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Heavy metals in seabed sediments beneath off-shore fish cages

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HERNÁNDEZ-SÁNCHEZ, C., R. RIERA, S. MARTÍNEZ-LÓPEZ, D. GONZÁLEZ-WELLER, A. J. GUTIÉRREZ, A. BURGOS, C. RUBIO, M.J. MARTÍNEZ-SÁNCHEZ, C. PÉREZ-SIRVENT, & A. HARDISSON. Metales pesados en los sedimentos de los fondos marinos bajo las jaulas "off-shore" de peces. *VIERAEA* 45: 367-380. https://doi.org/10.31939/vieraea.2017.45.21

ABSTRACT: The aquaculture industry has been steadily increasing worldwide in the last decade and currently there are more off-shore cages. Environmental impacts of off-shore cages have been focused on the effects of uneaten pellets and fish faeces on benthic assemblages. However, the release of heavy metals associated with aquaculture activities remains poorly studied. In the present study, the concentrations of heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) on sediments beneath off-shore fish cages were analyzed. Two aquaculture leases were sampled in two locations, NE and SW of Tenerife (Canary Islands, NE Atlantic Ocean). Sediments from unaffected locations were sampled to determine if there were significant changes in heavy metals composition on sediments due to aquaculture activities. There were significant differences in Cd, Co, Cr, Cu, Ni, Pb and Zn at both areas, with the exception of Mn that was in high amount. The high content of Mn collected in samples from both areas could have a volcanic origin. The concentrations of heavy metals find out in sediments beneath offshore seabed cages do not present risk for environment.

Keywords: Aquaculture, off-shore cages, heavy metals, marine sediments, Atlantic Ocean.

RESUMEN: La industria de la acuicultura ha estado aumentando constantemente en todo el mundo en la última década, existiendo en la actualidad numerosas jaulas "off-shore". Los impactos ambientales de las jaulas off-shore se han centrado en los efectos de los restos no consumidos y de las heces de peces en las estructuras bentónicas. Sin embargo, la liberación de metales pesados asociados con las actividades acuícolas sigue siendo poco estudiada. En el presente estudio se analizaron las concentraciones de metales pesados (Cd, Co, Cr, Cu, Mn, Ni, Pb y Zn) en los sedimentos de las jaulas de peces off-shore. Dos concesiones de acuicultura fueron muestreadas en dos localidades, NE y SO de Tenerife (Islas Canarias, NE Océano Atlántico). Los sedimentos de lugares no afectados fueron analizados para determinar si hubo cambios significativos en la composición de metales pesados en los debido a las actividades de acuicultura. Hubo diferencias significativas en Cd, Co, Cr, Cu, Ni, Pb y Zn en ambas áreas, con la excepción de Mn que estaba en grandes cantidades. El alto contenido de Mn recogido en muestras de ambas áreas podría tener un origen volcánico. Las concentraciones de metales pesados que se encuentran en los sedimentos debajo de las jaulas de fondo marino no presentan riesgo para el medio ambiente.

Palabras clave: Acuicultura, jaulas off-shore, metales pesados, sedimentos marinos, océano Atlántico.

INTRODUCTION

Aquaculture off-shore industry has been increasing steadily worldwide because of economic benefits and the improvements given to fisheries. However intensive activities can develop a negative impact on environment. Therefore, they have to be carefully studied and monitored. Metals are naturally present in earth and enter aquatic environments by various geochemical processes (Guardiola *et al*. 2013).

Sedimentary composition has been recognized as an important indicator of marine pollution since they act as depositories of contaminants, such as, heavy metals and hydrocarbons (Banat *et al.* 2005; Chen *et al*. 2005; Krishna & Govil, 2005; Idris *et al*. 2007; Li *et al.* 2009; Oyeyiola *et al.* 2011). Thus, sediments constitute a long-term record of pollutants from anthropogenic disturbances (Chapman *et al.* 1998; Santos-Bermejo *et al.* 2003; Idris *et al.* 2007; Rulian *et al.* 2008). Sediment accumulation of contaminants may cause severe adverse effects on ecosystems and even, could reach concentrations that may be unhealthy for humankind (Poté *et al.* 2008; Lagston *et al.* 2010; Freitas *et al.* 2012). High concentrations of heavy metals in sediments have been reported beneath offshore fish cages, being Zn and Cu the most abundant heavy metals (Uotila, 1991; Chow *et al.* 2002; Brooks & Mahnken, 2003; (no está en la bibliografía) 2004; Smith *et al.* 2005; Jaysankar *et al.* 2009). Other abundant heavy metals are Cd, Co, Cr, Mn, Ni and Pb (Alam *et al.* 2001; Wong *et al.* 2001; Belias *et al.* 2003; Álvarez-Iglesias *et al.* 2006; Mendiguchía *et al.* 2006; Li *et al.* 2007; Sutherland *et al.* 2007; Tabari *et al.* 2010; Basaran *et al.* 2010).

The main aims of the present study are (I) to determine heavy metals concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in sediments beneath fish cages and their feasibility as reliable bioindicators of environmental perturbations from aquaculture activities and (II) to establish if aquaculture activities are a consistent source of pollution on sedimentary composition, comparing caged sediments (impacted) and not affected (control) locations.

MATERIAL AND METHODS

Study area

A total of 111 sediment samples were collected in the Island of Tenerife (Figure 1). Fifty-seven samples were collected beneath offshore fish cages (27 from NE cages and 30 from SW cages), classified as “impact”. Fifty-four sediment samples were collected in non-affected areas (“control”), 20 from NE and 34 from SW.

Thus, sediments from NE and SW of the island have different composition and were not comparable between them. Impacted and control areas belonging to the same area (NE or SW) were compared.

The coordinates and depth of the four sampling areas were the following:

- Northeast impact: coordinates (28º32’08.73’’N/16º09’40.08’’W), depth 28 m
- Northeast control: coordinates (28º32’12.78’’ N/16º07’39.00’’W) , depth 25 m
- Southwest impact: coordinates (28º04’19.9’’N/16º44’21.16’’W) , depth 28 m
- Southwest control: coordinates (28º06’28.68’’N/16º45’42.36’’ W), depth 25 m.

Tenerife, is the largest (2,058km^2) and highest (3,718m) island of the Canarian Archipelago (Geyer and Martí, 2010), is characterized by its volcanic complexity, due to the accumulation of different volcanic materials (Dóniz Páez, 2010). The Canary Island climate is determined as semi-arid-subhumid (Hürlimann *et al.* 2001).

Tenerife has a volcanic origin and is characterized by heterogeneous environments, with a clear difference between the northern and the southern part of the island (Fernández-Caldas *et al.* 1982).

Grain size composition

To assess grain size composition of the analysed sediment, 100 g sediment from each sampling location was oven dried at 105º C, passed through a graded series of sieves (2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm and 0.063 mm), and weighed (Buchanan, 1984). These sieves characterized seven different sedimentary types (gravels, very coarse sands, coarse sands, medium sands, fine sands, very fine sands and silt/clay).

A sediment core (Hydro-Bios Apparatebau GmbH) of 600 mm length x 72 mm inner diameter was pushed into the sediment by scuba divers throughout field surveys. In the laboratory, the upper 5 cm were separated and dehydrated in a heater at 60-80ºC during 12-14 h.

The upper 5 cm layer of soil was more active biologically and chemically, and has the strongest influence on water quality and associated biota, because most of interactions between sediments and water occur superficially (Riera *et al.* 2012).

Mineralogical analysis

A semiquantitative estimation of the mineralogical composition of the samples was made by X Ray Diffraction (XRD) analysis using Cu Kα radiation with a PW3040 Philips Diffractometer. X-powder software (Martín, 2004) was used to analyse the X-ray diffraction diagrams obtained by the crystalline powder method. The powder diffraction file (PDF2) database was used for peak identification, taking into account that the determination of minerals from soils by XRD analysis is not accurate below a limit of 5% of the total weight in a sample (depending on the crystallography of individual minerals).

The software incorporates precise quantitative studies made by nonlinear least squares methods on a full profile of the diffractogram, and takes advantage of the information contained in the database records. wasWeighting was achieved with the standard Reference Intensity Ratios (RIR) method described by Chung (1974). The automatic use of this method assumes that the database contains the chemical composition of each phase.

Sediments analysis

Before sample processing, all laboratory materials used was washed with Acationox laboratory cleaning agent to avoid contamination and remove any possible trace metals, kept in 5% HNO_3 acid for 24 h followed by washing with milli-Q quality water.

To determine the Co, Cr, Cu, Mn, Ni, Pb and Zn contents, the samples were first ground to a fine powder using an agate ball mill. Then, 200 mg was placed in a Teflon vessel before adding 5 mL of concentrated HF acid solution, 2 mL of concentrated HNO_3 acid solution and 5 mL of pure water. When the digestion in the microwave system was complete, the samples were transferred to a volumetric flask and brought to 50 mL before measurement. Teflon or other suitable plastic ware was used for handling these liquids. (creo que falta alguna referencia aquí del método).

The samples were digested using a Milestone ETHOS Plus Microwave system operating with a standard program (applied power in watts 150, 0, 150, 0, 150, 0, 350, 400, 0, 450 and 0 for 1, 1, 1, 1, 2, 1, 5, 5, 1, 1 and 20 min, respectively). The method used to measure the soluble elements was based on the procedure described in European standard (EN 12457-1).

The reliability of the results was assessed through analysis of the NIST standard reference materials: SRM 2711 Montana Soil. Spikes, duplicates and reagent blanks were also used as a part of the quality control. The recovery obtained with the reference materials were all above 95%.

The Co, Cr, Cu, Mn, Ni, and Zn concentrations were determined using flame AAS. The spectrophotometer used to carry out the measurements was a Perkin-Elmer flame spectrophotometer. The Cd and Pb concentrations were determined using Perkin-Elmer model 4100 ZL Zeeman spectrophotometer, equipped with a graphite furnace tube and an automatic sampler.

Statistical analysis

Data were processed with SPSS v19.0. Normal Data distribution was tested with the Kolmogorov-Smirnov model (Xu *et al.* 2002), and Levene's test was applied to determine variance homogeneity (Pan, 2002). For inferential statistics, an ANOVA (post-hoc Tukey test) was applied as parametric test and the Mann-Whitney and Kruskal-Wallis as non-parametric tests (Choy *et al.* 2001).

RESULTS

Control areas were characterized by having a predominance of fine and medium sands, with a scarce content of silt and clay (Table 1). In NE area, fine sands were the dominant grain size fraction (49.89% at impacted area and 45.50% at control area). In SW area, medium sands are more abundant than in NE area (29.29% in impacted area and 49.12% in control area).

The content of silt and clay was better represented in impacted areas than in control areas because of the continuous input of organic matter from uneaten fish pellets and fish faeces. Higher content of silt and clay were found in NE impact area (4.49%) than in SW impact area (1.88%) (Table 2).

The concentration of the studied heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) were significantly different at both areas (NE and SW), with the exception of Mn ($p < 0.05$). At NE area, the control location showed higher concentrations of Mn, Ni and Pb than at the impacted site (Table 2). In contrast, higher concentrations of Co, Cd, Cr, Cu and Zn were observed at the impact site than at the control. No significant differences in Ni concentrations were found between impacted and control sites. Non parametric tests showed no significant differences of the remaining heavy metals (Cd, Co, Cr, Mn, Pb and Zn) between impacted and control sites. In contrast, Cu and Mn showed significant differences between both NE sites (impacted and control) (Figures 2 and 3).

Cu showed significantly higher concentrations at impacted site (14.69 mg kg^{-1}) than at the control (9.35 mg kg^{-1}) (Figure 2); while Mn concentrations in control site were higher (633.71 mg kg^{-1}) than impacted site (528.11 mg kg^{-1}) (Figure 3).

In SW area, Mn concentrations were higher in control sites than at impacted sites. In contrast, the remaining heavy metals (Co, Cd, Cr, Cu Ni, Pb and Zn) were measured in higher concentrations in impacted site than in control (Table 3). These differences were significant for Co, Cr, Cu and Ni (Table 4). Non-parametric tests showed no significant differences in Cd, Mn, Pb and Zn concentrations between impacted and control SE sites. Co was measured in higher concentrations in impacted site (15.49 mg kg^{-1}) than in control (6.87 mg kg^{-1}) (Table 4). The same trend occurred for the remaining heavy metals, with higher concentrations at impacted sites than in control (Cr, Impacted: 27.84 mg kg^{-1}, Control: 6.51 mg kg^{-1}; Cu, Impacted: 15.82 mg kg^{-1}, Control: 4.77 mg kg^{-1}; N, Impacted: 34.11 mg kg^{-1}, Control: 3.42 mg kg^{-1}) (Figures 4-7).

DISCUSSION

The Canary current is 1,000 km wide, and NE to SW direction at an intermediate speed (10-30 cm s^{-1}) and affects greatly the oceanographic conditions of the Canary archipelago and thus, the Island of Tenerife (Barton *et al.* 2004). The NE area is affected directly by this current, however, the SE area is on the leeward side of the island, and protected by the "island mass effect". The presence of continuous current in the Canaries could partially explained the low number of significant differences in heavy metals concentrations between impacted and control sites within the same area (NE or SW).

Cu was the only heavy metal which was measured in significant differences at both areas (NE and SW) and a higher concentration in impacted sites than in controls. Cu is extensively used as a biofouling product for aquaculture structures (cages and nets). This heavy metal is present as a mineral additive in the form of copper sulphate (Macleod &Eriksen, 2009; Basaran *et al.* 2010; Sneddon & Tremblay, 2011). The high content of Mn collected in our sediment samples could have a volcanic origin, i.e. piroclastic material or submarine emissions (Martínez-Frías, 1998; Canet *et al*. 2005).

The concentrations of heavy metals in sediments beneath offshore fish cages are not a risk for environment, because of continuous episodes of sediment resuspension and spreading in offshore areas where aquaculture cages are currently working in the Canary archipelago. In order to prevent Cu accumulation in sediments, Cu-free antifouling paintings and structures are strongly recommended, as well as, rotational movements of fish cages within the same lease are encouraged to impede punctual pollution on the same site.

Environmental monitoring studies of offshore fish cages are necessary with a fixed periodicity, i.e. two field surveys per year, as well as, a sustainable aquaculture production.

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TABLES AND FIGURES

Table 1.- Sedimentary types in control and impact sampling points.

	Impact NE	**Control NE**	**Impact SW**	**Control SW**
Gravels	0.02±0.03	0.01±0.01	2.78±0.47	0±0
Very coarse sands	0.77±0.17	1.05±0.32	10.25±1.99	0.38±0.89
Coarse sands	2.30±0.14	4.15±0.13	15.02±0.69	6.13±2.03
Medium sands	24.90±0.84	30.49±0.39	29.29±0.76	43.55±8.87
Fine sands	49.89±1.09	45.50±0.48	25.96±0.24	49.12±15.50
Very fine sands	17.63±1.74	18.02±1.00	14.82±1.93	0.76±0.41
Silt/clay	4.49±2.26	0.79±0.21	1.88±1.70	0.06±0.04

Table 2.- Average concentrations, standard deviation, maximum and minimum of heavy metals in sediments between northeast impact and control sampling points (mg kg^{-1} dry weight).

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Northeast control	**0.75±** 0.54	**25.59±** 0.33	**27.90±** 0.22	**9.35±** 0.13	**633.74±** 16.35	**40.52±** 8.35	**11.24±** 0.41	**90.69±** 8.89
Min	0.44	24.86	26.82	8.92	563.12	14.38	9.13	48.12
Max	1.03	27.96	29.39	10.33	694.92	68.02	12.84	139.86
Northeast impact	**4.32±** 2.62	**27.76±** 1.64	**47.49±** 8.53	**14.69±** 1.75	**528.11±** 27.22	**32.91±** 4.60	**9.69±** 0.93	**101.61±** 11.45
Min	0.47	10.32	16.68	7.06	48.62	1.70	0.33	35.22
Max	15,19	51.61	179.82	45.95	713.29	71.65	15.60	296.70

Table 3.- Average concentrations, standard deviation, maximum and minimum of heavy metals in sediments between south control and impact sampling points (mg kg^{-1} dry weight).

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Southwest control	**6.18±** 0.41	**6.87±** 0.37	**6.51±** 0.33	**4.77±** 0.26	**296.33±** 14.30	**3.42±** 0.26	**2.18±** 0.13	**46.29** ±3.03
Min	0.53	1.36	2.16	0.86	38.50	0.83	0.27	6.50
Max	11.95	10.92	9.96	7.37	428.14	11.15	3.65	100.90
Southwest impact	**7.54±** 0.13	**15.49±** 0.69	**27.84±** 2.06	**15.82±** 2.83	**290.87±** 2.45	**34.11±** 14.91	**2.31±** 5.66	**48.63±** 2.22
Min	4.16	3.90	12.39	5.43	165.83	7.19	1.20	30.24
Max	15.62	38.63	65.60	40.29	449.55	98.23	4.0	72.59

Table 4.- One-way ANOVA test for heavy metal concentrations at SW area (impacted vs control sites). Significant differences ($p < 0.05$) highlighted in bold.

Heavy metal	SS	df	MS	F	p
Co	1326.4	1	1326.4	24.2	**0.000**
Cr	8114.1	1	8114.1	81.4	**0.000**
Cu	2175.8	1	2175.8	29.3	**0.000**
Ni	16796.4	1	16796.4	43.1	**0.000**
Zn	98.325	1	98.32	0.3	0.569

Table 5.- Concentrations of heavy metals (mg kg-1) in sediments collected by other authors.

Place	Activity	Cu	Mn	Zn	Co	Cr	Ni	Pb	Cd	Reference
Salih Island (Turkey)	Fish farms	10.99	–	4.17	–	–	–	–	–	Basaran *et al.* 2010
Passamoquoddy Bay (Canada)	Salmon aquaculture cages	–	462	71.5	–	–	–	–	21.0±1.9	Chou *et al.* 2004
Lake Kasumigaura (Japan)	Carp aquaculture	44.76	0.22	154.98	14.48	23.32	14.79	25.77	BDL	Alam *et al.* 2001
Astakos Gulf (Greece)	Aquaculture	42.0	–	388	–	–	99.4	30.5	2.00	Belias *et al.* 2003
Nha Trang Bay	Aquaculture	–	–	–	–	–	–	0.078	0.069	Nghia *et al.* 2009
Van Phong Bay	Aquaculture	–	–	–	–	–	–	0.048	0.028	
Ecuador	Shrimp farms	6.4	–	9.5	–	–	–	4.1	–	Sonnenholzner and Boyd 2000
Sinaloa, Mexico	Shrimp farms	14.9	–	56.3	–	–	9.21	19.6	0.82	Frías–Espericueta *et al.* 2006
North Tenerife (Spain)	**Aquaculture**	**14.69**	**528.11**	**101.61**	**27.76**	**47.49**	**32.91**	**9.69**	**4.32**	**This study**
South Tenerife (Spain)	**Aquaculture**	**15.82**	**290.87**	**48.63**	**15.49**	**27.84**	**34.11**	**2.31**	**7.54**	**This study**

BDL: Below Detection Limit

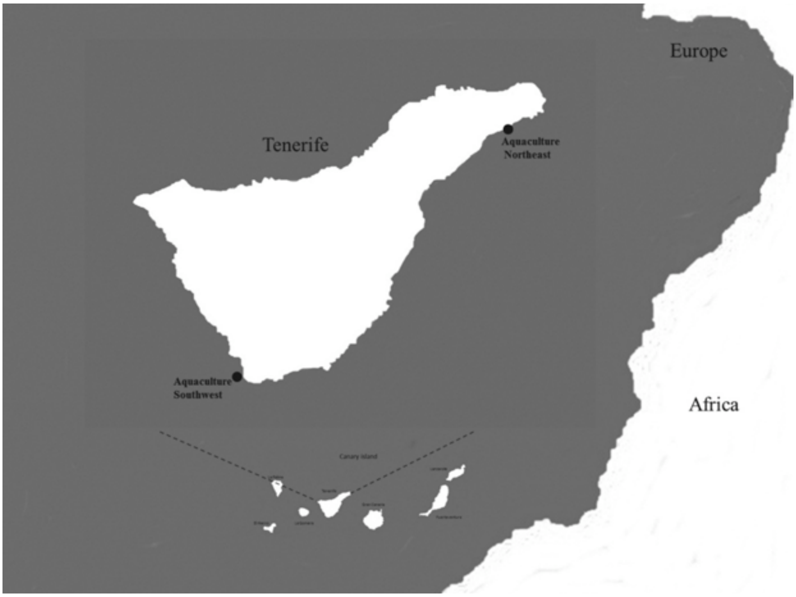

Figure 1.- Location map of aquaculture activities from Tenerife.

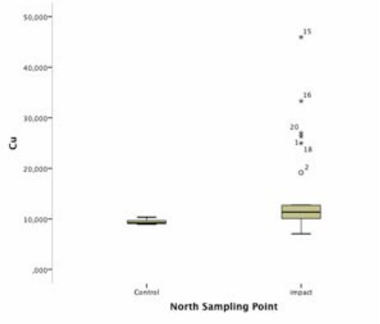

Figure 2.- Mean ± standard error concentrations of Cu at Control and Impacted sites at NE area.

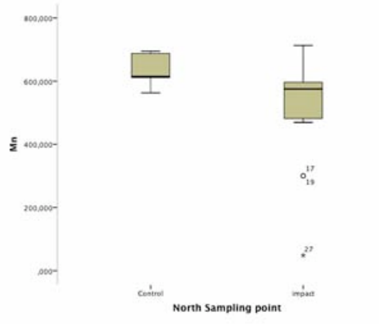

Figure 3.- Mean ± standard error concentrations of Mn between control and impacted sites at NE area.

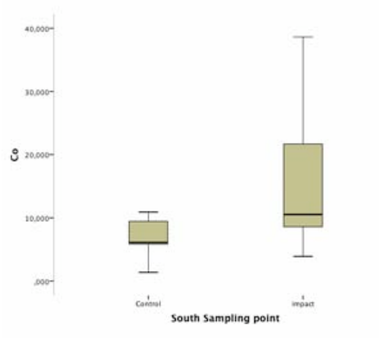

Figure 4.- Mean ± standard deviation of Co concentrations at impacted and control sites of SW area.

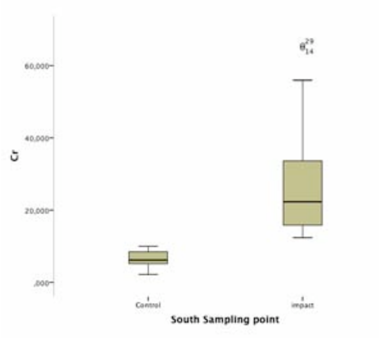

Figure 5.- Mean ± standard deviation of Cr concentrations at impacted and control sites of SW area.

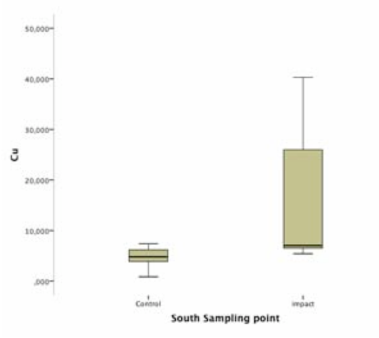

Figure 6.- Mean ± standard deviation of Cu concentrations at impacted and control sites of SW area.

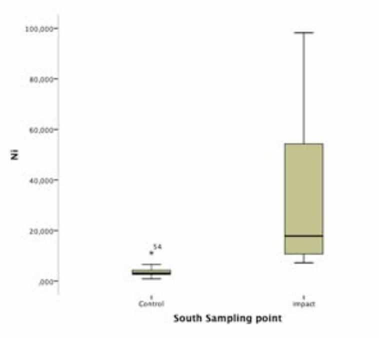

Figure 7.- Mean ± standard deviation of Ni concentrations at impacted and control sites of SW area.

Fecha de recepción: 17 mayo 2017 Fecha de aceptación: 27 junio 2017