

## Seasonal behavior of dissolved inorganic carbon, silica and barium along a salinity gradient in a shallow coastal lagoon (Etang de La Palme, Southern France)

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### ABSTRACT

The La Palme lagoon is a shallow coastal lagoon located close to the Mediterranean Sea in South West France. It is from time to time connected to the sea by an intermittent inlet ("grau de La Franqui") cutting through a 80 m wide sandy breach, that naturally opens after peculiar conditions (storms flooding the beach followed by days of seaward strong winds). North of the lagoon, water coming out of a karstic spring (Le Lavoir) forms a 300 m long river running through marshes before discharging into the lake. Such environments are of great ecological importance for example as resting and nesting areas for migrating birds. Investigating the hydrological and chemical budgets of the lagoon requires the evaluation of the contribution of seawater intrusions (SWI) and subterranean groundwater discharge (SGD). Deciphering the behavior of chemical tracers also requires investigating the eventual control of their concentrations by water-rock interactions.

Water samples have been collected at the spring, in the lagoon and in the narrow zone where the river water mix with the salty waters, at 8 different dates over a year. Temperature, pH, salinity, ORP and dissolved oxygen have been measured in situ. The complete compositions of the water samples (Na-K-Ca-Mg-Ba-Sr-Si-Cl-SO<sub>4</sub>-DIC-DOC) have been determined using ICP-OES, DIC (Dissolved Inorganic Carbon) and DOC (Dissolved Organic Carbon) analysis and ionic chromatography. We also analyzed radium isotopes for a few samples. Element-to-chloride concentration ratios show that Na/Cl, K/Cl, Mg/Cl and SO<sub>4</sub>/Cl are within 10% of the values for standard seawater over the investigated salinity range (4-45 ‰) while Ca/Cl, DIC/Cl and Sr/Cl depart from standard seawater values for salinities below 30 ‰, thus delimitating the transition from marine to continental waters. Temperature at the Lavoir spring has linearly decreased by 1 °C between April 2016 and January 2018 while salinity has decreased from 9 ‰ in April 2016 to 4‰ in April 2017 before increasing to values levelling off at about 6 ‰. This trend is also followed by pH, Na, Ca, SO<sub>4</sub> and to a lesser extend Sr while dissolved silica and inorganic carbon are roughly constant and Ba varied by a factor of two between 150 and 300 nmol/L. This salinity change can be due either to a freshening of salty formation waters by a freshwater contribution, or to an increase in salinity of fresh formation waters by a seawater intrusion.

The composition of samples collected in the very narrow zone where river waters discharge into the lagoon (estuary) change with the season. Whereas the Dissolved Inorganic Carbon (DIC) follows a first order dilution trend between the spring and the lagoon waters, barium varies in roughly the same way in the Lavoir and in the lagoon, displaying roughly parallel trends for each sampling date. The aqueous silica concentration is roughly constant at high values (100-120 μmol/L) in the karstic spring (Lavoir) and at low values (5-20 μmol/L) in the lagoon and follows a dilution trend for cold months. Data for summer 2017 show a local increase of the silica concentration of the estuarine waters that can be due to the degradation

of the plants and grass of the nearby marshes that form a thick back sediment layer at the mouth of the river.

The calculation of mineral saturation indices shows that barite, Ca-carbonates and  $\alpha$ -quartz are at equilibrium in the karstic spring waters at all dates. Ca-carbonates are supersaturated in the lagoon waters at values close to ocean surface waters, while barite changes from undersaturation to near equilibrium following seasons. Amorphous silica is always undersaturated in the entire salinity gradient and in the lagoon.

These results emphasize the seasonal dependency of the behavior of dissolved elements in an environment with large salinity changes and warn about conclusions that could be drawn from observations at a single date.

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