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# Heavy metal pollution index calculation in geochemistry assessment: a case study on Playa Las Petroleras

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Abstract This work is aimed to assess potential risk associated with the presence of metals and metalloids in soil at "Playa Las Petroleras" sector, located in Antofagasta (Chile). The zone under study has been affected by four oil spill events. This sector is located in an urban area by the sea. So, it has a great social and environmental relevance. The concentrations of 15 elements in soil samples were assessed, four of them presenting potential ecological risk: As, Co, Cu, and Pb. Nine pollution indices were applied to data: four single pollution indices and five integrated pollution indices to assess soil pollution. The single pollution indices show that the site bears potential ecological and environmental risk due to the presence of Cu, the site being classified as highly contaminated owing to a severe enrichment of this metal. For Co, all the

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Í. L. Montofré · F. A. Álvarez Mining Business School, ENM, Universidad Católica del Norte, Antofagasta, Chile indices allow classifying the site as little or uncontaminated, while the level of As and Pb pollution could be considered as ranging from uncontaminated to moderately contaminated. The integrated pollution indices show that average concentrations are highly contaminated mainly owing to the presence of Cu.

**Keywords** Pollution indices · Heavy metal · Ecological risk · Geoaccumulation index · Contamination factor

# Introduction

Heavy metals are highly accumulated in soils due to continuous human activities, resulting in increasing

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F. A. Álvarez Administration Department, Universidad Católica del Norte, C.P. 1270709 Antofagasta, Chile release and rapid spread of heavy metal pollution in human settlements and natural environments (Jia et al., 2019; Niu et al., 2020; Wei & Yang, 2010). Industrial activities, household, livestock, municipal waste, agrochemicals, and petroleum by-products can all be sources of chemicals and pollutants (Bundschuh et al., 2012; Luo et al., 2015; Reimann & Garrett, 2005). However, some potential sources of toxic elements (PTEs) and pollution in urban areas may also be related to the geological (natural) background (Biasioli et al., 2007; Cicchella et al., 2005; Luo et al., 2012). Several soil parental materials are PTE natural sources. When concentration increases, they may pose a threat to the environment and human health. Due to its impact on human health and ecosystems, urban soil pollution is one of the most challenging environmental problems (Albanese et al., 2010; Cicchella et al., 2005; Petrik et al., 2018). In addition, due to the acceleration of population growth, urbanization level, and industrialization, PTE are also increasing, resulting in various human-made pollution sources (Guillén et al., 2011; Wang et al., 2012; Wu et al., 2015).

This situation is particularly serious in Antofagasta Region (northern Chile), characterized by a high density of mining operations and the presence of a large number of fuel storage tanks along Antofagasta city coastline (Fig. 1), thus affecting recreational areas. An example is Playa Las Petroleras, where several hydrocarbon contamination events were reported from 2000 to 2006 (Merino & Herrera, 2006). One of the pollution events occurred in 2000, when the bottom of a hydrocarbon storage tank ruptured due to an earthquake, releasing about 140 m<sup>3</sup> of fuel. Only 120 m<sup>3</sup> were recovered. Due to irregular bedrock paleoreliefs, 20 m<sup>3</sup> of pollutants remained in the underground soil, forming a natural reservoir. Since then, several oil leaks have occurred from pipelines and fuel storage facilities and various remediation plans have been proposed and implemented to remediate groundwater and soil in the area. Specifically, in this area, surface soil samples recorded TPH values ranging from 18 to 495 mg/kg, while samples from 5 to 300 cm depth show TPH ranging between 5 and 53,168 mg/kg (CENMA, 2014). Short chain organic compounds such as BTEX (benzene, toluene, ethylbenzene, and o-, m-, and p-xylenes), and PAHs (polycyclic aromatic hydrocarbons), were not found in soil analyzed; this is attributed, on the one hand, to the fact that due to the long time that has passed there was a natural degradation of these, and on the other hand, to the fact that there are currently no sources that are generating them.

Assessing heavy metals levels in residential soils is necessary to evaluate human safety. The risk assessment of heavy metals would provide a certain theoretical support for risk management (Ma, Egodawatta, et al., 2016; Ma, Yang, et al., 2016; Zhu et al., 2012) and help to interpret soil quality (Prakruthi & Raju, 2017). Some methods used to evaluate the ecological risk of heavy metals in soil include the calculation of the enrichment factor, geoaccumulation (Müller, 1969; Zoller et al., 1974) and potential health risk index (Hakanson, 1980).

This study aims to assess the pollution levels and ecological risks of some heavy metals in an urban sector in Antofagasta City (Chile), known as "Playa Las Petroleras," caused by repeated hydrocarbon seepage events. Despite various remediation plans for the site, whether the soils are still contaminated by metals and metalloids has not been determined yet. The average, maximum, minimum, and 95% upper confidence limit (UCL) values of Antofagasta Region's background zones, together with the average, maximum, and 95% UCL values of concentration levels at the sector under study will be used. The National Environmental Center (CENMA, for its acronym in Spanish) (2014) has reported data on metal and metalloid concentrations in soils in the sector and 19 sites selected for not being anthropogenically impacted and therefore considered background zones in this study.

#### Materials and methods

#### Site description

The study was conducted at "Playa Las Petroleras" area, located in Antofagasta city, with more than 360.000 inhabitants (INE, 2017).

Rock and sediments outcropping in this area correspond to Quaternary colluvial, alluvial, eolian, and littoral deposits; Neogene marine, littoral, alluvial, colluvial, and eolian deposits; Lower Cretaceous continental sedimentary rocks, mostly carbonate in composition; and volcanic and intrusive Jurassic rocks (Fig. 2). The sedimentary Fig. 1 Study area location and soil samples analyzed. The blue squares correspond to the areas where the damaged storage tanks were located, which were removed during the aquifer remediation stage





Fig. 2 Background soil sampling points on Playa Las Petroleras geology. The total samples are from CENMA (2014) near Antofagasta

sequence is mainly matrix-supported gravel, whose matrix is mainly medium-grained sandstone, clasts corresponding to volcanic rocks of andesitic composition and fragments of marine shells. This gravel is intercalated with sandstone, siltstone, and clay lenses of low thickness and variable spatial distribution. The volcanic rocks of andesitic composition underlie the previous unit and are found along northern Chile's entire coast, being the main lithological unit of the Coastal Range (González & Niemeyer, 2004). These rocks are usually highly weathered and fragmented and consist of andesitic lavas, andesite-basalts, and andesitic breccia with interbedded volcanic tuffs and sandstones (Boric et al., 1990). These units are cut by dikes of basaltic, and esitic, and dacitic composition, while the intrusive rocks in the Coastal Range are mainly gabbros, diorites, granodiorites and tonalities, and granites to a lesser extent. Along the coast, outcrops of marine deposits, conglomerate, and calcareous sandstone dominate the geological features, where a succession of marine abrasion terraces and littoral cords can be found (Escribano et al., 2013).

The samples to estimate the background levels are distributed in 7 geological units (Fig. 2): alluvial, and subordinately colluvial deposits (Qa); clastic piedmont sedimentary sequences (MP1c); intrusive rocks (Jig); coastal marine sequences (PI1m); alluvial fan, piedmont or fluvial sedimentary sequences (M1c); continental and marine volcanic sequences (J3i); and eolian deposits (Qe). Playa Las Petroleras geological unit corresponds to the coastal marine sequences (PI1m), a few meters' thick, which overlies the volcanic sequences.

## Data Source

Two databases corresponding to the concentration values of metals and metalloids (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, and Zn) in surface soil (0–20 cm) from Antofagasta city were used. One of them represents the concentration levels at Playa Las Petroleras, while the second one represents the background levels at the same sector. The samples were collected and analyzed by personnel from CEMNA Environmental Chemistry Lab (CENMA, 2014). Values are reported in WSP-Emgrisa, 2019.

The chemical analyses of metals and metalloids was conducted by means of standardized and accredited procedures. Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn were determined by ICP on solid samples, following USEPA method 3052 "Microwave assisted acid digestion of siliceous and organically based matrices" and USEPA method 6010 C "Inductively coupled plasma-atomic emission spectrometry." The detection limits (mg  $kg^{-1}$ ) were Al (10.9), As (14.6), B (7.08), Ba (8.85), Cd (1.82), Co (2.44), Cr (4.61), Cu (0.97), Fe (17.3), Mn (8.45), Ni (1.39), Pb (3.67), V (1.45) and, Zn (2.70), while Hg was determined by means of EAA with atomic decomposition, USEPA Method 7473 "Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry," with a 0.0015 mg kg<sup>-1</sup> detection limit.

#### Background concentrations

For background assessment, a total of 94 soil samples were collected from Antofagasta town. The sampling points selected are not altered by human activity (CENMA, 2014), and some of them are shown in Fig. 2.

Since background soils must be the most representative of the study area (Ander et al., 2013; Chen et al., 2001), 19 out of the 94 background samples were selected, corresponding to the geological unit associated with Playa Las Petroleras. Eleven samples correspond to Pleistocene-Holocene alluvial deposits, while eight of them correspond to rock regolith from La Negra formation. The sampling points are shown in Fig. 2. To choose samples for establishing the background values, proximity to abandoned tailings from inactive mining activities and the geological units were considered. So, the samples closest to Antofagasta city, whose geological units are alluvial sedimentary deposits and volcanic rocks were considered. The volcanic rock geochemistry differs from the alluvial deposits, the latter units having more dispersed concentrations due to the different sources of these sediments.

To establish the concentration value representing the background level, according to US Environmental Protection Agency (US EPA) recommendations, 95% UCL mean concentration of the elements found was considered (US EPA, 2010). A 95% UCL of the mean describes an interval in which the true mean falls within a specified level of certainty (Chen et al., 2001). This ensures that the differences resulting from natural variability are included in the background level estimation.

The calculation of the background level using the 95% UCL value requires a logarithmic transformation of the concentration values, as shown in Eq. (1). This transformation can be useful to compare the evolution of the values of various elements when they are very different.

$$C^* = \log\left(C\right) \tag{1}$$

where C is background concentration and  $C^*$  its corresponding transformed variable.

To estimate 95% UCL, Eq. (2) was used (Chen et al., 2001; Gilbert, 1987).

$$UCL_{0.95} = \exp\left(\mu_{C^*} + 0.5\delta^2 + \delta \cdot \frac{H_{0.95}}{\sqrt{N-1}}\right)$$
(2)

where  $\mu_{C^*}$  is the mean value of the transformed background concentrations,  $\delta$  is the standard deviation of the transformed data, N is the number of background points, and  $H_{0.95}$  is the H-statistic tabulated constants of the 95% UCL (Gilbert, 1987).

The values of  $H_{0.95}$  were taken directly from the reference table (Gilbert, 1987), considering the standard deviation values, s<sub>v</sub>, and the number of experimental measurements, n. For the values not shown in the table, a double interpolation was made, assuming that two points are so close that they relate to each other by a straight line and, therefore, a slope equivalence can be made. For example, the value of  $H_{0.95}$  is estimated for Al. There are 19 concentration measurements whose standard deviation is  $s_v = 0.16$ . Table 1

shows no values for  $s_v = 0.16$ . So, an interpolation between 0.10 and 0.20 must be made. Neither are there values for n = 19. So, an interpolation between 15 and 21 must be made. The double interpolation values are shown in bold in Table 1.

By equating the slopes, the following relationships are obtained:

For 
$$s_y = 0.10$$
 y  $n = 19$ ,  
 $H_{0.95} = \left(\frac{19 - 15}{21 - 15}\right)(1.722 - 1.749) + 1.749 = 1.731$   
For  $s_y = 0.20$  y  $n = 19$ ,  
 $(19 - 15)$ 

 $H_{0.95} = \left(\frac{19 - 15}{21 - 15}\right)(1.771 - 1.809) + 1.809 = 1.784$ 

With the values obtained for n=19,  $s_v=0.10$ , and  $s_{y} = 0.20, s_{y} = 0.16 \text{ y} n = 19 \text{ are obtained}$ :

$$H_{0.95} = \left(\frac{0.16 - 0.10}{0.20 - 0.10}\right)(1.784 - 1.731) + 1.731 = 1.763$$

## Concentrations at Playa Las Petroleras

CENMA (CENMA, 2014; WSP-Emgrisa, 2019) took samples from the 9 surface points at Playa Las Petroleras soil area. Table 2 shows the mean, maximum, and 95% UCL values of metal/metalloid concentrations (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, and Zn). The 9 points are shown in Fig. 1.

# Reference norms and environmental risk elements selection

Since Chile has not established norms regulating admissible metal/metalloid concentrations in soils yet, international reference norms had to be selected to assess potential environmental risk. Table 3 shows the maximum admissible values for foreign residential norms: Basque Country, Spain (IHOBE, 2002),

<b>Table 1</b> Values of $H_{0.95}$ for computing a one-sided	sy	n									
upper 95% confidence limit on a lognormal mean (Gilbert, 1987)		3	5	7	10	12	15	21	31	51	101
	0.10	2.750	2.035	1.886	1.802	1.775	1.749	1.722	1.701	1.684	1.670
	0.20	3.295	2.198	1.992	1.881	1.843	1.809	1.742	1.742	1.718	1.697
	0.30	4.109	2.402	2.125	1.977	1.927	1.882	1.793	1.793	1.761	1.733
	0.40	5.220	2.651	2.282	2.089	2.026	1.968	1.856	1.856	1.813	1.830

**Table 2** Mean, maximum, and 95% UCL surface soil concentrations from 9 surface samples measured at Playa Las Petroleras (CENMA, 2014; WSP-Emgrisa, 2019)

Element	Mean value	Maximum value	95% UCL
	mg/kg		
Al	7331.24	13,905	9751.00
As	33.65	100.39	71.04
В	98.99	165.62	125.30
Ba	102.38	196.59	99.61
Cd	2.71	4.34	2.80
Co	15.11	26.72	18.63
Cr	28.19	67.76	47.99
Cu	1191.38	4447.55	3676.00
Fe	15,336	33,084	20,895.00
Hg	0.10	0.25	0.21
Mn	568.56	961.50	714.80
Ni	39.28	173.33	96.50
Pb	86.94	428.88	322.10
V	102.85	460.75	128.30
Zn	159.71	573.51	296.20

Australia (NEPC, 2003), US (EPA, 2021), Sao Paulo-Brazil (CETESB, 2016), Canada (CME, 2009), Mexico (NOM-147-SEMARNAT/SSA1-2004), Peru To select a reference norm, countries were prioritized according to similarity in environmental components, that is, metals and metalloids found on the study site. Next, the permissible values of each element were compared with their respective background level corresponding to 95% UCL. Norms with reference values higher than background values were selected.

For the elements under evaluation, measurements were made on 17 additional points, amounting to 26 sampling points, determining their extreme concentration values, mean value, standard deviation, and 95% UCL. These elements were then assessed according to ecological risk, by using nine different criteria.

The criteria used in each country are very different, depending on the legislated soil quality objectives and the background values of each region. Some countries consider generic quality standards, known as soil screening values (SSV), to regulate contaminated soil management. SSV are concentration thresholds above which some actions are necessary (Ferguson et al. 1998). Therefore, USEPA recommends using SSV as

 Table 3 Concentration limits allowed by international norms for residential soils

Element	Basque Country, Spain (2002) mg kg <sup>-1</sup>	Australia (2003)	Mexico (2004)	Canada (2009)	Peru (2013)	Bolivia (2015)	Ecuador (2015)	Brazil (2016)	US EPA (2021)
Al	_	_	_	_	_	_	_	_	77,000
As	30	100	22	12	50	12	12	55	0.68
В	-	4500	-	-	_	-	-	-	16,000
Ba	-	_	5400	500	500	-	500	1300	15,000
Cd	8	20	37	10	10	2	4	14	71
Co	-	100	-	50	-	40	50	65	23
Cr	200	100	280	-	400	65	64	300	0.3
Cu	10,000	6000	-	63	-	-	63	2100	3100
Fe	-	-	-	-	-	-	-	-	55,000
Hg	4	40	23	6.6	6.6	0.8	1	0.9	11
Mn	-	3800	-	-	-	-	-	-	1800
Ni	150	400	1600	45	-	50	100	480	840
Pb	150	300	400	140	140	100	140	-	400
V	_	390	78	130	_	-	130	-	390
Zn	10,000	7400	-	250	-	200	200	7000	23,000

an exploratory step and performing a risk analysis for each land use (US-EPA, 1996).

The first step consisted in comparing the concentration limits allowed by international norms for residential soils shown in Table 3, with the background concentrations estimated on the site under assessment. The reference values proposed, which are specific and exclusive of this study, are preliminary; however, they were used as a basis for discarding norms with permissible limit values lower than the background values of the site. Initially, 19 background soil samples with 95% UCL representative values were determined. Once the norm to be used for each element was selected, the reference value was compared with the concentrations of the 9 soil sample points, shown in Fig. 1 for the 15 metals/metalloids shown in Table 3.

The elements with concentrations lower than the corresponding reference values were considered as "without potential ecological risk" and, therefore, were not analyzed. On the contrary, the elements with values higher than the corresponding reference concentrations were considered as "potential ecological risk." Thus, they are included in the calculation of the indices below. For the elements still under evaluation, measurements were made on 17 additional points, amounting to 26 sampling points, determining their extreme concentration values, mean value, standard deviation, and 95% UCL. The 17 additional concentration points were specifically measured for those elements with values higher than the referential ones, mainly due to a matter of costs. These elements were then assessed according to ecological risk, by using nine methodologies.

Ecological risk assessment

# **Pollution Indices**

Nine Pollution Indices were applied to the data, consisting of four single pollution indices (Contamination Factor, Enrichment Factor, Geoaccumulation Index, and Single Risk Index) and five integrated pollution indices (Degree of Contamination, Modified Degree of Contamination, Potential Ecological Risk Index, Pollution Load Index, and Nemerow Pollution Index) to evaluate the soil pollution status. Tables 4 and 5 show the equations for calculating pollution indices, according to the criteria used.

# Results

### Background concentrations

Most methodologies assessing soil pollution indices require background concentration values considering the geologic complexity and diversity of soils. These values indicate the representative reference levels of the maximum admissible concentrations, without resulting in negative effects on soil organisms, considering aspects such as metal and metalloid bioavailability and the chemical properties and uses of the soil. This is particularly relevant in countries without environmental quality norms for soils, as in Chile. Before assessing risk to detect the soil contamination degree, it is necessary to determine their quality by using criteria based on background level. The mean values, 95% UCL, extreme metal/metalloid concentration values and 95% UCL BGV for the 19 samples are shown in Table 6. As shown in Fig. 2, the samples used to calculate the background value of the different elements analyzed were obtained from different geological units, ranging from volcanic rocks of andesitic composition to alluvial, colluvial, and marine deposits. Alluvial sedimentary deposits result from volcanic rocks, although their composition may differ due to soluble salts such as gypsum and halite, among others.

### **Reference norms selection and values**

To select the reference norms, the first step was prioritizing the international norms most similar to the diversity of metals and metalloids present at Playa Las Petroleras. Since 15 elements were assessed in this sector by comparing them with the elements in Table 3, the norms showing the most similarity concerning the presence of components were USEPA (15/15), NEPC (12/15), Ecuador (11/15), Canada (10/15), Sao Paulo-Brazil (9/15), IHOBE, Mexico and Bolivia (8/15), and Peru (6/15).

So, the first reference norms selected were USEPA, NEPC, and those from Ecuador. The second step was comparing the reference values of the three norms

Table 4 Single pollution index to assess the presence and intensity of anthropogenic contaminant deposition on surface soil

Common designation	Expression	Criteria
Contamination factor, $C_{\rm fi}$ Hakanson (1980) It describes a given toxic substance contamination. $C_{\rm i}$ is the concentration of the element (i) in substrate samples and $C_{\rm iB}$ is the reference value (background values) of the element (i)	$C_{\rm fi} = C_{\rm i}/C_{\rm iB}$	Hakanson (1980) $C_{fi} < 1$ , low contamination factor $1 \le C_{fi} < 3$ , moderate contamination factor $3 \le C_{fi} < 6$ , considerable contamination factor $C_{fi} \ge 6$ , very high contamination factor
Enrichment factor, <i>EF</i> Zoller et al. (1974) Used to quantify the enrichment of a potentially con- taminant-derived element in an environmental sample relative to a user-defined background composition. $C_i$ is the concentration of the element of interest and $C_{ie}$ is the concentration of a reference element for the purpose of normalization	$\mathrm{EF} = \frac{\left[C_{i}/C_{\mathrm{ic}}\right]_{\mathrm{Sample}}}{\left[C_{i}/C_{\mathrm{ic}}\right]_{\mathrm{Background}}}$	Chen et al. (2007) EF < 2, no mineral enrichment $2 < EF \le 3$ , minor enrichment $3 < EF \le 5$ , moderate enrichment $5 < EF \le 10$ , moderately severe enrichment $10 < EF \le 25$ , severe enrichment $25 < EF \le 50$ , very severe enrichment EF > 50, extremely severe enrichment
Geoaccumulation Index, $I_{geo}$ Müller (1969) Used to assess the intensity of anthropogenic contami- nant deposition on surface soil. $C_i$ is the concentration of the element of interest, while $C_{iB}$ is the geochemical background value. Constant 1.5 allows analyzing natural fluctuations in the content of a given substance in the environment and detecting very small anthropogenic influence	$I_{\rm geo} = \log_2\left(\frac{C_{\rm i}}{1.5C_{\rm iB}}\right)$	Loska et al. (1997); Gonzales-Macías et al. (2006) $I_{geo} < 0$ , unpolluted $0 < I_{geo} < 1$ , unpolluted to moderately polluted $1 < I_{geo} \le 2$ , moderately polluted $2 < I_{geo} \le 3$ , moderately to strongly polluted $3 < I_{geo} \le 4$ , strongly polluted $4 < I_{geo} \le 5$ , strongly to extremely polluted $I_{geo} > 5$ , extremely polluted
Single Risk Index, $E_r^i$ Hakanson (1980) It quantitatively expresses the potential ecological risk of a given contaminant. $C_{\rm fi}$ is the contamination factor and $T_r^i$ is the toxic response factor for the given substance. The $T_r^i$ values used were those given by Hakanson (As = 10; Co=5; Cu=5; Pb=5)	$E_r^i = T_r^i * C_{\rm fi}$	Hakanson (1980) $E_r^i < 30$ , low contamination $30 \le E_r^i < 60$ , medium contamination $60 \le E_r^i < 120$ , high contamination $120 \le E_r^i < 240$ , very high contamination $E_r^i \ge 240$ , extremely high contamination

prioritized with the 95%UCL background values shown in Table 6.

Figure 3 shows the background level concentration values transformed logarithmically, according to Eq. (1), and the reference levels of the three norms selected for the 15 elements. USEPA reference values are higher than Al, B, Ba, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, and Zn background values, i.e., 12 out of the 15 elements under assessment. This norm is well known and widely used as an assessment criterion. It is also used for determining maximum admissible environmental contamination levels, making decisions about risk management, and ruling authorized levels of dangerous residue emission, storage, and transport (Asante-Duah, 2021; Downie et al., 2012; Tepanosyan et al., 2017).

Since As is a highly toxic element, the reference values of the 9 norms (Table 3) were compared, showing that they greatly differ from one another.

USEPA is the most restrictive among the 9 norms for As (>0.68 mg/kg), as shown in Table 3. This limit is associated with the most toxic species, corresponding to As<sup>3+</sup>. On the contrary, the limits corresponding to NEPC and IHOBE are 100 mg/kg and 30 mg/ kg, respectively. Other international norms available for comparison, such as those from Germany (50 mg/kg, Lee et al. 2011), UK (32 mg/kg, Mtunzi et al., 2015), Taiwan (60 mg/kg, Lee et al., 2011), and China (30 mg/kg; Environmental Protection Ministry of China, 2015), reflect that average natural soils in the studied region are under these other limits, being slightly higher than the maximum admissible in Australia (20 mg/kg, EPA-Australia 2016) and Canada (20 mg/kg, CME, 2009). USEPA reference value for As is much lower than the background value of the study site. So, it could not be considered as a reference value, since the background values in soils without anthropogenic activity in the USA. are much

Common designation	Expression	Criteria
Degree of Contamination, $C_{\rm D}$ Lacatusu (2000) Defined as the sum of all contamination factors $(C_{\rm fi})$ for various heavy metals. n is the number of heavy metal species	$C_{\rm D} = \sum_{i=1}^{n} C_{\rm fi}$	Caeiro et al. (2005) $C_D < n$ , low contamination $n < C_D < 2n$ , moderate contamination $2n < C_D < 4n$ , considerable contamination $C_D > 4n$ , very high contamination
Modified degree of contamination, $mCd$ Abrahim and Parker (2008) Defined as sum of all the contamination factors ( $C_{\rm fi}$ ) for a given set of pollutants divided by the number of analyzed pollutants ( $n$ )	$mCd = \frac{\sum_{i=1}^{n} C_{fi}}{n}$	Abrahim & Parker, (2008) mCd < 1,5, no or low contamination $1,5 \le mCd \le 2$ , low contamination $2 \le mCd \le 4$ , moderate contamination $4 \le mCd \le 8$ , high contamination $8 \le mCd \le 16$ , very high contamination $16 \le mCd \le 32$ , extremely high contamina- tion $mCd \ge 32$ , ultra-high contamination
Potential Ecological Risk Index, RI Hakanson (1980) Used to quantitatively express the potential risk of metals measured in the soil. $E_r^i$ . is the ecological risk factors of the individual heavy metals (i)	$\mathrm{RI} = \sum_{i=1}^{n} E_r^i$	Hakanson, (1980) RI < 150, low toxicity $150 \le RI < 300$ , medium toxicity $300 \le RI < 600$ , considerable toxicity $RI \ge 600$ , extremely high toxicity
Pollution load index, <i>PLI</i> Thomilson et al. (1980) PLI is a measure of the degree of overall contamina- tion on a sampling site and provides simple but comparative means for assessing a site quality. n is the number of metals analyzed and $C_{\rm fi}$ is the contamination factor	$PLI = \sqrt[n]{\prod_{i=1}^{n} C_{fi}}$	Thomilson et al. (1980) PLI < 1, no pollution P = naseline levels of pollutant are present PLI > heavy pollution
Nemerow Pollution Index, PI <sub>Nemerow</sub> Nemerow (1985) It indicates the sediment quality. The index is similar to the modified degree of contamination index because it uses the average of the contamination factors of a suite of elements. However, it also con- siders an element contamination impact by using the maximum contamination factor to develop a weighted average. $C_{fi,max}$ is the maximum value of the single contamination factor of all heavy metals	$PI_{\text{Nemerow}} = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^{n}C_{\text{fi}}\right)^{2} + C_{\text{fi,max}}^{2}}{n}}$	Zhong et al. (2010) $PI_{Nemerow} < 0.7$ , safety domain $0.7 \le PI_{Nemerow} < 1.$ , warning limit $1 \le PI_{Nemerow} < 2.$ , slight pollution $2 \le PI_{Nemerow} < 3.$ , moderate pollution $PI_{Nemerow} > 3$ , heavy pollution

Table 5 Integrated Pollution indices to assess the presence and intensity of anthropogenic contaminant deposition on surface soil

lower than those in Antofagasta soils. In this sense, Chen et al. (2001) included a statistical analysis of background surface soils in Florida, considering 448 soil samples collected from seven soil types located throughout Florida state, finding that 95% UCL was 1.34 mg/kg. Their study also shows that the highest values occurred in histosols ( $2.06 \pm 2.41$  mg/kg) and the lowest values in spodosols ( $0.18 \pm 3.23$ ) (Chen et al., 2001; Missimer et al., 2018).

Arsenic mean concentrations between 4.8 and 13.6 mg/kg in several uncontaminated soil types in Canada are reported (Kabata-Pendias, 2011). Other authors found 91 background soil samples with a 9 mg/kg mean and a 9.03 standard deviation for As

(Lambert & Lane, 2004). Canadian norms consider a 12 mg/kg reference value. On the study site, As background values range between 3.5 and 24.7 mg/ kg, with an 8.5 mg/kg mean and a 5.5 mg/kg typical deviation. Considering As high toxicity and its great discrepancy with background values from other countries, the selection of the reference value was based on the criteria used to declare a soil as contaminated, according to Spanish legislation (R. D. 9/2005). Thus, the reference value adopted was estimated as the sum of the mean concentration plus twice the typical deviation of the concentrations in nearby uncontaminated zones with similar geological substrates (BOE, 2005; Mico et al., 2008; Recatalá et al., 2010). Thus,

Table 6       Background level         concentrations of metals       and metalloids in surface         soil, considering the 19       samples selected from Playa         Las Petroleras (WSP-       Selected from Playa	Element	Mean value mg/kg	Maximum value	Minimum value	95% UCL (BGV)
	Al	13,392.1	22,939.0	6805.0	15,112.3
	As	8.5	24.7	3.5	9.7
Emgrisa, 2019)	В	30.7	57.3	12.5	34.4
	Ba	34.3	148.0	15.4	38.3
	Cd	1.4	3.1	0.9	1.6
	Co	13.4	26.3	3.2	16.2
	Cr	25.3	36.0	15.5	27.6
	Cu	153.2	1269.0	14.1	157.3
	Fe	30,289.6	58,293.0	8152.0	35,942.9
	Hg	1.6	6.5	1.3	1.7
To evaluate ecological risk	Mn	1098.5	4657.0	102.0	1407.1
as suggested by US EPA (Chen et al., 2001; Darko et al., 2017; Townsend et al., 2004), 95% UCL was	Ni	10.7	20.6	3.0	12.8
	Pb	14.1	60.0	0.5	19.5
	V	89.9	148.0	32.7	103.2
used as Background value (BGV) for each element	Zn	210.5	667.0	7.9	302.9

Fig. 3 Comparison between logarithmic background concentrations and NEPC, USEPA, and Ecuador reference norms



the reference was determined as 19.5 mg/kg. For Cr and V, the norms selected were NEPC from Australia since the reference values for the 12 elements available are higher than the corresponding background values and Australia has climatic characteristics and soil similar to Chile (Lam et al., 2020). In conclusion, the reference values selected for each of the 15 elements allow comparing them with the background values, as shown in Table 7.

Selection of metals and metalloids of interest

The selection of metals and metalloids of interest to assess risk was based on the concentration of substances (9 surface samples) from Playa Las Petroleras, with values higher than the selected reference values. The maximum contents of each element (Table 2) were compared with the reference values of the adopted standards (Table 7). So, As, Co, Cu, and Pb were the elements whose concentration is higher than the reference one.

The elements considered for ecological risk assessment were As, Co, Cu, and Pb. A total of 17 additional samples were collected at Playa Las Petroleras

Element	Minimum value (mg/ kg)	Maximum value (mg/ kg)	Reference value (mg/ kg)	95% UCL (BGV) (mg/ kg)
Al	4000.2	13,905.5	77,000 <sup>a</sup>	15,112.3
As	18.6	100.4	19.5 <sup>c</sup>	9.7
В	43.7	165.6	16,000 <sup>a</sup>	34.4
Ba	<ld< td=""><td>196.6</td><td>15,000<sup>a</sup></td><td>38.3</td></ld<>	196.6	15,000 <sup>a</sup>	38.3
Cd	< 1.82	4.34	71 <sup>a</sup>	1.6
Co	8.2	26.7	23 <sup>a</sup>	16.2
Cr	11.53	67.76	100 <sup>b</sup>	27.6
Cu	35.2	4447.6	3100 <sup>a</sup>	157.3
Fe	6791.8	33,084	50,000 <sup>a</sup>	35,942.9
Hg	0.0111	0.2186	11 <sup>a</sup>	1.7
Mn	323.5	825.7	1800 <sup>a</sup>	1407.1
Ni	4.1	173.3	840 <sup>a</sup>	12.8
Pb	< 3.7	428.9	400 <sup>a</sup>	19.5
V	59.0	193.6	390 <sup>a,b</sup>	103.2
Zn	41.9	573.5	23,000 <sup>a</sup>	302.9

 Table 7
 Minimum, maximum, and reference value of the elements of interest

Bold values exceed the limits established by the normatives <sup>a</sup>USEPA

<sup>b</sup>NEPC

<sup>c</sup>O mean background value plus twice the typical deviation

sector and the concentration of these elements were measured. The results for all the samples (n=26) are shown in Table 8.

Figure 4 shows the logarithmically transformed values of the background concentrations; mean and maximum values; and reference concentration values of the elements selected as a priority, i.e., As, Co, Cu, and Pb, considering the 26 experimental points measured.

Great discrepancy is observed between Playa Las Petroleras maximum value and the corresponding As, Cu, and Pb background value. For Co, the values are slightly higher than the background value. For As, Cu, and Pb, the mean concentration exceeded background value, while it was lower for Co.

#### Pollution index assessment

To calculate pollution indices, the analysis considered the maximum and mean metal concentration values. Additionally, the reference value index was calculated to determine criteria applicability to the site.

## **Contamination factor, C**<sub>fi</sub>

The  $C_{\rm fi}$  values obtained were 2.0 (As), 1.4 (Co), 19.7 (Cu), and 20.5 (Pb). For the concentration factor to reach a value between 0 and 1, the soil should have metal concentrations between 0 and the background concentration value, at the most. Considering the maximum value of each metal found on the site for each of the metals under assessment, the concentration factor values were 10.4 (As), 92.9 (Cu), and 22.0 (Pb), thus indicating that the site is very highly contaminated by these three metals. For Co, a 1.6 concentration factor was obtained, thus classifying the site as moderately contaminated by Co.

Finally, considering the mean values of metals on Playa Las Petroleras, a 1.4 concentration factor was found for As, classifying the site as moderately contaminated by this toxic metal. For Co, a 0.7 concentration factor was found, classifying the site as little contaminated by Co. For Pb, a 2.2 concentration factor was found, classifying the site as moderately contaminated by Pb, the same as As. Lastly, for Cu, the concentration factor was the highest, 13.2, classifying the site as very highly contaminated by Cu.

Table 8	Results of UTP
WSP-En	ngrisa study for the
elements	assessed. Results
from the	whole surface soil
samples	(26)

Element	Minimum value (mg/kg)	Maximum value (mg/kg)	Mean value (mg/kg)	95% UCL (mg/kg)	95% UCL (BGV) (mg/ kg)
As	0.5	100.4	13.9	32.2	9.7
Co	1.39	26.72	11.46	13.65	16.2
Cu	26.9	14,608	2077	3726	157.3
Pb	0.5	428.9	43.9	124.5	19.5

**Fig. 4** As, Co, Cu, and Pb logarithmic concentrations of background values; mean and maximum values of the samples from Playa Las Petroleras; and reference values



## Enrichment factor, EF

EF requires data from a reference element. So, Fe concentrations were added. A reference element is an element particularly stable in the soil, characterized by the absence of vertical mobility and/or degradation phenomena (Jain et al., 2005). The constituent chosen should also be associated with finer particles (related to grain size), while its concentration should not be anthropogenically altered (Ackerman, 1980). Typical elements used in many studies are Al, Fe, Mn, and Rb. In this study, iron was chosen as a conservative element for analysis, because of its relative abundance in the regional earth's crust and, thus, its decreased tendency to be greatly influenced by human activity. The metal/Fe ratios minimize grain size effects on heavy metal data and, hence, are used to study the heavy metal mobility in the riverine environment (Jain et al., 2005).

Considering the worst scenario, i.e., applying maximum concentration values, no enrichment was found for Co, with a 1.8 enrichment factor, followed by a 11.2 factor for As and 23.9 for Pb, indicating severe enrichment. Lastly, the Cu enrichment factor was 100.9, indicating extremely severe enrichment.

Finally, in analyzing the mean concentration, only Co would indicate no mineral enrichment, with an 0.8 factor, followed by Pb with a 2.4 factor, indicating low enrichment; As with a 3.3 factor, indicating moderate enrichment; and Cu with a 14.3 factor, indicating severe enrichment.

## Geoaccumulation index, I<sub>geo</sub>

 $I_{geo}$  was calculated considering the maximum, mean, and reference values. Concerning reference values, the only element with a negative index was Co, showing that it does not contaminate the soil. For As, the index was 0.4, the site being classified as uncontaminated to moderately contaminated. The indices obtained were 3.7 (Cu) and 3.8 (Pb), the site being classified as strongly contaminated by Cu and Pb. Again, this shows that the reference values exceed the maximum limits admitted for these indicators to classify the site as contaminated by Cu and Pb.

Considering the worst scenario, i.e., applying maximum concentration values,  $I_{geo}$  was found to be positive for the 4 elements, in increasing order as follows: 0.1 (Co), 2.8 (As), 3.9 (Pb), and 5.9 (Cu). Thus, as to the extreme concentration points per element, the site is classified as uncontaminated or moderately contaminated by Co; moderately or strongly contaminated by As; strongly contaminated by Pb; and extremely contaminated by Cu.

Finally, in analyzing the mean concentration, negative values of -0.07 (As) and -1.1 (Co) were found, the site being classified as uncontaminated by As and Co. An 0.6 mean index was obtained for Pb, the site being classified as uncontaminated or moderately contaminated by Pb. The highest index was 3.1 for Cu, the site being classified as strongly contaminated by Cu.

# Single risk index, $E_r^i$

The potential single ecological risk was calculated for the four elements, considering maximum, mean, and reference values. As to the latter, the four elements were in agreement with an uncontaminated soil.

Considering the worst scenario, i.e., applying the maximum concentration values,  $E_r^i$  values lower than 30 were found for Co. Therefore, this element does not bear potential ecological risk, according to Hakanson's criteria. In addition, As and Pb show high contamination ( $60 \le E_r^i < 120$ ), with  $E_r^i$ values of 103 (As) and 110 (Pb). For Cu, the value obtained was 464, this point being classified as extremely high contaminated.

Finally, in analyzing mean concentration, As, Co, and Pb rendered  $E_r^i$  values of 14 (As), 3.5 (Co), and 11 (Pb), the site being classified as low contaminated by these elements. Co mean value was 66, the site being classified as highly contaminated by this metal.

After analyzing the four pollution indicators individually, the reference concentration values obtained were 19.5 (As) and 23 (Co), being coherent with the contamination criteria for all the pollution indicators.

Table 9 shows the results obtained from different methods for Playa Las Petroleras, showing a very high contamination and a severe enrichment of Cu. As shows low contamination; Co does not bear any risk; and Pb shows moderate contamination.

#### Integrated pollution indices

For  $C_D$  index, n value=4. For the site mean concentration, the pollution index = 17.6, the site being classified within range  $C_D > 4n$ , with a very high degree of contamination. Considering the maximum concentration values of the elements assessed, a very high index was obtained, 126.9, indicating very high contamination. The integral reference concentration assessment reveals a 9.4 index, the site being

Index	As Co		Cu	Pb
	1.4	0.7	13.2	2.2
Contamination	Moderate	Low	Very high	Moderate
factor, $C_{\rm fi}$	contaminati	contaminati	contaminati	contaminati
	on	on	on	on
Enrichmont	3.3	0.8	14.3	2.4
factor EE	Moderate	Without	Severe	Low
lactol, EF	enrichment	enrichment	enrichment	enrichment
	-0.07	- 1.1	3.1	0.6
Geoaccumulati	Without	Without	Heavy	Moderate
on index, $I_{\text{geo}}$	contaminati	contaminati	contaminati	contaminati
	on	on	on	on
	14	3.5	66	11
Single Risk	Low	Low	High	Low
Index, $E_r^i$	contaminati	contaminati	contaminati	contaminati
	on	on	on	on

Table 9Results obtainedwith different indices forAs, Co, Cu, and Pb usingthe mean concentrationvalues

<b>Table 10</b> Integratedpollution index results,	Pollution indices	Mean concentration	Maximum concentration
according to mean,	CD	17.6 (VH contamination)	126.9 (VH contamination)
maximum, and reference	mCd	4.4 (H contamination)	32 (EH contamination)
Cu, and Pb	RI	95 (L toxicity)	686 (EH toxicity)
	PLI	2.3 (H pollution)	14 (H pollution)
<i>VH</i> very high, <i>H</i> high, <i>EH</i> extremely high <i>L</i> low	PI <sub>Nemerow</sub>	6.9 (H pollution)	49.1 (H pollution)

classified within the  $2n < C_D < 4$  n range, thus showing a considerable degree of contamination.

Also, mCd shows high contamination, considering the mean concentrations of the elements assessed. Maximum concentrations show extremely high contamination. The index of the reference concentration values shows moderate concentration.

RI shows that average and reference concentrations indicate low toxicity in the soil. On the contrary, the maximum concentrations of the four elements in the soil show an RI index=686, indicating extremely high toxicity on the site.

PLI shows similar results for the maximum, mean, and reference concentrations, indicating heavy pollution on the site. Finally,  $PI_{Nemerow}$  shows heavy pollution on the site for mean and maximum concentrations and slight pollution for reference concentrations.

Table 10 shows the results obtained for the integrated pollution indices. Concerning the highest concentrations of the four elements, all the indices show that the site is heavily contaminated. Concerning mean concentrations, all the methods show that the site is heavily contaminated, except for *RI*, which shows low toxicity.

The application of the different methods to reference concentrations shows slight pollution to moderate contamination, indicating that the values selected as a standard do not represent a thoroughly uncontaminated site, considering that reference values should not be exceeded by any of the metals. The results also show that the As and Co values lie under the reference limits established, unlike Pb and mainly Cu, which exceed risk indices.

Therefore, according to this indicator and its corresponding criteria, the reference values do not represent a little contaminated site. According to the criterion for this indicator, a soil meeting the standards proposed could be classified as moderately contaminated by As and Co and highly contaminated by Cu and Pb.

### Conclusions

A study on soil contamination by petroleum by-products was conducted in Antofagasta (Chile), without having national reference norms to limit the maximum soil concentrations of potentially dangerous metals.

Comparing international norms with the value of background concentrations in the soil allowed selecting the reference values, choosing the most restrictive ones (US EPA and Australia NEPC) except in the case of As. For this metal, the Spanish indications for assessing the background level (Spain RD 9/2005) were used.

In this study, 4 single element contamination indices and another 5 integrated contamination indices were applied. Using the first ones, the 15 elements exceeding the maximum admissible values were determined, As, Co, Cu, and Pb being the metals above the reference levels.

As predicted, results show that Playa Las Petroleras sector after the oil spill episodes presents a degree of potential contamination mainly related to 4 of the 15 metals measured in the sector: As, Co, Cu, and Pb. Thus, the potential ecological risk assessment of the 4 single contamination indices shows that Co concentration does not involve risk, while As and Pb bear potential ecological risk at low and medium levels. Only Cu concentration produces high contamination and strong enrichment of this metal.

The integrated values of these four elements, when applying these indices to the mean and maximum concentrations, show high contamination in all the indices. Only the mCd and Potential Ecological Risk RI indices differentiate the degree of contamination from mean to maximum values in the results. The use of maximum values may be interesting for detecting contamination at specific points. Author contribution EJL was involved in conception/ research design/data acquisition/data analysis and interpretation/manuscript draft. JU was involved in conception/ research design/data acquisition/data analysis and interpretation/manuscript draft. CH was involved in conception/research design/acquisition of data/drafting the manuscript. ILM was involved in conception/research design/data acquisition/manuscript draft. VZ was involved in conception/ research design/ data acquisition/manuscript draft. Fernando ÁÁ was involved in data analysis and interpretation/manuscript draft. WZ was involved in conception/ research design/ data acquisition/manuscript draft. Fernando ÁÁ was involved in data analysis and interpretation/manuscript draft. MC was involved in data analysis and interpretation/manuscript draft. All the authors approved the final version to be submitted.

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**Conflicts of interest** The authors have no conflicts of interest relevant to the content of this article.

Animal research Since this study did not involve animal research, no consents were required to participate and publish data on animals. Therefore, the inclusion of these forms and other ethical issues related to the publication of this type of data do not apply to this study.

#### Consent to participate Yes.

**Consent to publish** All authors agreed on publishing the manuscript, respecting the current sequence of authors listed. Likewise, all authors agreed on designating Elizabeth J. Lam as the corresponding author.

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