

Micro-spatial variation of soil metal pollution and plant recruitment near a copper smelter in Central Chile

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“Capsule”: *Metal availability was different under shrub canopies than in open spaces.*

Abstract

Soil chemical changes produced by metal smelters have mainly been studied on a large scale. In terms of plant survival, determination of small scale variability may be more important because less toxic microhabitats may represent safe sites for successful recruitment and thus for plant survival. Three dominant microhabitats (open spaces and areas below the canopy of *Sphaeralcea obtusiloba* and *Baccharis linearis* shrubs) were defined in a heavily polluted area near a copper smelter and characterised in terms of microclimate, general soil chemistry, total and extractable metal concentrations in the soil profile (A_0 horizon, 0–5 and 15–20 cm depth), and seedling densities. Results indicated a strong variability in microclimate and soil chemistry not only in the soil profile but also among microhabitats. Air/soil temperatures, radiation and wind speed were much lower under the canopy of shrubs, particularly during the plant growth season. Soil acidification was detected on top layers (0–5 cm depth) of all microhabitats while higher concentrations of N, Cu and Cd were detected on litter and top soil layers below shrubs when compared to open spaces; however, high organic matter content below shrubs decreased bioavailability of metals. Plant recruitment was concentrated under shrub canopies; this may be explained as a result of the nursery effect exerted by shrubs in terms of providing a more favourable microclimate, along with better soil conditions in terms of macronutrients and metal bioavailability.

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1. Introduction

Soil chemical changes produced by metal smelters have mainly been studied on a macro-scale (e.g. kilometres, hundred metres), and thus mean metal values for an area have been more representative parameters than any measure of variability inside the area. However, from the plant point of view, small-scale variability in soil chemistry (e.g. metres, centimetres) in highly polluted areas may also be important; less toxic microhabitats may represent safe sites for successful recruitment and establishment of non-metal tolerant or sensitive plant species. Although metal tolerant plants

have been frequently considered the dominant species at metal smelter polluted sites (e.g. Cox and Hutchinson, 1980; Rauser & Winterhalder, 1985; Lolkema et al., 1986; Winterhalder, 1995), sensitive species have also been found in heavily polluted areas near a copper smelter in central Chile (Ginocchio, 1999) where mean total copper concentrations may reach up to 1500 mg kg⁻¹ (González & Ite, 1992; Pozo, 1993).

Climatic and edaphic factors can show great small-scale heterogeneity in many habitats, thus providing contrasting environments for plants in terms of resource supply (Skousen et al., 1990; Marshall and Price, 1997). Metal smelter polluted sites are no exception; great variability in metal levels may be found between microhabitats and within the soil profile. However, there are few reported studies where the small-scale heterogeneity of edaphic factors in metal rich areas has been carefully

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evaluated (e.g. McCarten, 1992; Winterhalder, 1995; Babilonas et al., 1997). Babilonas et al. (1997) demonstrated that the highly patchy distribution of plant species growing on a mineralised area in Greece was due to small-scale differences in soil properties, particularly metal content and texture. They found that the number of species occurring in different vegetation patches in the area was affected by the favourability or severity of soil conditions. Cox and Hutchinson (1980) showed that colonisation of barrens by *Deschampsia caespitosa* in Sudbury, Canada, occurred mainly in moist depressions where water availability was more favourable for plant establishment.

Small-scale variation of metal distribution in soils may represent considerable environmental heterogeneity where recruitment and establishment of plants with different tolerance/sensitivity to metals can occur. The main objectives of this study were (1) to characterise soil metal distribution at small spatial scales in a highly polluted area near a copper smelter; (2) to characterise variability of relevant climatic and edaphic factors for plant recruitment at small spatial scales in the same area; and (3) to investigate spatial patterns of plant recruitment in the area.

2. Materials and methods

2.1. Study site

A representative heavily polluted area of 50 × 50 m was selected as study site (see picture in Fig. 1). The site had a slope of 3–5° and was located approximately 2 km south-east of the ENAMI-Ventanas copper smelter, central Chile (34°45' S, 71°29' W). The general topography of the area exhibits undulating slopes ranging from 0 to 11° with some deep erosion gullies on sloping sites that have been exposed to heavy deposition of metal-rich particles and to SO₂ ground fumigations for the last three decades (Chiang et al., 1985; Alfaro, 1988). Smelter emissions have produced a significant reduction in plant cover and species richness (Ginoc-

chio, 2000). Approximately 60% of the landscape is occupied by bare soil, the remainder being occupied by *Sphaeralcea obtusiloba* and *Baccharis linearis*, two common shrubs which grow on degraded semiarid mediterranean-type ecosystems of central Chile (Ginocchio, 1997). Some herbaceous plants grow either in open spaces between shrubs (*Oenothera chilensis*, *Solidago chilensis*, *Noticastrum sericeum*, *Convolvulus chilensis*) or under the canopy of dominant shrubs (*Lolium perenne*; Ginocchio 1997). The two dominant shrubs have different canopy architectures; *S. obtusiloba* is a small (up to 0.6 m height), round, and dense shrub that grows close to the ground while *B. linearis* is a taller shrub (up to 2.0 m height) with a less dense canopy that sometimes grows close to the ground (Fig. 1). Three general microhabitats can be defined in this area: (1) open spaces between shrubs with sparse herbaceous cover, (2) areas below the compact canopy of *S. obtusiloba*, and (3) areas below the semi-compact canopy of *B. linearis* (Fig. 1).

2.2. Spatial distribution of seedlings

Seedling densities were estimated in the three microhabitats during the spring (September to October) 2000. Twenty-three parallel transects, 46 m long, were evenly located in the study site. Along each transect, ten 0.25 × 0.25-m quadrats were randomly distributed on open spaces between shrubs and 10 quadrats were also randomly distributed below the canopy of *S. obtusiloba*. Due to its lower density, all *B. linearis* individuals growing at the study site were sampled with two quadrats of 0.25 × 0.25 m, located at the northern and at the southern side of each shrub. A total of 230 quadrats were sampled on open spaces between shrubs and below the compact canopy of *S. obtusiloba* while a total of 36 quadrats were sampled under the semi-compact canopy of *B. linearis*. The total number of seedlings and the number of seedlings per plant species and growth form (shrubs and herb/grass) were recorded in all sampled quadrats.

Seedling densities between microhabitats were compared using the Kruskal–Wallis ANOVA test and non-

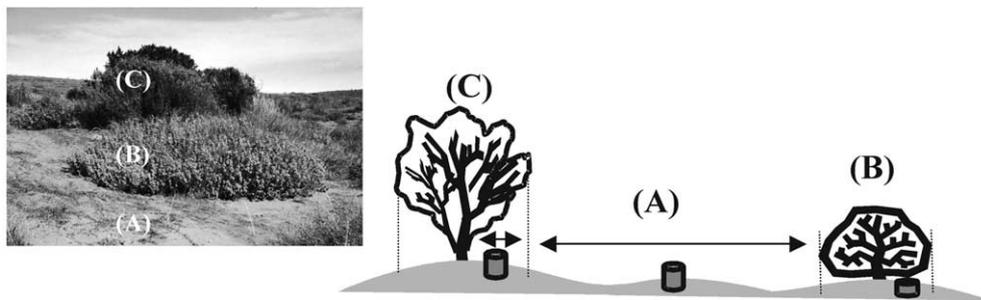


Fig. 1. General microhabitats defined in the study site. (A) open spaces between shrubs; (B) closed areas below the canopy of *Sphaeralcea obtusiloba*; (C) semi-closed areas below the canopy of *Baccharis linearis*. Soil and litter sampling points are indicated with a gray cylinder (0–20 cm depth).

parametric multiple comparisons (Siegel and Castellan, 1988), because the data could not be normalised. The relationship between mean and standard deviation of the number of seedlings per square meter was used to calculate a spatial distribution index ($DI = \text{standard deviation}/\text{mean}$) to determine the underlying pattern of spatial distribution in the study site: $DI > 1$ clumped distribution, $DI = 1$ random distribution, and $DI < 1$ homogeneous distribution (Ludwig and Reynolds, 1988).

2.3. Macro and microclimatic measurements

Daily macroclimatic data (air temperature, relative humidity, and wind speed) from January to December 2000 were obtained from the weather station of the ENAMI-Ventanas copper smelter. Temperature and gravimetric humidity of surface soil (0–10 cm) were determined every 2 months (April 2000–January 2001) between 12:00 and 13:30 h in all microhabitats. Soil temperature was registered using a stainless-steel thermocouple (Extech Instruments Corporation, Waltham, MA, USA) and soil gravimetric humidity was determined using a ThetaProbe ML2 soil moisture sensor (Delta-T Devices Ltd., Cambridge, UK). Ten replicate measurements were done for each microhabitat. Total radiation, photosynthetically active radiation (PAR), wind speed, air temperature, and relative humidity of air were determined 10 cm above ground level in all microhabitats at the end of November 2000 (a representative date when seedlings are actively growing in the study site), using LI-COR portable sensors and data logger (LI-COR, Lincoln, NE, USA). Seven replicate measurements per microhabitat were obtained.

ANOVA tests were used to compare microclimatic factors between microhabitats and time of the year; the Tukey Honest Significant Difference test was used as a posteriori test. Logarithmic transformations were applied when needed (Zar, 1984). Kruskal Wallis ANOVA test and non-parametric multiple comparisons were used to compare microclimatic factors between microhabitats and months (Siegel and Castellan, 1988), when the data could not be normalised.

2.4. Soil and litter collection

Samples were collected in April 2000 before the beginning of the rainy season. Fifteen surface soil samples (0–20 cm, region of intensive root exploration) were taken randomly in each microhabitat, using PVC soil core samplers (12 cm diameter, 30 cm long). Samples in open spaces were taken at a halfway distance between the closest shrubs while samples below shrubs were taken halfway between the trunk and the external projection of the canopy (Fig. 1). Each soil sample was

separated into five or four layers to reveal whether a gradient of metal contents and other chemical factors existed with depth. Samples were divided into litter (A_0 horizon), when present, and four other soil sections: 0–5, 5–10, 10–15 and 15–20 cm depth. Soil samplers were introduced into the soil with a rubber hammer and each layer was carefully extracted with a plastic spoon following an internal metric graduation in the soil sampler. Each layer was stored in clean polyethylene bags and transported in clean plastic containers to the laboratory. Litter, 0–5 and 15–20 cm samples were chemically analysed as described below.

Two-way ANOVA tests were used to compare the soil chemistry between microhabitats and soil depth; the Tukey Honest Significant Difference test was used as a posteriori test. Logarithmic transformations were applied when needed (Zar, 1984).

2.5. Soil and litter chemical analyses

Soil samples were dried in a forced air drying cabinet at 30 °C and sieved through a 2-mm nylon sieve. Aliquots (50 mg) of each soil fraction < 2 mm were ground in an agate ball mill (RETSCH S100) and stored in polyethylene sample bottles. Soil pH was determined in 1:1 soil–water. Soil organic matter (OM) was analysed by the Walkley–Black method, using USDA protocols (1996). Total N was determined by the Kjeldahl method (Allen, 1974).

Soil samples were subjected to microwave acid digestion (1200 mega microwave system, Milestone Microwave System, Monroe, CT, USA) and extraction (modified US EPA method 3052; US EPA, 1996) prior to determination of Cu, Zn, Fe, Pb, and Cd. Each digestion batch had one blank, one standard reference material sample, one duplicate sample and one quality control sample (a previously characterised soil sample with a known concentration of metals). The QA/QC criteria was satisfied when the measured parameter of the standard reference material (Loam-B, cat# CRM-LO-B purchased from High-Purity Standard, Charleston, SC) and the quality control sample differed from the known value by less than 5%. The digested soil samples were analyzed for total metal contents (Cu, Zn, Fe, Cd, and Pb) using US EPA method SW-486 (US EPA, 1997). Soil Cu fractions were also extracted with demineralised water (1:0.8 soil:water), CaCl_2 0.01 M (1:1 soil:solution), and HCl (1:10 soil:solution). Total metal concentrations and Cu soil fractions were measured by either flame or graphite atomic absorption spectrometry (Perkin-Elmer Analyst 300; HGA 800 graphite furnace).

Litter samples were dried in a forced air drying cabinet at 30 °C, ground in an agate ball mill, and stored in polyethylene sample bottles. These were digested following the same protocol used for soils (US EPA, 1996).

Each digestion batch had one blank sample, one standard reference material sample (SRM 1573a Tomato Leaves from National Institute of Standards and Technology or SRM 1570a Spinach Leaves from National Institute of Standards and Technology), one duplicate sample and one quality control sample (QCPS). Total Cu was measured by flame atomic absorption spectrometry (Perkin-Elmer Analyst 300).

2.6. Statistical analyses

All statistical analyses were performed using Statistica software for Windows (StatSoft Inc., 1993).

3. Results

3.1. Spatial distribution of seedlings

Seedlings were not homogeneously distributed in the microhabitats of the study area. Total seedling densities significantly differed between microhabitats ($KW = 174.1$, $P < 0.01$), as shown in Table 1. There are 16 times more seedlings under the canopy of *B. linearis* and 193 times more seedlings under the canopy of *S. obtusifolia* than in open spaces. Significant differences between microhabitats are also found for seedling den-

sities of herbs/grasses ($KW = 160.7$, $P < 0.01$) and shrubs ($KW = 47.83$, $P < 0.01$). Herbaceous plants seedlings are more abundant than woody species seedlings in all microhabitats (Table 1) and both woody and herbaceous species are much more abundant below shrubs than in open spaces (251 versus 2.4 seedlings per m^2 , respectively). No recruitment of woody species was detected in open spaces (Table 1).

Seedlings do not only have a clumped distribution under the shrubs, but they also show clumped distribution in each microhabitat, as indicated by DI values greater than 1 (Table 1). They are clumped under the canopy of dominant shrubs, particularly under the compact canopy of *S. obtusifolia*. In addition some patches of shrubs and open spaces have much higher densities of seedlings than others.

Seedling species richness is higher under the canopy of *S. obtusifolia* than under *B. linearis* shrubs and very low in open spaces; there is a lack of recruitment of *S. obtusifolia*, *Noticastrum sericeum*, and *Eschscholzia californica* plants under *B. linearis* shrubs (Table 2). The grasses *Lolium perenne* and *Bromus* spp. show a significantly higher density under the canopy of *S. obtusifolia* ($KW = 7.9$, $P < 0.01$ and $KW = 5.5$, $P < 0.01$, respectively; Table 2). Few herbaceous plants recruit in open spaces between shrubs (*L. perenne*, *E. californica*, and *Solidago chilensis*; Table 2).

Table 1
Density of seedlings in different microhabitats

Microhabitat	Shrubs		Herbs & Grasses		Total	
	Density (seedlings / m^2)	DI	Density (seedlings / m^2)	DI	Density (seedlings / m^2)	DI
Open spaces	0.0±0.00	–	2.4±15.04	6.27	2.4±15.04	6.27
<i>S. obtusifolia</i>	6.2±19.69	3.18	456.2±744.46	1.63	462.1±747.33	1.62
<i>B. linearis</i>	4.4±16.37	3.72	34.8±71.37	2.05	39.2±73.82	1.88

The mean and standard deviation are reported; DI, spatial distribution index.

Table 2
Species richness and density of seedling species present under *Baccharis linearis* ($N = 36$) and *Sphaeralcea obtusiloba* ($N = 230$) shrubs

Species	Nursery Shrub		Open Spaces (seedlings / m^2)
	<i>B. linearis</i> (seedlings / m^2)	<i>S. obtusifolia</i> (seedlings / m^2)	
<i>Baccharis linearis</i>	4.4±16.37	4.4±15.44	0.0
<i>Sphaeralcea obtusiloba</i>	0.0	1.9±7.55	0.0
<i>Lolium perenne</i>	19.4±52.32	381.6±708.28	1.6±11.81
<i>Bromus</i> spp.	10.1±42.45	66.0±249.17	0.0
<i>Noticastrum sericeum</i>	0.0	0.8±8.55	0.0
<i>Solidago chilensis</i>	4.4±15.46	5.2±22.36	0.7±6.76
<i>Rhodophiala advena</i>	0.4±2.65	0.1±1.48	0.0
<i>Eschscholzia californica</i>	0.0	1.8±8.20	0.1±1.48
<i>Convolvulus</i> spp.	0.6±2.65	0.4±4.37	0.0
Species richness	6	9	3

The mean and standard deviation (SD) are reported.

3.2. Macro and microclimates

Relative humidity is high (78–89%) throughout the year (Fig. 2A), due to the proximity of the area to the Pacific Ocean (2 km) and the frequent occurrence of early-morning fogs throughout the year. Mean air temperature decreases in winter from 16 to 10 °C and increases in summer up to 16 °C (Fig. 2A) while wind speed increases in spring, reaching an average of 3 m s⁻¹ in December (Fig. 2B).

Soil temperature differs significantly between microhabitats (KW = 74.38, $P < 0.01$) and time of the year (KW = 163.6, $P < 0.01$). It is always higher in open spaces than under the canopy of *S. obtusifolia* and *B. linearis* (Fig. 3A). It decreases during winter months and increases during summer months in all microhabitats, but the extent of the variation is much higher in open spaces than under the shrubs canopies (Fig. 3A). In summer (January), mean noon soil temperature in open spaces can reach 39 °C, showing a 15 °C increase compared to the temperature under shrub canopies. During winter (July), this difference is reduced to approx. 6 °C.

There are no differences between mean soil temperatures measured under both shrub species throughout the year (KW = 1.11 $P = 0.293$; Fig. 3A).

Humidity of the surface soil is low throughout the year (up to 10% in winter; Fig. 3B) due to its sandy texture. However, this factor significantly differs with the time of the year (KW = 214.73, $P < 0.01$). It shows an opposite annual trend to soil temperature, increasing in winter months (July) and decreasing in summer (February–March; Fig. 3B). No significant differences in soil humidity were found between microhabitats ($F = 3.4$, $P = 0.065$; Fig. 3B).

Total radiation is approximately 3-times higher in open spaces than below the canopy of both shrub species ($F = 49.24$, $P < 0.01$), but photosynthetically active radiation (PAR) significantly differs among all microhabitats ($F = 55.0$, $P < 0.01$). PAR is 6.5 times greater in open spaces when compared to *S. obtusifolia* and 4 times greater when compared with *B. linearis* (Table 3). Relative air humidity is significantly higher under the canopy of *B. linearis* than in open spaces ($F = 11.82$, $P < 0.01$) but it is similar below the canopy of both species

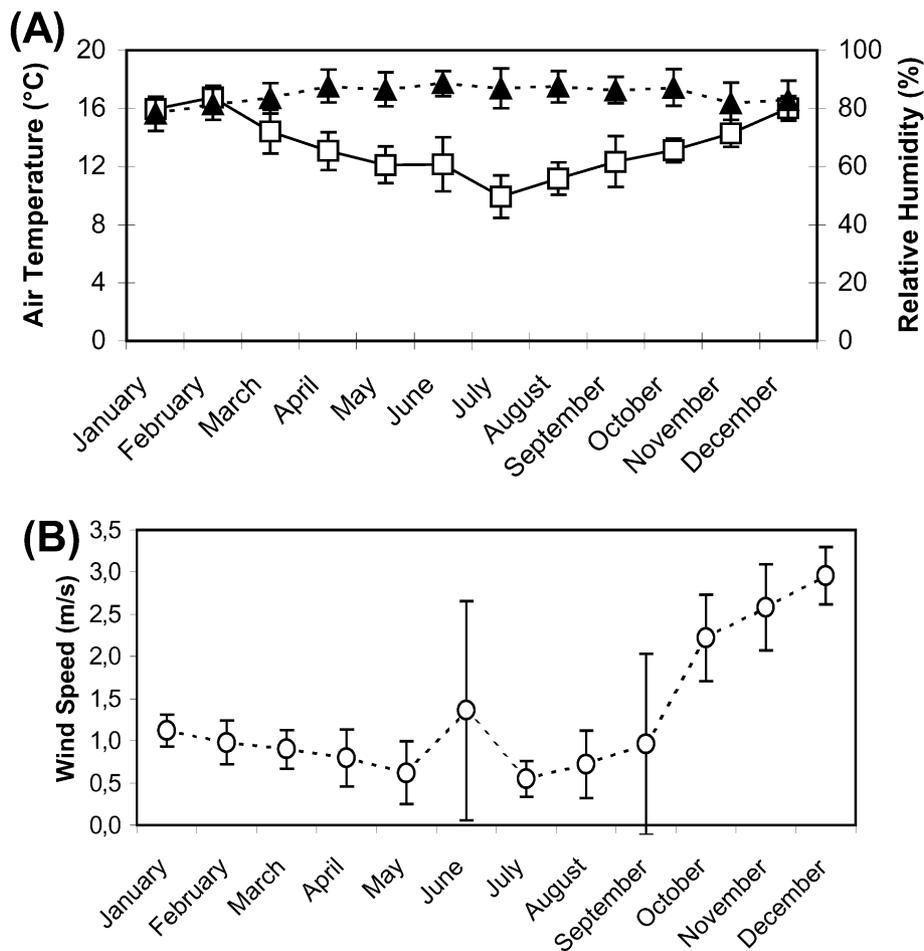


Fig. 2. Annual course of (A) air temperature (□), relative humidity (▲) and (B) wind speed (○) in the study site during the year 2000. Mean values and standard deviations are reported.

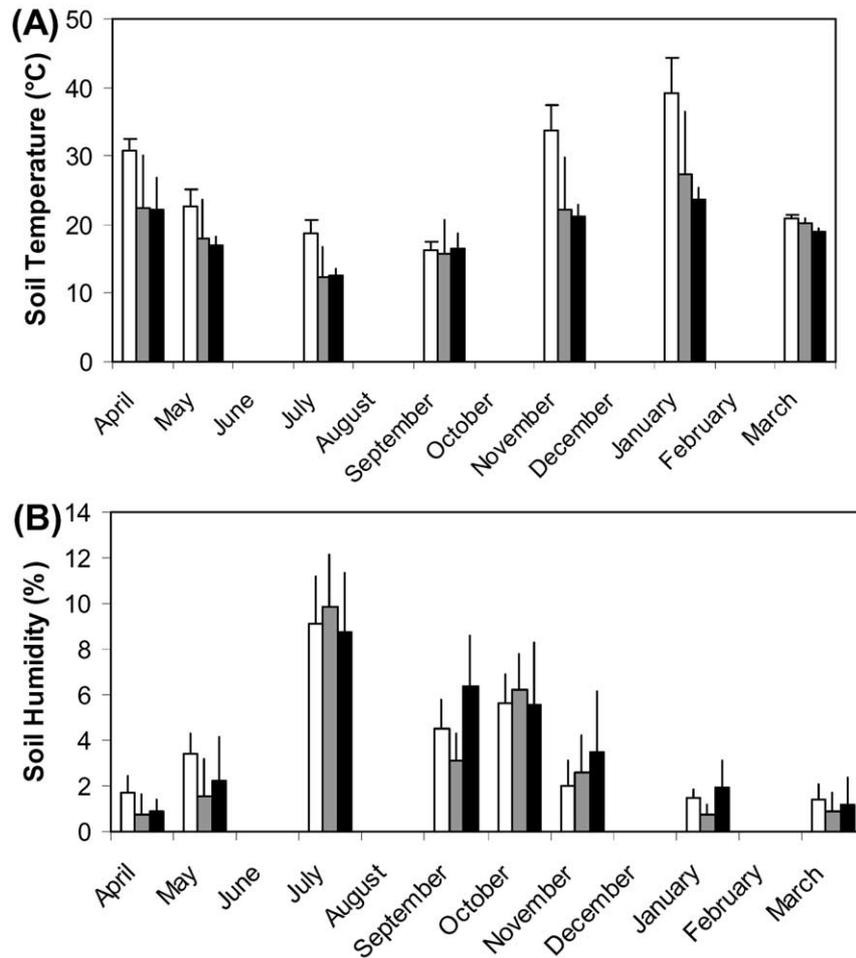


Fig. 3. Annual course of soil temperature (A) and soil humidity (B) in different microhabitats: open spaces between shrubs (□), and under the shrubs *Sphaeralcea obtusiloba* (■), and *Baccharis linearis* (■). Mean values and standard deviations of twenty or ten replicate measurements are reported.

Table 3
Abiotic parameters measured in different microhabitats at the end of November 2000

Microhabitat	PAR ($\mu\text{mol s}^{-1} \text{m}^{-2}$)	Total radiation (Wm^{-2})	Relative humidity (%)	Wind speed (m s^{-1})	Soil temperature ($^{\circ}\text{C}$)	Air temperature ($^{\circ}\text{C}$)
Open spaces	1638.7±656.1	797.0±316.1	43.1±3.1	1.2±0.4	33.4±2.6	24.2±1.2
<i>S. obtusiloba</i>	252.1±120.1	234.9±113.4	48.3±5.2	0.0±0.0	22.9±3.5	21.1±1.8
<i>B. linearis</i>	412.7±102.9	249.1±59.6	53.8±5.0	0.7±0.5	22.2±1.1	22.2±1.1

The mean and standard deviation of seven replicate measurements are reported.

(Table 3). Soil temperature is similar under the canopy of both shrubs but it is 10 °C higher in open spaces ($F=86.8$, $P<0.01$). Air temperature is significantly higher in open spaces ($F=6.82$, $P<0.05$), but the difference between open spaces and shrub canopies is not as marked as it is with soil temperature. Wind speed significantly differs between microhabitats ($F=18.68$, $P<0.01$); it is higher in open spaces (1.2 m s^{-2}), much lower under the semi-compact canopy of *B. linearis* (0.7 m s^{-2}) and null (0), under the compact canopy of *S. obtusiloba*.

3.3. Soil and litter chemistry

There are significant differences in litter accumulation between microhabitats ($F=27.36$, $P<0.01$; Table 4). Litter is accumulated under the canopy of dominant shrubs, where an A_0 horizon is well defined, but there is significantly more litter under the canopy of *B. linearis* than under the canopy of *S. obtusiloba* (Table 4). Litter composition under shrubs is very homogeneous, as dead leaves of a shrub species seem to be accumulated under the canopy of the same shrub. Organic matter content

depends on microhabitat and soil depth, showing greater variation under the canopy of *S. obtusifolia* than in the other microhabitats (2.2 times and 1.2 times, respectively; Table 5). A higher rate of litter accumulation and/or degradation under *S. obtusifolia* shrubs may explain the higher total organic matter content detected in upper soil layers. Soil nitrogen content varies significantly in the soil profile but not between microhabitats (Table 5). There is a significantly higher concentration of nitrogen in the upper soil layers than at 15–20 cm soil depth in both open spaces and under the shrub canopies.

Total Zn, Pb, and Fe did not differ between microhabitats, depth, and microhabitat \times depth, but pH and Cd significantly differed with soil depth (Table 5). Soil pH increases approx. 1 unit in the deeper soil layers, from acidic (4.7–4.8) to less acid values (5.6–5.8, the background levels described for the area) at a depth of 10 cm. Cd concentration decreases about 13–20 times from the uppermost soil layer (0–5 cm depth) to the

deeper soil layers (15–20 cm depth), but the same trend is observed in all microhabitats (Table 5).

Total Cu concentration depends on both the microhabitat and the depth of the soil profile (Table 5). Total Cu concentration decreases with soil depth in all microhabitats but the decline is steeper under the canopy of shrubs than in open spaces, maybe due to the presence of a copper-rich litter horizon (Table 5). Although Cu is being accumulated under the canopy of dominant shrubs, its concentration at a soil depth of 15–20 cm is the same for all microhabitats. Copper solubility does not differ between microhabitats although it tends to be slightly higher below shrubs where total Cu content is also higher than in open spaces (Table 5). Soluble Cu is low in all microhabitats (up to 2% when extracted with water and up to 4% when extracted with HCl), but there is a significant decrease with soil depth in all Cu fractions extracted (Cu_{water} , Cu_{CaCl_2} , and Cu_{HCl} ; Table 5).

Table 4
Quantification of litter in every microhabitat

Microhabitat	Litter (g cm ⁻²)
Open spaces	0.0 \pm 0.00a
<i>S. obtusifolia</i>	0.3 \pm 0.07b
<i>B. linearis</i>	0.7 \pm 0.38c

The mean and standard deviation of five replicate measurements are reported. Different letters indicate significant differences.

4. Discussion

These results show that pollutants released by the copper smelter have produced highly heterogeneous chemical changes at small-scales which restrict plant recruitment and establishment to specific microhabitats in heavily polluted sites. On the one hand, although the study area has been heavily polluted over the past 30 years, there are marked chemical differences in the soil

Table 5
General soil chemistry of selected microhabitats at different soil depths

	pH (water)	OM (%)	N (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Cu_{water} (mg l ⁻¹)	Cu_{CaCl_2} (mg l ⁻¹)	Cu_{HCl} (mg l ⁻¹)
<i>Open spaces</i>											
Litter	–	–	–	–	–	–	–	–	–	–	–
0–5 cm	4.8	0.58	645.2	361.6	157.8	50024.7	79.9	0.8	1.25	12.68	15.64
15–20 cm	5.8	0.51	542.5	46.3	124.8	47531.3	23.2	0.06	0.97	0.45	1.03
<i>Below</i>											
<i>B. linearis</i>											
Litter	–	–	–	3718.0	–	–	–	–	–	–	–
0–5 cm	4.8	0.99	1218.0	535.9	165.4	47252.0	79.9	1.0	1.93	7.07	25.12
15–20 cm	5.7	0.82	560.7	48.1	126.8	48488.0	21.3	0.05	0.43	0.06	0.12
<i>Below</i>											
<i>S. obtusifolia</i>											
Litter	–	–	–	1854.6	–	–	–	–	–	–	–
0–5 cm	4.7	1.2	933.3	679.9	174.4	50261.0	104.7	1.0	4.27	16.38	30.01
15–20 cm	5.6	0.55	452.7	45.4	126.8	48160.0	21.3	0.05	0.09	0.19	0.60
<i>2-way ANOVA</i>											
F_{habitat}	2.51	6.02	2.56	73.35	0.0003	0.38	0.92	1.18	1.73	2.33	0.78
P_{habitat}	0.089	<0.01	0.105	<0.01	0.999	0.767	0.405	0.315	0.186	0.107	0.461
F_{depth}	71.65	7.81	17.78	65.68	0.54	0.63	1.20	210.29	23.52	61.70	5.02
P_{depth}	<0.01	<0.01	<0.01	<0.01	0.653	0.535	0.319	<0.01	<0.01	<0.01	<0.01
$F_{\text{depth} \times \text{habitat}}$	0.39	4.07	2.42	65.73	0.81	0.60	1.48	1.41	0.23	0.24	2.94
$P_{\text{depth} \times \text{habitat}}$	0.886	<0.05	0.117	<0.01	0.570	0.727	0.199	0.253	0.963	0.963	<0.01

profile. The strongest effects are restricted to the upper layers of the soil where plant recruitment occurs. The intense decrease in metal content with depth, particularly for Cu and Cd, and the evident increase in soil pH may be assumed mostly to the dryness of the area which may restrict proton and cation leaching to deep soil layers. The high acidity of the upper soil layer (0–5 cm depth) due to the acid deposition generated by the smelter should favour cation leaching to deep soil layers (Kelly and Strickland, 1986), particularly in a sandy soil with low organic matter content. However, the low water availability in this semiarid Mediterranean environment may restrict metal solubility and thus cation loss. Although air humidity is quite high throughout the year (Fig. 2A), the mean annual precipitation registered for the area is 300 mm, concentrated in winter months, and droughts are not infrequent (Poza, 1993). Concentration of Cu and Cd in the upper soil may be also a result of metal sequestration in the organic layer for long periods of time due to the low decomposition rate of the sclerophyll litter that characterises this semiarid Mediterranean area (Cisternas and Yates, 1982; Yates et al., 1987).

On the other hand, it is interesting to note that edaphic changes that may strongly restrict plant recruitment, such as soil acidification and high metal concentration, are also strongly dependent on the type of microhabitat. Although distribution of metal-rich particles in the atmosphere at small spatial scales can be assumed to be homogeneous in a smooth undulating environment dominated by a grassland community, the magnitude of the soil-metal changes produced by its deposition varies markedly. Metal deposition is much higher under the canopy of dominant shrubs than in open spaces, particularly for total Cu. Several explanations can be made for this phenomenon. First, the canopy of dominant shrubs (*B. linearis* and *S. obtusiloba*) may act as an effective collector of metal-rich particles released by the smelter, due to their evergreen status, the small size of their leaves (particularly for *B. linearis*; Table 6), the high leaf densities per plant, the high density of trichomes (particularly for *S. obtusiloba*; Table 6), and the presence of resiniferous glands and resins on leaf surface (particularly for *B. linearis*; Table 6). These characteristics increase the canopy

surface exposed to air or the capability of leaf surface to retain particles, thus resulting in a high capability for collecting air particles, as it has been demonstrated by others for other plant species (e.g. Kovacs et al., 1982; Harris, 1992; Nowak, 1994). Pollutants may be then washed on to the soil by precipitation or transferred into the soil as leaves are shed by the plant. Second, incorporation of metals into plant tissues may result in subsequent translocation to senescent leaves, a detoxifying mechanism described for plants (Heelmisaari et al., 1995; Mooni et al., 2000). The soil may become enriched as leaves are shed and litter accumulates under the shrub canopy. This phenomenon of strong soil metal gradients below plants has been previously described by Dahmani-Muller et al. (2000) near a metal smelter, but for herbaceous absolute metallophyte plant species.

Although elevated metal levels are found in the acidified upper soil layers under shrub canopies, plant recruitment is more or less restricted to this microhabitat. This may be the result of litter accumulation under the shrubs, a good cation chelating agent that may reduce the excessive metal concentration being deposited into soils and thus avoid their phytotoxicity (e.g. Sauvé, 2001), and also a good source of macronutrients in a nutrient-poor environment. The low cycling rate of minerals under the semiarid Mediterranean conditions of the area (Cisternas and Yates, 1982; Yates et al., 1987) may also determine the low bioavailability of metal pollutants in soils. Low Cu solubility was detected in this study, although very high total Cu concentrations were registered under shrubs (Table 5). Plant recruitment may be also restricted to areas below shrubs, because higher availability of macronutrients, such as nitrogen, and better microclimatic conditions, such as soil temperature and humidity, are more favourable for seed germination and seedling establishment. The nursery effect of shrubs against harsh climatic and edaphic conditions has been previously described by others in non-polluted semiarid Mediterranean-type ecosystems (e.g. Fuentes et al., 1986; Holmgren et al., 2000). However, its importance may be greater in polluted environments where heavy soil erosion occurs in bare areas, severely restricting plant establishment under the shrubs.

Table 6

General leaf morphological characteristics of dominant shrubs present in the study area (modified from Ginocchio, 1997)

Species	Area (cm ²)	Length (cm)	Thickness (µm)	Upper leaf surface	
				Trichomes (% ^a)	Glands (% ^a)
<i>B. linearis</i>	0.3	1.3	451.9	0	1
<i>S. obtusiloba</i>	1.6	1.2	197.1	100	2

^a Percentage of the upper leaf surface covered with trichomes and/or glands.

The efficiency of the nursery effect of shrub species also depends on the architecture of the shrub canopy. Although soil and air temperature, soil humidity and air relative humidity are similar below the canopy of both dominant shrub species, seedling densities are higher under *S. obtusiloba* than under *B. linearis*. It has been shown that in heavily polluted areas of the study site, seeds accumulate under the canopy of the dominant shrubs, reaching densities of 4786 seeds per 1188 cm³, a seed density normally found between shrubs in non-polluted sites of the area (Ginocchio, 2000); we describe here the same pattern for litter. Seeds and litter that reach the bare soil surface between shrubs are rapidly washed or blown out into the shrub canopies by water runoff and winds. However, the densely packed canopy of *S. obtusiloba* may be a more efficient seed and litter keeper and collector than the semi-compact canopy of *B. linearis*, as indicated by differences in wind speed measured inside the canopy of both species. Seed distribution was highly clumped not only below the canopy of dominant shrubs but was also highly heterogeneous between shrubs of the same species. Seed production of the species belonging to a specific patch of vegetation may be retained under the canopy of the same patch where they may germinate and establish unless they have wind dispersal mechanisms, such as *B. linearis*. Although we did not evaluate the efficiency of canopies in reducing gaseous ground fumigations (SO₂ and NO_x), the densely packed canopy of *S. obtusiloba* may also provide a good physical barrier to the ground-SO₂ fumigations generated by the smelter, as it is closer to the soil surface than the canopy of *B. linearis*.

Finally, although we did not evaluate the fate of seedlings established under the shrubs, it is frequent to find mature herb and grass plants growing through the canopy of *S. obtusiloba* and *B. linearis* shrubs. Indeed, high densities of mature annual grasses are normally observed growing through the canopy of *S. obtusiloba* shrubs; in this case it is evident that seedlings are able to develop to maturity, reproduce and die, even under the compact canopy of *S. obtusiloba* shrubs, because high densities of reproductive spikes are frequently seen over the edge of the shrub canopy in summer time. However, a further evaluation of the canopy effect on the proportion of mature plants of each species present at the site and on their productivity and seed yield is needed.

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