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Short Communication

Laguna Verde Bay's sediments origin and its heavy metals content (Al, Fe, Cu, Mn, Pb, and Hg), Valparaíso, Chile

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ABSTRACT. Laguna Verde Bay, a World Biosphere Reserve, seems to be barely uncontaminated due to its isolated geographical position (18 km south of Valparaíso, Chile) and low amount of anthropogenic activities. At its coastal border, there is a thermoelectric generator (using coal since 1939 and diesel since 2007 as fuel), a small village (≈10.000 inhabitants) and a local fishermen's wharf. A freshwater creek flows into the beach, creating a small coastal pond that sporadically overflows into the bay. With the objective of estimating the origin of the Laguna Verde Bay surface sediments and its heavy metal pollution level, the content of Total Organic Matter (TOM), organic carbon to total nitrogen ratio (C:N ratio), stable carbon isotope ratio ($\delta^{13}C$), Al, Fe, Cu, Mn, Pb and Hg in samples collected in August 2015, were measured. According to the $\delta^{13}C$ values, the sediment origin was mostly terrestrial, with an allochthonous content greater than 50%. Since there is no legislation in Chile to establish the heavy metal concentrations for unpolluted marine sediments, a normalized metal enrichment factor (NEF) was computed to infer the contamination level. Despite the high Fe and Pb contents in the bay's sediment at two stations (13.3 mg g^{-1} and 18.0 µg g^{-1}, respectively), the NEF values in the bay generally correspond to a low level of pollution.

Keywords: heavy metals, marine pollution, marine sediments, allochthonous content, Laguna Verde, central, Chile.

Most of the pollution compounds found in the ocean water come from land-based anthropic activities. These pollutants are released into the atmosphere, continental waters and wastewaters to be finally deployed into the ocean water column and sediment. There, they may remain as dissolved or particulate matter, constituting a risk for the marine biota and/or for human health.

Some of the most common pollutants found along the coastal border are the heavy metals derived mostly from urban and industrial activities. In coastal marine sediments, depending on their physical and/or chemical environmental conditions, the heavy metals are usually adsorbed in organic and inorganic particles (Buccolieri *et al*., 2006). Since the heavy metals are generally toxic and some organisms bio-cumulate them, their concentrations in sediments constitute an important indicator of the sediment environmental quality (Purves, 1985; Moalla *et al*., 1998).

Laguna Verde Bay, declared as a World Biosphere Reserve (UNESCO, 2009; Moreira-Muñoz & Borsdorf, 2014), is located 18 km south of Valparaíso, Chile (33°06'0.66"S, 71°39'51.36"W; Fig. 1). It is under the influence of coastal upwelling associated with a subsurface dissolved oxygen minimum zone (Silva & Valdenegro, 2003). At its coastal boundary, there is a 1700 m long beach, which is occasionally divided in two by the freshwater overflow of the coastal El Sauce Pond (mean volume: 5.708.016 m^3; C. Rivera, *unpubl. data*).

Since 1939, a thermoelectric generator has been located at its southern border. Initially, coal was used as fuel, but in 2007, the fuel was changed to diesel. Du-

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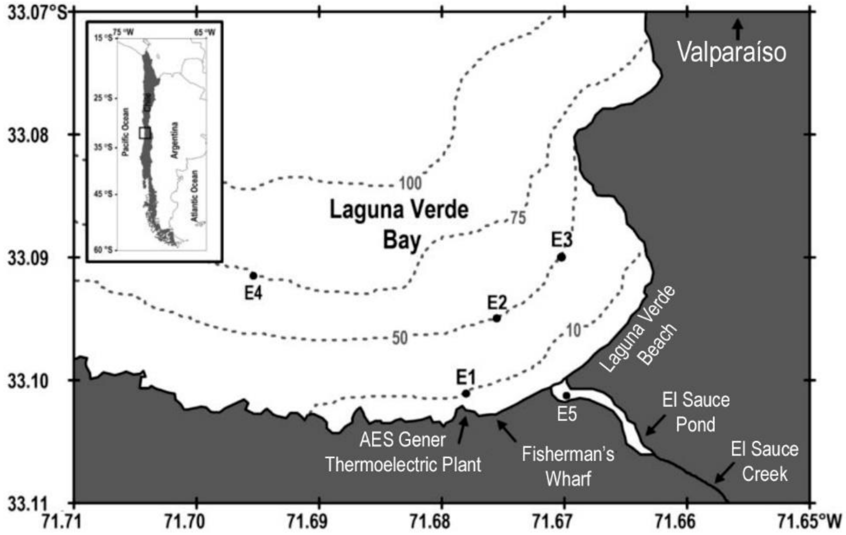

Figure 1. Geographic positions of sediment sampling stations in Laguna Verde Bay and El Sauce Pond, Chile.

ring this second period, the thermoelectric generator has been sporadically used. Due to the burning of these fossil fuels, several toxic substances such as heavy metals (*e.g.*, Fe, Cu, Mn, Pb and Hg) are released during combustion of the coal or diesel fuel (Gaur *et al.*, 2005; Wegoszewski & Kuhn, 2014; Gao *et al.*, 2016). These metals are incorporated into the thermoelectric generator's smoke, cooling water, vapor and/or wastewaters and finally deposited in the bay's surface sediments.

In addition to the thermoelectric generator, freshwater from the El Sauce Pond overflows into the bay during episodic stormy events. Additionally, there is a small village of approximately 10,000 inhabitants and the local fishermen's wharf activities.

Analyses of the total organic matter (TOM), organic carbon to total nitrogen ratios (C:N), stable carbon isotope ratios (δ^{13}C), Al, Cu, Fe, Mn, Pb and Hg were conducted with the aim to establish a baseline for the sediment origin of Laguna Verde and its heavy metal content. Al was used as a normalized enrichment factor (NEF) for the heavy metals to establish their possible pollution level (Marmolejo-Rodríguez *et al.*, 2007a, 2007b).

On August 24th, 2015, sediment samples from four marine stations (Laguna Verde Bay; Stations E1-E4) and one station in the freshwater El Sauce Pond (Station E5) were collected (Fig. 1). Stations E2-E4 were sampled with a polycarbonate gravity corer. Station E1 was sampled with a Van Veen dredge, and a subsample from its center was taken with a polycarbonate tube. Station E5 was manually sampled with a polycarbonate tube.

The upper 5 cm of each sediment sample was immediately withdrawn from the polycarbonate tube and then thoroughly mixed. A subsample was frozen in an aluminum foil bag for the chemical analyses of organic carbon, total nitrogen, and δ^{13}C. These analyses were performed at Laboratorio de Isótopos Estables (LABASI), Pontificia Universidad Católica de Chile, with an elemental analyzer coupled to an isotope-ratio mass spectrometer Delta V Advantage IRMS, Finnigan Delta Plus) according to Harris *et al.* (2001).

A second subsample was frozen in a plastic bag for chemical analysis of the TOM and heavy metals. The TOM was determined by loss on ignition (Byers *et al.*, 1978) at Laboratorio de Biogeoquímica Marina, Pontificia Universidad Católica de Valparaíso. The heavy metal content in each sediment sample was analyzed in triplicate with a Shimadzu atomic absorption spectrophotometer, model AA-7000, following the procedure described for metals in solids in US EPA 3050B for Al, Cu, Fe, Mn and Pb and 7471A for Hg (US EPA, 1996). The analytical procedure was verified by the use of Merck aqueous standards (119770 for Al, 119786 for Cu, 119781 for Fe, 119789 for Mn, 119776 for Pb and 170276 for Hg). These analyses were performed at Laboratorio de Investigación Química Ambiental, Universidad de Playa Ancha.

The origin of organic matter in the sediment samples was inferred using their C:N ratio and δ^{13}C values as source *proxies* (Meyers, 1994, 1997; Perdue & Koprivnjak, 2007). The sediment C:N ratio in the studied area fluctuated between 7 and 16 (Table 1). In the bay stations, the C:N ratio was larger than expected according to the marine phytoplankton composition (C:N ~6.6; Redfield *et al.*, 1963). Nevertheless, an in-

Table 1. TOM, C:N, δ^{13}C, percentage of allochthonous participation and metal concentration in the surface sediments of Laguna Verde Bay (marine stations E1-E4) and El Sauce Pond (freshwater station E5), Chile.

Station	TOM (%)	C:N	δ^{13}C (‰)	Allochthonous (%)	Al (mg g^{-1})	Fe (mg g^{-1})	Cu (µg g^{-1})	Mn (µg g^{-1})	Pb (µg g^{-1})	Hg (µg g^{-1})
E1	0.35	11.51	-23.83	54.68	4.2 ± 0.03	13.3 ± 0.02	10.2 ± 0.06	59 ± 0.34	1.4 ± 0.19	0.13 ± 0.002
E2	4.26	15.93	-24.53	64.76	13.0 ± 0.22	18.5 ± 0.34	73.8 ± 0.40	158 ± 0.49	18.0 ± 0.17	0.15 ± 0.002
E3	1.87	16.58	-25.00	71.49	12.7 ± 0.40	15.9 ± 0.19	41.5 ± 0.18	144 ± 0.74	5.5 ± 0.23	0.10 ± 0.004
E4	5.27	11.45	-23.51	50.17	15.9 ± 0.24	23.4 ± 0.11	101.3 ± 0.26	186 ± 0.15	17.5 ± 0.35	0.25 ± 0.006
E5	2.28	8.70	-25.34	76.29	7.5 ± 0.06	9.9 ± 0.16	18.8 ± 0.08	100 ± 0.92	2.6 ± 0.11	0.05 ± 0.004

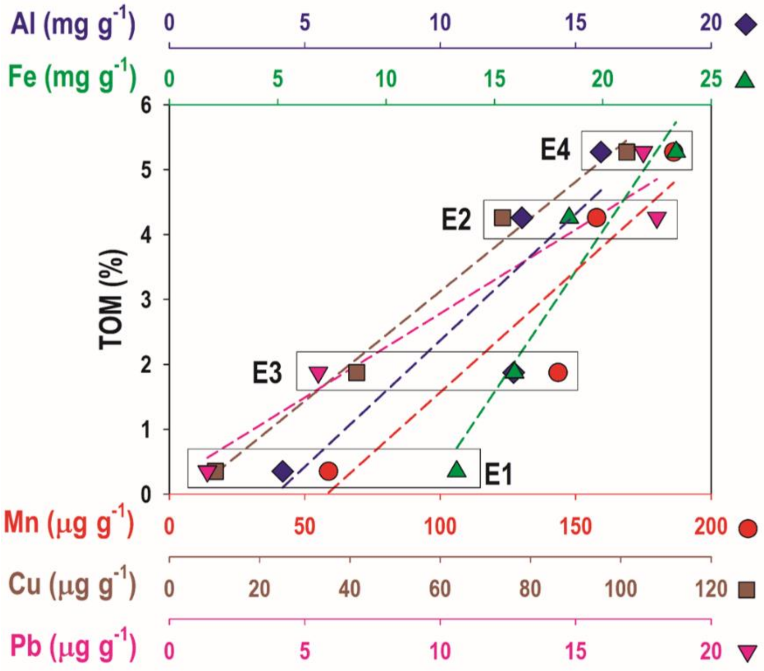

Figure 2. Total organic matter content *versus* heavy metal (Al, Fe, Mn, Cu, and Pb) direct association content in the marine sediments of Laguna Verde Bay, Chile.

crease in the C:N ratio is usually expected in marine sediment since the organic nitrogen compounds degrade faster than the organic carbon as the sediment ages (Price, 1976; Jorgensen, 1982). Rullköter (2000) stated that C:N values of 7-10 are expected for remnants of degraded marine phytoplankton. Since the terrestrial vegetables have a higher C:N ratio (*e.g.*, 98, Deevy, 1973; 126, Delwiche & Likens, 1977; 55-64, Silva *et al.*, 2011), the observed C:N ratio increase in the bay sediments may also be due to a partial input from land sources. The C:N ratio at station E5, El Sauce Pond (8.7), was lower than expected for terrestrial samples. According to Barros *et al.* (2010), these low values are present in zones where untreated wastewater is released into bays. Also been observed in Laguna Verde Bay (C. Rivera, *unpubl. data*).

The TOM fluctuated between 0.4% and 5.3% (Table 1). The TOM is an important factor in the sediment heavy metal concentration since it adsorbs heavy metals as it sinks through the water column, increasing the heavy metal concentration in the sediment (Tribovillard *et al.*, 2006). In Laguna Verde Bay, this association was observed as a direct association between the marine sediment heavy metal content and TOM concentration (Fig. 2, Table 2).

The allocthonous content in the sediments (terrestrial) was quantified utilizing a two-source mixing model using the δ^{13}C values from a terrestrial source and a marine source (Bianchi, 2007):

$$\%OC_{terrestrial} = [(\delta^{13}C_{sample} - \delta^{13}C_{marine}) / (\delta^{13}C_{terrestrial} - \delta^{13}C_{marine})] \times 100$$

where $\delta^{13}C_{sample}$ is the sample stable carbon isotope ratio; $\delta^{13}C_{terrestrial}$ is the typical stable carbon isotope ratio of terrestrial sediment (≈27‰), and $\delta^{13}C_{marine}$ is the typical stable carbon isotope ratio of marine sediment (≈20‰) (Fry, 2006).

Table 2. Linear equations for heavy metals *versus* total organic matter (TOM).

$\mathrm{Al} = 0.389[\mathrm{TOM}] - 1.527;\ R^2 = 0.778$

$\mathrm{Fe} = 0.496[\mathrm{TOM}] - 5.870;\ R^2 = 0.912$

$\mathrm{Cu} = 0.056[\mathrm{TOM}] - 0.253;\ R^2 = 0.986$

$\mathrm{Mn} = 0.038[\mathrm{TOM}] - 2.179;\ R^2 = 0.843$

$\mathrm{Pb} = 0.259[\mathrm{TOM}] + 0.197;\ R^2 = 0.949$

The $\delta^{13}C$ values in bay sediments fluctuated between -23 and -26‰ (Table 1), indicating mixing between terrestrial and marine sediments. The two-source mixing model showed that the allochthonous content of the bay sediment was higher than 50% (Table 1), which implies a higher input from terrestrial sources than from marine sources into the bay. The El Sauce Pond sediment showed a $\delta^{13}C$ of -25.3‰ and an allochthonous content of 76.3%, which is consistent with its coastal position.

The surface sediment heavy metals distribution in the bay was characterized by high concentrations, while in the El Sauce Pond sediment (E5), the concentrations were low for all metals (Table 1). The Al and Fe showed the highest sediment concentrations of all the heavy metals in the bay, with a mean value of 11.45 and 17.77 mg g^{-1}, respectively, in accordance with the lithosphere's high heavy metal concentrations, where the sediment metal originated.

The Cu concentrations fluctuated between 10 and 101 µg g^{-1}, with the highest concentration registered at station E4. The Mn concentrations ranged between 59 and 186 µg g^{-1}, with the highest concentration registered at station E4. The Pb concentrations fluctuated between 1.4 and 18.0 µg g^{-1}, with the highest concentration recorded at station E2. The Hg concentrations ranged between 0.05 and 0.25 µg g^{-1}, with the highest concentration at station E4 (Table 1). The Hg concentrations were the lowest of all the heavy metal concentrations in the bay, which is in accordance with the heavy metal content of marine sediments from other places (Prego & Cobelo-García, 2003).

In Chile, no legislation establishes the acceptable heavy metal concentrations in marine sediments. Thus, to infer the level of heavy metal pollution in the Laguna Verde Bay sediments, we used the NEF (Marmolejo-Rodríguez *et al.*, 2007a, 2007b) and a pollution classification level proposed by Prego *et al.* (2008) (Table 3), performed by computing a linear regression between the content of Al and the content of a given trace metal from a sediment sample (Fig. 3).

The computed regression, within 95% prediction intervals, was then used to calculate the theoretical natural or background heavy metal concentration of a given sample based on its Al content (Marmolejo-Rodríguez *et al.*, 2007a, 2007b). Al is a suitable normalizer because it is a major constituent in the sediment (Hanson *et al.*, 1993) and pollution does not usually change its concentration (Ackerman, 1980).

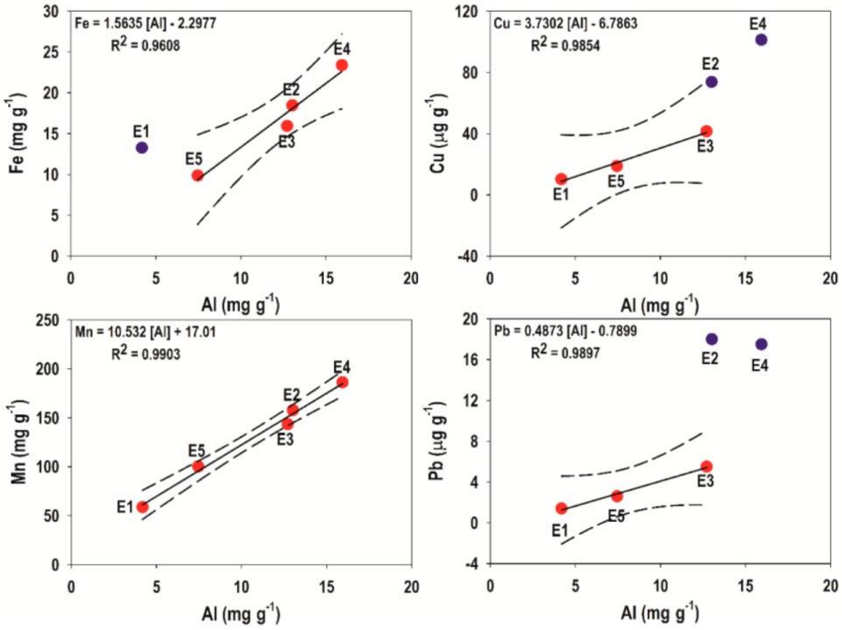

Figure 3. Heavy metal content (Fe, Cu, Mn, and Pb) *versus* Al content for the sediments of Laguna Verde Bay (E1-E4) and El Sauce Pond (E5), linear regression. The blue dots are outliers not considered in the equation computation, and the segmented lines correspond to a 95% confidence interval.

Table 3. Normal enrichment factors (NEF) for heavy metal contents of the surface sediments of Laguna Verde Bay (E1-E4) and El Sauce Pond (E5), Chile. The NEF classification proposed by Prego *et al.* (2008) (adapted from Hakanson, 1980) is also included.

Station	NEF(Fe)	NEF(Cu)	NEF(Mn)	NEF(Pb)
E1	3.1	1.2	1.0	1.1
E2	1.0	1.8	1.0	3.2
E3	0.9	1.0	1.0	1.0
E4	1.0	1.9	1.0	2.5
E5	1.1	0.9	1.0	0.9

Importance	Ranks
Insignificant	NEF < 1
Possible	1 < NEF < 2
Moderate	2 < NEF < 3
Severe	3 < NEF < 6
Very severe	6 < NEF < 9
Heavy	NEF > 9

Outlier values, beyond the 95% prediction intervals, were considered to belong to polluted sediment samples.

The NEF is defined as the number of times that the natural heavy metal concentration is surpassed in the measured sediment.

$$\mathrm{NEF}_{Me} = \frac{[\mathrm{Me}]}{[\mathrm{Me}]_{Al}}$$

where [Me] is the measured heavy metal concentration in a given sample and $[\mathrm{Me}]_{\mathrm{Al}}$ is the theoretical natural concentration that the sediment sample must have according to the linear regression Al-Metal. Therefore, on this basis, it is possible to infer the sediment pollution level for a given sample (Table 3).

Out of the 20 computed NEF values, only Fe and Pb from E1 and E2 showed severe pollution. Pb showed moderated pollution at E4. Despite those relatively high NEF values, the other 17 NEF values for Fe, Pb, Mn, and Cu showed insignificant or possible pollution levels (Table 3).

No correlations were found between the Hg and Al or Hg and TOM concentrations. Birkett *et al.* (2002) indicated that particulate organic matter is not a major factor that controls the Hg distribution. Other factors such as the presence of benthic macro-organisms produce Hg physical and chemical changes that may contribute to the mobilization of Hg from the bottom to the superficial sediment and the water column. Canário *et al.* (2005) indicate that this lack of association between the Hg and Al or TOM concentrations reflects mainly historical episodes of anthropogenic discharges, which have been observed in various coastal areas

Table 4. Metal levels in surface sediments from Laguna Verde Bay and other coastal areas.

Region	Al (mg g^{-1})	Fe (mg g^{-1})	Cu (µg g^{-1})	Mn (µg g^{-1})	Pb (µg g^{-1})	Hg (µg g^{-1})	Reference
Laguna Verde Bay	11.4 ± 5.1	17.8 ± 4.3	56.7 ± 39.5	136.6 ± 54.8	10.6 ± 8.4	0.2 ± 0.1	This study
Caldera Bay	-	-	125.5	-	33.1	-	Valdés & Castillo (2014)
Chañaral Bay	-	12.5 ± 0.003	1659	2367 ± 2	21.2 ± 0.1	-	Ramírez *et al.* (2005)
San Jorge Bay	-	-	14.3 - 327.5	-	5.6 - 45.9	-	Calderón & Valdés (2012)
Concepción Bay	-	-	41.0	-	40.1	-	Salamanca *et al.* (1988)
Chiloé Inland Sea	-	45.4 ± 11.6	36.6 ± 24.0	-	9.3 ± 1.8	-	Silva *et al.* (2009)
Cleveland Bay (Australia)	21.3 ± 3.6	17.4 ± 1.4	5.9 ± 0.9	505.4 ± 65.9	9.1 ± 1.0	-	Doherty *et al.* (2000)
San Francisco Bay (USA)	-	-	40 - 75	-	20 - 40	0.3	Hornberger *et al.* (1999)
Unpolluted marine sediments	-	1.5	5 - 25	240 - 600	5 - 25	0.03	Prego & Cobelo-García (2003)

(Table 4). Therefore, no NEF values were computed for Hg.

A comparison of our results with those previously obtained in other coastal regions was performed (Table 4). The comparison of our Fe and Mn data with those of Chañaral Bay (a bay subject to high mining and industrial activity), obtained by Ramírez *et al*. (2005), showed that Laguna Verde Bay has similar Fe concentrations but lower Mn concentrations than Chañaral Bay. The Hg content in the Laguna Verde Bay sediments was lower than the reported values for San Francisco Bay, in which most the Hg mining in the world occurred between 1850 and 1900 (Hornberger *et al*., 1999). According to the reported heavy metal values for the unpolluted marine sediment from different bays (Prego & Cobelo-García, 2003), the Fe, Cu and Hg contents in the sediments from Laguna Verde Bay were comparatively high, whereas the Mn and Pb contents were low (Table 4). Nevertheless, Fe and Cu showed mostly a low level of pollution (Table 3).

Even though the measurements were performed in one campaign and considering that the sediment is a "time integrator" of the local sedimentation, our results allowed us to infer a generally low level of heavy metal pollution (Fe, Cu, Mn, and Pb) in the Laguna Verde Bay and El Sauce Pond.

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