Determination of heavy metals in coastal seawater of Gran Canaria Island using a matrix elimination step

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INTRODUCTION

Coastal areas are highly valued territories with many competing economic activities, which added to its ecological and environmental wealth and importance, makes necessary to manage them under the **"Sustainable Development"** philosophy with the aim to preserve and protect them from impacting pressures, but continuing being an economic resource. For this reason, it is necessary, among other things, to study the possible disturbances affecting the marine environment to know their origin, predict their behavior and propose measures to avoid and reduce its harmful effects.

In this sense, the natural concentrations of **metals** that present **toxicity, persistence and bioaccumulation** in the aquatic environment can be increased by anthropogenic sources such as industrial activities, wastewater discharges (urban and industrial), traffic (road and maritime), the use of chemicals in agriculture (pesticides, fungicides, fertilizers, etc.) and cooling water discharges (Bergasa et al, 2007, Rosas, 2001). Assessment of the heavy metals concentrations in water is essential to know its chemical status.

OBJECTIVE

This work, proposed under the **Water Framework Directive** (WFD), falls within the task called "Evaluation of specific pollutants in coastal waters" of the **OMARCOST** project "Strategy for the environmental sustainability of transboundary coastal environment" (**www.omarcost.org**), funded by the Program of Cross-border Cooperation Spain - External Borders (**POCTEFEX**).

Its objective was to determine the presence in coastal waters of Gran Canaria island of five **metals** listed in the WFD and classified as **priority and preferred substances** to evaluate their chemical quality based on the fulfillment of the established **Environmental Quality Standards** (EQS), showed in the following table (Table 1).

Table 1. Established environmental quality standards at the Royal Decree for metals to study

Analyte	EQS-AA (annual average), µg/L	EQS-MAC (maximum allowable concentration), µg/L
Cd	0,2	1,5
Cu	25	Not applicable
Ni	20	Not applicable
Pb	7,2	Not applicable
Zn	60	Not applicable

METHODOLOGY

Analysis method set up

For the elimination of the **matrix effect** caused by the salts present in seawater, it was decided to use a resin called **SPR-IDA** (suspended particulate reagent-iminodiacetate) of the trading house CETAC, formed by 10 micron diameter beads with the chelating agent **iminodiacetic**, capable of immobilizing the elements shown in light blue in the picture below (Figure 1).

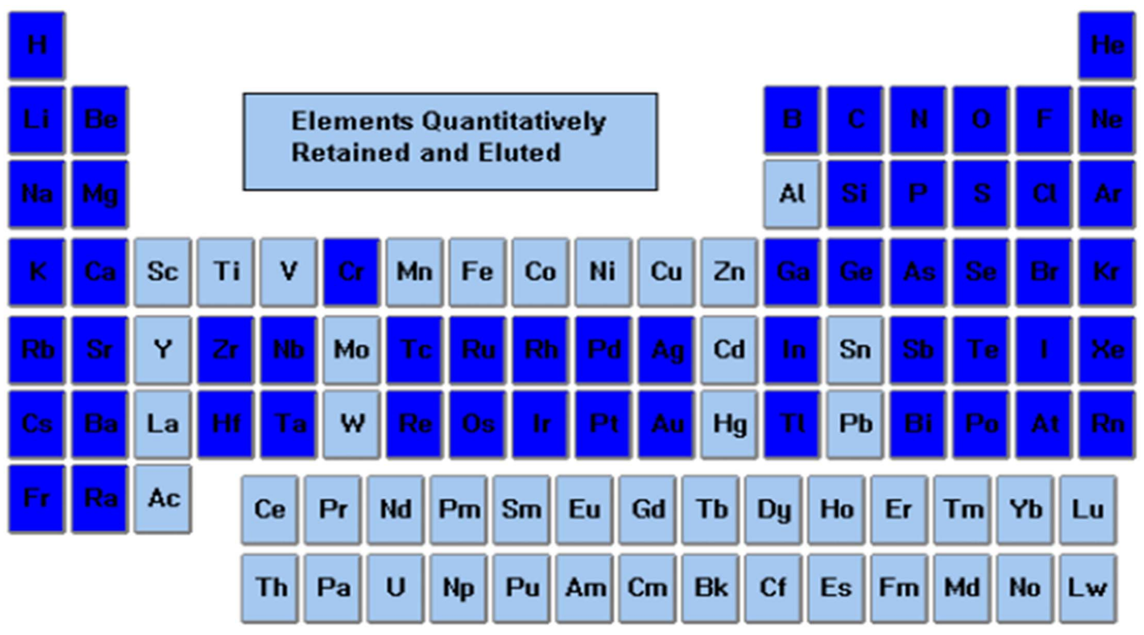


Fig. 1. Selectivity of iminodiacetate (Source: CETAC)

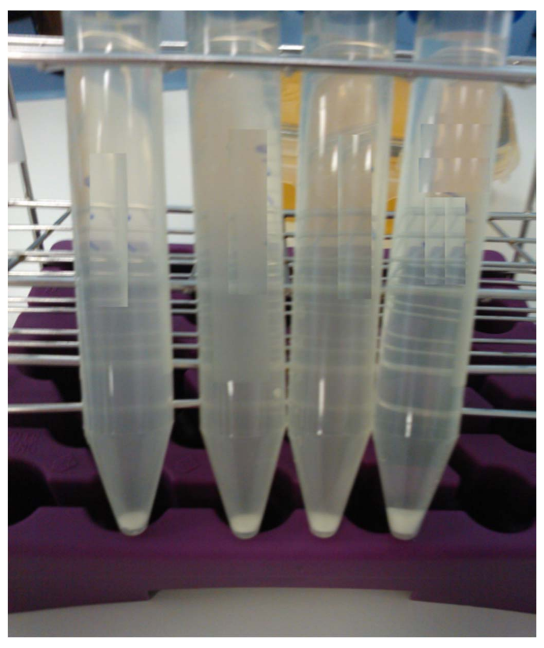


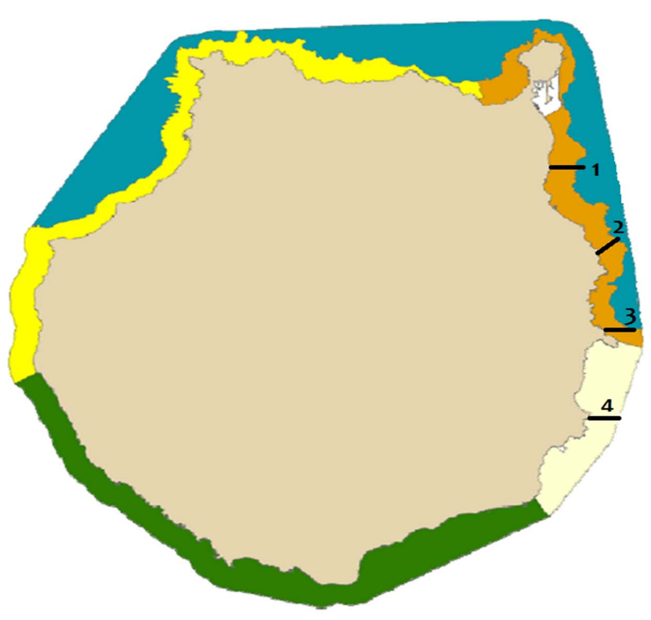
Fig. 2. Seawater samples with the SPR-IDA

The treatment of seawater samples, once filtered through 0,45 µm and acidified to pH<2, was performed following the procedure described by Smith (Smith and Doeschot, 2012), involving the aliquot addition of the 10% suspension of the SPR-IDA resin and the pH adjust to 8 ± 0,5. The resin retains the metals of interest, whereas the Na, K, Ca, Mg and Cl remain in the suspension and can be removed by settle or centrifugation (Figure 2). Metals are resuspended in 7% nitric acid. Treated samples were analyzed by an Inductively Coupled Plasma Atomic Optical Emission Spectrometer (ICP-OES) from Perkin Elmer, model DV 2100.

The method agreement was tested by the participation in a **proficiency exercise** for metals in seawater organized by Quality Reliable Lab Services, S.L. in November 2012.

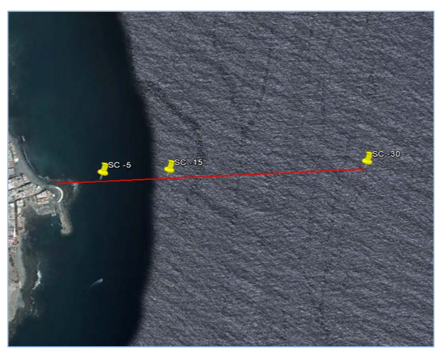
Sampling campaigns in coastal areas

Four coastal areas in the east of the Gran Canaria Island shoreline (Fig. 4) were selected. In each of them a four-point transect was chosen for surface sampling (0,3 and 1 m deep), corresponding to the bathymetric levels of -5, -15, -30 and-50 m (always within a nautical mile). Samples were collected in amber glass bottles (Fig. 3) and stored in dark at 4 ° C until analysis or treatment within 24 hours. Sampling was conducted bimonthly between April and December 2013.



Figures 3 and 4. Images of one of the sampling (left) and overview of the sampling transects (right)

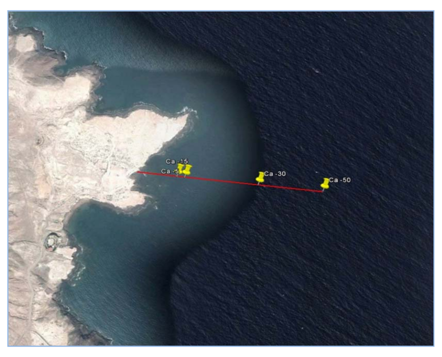
Coastal study areas



1.-San Cristóbal area
Main **uses**: bathing area and recreational fishing
Main **pressures**: small fishing port and discharge of treated wastewater from Barranco Seco WWTP sea outfall

2.-La Estrella area
Main **uses**: bathing area and recreational fishing
Main **pressures**: treated wastewater discharges from Jinámar WWTP and Hoya Pozuelo WWTP

3.-Gando area
Main **uses**: bathing area and recreational fishing
Main **pressures**: greenhouses, Silva outfall discharges (treated wastewater and brine) and discharge of industrial wastewaters from industrial sites of Salinetas and El Goro. Very close to Gando airport



4.-El Cabrón area
Main **uses**: bathing and diving area
Main **pressures**: No significant pressures identified (a discharge from a WWTP is located 4 km east south)

RESULTS AND DISCUSSION

Results of the proficiency exercise

In the table below (Table 2), the results obtained with the described method together are shown with the assigned values in the exercise and the Z'-score values, all **satisfactory** for the five analyzed metals (values between -2 and +2).

Table 2. Concentrations reported, assigned values and Z'-score

Analyte	Reported value, µg/L	Assigned value, µg/L	Z'-score
Cd	0,50	0,49	**0,26**
Cu	2,58	3,22	**-0,42**
Ni	2,80	2,48	**0,54**
Pb	2,34	2,02	**0,93**
Zn	198,00	178,38	**0,48**

Metal concentrations on the east coast of Gran Canaria

At all the sampling points and during the five sampling campaigns, the concentrations of Cu, Ni and Pb were below the limit of quantification (Lq) of the method and meet their corresponding EQS-AA. For Cd, concentrations were also always lower than Lq, but since Lq is greater than the EQS-AA, it can only be ensured that they meet the EQS-MAC. In the case of Zn, all samples presented concentrations below the EQS-AA and only some of the samples taken in December exceed the Lq, with concentrations in the order of few tens of µg/L.

This **presence of Zn** could be explained as a consequence of the fact that three of the four industrial complexes in the study area declare Zn emissions to water, making a total of more than 2200 kg/year (PRTR-Spain). In the Canary Islands, the possible sources of Zn input to the marine environment may be urban and industrial wastewater discharges, traffic and agriculture (Mendiguchia, 2005). At the industrial level, the Zn is one of the most commonly additive present in the products used for corrosion inhibition in cooling circuits.

CONCLUSIONS

- ✓ The **method** comprising the use of the SPR-IDA resin for analysis of Cd, Cu, Ni, Pb and Zn in seawater is **valid**.
- ✓ **Advantages** of the use of SPR-IDA resin for the analysis of seawater samples:
  - It is not necessary to dilute samples
  - washing time is reduced (shorter analysis and lower argon consumption)
  - external calibrations in ultrapure water can be performed (because of the elimination of the matrix effect on the samples)
  - lower consumption of high purity reagents
  - lower deterioration of the equipment
- ✓ **All analyzed metals meet EQS-AA**, except Cd, for which we can only ensure compliance with the EQS-MAC.
- ✓ The Zn was the only element quantified, but only during the December sampling and always in concentrations around few tens of µg/L.
- ✓ This study contributes to **knowledge** about the presence of heavy metals in the canarian coastal marine environment.
- ✓ Given the low concentration and high variability of these pollutants in the marine environment, it would be desirable to establish more appropriate sampling systems, such as **passive samplers devices**.

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