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A new index to evaluate anomalies of trace elements in soils: the case of SE Spain

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Abstract

In this work, an index is established to detect anomalies in trace elements in the soil. This index, which relates the total concentration of each element with the regional geochemical background value of the element considered, was defined by studying the levels of trace elements from different soils located in SE Spain. In the area, a previous screening of trace elements detected seven zones with anomalies and revealed two conflictive areas: Sierra Gador and Cabo de Gata. In each zone, a second sampling was undertaken at two different depths (0-20 cm and 20-40 cm). The results indicate that the main anomalies were due to arsenic (As), lead (Pb), and zinc (Zn). In Sierra Gador Pb was the element that registered the highest rate of enrichment with respect to the regional geochemical background, reaching values up to 270-fold higher in some samples. In this zone, more than 50% of the samples were anomalous in any of the trace elements studied (higher than regional geochemical background). In Cabo de Gata, As concentration was higher than the geochemical background in more than 40% of the samples; meanwhile Pb concentration was higher in 50% of the samples.

Additional key words: enrichment index, geochemical background, soil pollution.

Resumen

Nuevo índice para evaluar anomalías de elementos traza en suelos: el caso del SE español

En este trabajo establecemos un índice para detectar anomalías en el contenido de elementos traza en suelos. Este índice relaciona el contenido total de cada elemento traza con el fondo geoquímico regional, definido mediante el estudio de los niveles de elementos traza en diferentes suelos localizados en el sureste español. En un primer estudio sobre niveles de electos traza en suelos del área de estudio detectaron siete zonas con anomalías, de las cuales dos fueron consideradas conflictivas: Sierra de Gádor y Cabo de Gata. En cada una de estas dos zonas se realizó un segundo estudio más exhaustivo a dos niveles de profundidad (0-20 y 20-40 cm). Los resultados indican que las principales anomalías correspondes a los niveles de As, Pb y Zn. En Sierra de Gádor el Pb es el elemento que presenta una mayor tasa de enriquecimiento con respecto al fondo geoquímico regional, con valores puntuales que lo superan hasta 270 veces. También en esta zona más del 50% de las muestras presentan anomalías en alguno de los elementos analizados. En Cabo de Gata el As supera el fondo geoquímico regional en más del 40% de las muestras; mientras que el Pb lo supera en el 50% de las muestras.

Palabras clave adicionales: contaminación de suelos, fondo geoquímico, índice de enriquecimiento.

Introduction

The study of the concentrations of potentially hazardous elements in soils from south-eastern Spain arose from the need to ascertain the risks and their intensity so as to establish corrective measures or at least compile enough information to act appropriately in the case of environmental accidents.

South-eastern Spain has traditionally been unproductive due to its aridity. Nevertheless, since the 1960s,

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Abbreviations used: CEC (cation exchange capacity), OM (organic matter), RGL (regional geochemical level), SASL (soil anomaly screening level).

it has developed intensive agriculture under plastic (primarily greenhouses), which today is one of the three pillars of its economy, together with mining and tourism (Montoya *et al*., 1999).

Mining is another pillar of the traditional economy of south-eastern Spain. Around 3500 BC, the Los Millares civilization began to use Cu for making tools in this part of the Iberian Peninsula. The zone of Adra, since 700 BC, was the prime enclave in metallurgy. Mining sites in the Sierra Gádor and Sierra Contraviesa were exploited mainly for Fe, Pb, and to a lesser extent silver and gold.

Another zone of great socio-economic importance is located in the Sierra Almagrera, with its vein of Pb and silver, discovered in 1838 in Jaroso ravine. The effects of mining in the Sierra Almagrera have been studied by Collado *et al*. (1996, 1999), Navarro *et al*. (1999) and Collado (2001). Collado (2001) emphasizes the volume and potential pollution from tailings in El Arteal, which reach very high values in Pb, As, Ba, Sb and Zn, among other elements.

From the Sierra Almagrera to Cabo de Gata, there are other mining zones of different degrees of interest: Sierra Cabrera for Pb, iron, and cinnabar; Bédar for iron from 1950 to 1970; Sorbas for gypsum; Carboneras and Cabo de Gata for bentonites, Pb, Zn, and Ag; and Rodalquilar for extensive mining of auriferous mineral.

Industry (Michelín, Campsa, Endesa, etc.) and thermal plants (Carboneras) are another notable focus of environmental contamination. Near Villaricos, soils are polluted due to past mining, and the normal activity of current industrialized zones is an additional source of pollutants.

The present work seeks to establish a new index to detect anomalies of trace elements in soils. It is demonstrated that background may change from area to area within a region and between regions (Reimann and Garrett, 2005). To define a baseline for a large region is fraught with problems due to the natural heterogeneity of the soils but this can be reduced by distinguishing areas according to the geological domains. The SASL has as main advantage the use of the local background level in relation to the geological domain of each sample, this allows to identify anomalies in a more realistic way than other indexes based on general background levels (countries or world wide) (Alloway, 1995; Baize, 1997; Reimann and Caritat, 1998; Adriano, 2001; Kabata-Pendias, 2001). Soil is under increasing environmental pressure, exacerbated by human activity, such as inappropriate agricultural and forestry practices, industrial activities, tourism or urban development. These activities are damaging the capacity of soil to perform its variety of crucial functions. It is essential to develop identification methods of areas at risk of accumulation of dangerous substances that would hamper soil functions and create a risk to human health and the environment.

Material and methods

The study area is located in south-eastern Spain and includes the province of Almería and the eastern part of Murcia (Fig. 1). The geology and lithology of the province of Almería were studied and mapped by the Geological and Mining Institute of Spain, and published in the Geoscientific Map of the Environment of the province of Almería (IGME, 1982). Also, information was found in the Geological and Mining Map of Andalusia at a scale of 1:400,000 (Borja *et al*., 1985). All the soil maps (1:100,000) of the province of Almería are published and there is even a map at a scale of 1:100,000 for the entire province (Aguilar *et al*., 2004). Also, there are numerous publications on Almerian vegetation (Valle *et al*., 2003). The climate is mainly semiarid although there are some small zones with an arid climate.

Initially, the study area was divided into 106 sampling sectors, each 100 km^2. A square plot was laid out (2×2 m) and georeferenced by Global Positioning System (GPS) approximately at the centre of each sector. Five

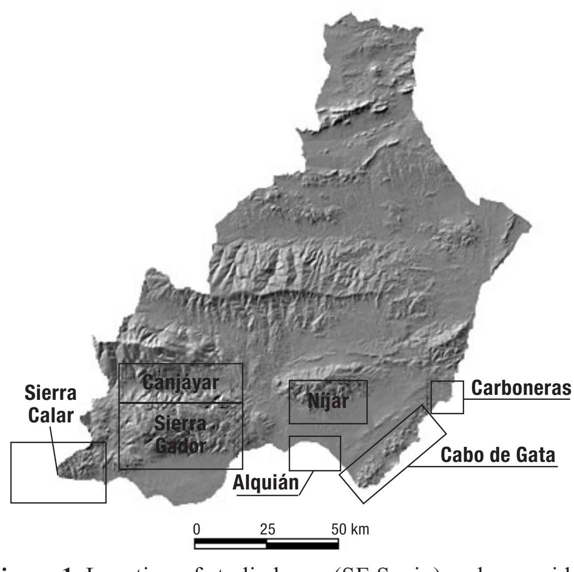

Figure 1. Location of studied area (SE Spain) and seven identified anomalous zones (Sierra Calar, Sierra Gador, Canjáyar, El Alquián, Níjar, Carboneras and Cabo de Gata).

samples were taken from the four corners and centre of each plot at depths of 0-20 and 20-40 cm. Then the samples taken at each depth were pooled.

This sampling was intended as a screening in order to detect zones with significant levels of trace elements. Seven zones which contained at least one sample with some anomaly were differentiated (Fig. 1): 1) Sierra Calar, 2) Sierra Gador, 3) Canjayar, 4) El Alquián, 5) Níjar, 6) Carboneras and 7) Cabo de Gata (Junta de Andalucia, 2005). Two of these zones were selected for a fuller study because of their abundance of samples with anomalous contents in at least one trace element: Sierra Gador and Cabo de Gata. In these zones, a second sampling was made, increasing the density of the studied points in the surroundings of areas where outliers were identified previously. In any case, some samples pertained only to the superficial layer, due to the predominance of Leptosols in the study area. Soils were classified according to World Reference Base (FAO, 1998) and the underlying lithology was described.

Soil samples were air dried on a non-absorbent surface, breaking down the aggregates with a wooden roller, and passed through a 2-mm sieve. Afterwards, the samples were ground in a Retsch mill for specific analyses. For the granulometric analysis, the fine fractions were determined by sedimentation and submitted to the Robinson pipette method (Soil Conservation Service, 1972). The pH was measured in a 1:2.5 water extract. Calcium carbonate content (% $CaCO_3$) was evaluated by gas volumetry (Barahona *et al*., 1984) and the percentage of organic matter (% OM) was determined by a oxi-reduction tritation with $K_2Cr_2O_7$ and $FeSO_4 \cdot 7H_2O$ (Tyurin, 1951). The cation-exchange capacity (CEC) was determined with ammonium acetate 1 N at pH 7.0 (Soil Conservation Service, 1972). In specific samples, the oxidation pH was determined to detect sulphides: 10 mL of 15% hydrogen peroxide were added to 5 g of fine earth measuring the pH at 2 min, 30 min, 2 h and 6 h (Urrutia *et al*., 1992).

Cd, Cu, Ni, Pb and Zn were determined by the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (detection limit, in mg kg^{-1}: Cd = 0.3; Cu = 1; Ni = 1; Pb = 3; Zn = 1) (upper limit, in mg kg^{-1}: Cd = 2,000; Cu = 1,000; Ni = 100,000; Pb = 5,000; Zn = 100,000). As, Cr, Co and Hg were quantified by the Instrumental Neutron Activation Analysis (INNA) (detection limit, in mg kg^{-1}: As = 0.5; Cr = 2; Co = 1; Hg = 1) (upper limit, in mg kg^{-1}: As = 10,000; Cr = 100,000; Co = 5,000).

The statistical study was made with the program SPSS, version 13.0. The anomalies were estimated on

Table 1. Regional geochemical level (RGL) for soil samples (at 0-20 and 20-40 cm) depending on the underlying geochemical formation (Junta de Andalucía, 2004)

Element (mg kg^{-1})	Geological formation			
	Internal areas of the Betic mountain ranges	**External areas of the Betic mountain ranges**	**Other post-orogenic basins**	**Volcanic rocks**
0-20 cm				
As	54	54	54	54
Co	36	32	32	32
Cr	193	144	144	144
Cu	62	62	62	62
Ni	95	69	69	69
Pb	109	109	109	109
Zn	145	145	145	145
20-40 cm				
As	49	49	49	48
Co	43	31	31	31
Cr	195	151	151	151
Cu	62	62	62	52
Ni	95	71	71	71
Pb	83	83	83	83
Zn	123	123	123	123

RGL: Regional Geochemical Level.

the basis of the calculation of a new index called Soil Anomaly Screening Level (SASL) and defined as the ratio between the value of the total concentration of each element and the value of the regional geochemical level (RGL). A pedo-geochemical anomaly was considered to exist when the value of SASL was higher than 1. The RGL values used in the study area (Table 1) are based in the different geological domains defined in Andalucía (Junta de Andalucía, 2004). The RGL is determined as 90 percentile of its geochemical background concentration.

Results

Table 2 reveals that Co, Cr, and Ni did not surpass the RGL in Sierra de Gador; Hg and Cu exceeded the RGL in the sample 2AL186, while Cd surpassed this value in that sample and in the sample 2AL187.

Meanwhile, As varied greatly, between 9 and 196 mg kg^{-1} at the surface level, and many samples surpassed the RGL, and even the mean exceeded this value. In depth something similar was found, though the mean did not surpass the RGL. Also, Pb presented great variability in this sector, which translated as minimum and maximum values of 22 and 29,529 mg kg^{-1} at the surface and 15 and 5,443 mg kg^{-1} in depth. It was striking that almost half the samples, at both depths, as well as the respective means, exceeded the RGL. With respect to Zn, levels were similar to those of Pb as practically all the same samples had a Zn concen-tration greater than the corresponding RGL and means, both on the surface as well as in depth, that also greatly exceeded this limit.

Table 2. Total concentrations of trace elements (mg kg^{-1}) for samples at 0-20 and 20-40 cm in Sierra Gador. Concentrations above the RGL (regional geochemical level) are shown in bold

Sample[a]	As	Co	Cr	Hg	Cd	Cu	Ni	Pb	Zn
0-20 cm									
AL035	**65**	14	114	bl[b]	bl	41	48	70	134
2AL200	19	9	42	bl	bl	20	20	**5,521**	**146**
2AL202	9	13	69	bl	bl	23	29	24	63
2AL203	**196**	23	117	bl	bl	81	57	**592**	**336**
2AL182	49	14	68	bl	bl	24	38	63	74
2AL183	15	14	88	bl	bl	7	29	22	50
2AL184	**63**	20	83	bl	bl	31	49	**158**	**259**
2AL185	**99**	25	123	bl	bl	35	48	**1,149**	123
2AL186	**72**	15	81	**12**	**4**	**62**	43	**29,529**	**1,475**
2AL187	**148**	16	78	bl	**5**	30	31	**616**	**1,488**
2AL189	42	17	79	bl	bl	27	44	41	98
2AL190	40	9	67	bl	bl	31	30	95	86
2AL191	29	9	56	bl	bl	17	25	61	75
2AL194	23	10	52	bl	bl	17	21	33	60
2AL172	31	15	71	bl	bl	23	30	**133**	60
Mean	**60**	15	79	—	—	31	36	**2,540**	**302**
Median	42	14	78	—	—	27	31	95	98
St. Dev.	52	5	24	—	—	11	11	7,596	486
20-40 cm									
AL035	**55**	9	79	bl	bl	28	24	35	103
2AL200	20	8	46	bl	bl	21	24	**5,443**	**151**
2AL202	5	11	53	bl	bl	53	25	15	62
2AL184	**79**	23	101	bl	bl	40	63	**176**	**336**
2AL190	48	12	102	bl	bl	37	46	60	**126**
Mean	41	13	76	—	—	36	37	**1,146**	**155**
Median	48	11	79	—	—	37	25	60	126
St. Dev.	29	6	26	—	—	12	18	2,403	106

[a] Soil samples data are extracted from research Project nº 1550 of the Regional Environmental Department of the Andalusian Government maintaining its nomenclature. [b] bl: below the detection limit.

In the Sierra Gador, limestones strongly predominated and soils changed from calcareous to strongly calcareous, generally surpassing 20% in calcium carbonate (Table 3). The high content in carbonates caused the soils to have basic pH values, exceeding 7.5 in all cases, and in some samples reaching 8.5.

Soils with organic, mollic, and rendzic horizons were predominant, as well as lithic units, which for lack of thickness did not become mollic. The notable content in organic matter and clay resulted in a high exchange capacity, especially at the superficial layer.

The total trace-element concentrations in soil samples in the volcanic zone (Cabo Gata) are listed in Table 4. Statistical data are also shown in this table.

In a large part of the soils in Cabo Gata, the As concentrations were higher than the RGL both in the upper part of the soil (0-20 cm) as well as in the lower part (20-40 cm).

The quantities of Co in the soils of the study area were below the RGL at the surface and in depth, except in sample 2AL220 (44 mg kg^{-1}) in depth, which was higher than the RGL (31 mg kg^{-1}). None of the samples of the sector of Cabo Gata had a total Ni or Cr concentration higher than the RGL. With respect to Cu, only the sample 2AL251 in depth (20-40 cm) was the total content in this element (98 mg kg^{-1}) higher than the RGL (52 mg kg^{-1}), while the lowest concentration belonged to soil 2AL229, with 5 and 1 mg kg^{-1}, depending on the depth considered. Pb presented strong variations in the total contents of soils; concentrations ranged from 32 to 261 mg kg^{-1} in the superficial layer and from 6 to 296 mg kg^{-1} in depth. Most of the soils had contents higher than the RGL (109 mg kg^{-1} for the superficial layer, and 83 mg kg^{-1} in depth). In the case of Zn, the total content varied from 22 to 249 mg kg^{-1} in the surface and from 1 to 341 mg kg^{-1} in depth.

Table 3. Soil parameters at 0-20 and 20-40 cm for soil samples in Sierra de Gador and Cabo de Gata

Sample	pH	OM[a] (%)	CEC[b] (cmolc kg^{-1})	$CaCO_3$ (%)	Clay (%)	Silt (%)	Sand (%)
Sierra de Gador							
0-20 cm							
Mean	8.2	4.50	20.33	22	33.2	31.5	33.4
Median	8.3	3.99	17.35	20	36.5	33.2	29.7
Minimum	7.6	1.59	6.66	11	11.4	27.2	16.0
Maximum	8.6	8.45	33.05	55	52.1	40.5	64.8
St. Dev.	0.3	2.19	9.78	12	10.4	9.3	13.9
20-40 cm							
Mean	8.3	0.87	9.41	30	28.3	19.9	41.7
Median	8.4	0.98	7.51	24	24.9	28.8	46.3
Minimum	8.0	0.48	4.65	19	13.9	21.8	17.8
Maximum	8.5	1.15	16.88	50	49.5	38.3	64.3
St. Dev.	0.2	0.30	4.88	12	14.3	6.1	19.1
Cabo de Gata							
0-20 cm							
Mean	8.1	1.80	14.71	10	35.3	20.7	43.9
Median	8.0	1.70	14.97	9	35.6	20.8	44.0
Minimum	7.3	0.63	7.73	0	17.8	14.0	25.0
Maximum	8.6	3.20	24.46	18	48.9	27.8	61.5
St. Dev.	0.5	0.70	4.49	7	12.1	4.8	11.7
20-40 cm							
Mean	8.2	0.65	8.96	12	33.8	21.6	45.3
Median	8.1	0.68	8.99	11	33.6	19.8	44.5
Minimum	7.3	0.39	4.41	0	15.7	15.4	26.6
Maximum	8.7	1.01	13.34	20	50.3	31.7	65.9
St. Dev.	0.4	0.19	2.36	8	12.4	4.7	13.6

[a] OM: organic matter (%). [b] CEC: cation exchange capacity.

Table 4. Total trace-element concentrations at 0-20 and 20-40 cm (mg kg^{-1}) for soil samples in Cabo de Gata. Concentrations above the RGL (regional geochemical level) are shown in bold

Sample	As	Co	Cr	Hg	Cd	Cu	Ni	Pb	Zn
0-20 cm									
2AL229	11	8	24	bl[a]	bl	5	14	32	22
2AL210	10	22	103	bl	bl	34	35	33	54
2AL232	8	27	95	bl	bl	26	34	34	66
2AL220	**131**	20	56	1.1	1.1	39	11	**225**	**225**
2AL227	**68**	12	79	bl	bl	27	38	**109**	138
2AL225	**95**	5	43	bl	bl	43	8	**261**	85
2AL226	**67**	16	41	bl	bl	35	23	**148**	**182**
2AL242	38	13	30	bl	bl	25	16	**255**	**233**
2AL243	23	17	57	bl	bl	41	28	52	94
2AL244	50	14	62	bl	bl	16	16	38	84
2AL246	**66**	13	43	bl	bl	61	21	**167**	**159**
2AL250	47	15	24	bl	bl	15	12	56	99
2AL251	**55**	17	32	bl	bl	15	28	56	78
2AL252	50	13	57	bl	bl	25	26	**181**	**249**
Mean	51	15	53	—	—	29	22	**118**	126
Median	50	15	50	—	—	27	22	82	96
St. Dev.	34	6	25	—	—	15	10	87	72
20-40 cm									
2AL229	5	4	13	bl	bl	1	7	13	1
2AL210	10	19	104	bl	bl	34	35	33	55
2AL220	**123**	**44**	50	bl	3.7	44	14	**121**	**341**
2AL227	**77**	13	79	bl	bl	24	38	**89**	**125**
2AL225	**83**	5	45	bl	bl	36	15	**296**	102
2AL226	**64**	16	38	bl	bl	36	25	**144**	**171**
2AL242	**77**	13	79	bl	bl	24	38	**89**	**125**
2AL243	13	15	34	bl	bl	59	16	6	43
2AL244	**56**	14	65	bl	bl	15	26	41	92
2AL246	**64**	11	45	bl	bl	17	22	**179**	**157**
2AL250	41	16	29	bl	bl	16	11	50	100
2AL251	**53**	17	72	bl	bl	**98**	24	41	72
2AL252	**109**	14	64	bl	bl	19	24	**102**	**247**
Mean	**59**	15	55	—	—	33	23	**93**	**125**
Median	**64**	14	50	—	—	24	24	89	102
St. Dev.	36	10	25	—	—	25	10	80	90

[a] bl: below the detection limit.

For Hg, concentrations were lower than 1 mg kg^{-1} in all the samples, while Cd reached its highest concentration (3.7 mg kg^{-1}) in the deep soil sample 2AL220.

In Cabo de Gata, the clay content was higher than 20% in many cases (Table 5) and therefore the most frequent texture was loamy clay to clay (especially the latter). The content in calcium carbonate at the surface fluctuated between 10 and 20%; the pH presented no significant variations with depth and ranged from 7.3 to 8.7 throughout practically the entire zone, at the two levels sampled. The percentage of organic matter remained between 0.6 and 1.5% in the central zone; on the other hand, in the protected zone of the national park, the vegetation increased and so did the organic content of the soil. The exchange capacity was higher in the strip of volcanic rocks (> 12 cmolc kg^{-1}), where, together with a greater quantity of organic matter, there were soils with clay contents higher than 20%. In the rest of the zone, the values for CEC fell within the range of 8-12 cmolc kg^{-1} and occasionally diminished in the most westerly part.

Table 5. Pearson's correlation matrix for trace-element concentrations against soil parameters in Sierra Gador and Cabo de Gata

	Clay (%)	$CaCO_3$ (%)	pH	CEC[a] ($cmol_c$ kg^{-1})	Clay (%)	$CaCO_3$ (%)	pH	OM[b] (%)	CEC ($cmol_c$ kg^{-1})
Sierra de Gador									
	0-20 cm; N = 15				20-40 cm; N = 5				
As									
Co	0.526*	–0.382*	–0.445*	0.581*	0.873*	–0.894*	–0.809*		0.928**
Cr	0.553*	–0.600*	–0.403*	0.564*	0.963**	–0.957**	–0.867*	–0.885*	0.892*
Cu									
Ni	0.574*	–0.634*	–0.563*	0.587*	0.906*	–0.877**	–0.923**	–0.870*	0.918**
Pb									
Zn		0.417*				0.910*			
Cabo de Gata									
	0-20 cm; N = 14				20-40 cm; N = 13				
As	0.769**				0.719**				0.548*
Co	0.610**	–0.576*		0.582*	0.527*				0.588*
Cr									
Cu		–0.593*		0.593*					0.585*
Ni									
Pb		–0.594*	–0.573*						
Zn		–0.567**			0.627*				

[a] CEC: cation exchange capacity. [b] OM: organic matter (%). *,**: significant correlation at the level 0.05 and 0.01, respectively.

The results of the correlation analysis between soil parameters and trace element concentrations are shown in Table 5 for the two studied areas. Correlation between trace element concentrations and pH and carbonates are negative, but they are positive with clay content and CEC.

The correlations between trace elements are highly abundant in the superficial layer in Sierra de Gador (Table 6) but they decrease in the subsupericial layer probably due to the scarcity of data because of leptic character of the soils in the area.

Oxidation pH values (Table 7) in selected samples are practically constant over time. This can be the consequence of the absence of sulphur in the superficial level or the presence of carbonates which produce a buffering effect.

Finally, Table 8 shows the relationships corresponding to the total concentrations of the studied elements in the superficial layer of the soils sampled in the Sierra Gador and Cabo de Gata with respect to the RGL values corresponding to the internal zones of the Betic range and Volcanic Rocks, respectively. SASL values reveal the existence of areas with anomalous concentration in As, Cu, Pb and Zn, in Sierra de Gador, and As, Pb and Zn in Cabo de Gata.

Discussion

Sierra Gador

The significant statistical relationships with the soil parameters centred fundamentally on Co, Cr, and Ni, which presented a positive correlation with the content in clay and with the CEC. In turn, this parameter correlated negatively with the carbonate content and pH, so that Co, Cr, and Ni tended to concentrate in those areas where the carbonate content was lower and so was the pH. The opposite was true with Zn, which was more abundant in heavily carbonated zones. There was a striking absence of significant relationships between Pb and organic matter, as widely noted in the literature (Zimdahl and Skogerboe, 1977; Reimann and Caritat, 1998; Bellido, 2004).

The high correlations between trace elements are highly abundant, which could suggest a natural origin of these elements. Many correlations have been described by Reimann and Caritat (1998) as a function of the geochemical nature of the parent materials. The presence of As together with Ag and Au in the zone can be explained by the influence that hydrothermalism exerts in a province, such as Almería, marked by volcanism

Table 6. Pearson's correlation matrix for total trace-element concentrations in Sierra Gador and Cabo de Gata

	As	Co	Cr	Cu	Ni	Pb	Zn
Sierra de Gador							
0-20 cm, N = 15							
As	1						
Co	0.681**	1					
Cr	0.634*	0.819**	1				
Cu	0.775**	0.541*	0.586*	1			
Ni	0.651**	0.829**	0.846**	0.743**	1		
Pb						1	
Zn						0.662**	1
20-40 cm, N = 5							
As	1						
Co		1					
Cr			1				
Cu				1			
Ni		0.922*			1		
Pb						1	
Zn		0.882*					1
Cabo de Gata							
0-20 cm, N = 14							
As	1						
Co		1					
Cr		0.613*	1				
Cu				1			
Ni			0.702**		1		
Pb	0.687**					1	
Zn						0.742**	1
20-40 cm, N = 13							
As	1						
Co		1					
Cr			1				
Cu				1			
Ni			0.869**		1		
Pb	0.581*					1	
Zn	0.887**	0.703**					1

*,**: significant correlation at the level 0.05 and 0.01, respectively.

(Reimann and Caritat, 1998). In addition, the simultaneous presence of Cu-Ni-Co-As-Ag-Fe is characteristic in zones of sulphur deposits, also found in the Sierra Gádor.

Co, Cr, and Ni were the elements geochemically related in deposits and veins of sulphides (Reimann and Caritat, 1998), which in turn appear correlated in the Sierra Gador.

The main sources of trace elements are sulphides and oxides, accompanied by other minerals in the metal sites. Given that the sulphides are easily oxidized, producing very soluble sulphates, in order to determine whether the origin of the trace elements present in this zone was due to sulphides, the pH of oxidation was determined in a number of samples from this zone. The oxidation pH was not lower, perhaps due to the absence of sulphides by previous oxidation or to an insufficient quantity to overcome the buffering power of the carbonates.

Evaluation of the anomalies

Pb was the element that presented the highest enrichment rate with respect to the RGL, especially in

Table 7. Oxidation pH of the samples selected in Sierra Gador and Cabo de Gata

Samples	Oxidation pH				$CaCO_3$ (%)
	2 min	30 min	120 min	6 h	
Sierra de Gador					
AL035	6.63	6.86	6.88	7.53	20
2AL200	6.48	6.69	6.63	7.41	55
2AL202	6.39	6.64	6.73	7.47	16
2AL203	6.44	6.51	6.51	6.95	12
2AL182	6.42	6.69	7.42	7.97	16
2AL183	6.43	6.66	6.68	7.43	26
2AL184	6.39	6.74	7.80	8.14	15
2AL185	6.60	6.80	7.06	7.64	22
2AL186	6.75	6.73	6.84	7.17	17
2AL187	6.32	6.59	6.63	6.71	11
2AL189	6.46	6.50	7.40	7.68	20
2AL190	6.44	6.49	6.45	6.50	30
2AL191	6.67	6.60	7.39	7.70	42
2AL194	6.55	6.62	6.71	6.82	13
2AL172	6.54	6.74	6.82	7.09	23
Cabo de Gata					
2AL210	6.26	6.53	6.59	6.82	2
2AL220	6.18	6.38	6.38	6.43	0
2AL243	6.21	6.43	6.40	6.58	1
2AL252	6.51	6.66	6.79	6.83	15

some samples, particularly sample 2AL186, for which the SASL was 270.9-fold the RGL. This sample was truly anomalous, with respect to Zn (10.2-fold higher) and As (1.33-fold), although the total concentration in the rest of the elements was within the normal range of the domain. Also, the sample 2AL200 was anomalous with respect to Pb, its content being more than 50.6-fold higher, though the concentrations in the other elements except Zn were even lower than the reference value. With respect to As, sample 2AL203 presented the highest SASL, being more than 3.6-fold higher than the RGL of the geological domain. Also, Pb, Zn, and Cu were anomalous, although to a lesser degree in the case of the latter two. A similar case was sample 2AL187, with a SASL value of around 2.7 in As, 5.6 in Pb, and 10.3 in Zn. In general, the As was the element showing the highest number of anomalies in this zone, because almost 50% of the samples presented a SASL higher than 1.

Cabo de Gata

Trace elements in Cabo de Gata frequently correlated negatively with pH and carbonates, as in the case of Co, Cu, Pb, Zn, although these reached significant values only in the superficial layer. As and Co correlated with clay in both sampling levels, but Zn only in depth.

The correlations between the elements determined were associated geochemically with the volcanic and hydrothermal influence of the zone. Thus, Reimann and Caritat (1998) associated the presence of Zn-Pb-Co-Ag-Au with veins and deposits of volcanogenetic stratiform sulphides, which on the surface were oxidized, as the oxidation-pH values remained practically constant.

Evaluation of the anomalies

As concentration was higher than the geochemical background in more than 40% of the samples and the sample 2AL220 exceeded the SASL by more than double.

Pb followed the same pattern, 50% of the samples exceeding the RGL and some samples (2AL220, 2AL225 and 2AL242) being more than 2-fold higher.

Table 8. Soil anomaly screening level (SASL) and regional geochemical level (RGL) values for As, Co, Cr Cu, Ni, Pb and Zn in soil samples in Sierra Gador and Cabo de Gata

	As	Co	Cr	Cu	Ni	Pb	Zn
RGL	**54**	**36**	**193**	**62**	**95**	**109**	**145**
Sierra de Gador							
Al035	1.20	0.39	0.59	0.66	0.51	0.64	0.92
2AL200	0.35	0.25	0.22	0.32	0.21	50.65	1.01
2AL202	0.17	0.36	0.36	0.37	0.31	0.22	0.43
2AL203	3.63	0.64	0.61	1.31	0.60	5.43	2.32
2AL182	0.91	0.39	0.35	0.39	0.40	0.58	0.51
2AL183	0.28	0.39	0.46	0.11	0.31	0.20	0.34
2AL184	1.17	0.56	0.43	0.50	0.52	1.45	1.79
2AL185	1.83	0.69	0.64	0.56	0.51	10.54	0.85
2AL186	1.33	0.42	0.42	1.00	0.45	270.91	10.17
2AL187	2.74	0.44	0.40	0.48	0.33	5.65	10.26
2AL189	0.78	0.47	0.41	0.44	0.46	0.38	0.68
2AL190	0.74	0.25	0.35	0.50	0.32	0.87	0.59
2AL191	0.54	0.25	0.29	0.27	0.26	0.56	0.52
2AL194	0.43	0.28	0.27	0.27	0.22	0.30	0.41
2AL172	0.57	0.42	0.37	0.37	0.32	1.22	0.41
RGL	**54**	**32**	**144**	**62**	**69**	**109**	**145**
Cabo de Gata							
2AL229	0.20	0.25	0.17	0.08	0.20	0.29	0.15
2AL210	0.19	0.69	0.72	0.55	0.51	0.30	0.37
2AL232	0.15	0.84	0.66	0.42	0.49	0.31	0.46
2AL220	2.43	0.63	0.39	0.63	0.16	2.06	1.55
2AL227	1.26	0.38	0.55	0.44	0.55	1.00	0.95
2AL225	1.76	0.16	0.30	0.69	0.12	2.39	0.59
2AL226	1.24	0.50	0.28	0.56	0.33	1.36	1.26
2AL242	0.70	0.41	0.21	0.40	0.23	2.34	1.61
2AL243	0.43	0.53	0.40	0.66	0.41	0.48	0.65
2AL244	0.93	0.44	0.43	0.26	0.23	0.35	0.58
2AL246	1.22	0.41	0.30	0.98	0.30	1.53	1.10
2AL250	0.87	0.47	0.17	0.24	0.17	0.51	0.68
2AL251	1.02	0.53	0.22	0.24	0.41	0.51	0.54
2AL252	0.93	0.41	0.40	0.40	0.38	1.66	1.72

In the case of Zn, samples varied markedly, almost 40% exceeding the RGL. Nevertheless, these elements showed no significant correlation, except between Pb and Zn at the surface of the soils.

Finally, the elements Co, Cr and Ni did not exceed the SASL value in any sample, while Cu exceeded the cited index only in sample 2AL251. The foregoing results imply a certain pollution, although a more detailed investigation of the soluble and bioavailable fractions of these trace elements is needed to evaluate the risk to ecosystem health and, subsequently, to recommend remediation actions. The above also implies that the SASL index proposed could be of great value to detect anomalies in a region, such as the province of Almería, where serious problems exist and require more detailed investigation.

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