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# Hydrogeochemical and isotopic signature of surface and groundwater in a highly industrialized sector of the Rio de la Plata coastal plain (Argentina)

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ABSTRACT

The coastal plain of the middle estuary of the Río de la Plata is a highly industrialized area and is densely populated by sectors. The main human activity in the sector encompassed between the cities of Ensenada and Berisso is associated with the petrochemical industry. In this work, hydrogeochemical and isotopic characteristics of surface and groundwater in the impacted area are analyzed and the results are contrasted with those obtained in an undisturbed protected area. Major and trace elements were determined using standardized methods while the stable isotopes $\delta^{18}O$ y $\delta^{2}H$ were analyzed by mass spectroscopy. Human impact is evidenced by the occurrence of large variations in the major chemical composition of water, and also by the elevated concentrations of some trace elements that are not contributed from natural sources. These results may contribute to the understanding of chemical processes and pollutants distribution in highly industrialized coastal plain areas.

Coastal plains are complex hydrological environments where the chemical composition of water is controlled by multiple natural factors such as regional discharge, rainfall, tides, and evapotranspiration (e.g., Vandenbohede and Lebbe, 2012; Da Lio et al., 2015). In addition, these regions located at the interface between oceans and the continents are highly stressed owing to their intensively use and the accumulation of the byproducts of inland human activities, that are discharged from rivers and atmospheric deposition (Pruden et al., 2006; Da et al., 2014; Wu et al., 2014; Zhu et al., 2017; Herlinger and Viero, 2007; Graber et al., 2008; Güler et al., 2012). Therefore, an integrated understanding of fundamental physical and chemical processes is required to manage coastal resources more efficiently, based on site-specific comparative studies of coastal environments.

Modifications to the hydrological functioning and to the water quality are commonly registered in coastal plains with industrial development worldwide (e.g., Vecchioli, 1998; Herlinger and Viero, 2007; Botté et al., 2010; Marcovecchio et al., 2010; La Colla et al., 2015; Sá et al., 2015). The coastal plain of the Río de la Plata is one of the most extensive of the Atlantic coast of South America. Its hydrochemical characteristics have been mostly studied in pristine areas (e.g. Logan and Rudolph, 1997; Logan and Nicholson, 1998; Carol et al., 2009; Carol et al., 2013) while just a few local works have been performed in industrialized sectors. Thus, in this work the hydrogeochemical characterization of groundwater highly affected by the discharge of effluents derived from the petrochemical pole located between Berisso and Ensenada cities (Fig. 1) is performed, with the aim of contributing to the knowledge of the water chemical composition in impacted areas of the Río de la Plata coastal plain. The obtained results are contrasted with those of a pristine sector located in the Punta Lara Natural Reserve in order to assess the impact of the industrial activity.

The study area is located between the cities of Ensenada and Berisso and corresponds to a ~10 km wide coastal strip, formed on the right margin of the middle Río de la Plata estuary (Fig. 1). The estuary has a semidiurnal, microtidal regime, with water salinity varying in this section between 1.0 and 2.0 g $L^{-1}$ (Kind, 2004). Climate in the area is mild and humid with annual rainfall averaging 1010 mm $yr^{-1}$ (period: 1900–2012) and a mean annual temperature of 16.2 °C (Carol et al., 2012).

The coastal plain is bounded by the Río de la Plata in the East and by the Pleistocene loess plain in the West (Schnack et al., 2005). Clayed-silty sediments deposited in the tidal plain cover most parts of the study area and they are overlain by present-day alluvial deposits of the levee in the vicinity of the Río de la Plata (Fig. 1). In the Punta Lara Natural Reserve the geological, hydrological and environmental characteristics are preserved from human alterations. In this protected area, the main water course is Las Cañas stream which crosses the zone following a

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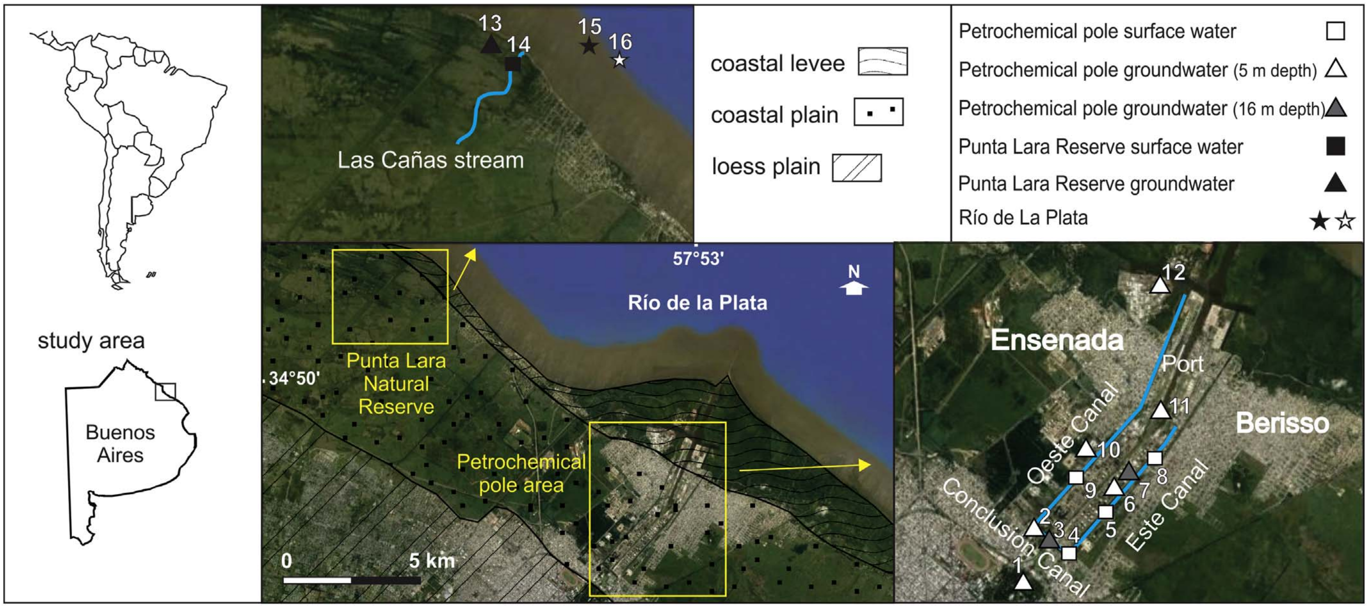


**Fig. 1.** Map of the study area and location of sampling points.

SW-NE direction and finally discharges into the Río de la Plata (Fig. 1). The Punta Lara Natural Reserve is the only pristine area in this urbanized and industrialized sector where one of the biggest ports and refineries of Argentina were emplaced since the early 1920s (Fig. 1). The petrochemical pole occupies an area of about 605 ha transversal to the Río de la Plata coast and is limited by three canals (Conclusión, Este, and Oeste) and by the La Plata port, located in the North. Because the area was originally affected by continuous flooding, it has been elevated for nearly 2 m above the natural level with loessic sediments during the construction of the petrochemical pole.

Surface water samples were collected in 2015 from the three canals dug around the petrochemical pole (Conclusión, Este and Oeste), while groundwater samples were collected from exploration boreholes drilled on the margins of the canals (Fig. 1). In the Punta Lara Reserve, surface water samples were collected from Las Cañas stream, while groundwater was sampled from an exploration borehole drilled a few meters northward the stream. Most of the sampled boreholes were manually drilled and fitted with a 4-in. PVC casing, with grooved filter and a siliceous gravel prefilter. Deeper boreholes located near the Conclusión and Este canals (16 m depth) were drilled using a water circulation rotary drill, and built as described above. A detailed record of the lithological and mineralogical characteristics of the sediment layers penetrated by the boreholes was performed during well logging. In addition to surface and groundwater samples collected in the study sector of the Río de la Plata coastal plain, two water samples were collected in the Río de la Plata in order to evaluate the influence of the tidal flow on the chemical composition of water in the coastal plain.

Field determinations consisted of pH and electrical conductivity (EC). In the Punta Lara Natural Reserve periodic measures of pH and EC were recorded along the Las Cañas stream, from the catchments to its mouth. After collection, samples were filtered through 0.22 μm cellulose acetate membrane filters (Millipore Corp.). The filtration equipment was repeatedly rinsed with sample water prior to filtration. The aliquots used for trace elements determination (15 ml) were acidified to pH $< 2$ with ultrapure $HNO_3$ ($> 99.999\%$, redistilled, Aldrich Chemical) and stored in pre-cleaned polyethylene bottles. A 1000 ml aliquot was stored in polyethylene bottles, without acidifying, at 4 °C for the determination of major ions. Unfiltered samples were stored in 500 ml polyethylene bottles at 4 °C, for stable isotopes determinations.

Determinations of major ions ($HCO_3^-$, $Cl^-$, $SO_4^{-2}$, $Ca^{+2}$, $Mg^{+2}$, $Na^+$, $K^+$) were performed following standard methods outlined by the American Public Health Association (APHA, 1998). Calcium was determined by titration using a 0.01 M EDTA solution, and Magnesium was calculated as the difference between total hardness and calcium expressed as $CaCO_3$. Sodium and potassium were determined by flame photometry using a Metrolab 315 photometer. Chloride was determined by titration using the argentometric method. Sulphate was precipitated in an acetic acid medium with $BaCl_2$ and its concentration was determined by turbidimetry. Bicarbonate and carbonate were determined by titration using a 0.01 N sulfuric acid solution and methyl-orange and phenolphthalein were used as end-point indicators, respectively. Ion balances were typically lower than 10% in all cases.

Minor and trace elements were measured by ICP-MS (Perkin Elmer Sciex Elan 6000 – quadrupole mass spectrometer). The validity of the results for major and trace elements were checked with NIST-1643e (Trace Elements in Water Reference Material certified by the National Institute of Standards & Technology, USA) and SRLS-5 (River Water Reference Material for Trace Metals certified by the National Research Council of Canada), carried out along with sample analysis. The accuracy of standard measures ranged between 1 and 10% in both cases. In addition, duplicated analysis were performed every 10 samples in order to check the reproducibility of results, and the precision ranged between 1 and 8% in all analyzed elements. Isotope ratios $\delta^{18}O$ and $\delta^2H$ were measured using mass spectroscopy (Thermo Finnigan MAT Delta Plus XL continuous flow mass spectrometer). The analytical accuracy is $\pm$ 0.05‰ and $\pm$ 0.3‰, for $\delta^{18}O$ and $\delta^2H$, respectively. Results are reported in δ (‰) relative to V-SMOW (Gonfiantini, 1978).

The lithological and textural descriptions carried out during drilling show that the unconfined aquifer in the loess plain region is composed of silty to silty-clayed sediments with calcium carbonate concretions. The mean aquifer thickness is 31.5 m and it generally wedges out towards the Río de la Plata. In the coastal plain, the unconfined aquifer corresponds to ~6 m thick silty to clayed sediments that alternate with lenses of fine-grained sands and marine shells deposited over the loess sediments (Fig. 2). In the petrochemical pole groundwater is also in contact with the 2 m thick sediments that fill the area. Finally, the uppermost sediments consist of fine-grained sands corresponding to alluvial deposits of the levee in the vicinity of the Río de la Plata. In both, the loess plain as well as in the coastal plain, the unconfined aquifer overlays a 3 m thick silty-clayed layer which hinders the hydraulic transmission between the unconfined aquifer and the under-