions under the action of physicochemical and biological factors. Such decompositions lead to a final compound called “humus”. The properties of organic matter are mainly due to the presence of this substance (Harrison, 1999; Bohn et al., 1993).

According to the above mentioned facts, the aim of our work was to perform an exhaustive physicochemical characterization of sediments collected in the southern part of the coastal wetland of Samborombón Bay (Buenos Aires province, Argentina) to determine the source of the nitrogen and phosphorous present in that environment.

2. Study area

The Samborombón Bay wetland extends along 180 km on the western coast of the Río de la Plata estuary, from Punta Piedras to Punta Rasa (Fig. 1). It includes a wide coastal plain with a strong interaction between surface water and groundwater. This mixohaline wetland was declared as a RAMSAR site in 1997. The sector corresponding to the external estuary of the Río de la Plata has a semidiurnal tidal regime, with ranges of less than 2 m (NHS, 2008). The geological evolution of the bay and the sedimentation on the plain occurred during the Holocene. These sediments originated in successive displacements of the shoreline due to sea level oscillations (Violante et al., 2001). The current configuration is the result of a simultaneous development of a sand spit, salt marshes, muddy tidal flats and channels.

The coastal plain is drained by the Ajó River toward the bay. The main contributions come from the El Palenque Channel, which flows toward the southernmost sector, and the Channel 2, which carries allochthonous waters originating in a higher area located to the southwest. All of these surface courses receive groundwater discharge from a shallow phreatic aquifer (Carol et al., 2008). The Ajó River is the main course for tidal propagation from the estuary toward the continent. At present, the Channel 2 has a floodgate that blocks the entrance of the tide.

Within the coastal plain, two geomorphologic subunits are recognized: the intertidal plain and sand sheets. The intertidal plain develops along the bay coast, the tidal channels, and the margins of both the Ajó River and the El Palenque Channel. It is a topographically low area (with an elevation of less than 1.10 m above sea level) which is flooded periodically by the tide. The sand sheets have different morphologies, normally occurring over a reduced area (usually less than 0.1 km²), and with elevations of about 2.5 m above the intertidal plain. Lithologically, they are composed by fine sand with shell fragments.

3. Materials and methods

Nine samples were collected from different geological environments: the coastal plain (CP1, CP2), sand sheets (SS1, SS2), the intertidal plain (IP1, IP2) and water courses (WC1, WC2, WC3). Sediments were extracted at a depth of 0–10 cm and stored in plastic bags. Fig. 1 shows sample extraction sites.

The identification of the major species present in sediments was carried out by X-ray diffraction (XRD), differential thermal analysis (DTA), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM) with the measurement of surface chemical composition.

XRD analyses were made with a Philips 3 kW X'Pert equipment, using Cu K α radiation and Ni filter. Thermal analyses (DTA and TGA) were performed simultaneously with a Netzsch STA 409 equipment. The sample was placed in a platinum crucible and α -Al₂O₃ (α -alumina) was employed as reference substance. The heating rate was 10 °C min⁻¹ and tests were carried out under nitrogen dynamic atmosphere with flux rate of 0.05 L min⁻¹.

SEM studies were made with a JEOL JSM–6360LV microscope. The surface chemical composition was determined by energy dispersive X-ray analysis (EDX) with the EDAX microanalysis system and a Philips 505 microscope. Percentages of sand (>63 μ m), silt (2–63 μ m) and clay (<2 μ m) were established in all sediments. The sand fraction was removed by washing the sample through a 63 μ m sieve. The silt and clay fractions were analyzed by the pipette method (Carver, 1971). The procedure began with the dispersion of the sample in water using vigorous stirring (180–230 rpm) for 30 min. The physicochemical characterization of sediments was completed by measuring the BET specific surface with a Micromeritics Accusorb 2100E equipment by means of nitrogen adsorption.

The organic carbon was valued by wet oxidation with potassium dichromate in a concentrate sulfuric acid medium, according to the Walkley-Black procedure. The remaining dichromate was titrated with ferrous ammonium sulfate. As regards the total and inorganic nitrogen contained in sediments, both concentrations were measured by the semi-micro Kjeldahl method. Nitrate and nitrite reductions were performed with aluminum, before digestion.

The total phosphorus was determined by the method described in Molins (1991), which is a specific analysis for orthophosphate, whereas other forms (polyphosphate and organic species) require a previous conversion. Transformation reactions were performed with sodium carbonate (fluxing salt) and perchloric acid (oxidizing agent). After converting phosphorus to orthophosphate, ammonium molybdate dissolved in a nitric medium was added to produce a yellow ammonium phosphomolybdate precipitate. Then, the insoluble substance was dissolved with NaOH excess and the alkali amount consumed was back titrated with standard acid. With a comparative criterion, the phosphorus content of sediments was also measured by EDX (non-destructive test).

4. Results and discussion

Table 1 includes all the data presented in this work: weight losses (200 °C, 200–500 °C); percentages of sand, silt, clay; specific surface; contents of organic carbon, total nitrogen, organic nitrogen, total phosphorus; organic carbon:total nitrogen ratio and water pH in contact with each sediment.

4.1. Physicochemical characterization of sediments

The diffractograms obtained showed the presence of quartz and small amounts of feldspars in all sediments (CP1, CP2, SS1, SS2, IP1, IP2, WC1, WC2, WC3). Besides, traces of calcite (WC1, WC3), hematite (WC3) and kaolinite (SS1, SS2) were determined in some sediments. According to these results, XRD was not an effective tool to identify organic matter.

The samples observed by SEM allowed us to confirm that grains had irregular sizes and shapes (Fig. 2(a), (b), (c)). Likewise, most of them were covered by precipitated particles (Fig. 2(b), (c), (d)). The EDX analysis demonstrated that sediments are formed mainly by

silicon, oxygen, aluminum and in lower proportion calcium, potassium and iron. Although with this technique it is possible to establish the surface chemical composition of sediments, it can be stated with a fair degree of certainty that the major minerals are quartz and feldspars.

In all sediments an endothermic peak at 92.4–123.3 °C with weight loss and an exothermic peak at 312–348 °C with weight loss were determined. The first transformation was connected with the release of hydration water and it appears to have concluded at 200 °C. This temperature in a chemical reaction expresses the position at which the peak reached its maximum value, even when from a kinetic point of view the phase change does not happen instantaneously. In turn, the second transformation was attributed

to the thermal breakdown of organic matter (Mitchell and Birnie, 1970). Thus, it is possible to assume that the organic matter would be eliminated in a quasi-quantitative manner during ignition between 200 and 500 °C. Such temperature range does not coincide with the conditions proposed by other authors, who suggest that transformations occur between 250 and 540 °C (Galbács et al., 1998) or 105–400 °C (Al-Khafaji and Andersland, 1992) and by ignition at 375 °C for 16 h (Ball, 1964). Table 1 shows weight losses at 200 and between 200 and 500 °C. The thermal behavior for the sample with the highest organic matter content is illustrated in Fig. 3.

Sediments had a variable content of sand, silt and clay (Table 1), including those collected in similar sectors (SS1 and SS2; WC1, WC2

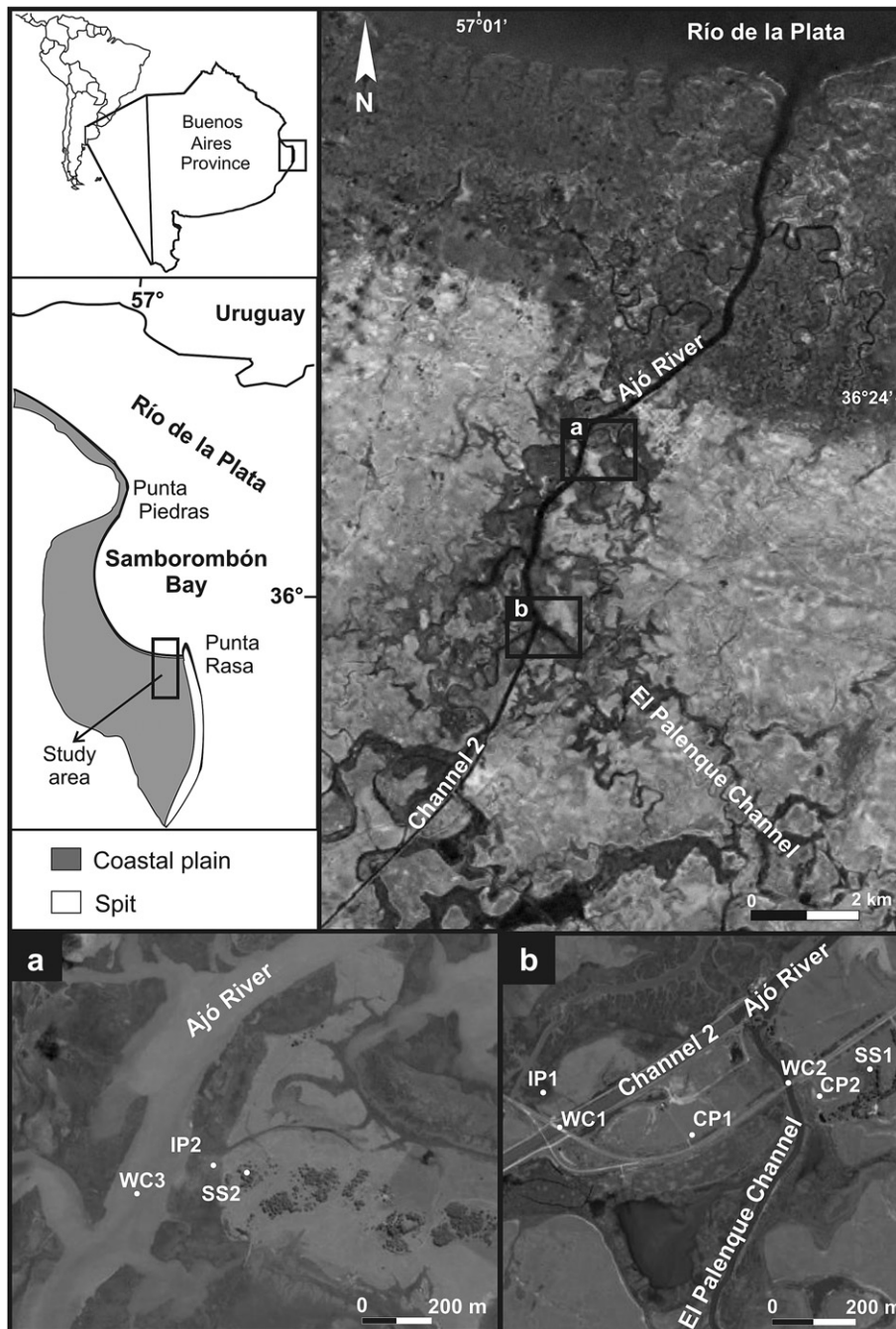


Fig. 1. Location of the study area and extraction points of sediments.

Table 1

Weight losses at 200 °C and 200–500 °C; percentages of sand, silt, clay; specific surface (SS); contents of organic carbon (C), total nitrogen (N), organic nitrogen (ON), total phosphorus (P); organic carbon:total nitrogen (C:N) ratio and water pH in contact with each sediment.

Sediment	Weight loss (% w/w)		Percent (% w/w)			SS m ² g ⁻¹	Content (% w/w)				C:N	pH
	200 °C	200–500 °C	Sand	Silt	Clay		C	N	ON	P		
CP1	4.6	2.9	11.5	88.0	0.5	74.75	0.839	0.342	0.334	0.028	2.45	7.8
CP2	8.5	3.4	15.8	83.6	0.6	55.10	0.656	0.324	0.305	0.047	2.02	7.1
SS1	3.7	6.0	42.1	56.3	1.6	19.80	2.840	0.522	0.480	0.185	5.44	7.7
SS2	1.2	2.7	86.5	11.9	1.6	4.32	1.409	0.351	0.330	0.064	4.01	7.3
IP1	3.5	2.5	23.1	76.4	0.5	30.65	1.590	0.229	0.223	0.063	6.94	7.6
IP2	2.1	5.2	23.6	75.8	0.6	23.49	2.051	0.470	0.440	0.062	4.36	7.2
WC1	5.4	2.0	39.4	59.7	0.9	62.17	0.279	0.200	0.190	0.092	1.40	7.9
WC2	3.8	2.6	66.9	32.3	0.8	18.93	0.563	0.357	0.345	0.029	1.58	7.6
WC3	2.7	2.1	58.5	40.8	0.7	15.82	0.499	0.255	0.243	0.067	1.96	7.7

and WC3). The percentage of clay was considerably low for the totality of the samples (<2% w/w). Results show that the silt was the main fraction, with a range from 11.9 to 88.0% w/w. No relationship among the three fractions (sand, silt, clay) and organic matter could be established.

Specific surface values showed a reasonable agreement with the type of geological environment from which each sample was extracted. Sediments associated with sand sheets had an irregular behavior, the specific surface of SS2 was smaller compared with SS1 (different silt:sand ratio and organic matter content). The partial elimination of organic matter in SS1 by physical means produced an appreciable decrease in its specific surface. Therefore, it can be assumed that the variance of this parameter for both samples is originated by the high content of organic matter in one of them.

Sediments WC2 and WC3 were collected in two water courses (Ajó River and El Palenque Channel) with tidal fluxes that drag the finest particles; consequently their specific surfaces are relatively lower. Sediment WC1 comes from Channel 2 and its large

specific surface may be due to the content of fine particles. Such a channel does not have bed flow and only the surface water layer is drained when its level surpasses the floodgate that regulates it. Sediments IP1 and IP2 were extracted from the intertidal plains of a channel and a river, respectively. The small slope (0.5%) of both sectors determines that the water flow and, hence, less dragging of fine particles in the bed. Then, there is a slight increase in the specific surface of the sediments IP1 and IP2 with respect to WC2 and WC3.

The largest specific surfaces were found in CP1, WC1 and CP2, which had a high silt percentage and low organic matter content. Sediments CP1 and CP2 are in the same coastal plain with an elevation between 1.17 and 1.55 m above sea level. Such area is not affected by the overflows of water courses, which favors the deposit of fine particles. The smaller value of CP2 with relation to CP1 may be caused by the sediment receiving a supply of coarse particles from nearby sand sheets (SS1). Briefly, the hydrology appears as a key aspect that helps to explain how the specific surface varies.

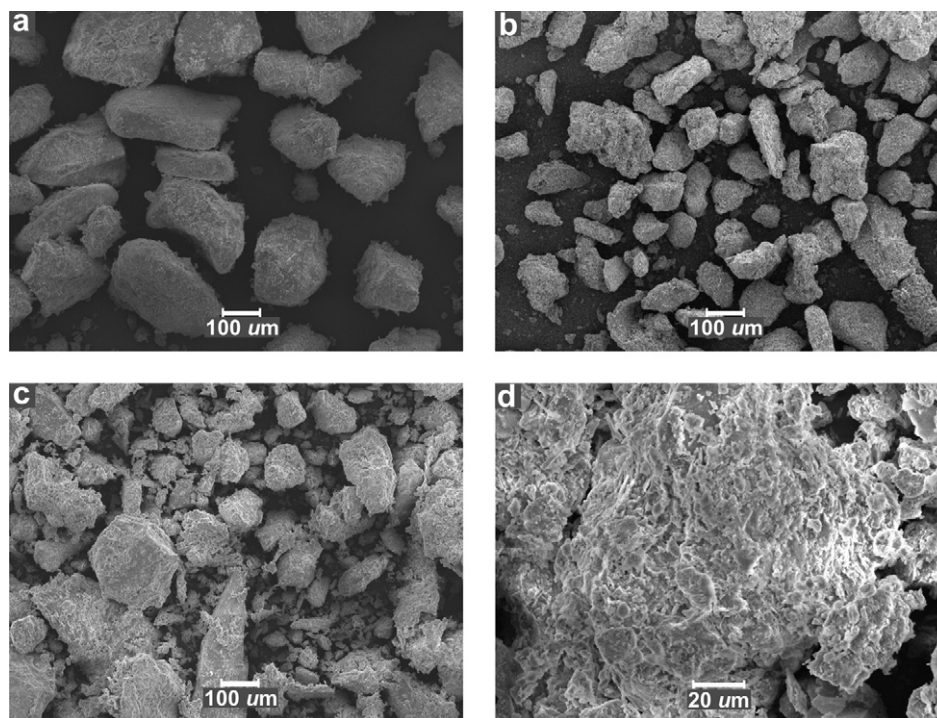


Fig. 2. SEM micrographs illustrating the main features of sediments. The major mineralogical components were quartz and, in smaller proportion, feldspars. (a) SS2: angular to sub rounded grains. (b) WC1: smaller grains of angular to sub rounded shapes, some of them have particles deposited on the surface. (c) WC2: sub rounded to sub angular grains very covered by precipitated particles. (d) Magnified surface view of a grain from WC2.

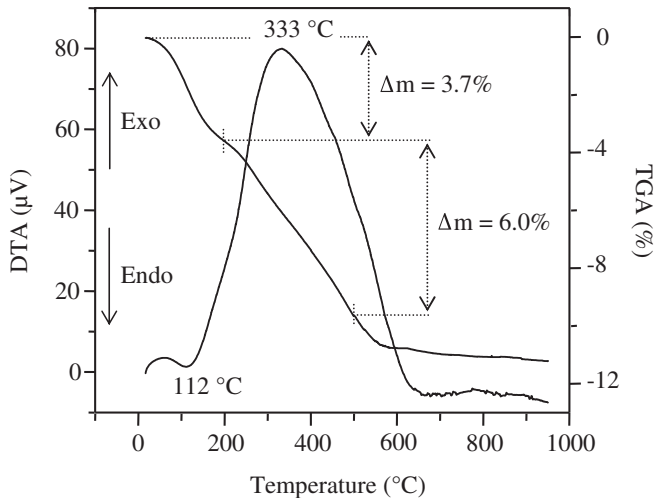


Fig. 3. DTA-TGA of SS1, sediment with the highest organic matter content.

4.2. Organic carbon

Organic carbon is the most abundant among the three nutrients examined (Table 1). Its content spans a range from 0.279 (WC1) to 2.840% w/w (SS1). Fig. 4 displays the ratio between organic carbon and organic matter. For a 5% significant level (NIST/SEMATECH, 2003), the linearity of the straight line evaluated by the minimum square method was: $r^2 = 0.738$; $p < 0.05$. This positive correlation confirms an acceptable dependence between both substances, as assumed when the regression line was drawn so that the absence of organic matter results in a null content of organic carbon.

A widely accepted criterion is based on the fact that particulate organic material and very fine-grained minerals (silts and clays) precipitate at a similar rate (Burone et al., 2003). Hence, the highest accumulation of organic carbon should be found in sediments of smaller granulometry (CP1 and CP2). The results in our samples do not confirm this behavior. The adsorption is the other mechanism habitually used to justify the accumulation of the cited nutrient although in our system, due to the low content of clays, the phenomenon is considered irrelevant.

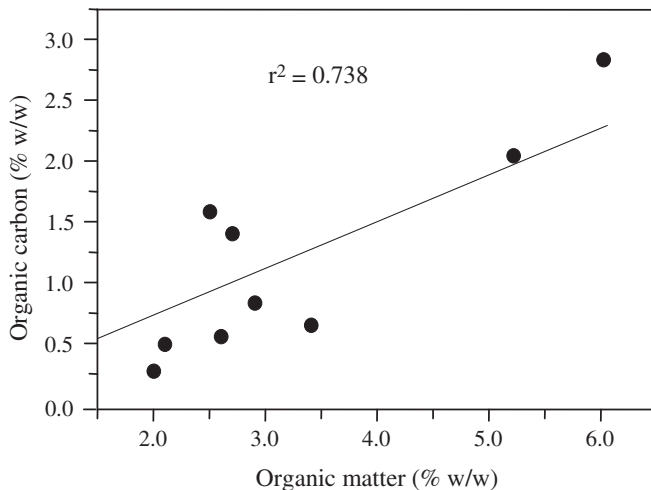


Fig. 4. Organic carbon as a function of the organic matter content.

It is well known that water courses (rivers and channels) produce a substantial contribution of organic matter together with an important dragging of those sediments that have smaller particle size. The situation is even more unpredictable in the case of strong currents (Burone et al., 2003; Prah et al., 1994). According to these authors, the hydrological regime of the wetland becomes a decisive factor to explain the distribution of organic carbon (organic matter) in the sectors selected for the sampling. This reasoning was applied in the previous point to justify the specific surface variation, whose values did not coincide with the ones expected.

4.3. Nitrogen

Nitrogen participates in the formation of a large diversity of organic and inorganic substances. Its most important resource is molecular nitrogen (N_2), a major constituent of the atmosphere, although it is a relatively inert species. Other atmospheric components, though chemically active, are the ones called nitrogen oxides ($NO_x = N_2O, NO$ and NO_2). These gases can be combined with atmospheric water to produce nitric acid (HNO_3). Nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) are the forms most easily incorporated to sediments. The inorganic nitrogen cycle involves several oxidation states of the element and its salts are appreciably soluble. In wetlands, very complex soluble substances containing nitrogen (aminoacids, amines, purines, urea, etc.) together with the particulate organic nitrogen resulting from living and dead matter are also found.

Fig. 5 shows the ratio total nitrogen to organic matter in sediments. The results obtained reveal that the nitrogen concentration increased in samples with a high content of organic matter. The slope of the straight line drawn indicates the average content of total nitrogen in the organic matter and its value was 6.96% w/w. Neither in this case nor in the following ones, the above mentioned idea that organic matter is the only source of nutrients can be applied. The analysis was completed evaluating the respective linearity by the minimum square method, reaching an elevated correlation ($r^2 = 0.845$; $p < 0.05$) for the two magnitudes.

The analytical techniques used in this work made the determination of total nitrogen and inorganic nitrogen possible, while the organic nitrogen was calculated by difference between those two

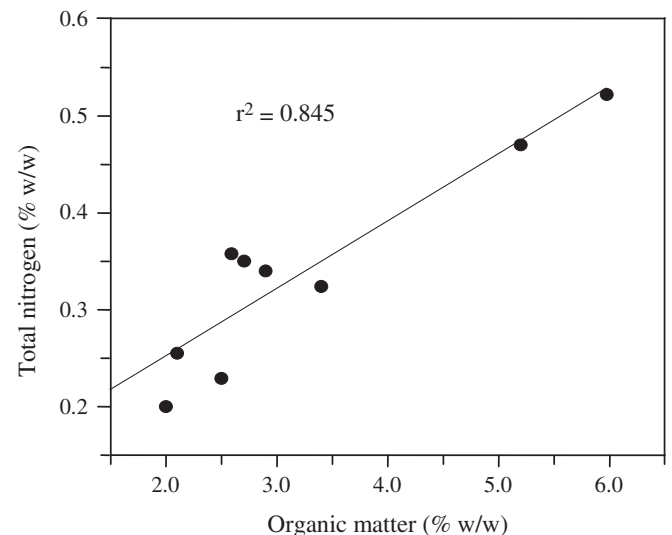


Fig. 5. Total nitrogen concentration versus organic matter content.

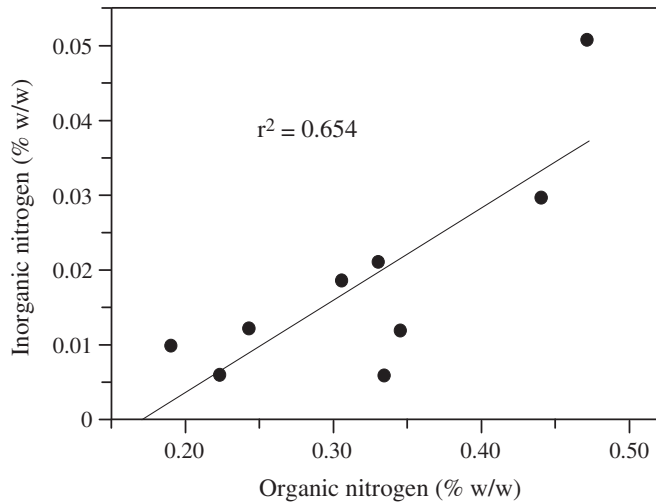


Fig. 6. Inorganic nitrogen concentration as a function of the organic nitrogen content.

amounts. The presence of organic nitrogen was much higher than the one of inorganic nitrogen in the nine samples.

The ratio of inorganic to organic nitrogen corresponds to the straight line slope plotted when one of the variables is a function of the other (Fig. 6). The average content of inorganic nitrogen with respect to organic nitrogen was 12.34% w/w ($r^2 = 0.654$; $p < 0.05$). This percentage indicates that almost all of the nitrogen determined in sediments is of organic nature, and its results are consistent with those mentioned by other authors (Bohn et al., 1993). According to such considerations, it can be assumed that the organic matter – and not the minerals in sediments – is the component that makes it possible to explain the evolution of nitrogen in the different geomorphological environments of the wetland.

From data shown in Table 1 it was possible to calculate the C:N ratio, noticing variations from 1.40 (WC1) to 6.94 (IP1). Such parameter has been used to determine the marine or terrestrial origin of organic matter. Thus, the algae have a C:N ratio which is lower than 6–7 and land vascular plants register values up to 30 (Burone et al., 2003; Prahel et al., 1994). Our results indicate that the organic matter is mainly of marine origin.

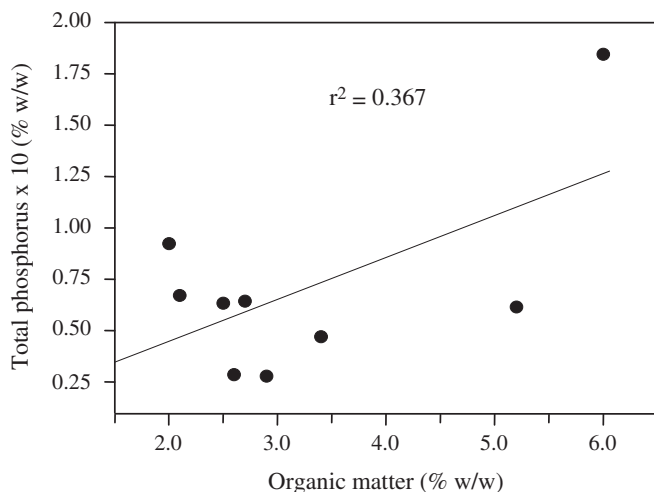


Fig. 7. Total phosphorus concentration versus organic matter content.

4.4. Phosphorus

Organic matter and kaolinite are two components of sediments that deserve special attention when the presence of phosphorus is analyzed in wetland. Phosphorus can be formed by organic matter decomposition. Such transformation depends on the type of substances present in each case (Bohn et al., 1993).

Some sediments had a very high phosphorus content that was not related to the amount of organic matter (Table 1). In order to carry out a quantitative valuation of such tendency, Fig. 7 expresses the concentration of total phosphorus versus organic matter content. Total phosphorus comprises the element present under inorganic and organic forms. The linearity of the straight line showed a very low correlation ($r^2 = 0.367$; $p > 0.05$), which suggests that the organic matter makes a minor contribution of phosphorus to the sediments.

In summary, organic matter is a component that does not explain in a satisfactory way the presence of phosphorus in the system. Besides, in those samples that had kaolinite (SS1, SS2) quite different phosphorus contents were determined. From the analysis of certain physicochemical aspects of the medium, it appears that the pH of the water which is in contact with the sediments provides an alternative explanation for the behavior observed. The pH in sectors associated to sediments WC1, WC3, CP1 and SS1 is favorable for the precipitation of calcium phosphate. However, the calcium ion in aqueous medium is necessary for the occurrence of such a reaction.

Calcium carbonate is scarcely soluble and, in aqueous medium, it is dissociated into carbonate and calcium ions ($K_{sp} = 4.8 \times 10^{-9}$). This salt crystallizes as calcite (trigonal system) and as aragonite (orthorhombic system). Sediments WC1 and WC3 contain calcite, so in such sectors sufficient calcium ions could be found to react with the phosphate. Kaolinite is considered an adverse substance for the salt precipitation ($\text{Ca}_3(\text{PO}_4)_2$) since the calcium is adsorbed very efficiently on the surface of such a clay. On the other hand, in a recent paper it was established that organic matter is a key factor in phosphogenesis (Brookfield et al., 2009). The sample with highest phosphorus content is SS1, which is characterized by the presence of organic matter plus kaolinite and it does not have calcite. These facts indicate, to some extent, the relative importance of each cited component in the reaction mechanism of phosphate and calcium.

The analysis by EDX made it possible to determine the surface total phosphorus in sediments. The number of counts for the phosphorus K-line was small in all samples. Nevertheless, it was viable to establish a marked difference in the amount of elements present in the respective sediments. The sample with the largest abundance of phosphorus was SS1 (2.33% w/w), although its concentration was very superior with respect to that measured by destructive chemical analysis. Particles deposited on the surface of most grains can be observed. These phases had a phosphorus content between 3.58 and 5.27% w/w, while the average value in grains was lower. Such relations corroborate that a significant amount of the phosphorus present in sediments is of inorganic nature.

5. Conclusions

The major mineralogical species identified in the sediments collected in different geological environments of the coastal wetland of Samborombón Bay (Buenos Aires province, Argentina) were quartz and, in smaller proportion, feldspars. In some cases traces of calcite, hematite and kaolinite were detected.

The organic matter content varied between 2.0 and 6.0% w/w. For its analysis, the weight loss produced by ignition from 200 to 500 °C was considered. These temperatures were selected in order to start the measurement once the release of the hydration water was concluded, and to assure the organic matter breakdown.

Percentages of sand (11.5–86.5% w/w), silt (11.9–88.0% w/w) and clay (0.5–1.6% w/w) were established. No relationship among these three fractions and the organic matter could be confirmed.

Extremely uneven values were determined for specific surface ($4.32\text{--}74.75\text{ m}^2\text{ g}^{-1}$) depending on the sector where the sediments were collected. At the same time, we could confirm that this parameter was conditioned by the hydrology of the system.

It was established that sediments had a very different organic carbon content, from 0.279 to 2.840% w/w. Concerning nitrogen, its extreme total values were 0.200 and 0.522% w/w. Likewise, it was determined that such a constituent mainly derives from organic matter. The total phosphorus concentration ranged between 0.028 and 0.185% w/w, noticing this element was mainly formed from inorganic substances. The results discussed in this work clearly indicate a different source for the two macronutrients contained in the wetland. Finally, it was demonstrated by calculations performed with the C:N ratio that the organic matter is chiefly of marine origin.

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