

## **Influence of ore processing activity on Hg, As and Sb contamination and fractionation in soils in a former mining site of Monte Amiata ore district (Italy)**

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**Abstract:** This paper presents the results of a biomonitoring study to evaluate the environmental impact of airborne emissions from a municipal solid waste landfill in central Italy. Concentrations of 11 heavy elements, as well as photosynthetic efficiency and cell membrane integrity were measured in Evernia prunastri lichens transplanted for 4 months in 17 monitoring sites around the waste landfill. Heavy element contents were also determined in surface soils. Analytical data indicated that emissions from the landfill affected Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn concentrations in lichens transplanted within the landfill and along the fallout direction. In these sites moderate to severe accumulation of these heavy elements in lichens was coupled with an increase in cell membrane damage and decrease in photosynthetic efficiency. Nevertheless, results indicated that landfill emissions had no relevant impact on lichens, as heavy element accumulation and weak stress symptoms were detected only in lichen transplants from sites close to solid waste. The appropriate management of this landfill poses a low risk of environmental contamination by heavy elements.

1   **Heavy element accumulation in *Evernia prunastri* lichen transplants**  
2   **around a municipal solid waste landfill in central Italy**

3  
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36 **ABSTRACT**

37 This paper presents the results of a biomonitoring study to evaluate the environmental  
38 impact of airborne emissions from a municipal solid waste landfill in central Italy.  
39 Concentrations of 11 heavy elements, as well as photosynthetic efficiency and cell  
40 membrane integrity were measured in *Evernia prunastri* lichens transplanted for 4  
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48 accumulation and weak stress symptoms were detected only in lichen transplants from  
49 sites close to solid waste. The appropriate management of this landfill poses a low risk  
50 of environmental contamination by heavy elements.

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52 *Keywords:* Lichens; Solid waste landfill; Heavy elements; Biomonitoring; Soils.

53

## 54 **1. Introduction**

55 Landfilling is currently the main method of solid waste disposal worldwide, as it is the  
56 simplest, cheapest and most cost-effective practice to store municipal solid waste  
57 (Giusti, 2009). However, the disposal of municipal solid waste in landfills causes  
58 concern about possible adverse effects on the environment and human health, such as  
59 fires and explosions, unpleasant odours, damage to vegetation, as well as air, soil and  
60 groundwater contamination (Chrysikou et al., 2008; El-Fadel et al., 1997; Vrijheid,  
61 2000). These adverse effects are mainly related to the release of inorganic and organic  
62 contaminants from the waste landfills via leachate and production of gases and  
63 particulate matter (Bogner and Matthews, 2003; Chalvatzaki et al., 2010; Koshy et al.,  
64 2009). Much attention has therefore been given to landfill emissions affecting air  
65 quality, and the EU has recently prescribed strict regulations on waste disposal in  
66 landfills (European Union, Directive 2008/98/EC).

67 Gas emissions from municipal solid waste landfills are a complex mixture of  
68 contaminants such as carbon dioxide, methane, hydrogen sulphide, nitrous compounds  
69 and hazardous volatile organic compounds (i.e., polycyclic aromatic hydrocarbons). The  
70 characteristics of landfill particulate matter reflect the nature and chemical composition  
71 of the disposed waste. Several contaminants such as toxic heavy elements (i.e., Pb, Cr,  
72 Cd and Zn) are associated with the airborne particles released from the landfill (Koshy  
73 et al., 2009). Municipal solid waste landfill is thus a reservoir and source of several  
74 inorganic and organic contaminants in the surface environment.

75 In the landfill, particulate matter is mainly generated by re-suspension and dispersal by  
76 wind of decomposed and altered waste materials. It is also generated by mechanical  
77 processes linked to landfill management such as: i) the movement of dustcarts and  
78 vehicles over previously deposited waste; ii) the tipping, sorting and compaction of  
79 waste by bulldozers; iii) the stockpiling of soil and rubble required for daily waste  
80 coverage (Chalvatzaki et al., 2010; Fitz and Bumiller, 2000).

81 Gaseous and particulate emissions from municipal solid waste landfill may fall down  
82 close to the source and accumulate contaminants in soil (Iwegbue et al., 2010; Rizo et  
83 al., 2012; Waheed et al., 2010). The contaminants accumulated in soil may be released  
84 into watercourses and groundwater (Rajkumar et al., 2010) and be taken up by  
85 vegetables and animals, thus constituting a threat to living organisms, including humans  
86 (Acosta et al., 2011; Gupta et al., 2010; Krishna and Govil, 2007).

87 The levels and distribution of contaminants should be monitored in any study assessing  
88 the environmental impact of activities related to the management of municipal solid  
89 waste in landfill (Biswas et al., 2010; Paoli et al., 2012). In this context, lichens are  
90 valuable biomonitoring tools for evaluating air quality and controlling contamination in  
91 areas around waste landfills (Nimis et al., 2002; Pirintsos and Loppi, 2008).

92 Lichens are one of the most sensitive components of the ecosystem. These organisms  
93 are able to absorb and accumulate contaminants in their thallus, intercepting airborne  
94 materials and solutes of wet and dry precipitations, as well as atmospheric gases (Nash,  
95 2008). Lichens are thus widely used as biomonitors and bioaccumulators of  
96 contaminants in air quality and environmental contamination surveys (i.e., Conti and  
97 Cecchetti, 2001; Loppi et al., 1997; Nimis et al., 2002; Wolterbeek, 2002).

98 Lichens are symbiotic, perennial and slow-growing organisms that maintain a fairly  
99 uniform morphology over time. They are highly dependent on the atmosphere for their  
100 macro and micronutrients. However, due to their large surface area, relatively low  
101 growth rate, and lack of waxy cuticle and stomata, lichens can also absorb and  
102 accumulate inorganic and organic contaminants such as heavy elements directly from  
103 the air. Moreover, several authors have shown that a direct relationship exists between  
104 heavy element concentrations in thalli and those in the environment (Bari et al., 2001;  
105 Ng et al., 2006; Rodrigo et al., 1999; Sloof, 1995).

106 Lichens are widely used in biomonitoring studies, which employ either native species,  
107 that is species naturally present in the study area (Augusto et al., 2007; Blasco et al.,  
108 2008), or transplanted species (Baptista et al., 2008; Bergamaschi et al., 2007; Frati et  
109 al., 2005; Sorbo et al., 2008). The latter technique involves the use of thalli removed  
110 from areas with little or no contamination and transplanted for a period in selected  
111 monitoring sites. Transplant techniques are frequently used when lichens are scarce or  
112 absent in the study area.

113 Changes in the physiology and chemical composition of lichen transplants provide  
114 information on the concentration of inorganic and organic contaminants in the air  
115 (Demiray et al., 2012; Guttova et al., 2011; Oztetik and Cicek, 2011). In urban and  
116 industrial settings, the accumulation of air contaminants such as heavy elements can  
117 damage the photosynthetic apparatus (Piccotto et al., 2011; Zambrano and Nash, 2000),  
118 decrease the integrity of cell membranes (Paoli et al., 2011) and induce oxidative stress  
119 (Carreras et al., 2009; Oztetik and Cicek, 2011) in transplanted lichens.

120 Lichens accumulate heavy elements through uptake of soluble species in wet  
121 depositions and trapping of airborne particles (Williamson et al., 2004). Trapped  
122 particles can remain within lichen thalli over long periods of time and may be leached  
123 out by acid precipitation or lichen organic compounds (Brown, 1987). As lichens lack a  
124 vascular system and roots, there is no interaction with the substratum. This feature  
125 eliminates any doubts as to the origin of contaminants, an issue when vascular plants are  
126 used to biomonitor air quality.

127 Besides being useful bioindicators, these characteristics make lichens very sensitive to  
128 changes in the chemical composition of air. Lichens can thus serve as “early-warning”  
129 indicators of environmental changes and are very helpful in monitoring spatial patterns  
130 and temporal trends in heavy element deposition and accumulation (Bennett and  
131 Wetmore, 1999, 2000).

132 The study determined some physiological parameters (photosynthetic efficiency and  
133 electrical conductivity) and concentrations of 11 heavy elements (As, Cd, Co, Cr, Cu,  
134 Ni, Pb, Sb, Tl, V and Zn) in transplants of *Evernia prunastri* (L.) Ach. lichen and in  
135 surface soils collected within and around a municipal solid waste landfill in central  
136 Italy. Variations in photosynthetic efficiency and cell membrane integrity, as well as the  
137 accumulation of heavy elements in transplanted lichens were used to assess the  
138 environmental impact of emissions from the municipal solid waste landfill and define  
139 the extent of heavy element distribution in air.

140 This lichen biomonitoring study contributes to understanding of how municipal solid  
141 waste landfills affect air quality. To our knowledge, few researches have focused on this  
142 topic (Paoli et al., 2012; Protano et al., 2014). The study also provides analytical data on  
143 toxic heavy elements in lichens such As, Sb and Tl, which are generally little  
144 investigated in such surveys.

145

146

## 147 **2. Material and methods**

148

### 149 **2.1. Study area**

150 The study area is centred on the Cà Mascio municipal solid waste landfill (MSWL),  
151 located about 1 km NNW of the urban centre of Montecalvo in Foglia (Province of  
152 Pesaro and Urbino, Marche) in central Italy (Fig. 1). The landfill is located in a hilly  
153 zone with reliefs between 200 and 250 m a.s.l. The land is mostly used for agriculture

154 (cereals), but there are also pastures and woodlands. The prevalent direction of winds is  
155 from SSW and SW (Fig. 1).

156 In the study area, pliocenic marine sediments belonging to the Argille azzurre formation  
157 crop out. This lithostratigraphic unit mainly consists of blue-gray clays and marly clays,  
158 with interbedded yellowish sandstones and silty clays.

159 According to the Italian law (Italian Legislative Decree n° 36/2003), the Cà Mascio  
160 landfill is classified as “landfill for municipal and not hazardous waste”. This landfill  
161 consists of seven batches: the old batches, numbered from 1 to 6, were used from 1984  
162 to 2000, and overall they contain about 600,000 m<sup>3</sup> of solid waste. These old batches  
163 were covered by a layer of soil and vegetation. The batch 7 was utilized since 2001 and  
164 is still in use when this research was carried out (2011).

165

## 166 **2.2. Lichen sampling, transplant and laboratory treatment**

167 The lichen transplantation is an effective technique widely used for the determination of  
168 heavy element accumulation and for assessing the variation of physiological  
169 characteristic (Ayrault et al., 2007; Conti et al., 2004; Godinho et al., 2008; Mikhailova,  
170 2002; Pacheco et al., 2008 Sloof, 1995).

171 The use of lichen transplants in place of native lichens (lichens grown *in situ*) is mainly  
172 due to the following reasons: absence of native lichens in the study area, uniformity of  
173 the lichen species utilized in biomonitoring and of the exposure period, possibility to  
174 choose the monitoring sites and their number, knowledge of the concentration of  
175 chemical elements before exposure, possibility to evaluate the accumulation trend of  
176 chemical elements.

177 For these reasons, and especially because of the absence of native lichens, the transplant  
178 technique was employed to assess the influence of Cà Mascio landfill emissions on the  
179 air distribution of some heavy elements of environmental concern.

180 In February 2011 thalli of the fruticose *Evernia prunastri* (L.) Ach. lichen were  
181 randomly collected from tree twigs in a woody zone far from contamination sources,  
182 located about 25 km S of Siena (central Italy). The *E. prunastri* lichen was chosen  
183 because it is easily collected and transplanted. In addition, this species is one of the  
184 most used lichens in biomonitoring studies due to its bioaccumulation capacity and  
185 widespread distribution (Garty, 2001; Guttova et al., 2011; Loppi and Frati, 2006; Paoli  
186 et al., 2011).

187



## Figure 1

The samples of native lichens were immediately transferred to laboratory in polyethylene bags, and left 48 h to acclimate in a climatic-chamber at 15 °C with relative humidity at  $60 \pm 5\%$  and photoperiod of 12 h at  $40 \mu\text{mol m}^{-2} \text{s}^{-1}$  photons of photosynthetically active radiation. In laboratory, the lichen samples were carefully cleaned with plastic tweezers under a binocular microscope to remove extraneous materials such as moss, leaves, bark pieces and soil particles. Finally, the lichen samples were rinsed with ultra-pure water to remove smaller particles from the surface of thalli and were stored in paper bags. The samples used for analytical determinations ( $n=4$ ) were frozen at -20 °C.

In the study area, the samples of native lichens were transplanted in sites located at different distance from the Cà Mascio MSWL and positioned according to the prevalent directions of winds. Lichen transplants were exposed in 17 sites clustered into the following 4 groups (Fig. 1): landfill sites situated around the Cà Mascio MSWL within a distance of 100 m ( $n=5$ ); fall-out sites placed along a NNE transect aligned with the prevalent direction of winds, at a distance of between 50 and 500 m from the landfill ( $n=4$ ); rural sites not affected by the direct influence of the landfill fall-out, at a distance of 250 and 500 m from the plant ( $n=4$ ); background sites distant from contamination sources including the landfill, at distances of more than 1500 m from the stored waste ( $n=4$ ).

In each monitoring site, a tree was selected and three lichen thalli were fixed on the branches at a height of about 2.5 m above the ground, using plastic strings. Lichens were exposed for 4 months, from March to June 2011. At the end of the exposure period, lichen samples were detached from the tree and placed in clean plastic bags to avoid contamination.

In the laboratory transplanted lichens were stored in paper bags and frozen at -20 °C. Before the analysis lichen thalli were removed from the freezer and left at room temperature for about 15 minutes and were then carefully cleaned with plastic tweezers under a binocular microscope to remove extraneous material deposited onto the surface. Samples were not washed as the washing procedure may alter their chemical composition (Bettinelli et al., 1996).

Native and transplanted lichens were air-dried and immersed in liquid nitrogen, pulverized and homogenized using a ceramic mortar and pestle. Only peripheral parts of

thalli (up to 2 cm from lobe tips) were used for analysis. Each transplanted sample was a mixture of all lichen thalli exposed in the monitoring site.

### **2.3. Lichen analysis**

About 200 mg of powdered lichen material were solubilised with a mixture of 6 mL HNO<sub>3</sub> 70%, 1 mL H<sub>2</sub>O<sub>2</sub> 30% and 0.2 mL HF 60%, in Teflon bombs placed in a microwave digestion system (Milestone Ethos 900) for 30 min. Ultra-pure trace-grade reagents were employed and ultra-high-purity water was used for dilution. Solutions were filtered, diluted to 50 mL and stored in PE bottles before analysis. A certified reference material and a blank of the employed reagents were included in each digestion batch.

The concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, V and Zn in native and transplanted lichens were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using the Perkin Elmer Sciex Elan 6100 spectrometer. Concentrations were expressed as dry weight basis (mg/kg dry weight).

The Standard Reference Material IAEA-336 (Trace and minor elements in lichen) of the International Atomic Energy Agency (Vienna, Austria) was used to check the analytical accuracy. The recoveries were from 90% (Co) to 106% (Cr). Precision was determined by five replicate analyses of each lichen sample and expressed as percent relative standard deviation (% RSD). The analytical precision was within 10% for all the analyzed chemical elements.

### **2.4. Integrity of cell membranes**

To check the integrity of the plasma membrane, the difference in electrical conductivity was carried out by placing a fragment of lichen thalli in deionized water (Munzi et al., 2009; Paoli et al., 2011). This is a simple test to assess the integrity of the plasma membrane: the value of electrical conductivity is related to the degree of damage endured by cell membranes (Marques et al., 2005). In fact, permeability is altered in damaged cell membranes and electrolyte leakage (mainly K<sup>+</sup>) occurs (McKersie et al., 1982).

Each lichen sample (about 100 mg of young portion of thalli up to 2 cm from lobe tips) was rinsed several times in deionised water for 3-5 seconds, until stable values of electrical conductivity were obtained. This rinsing was carried out to remove the particles deposited onto the lichen surface that contribute to the electrical conductivity

of sample. Afterwards, the lichen sample was immersed into a glass bottle with 50 mL of deionised water and shaken for 60 min. The electrical conductivity of water was measured before and after the lichen was soaked using the conductivity-meter Delta Ohm HD/8706. Thalli were thus boiled for 10 min at 100 °C to determine the total disruption of cell membranes, and electrical conductivity of water was measured again. The values of electrical conductivity were expressed in  $\mu\text{S cm}^{-1} \text{ mL mg}^{-1}$  dry weight at a normalized temperature of 25 °C.

## **2.5. Photosynthetic efficiency**

Photosynthetic efficiency was measured with a plant efficiency analyzer (Handy PEA, Hansatech Instruments Ltd) on well-wet and dark-adapted lichen samples, applying a saturating flash of red light (650 nm) of  $2400 \mu\text{mol s}^{-1} \text{ m}^{-2}$  for 1 sec. To block the physiological state at the time of the end of the transplant, lichen samples were air-dried and stored at -20 °C in paper bags. Before measurements, a physiological recovery of the samples was carried out. To avoid any osmotic stress by air humidity during de-freezing, lichens were left in dry ambient conditions for 15 min. Thalli were subsequently sprayed with water until wet and the water in excess was removed. Samples were then stored at 4 °C in the dark for 24 h. The outermost 2 cm of thalli was randomly selected for measurements. The selected lichen material was placed within a clip for 10 min to allow full dark adaptation of the photosynthetic pigments. The ratio of variable fluorescence to the maximal fluorescence ( $F_v/F_M$ ) was used to assess the potential quantum yield of primary photochemistry of PS II (Maxwell and Johnson, 2000).

## **2.6. Soil sampling, laboratory treatment and analysis**

In the 17 sites where lichens were exposed, surface soil samples (5 cm deep) were collected. Each soil sample was a composite sample consisting of 3 sub-samples taken a few metres apart.

In laboratory litter material was manually removed and soil samples were dried at +40 °C and sieved through a 2 mm mesh. Homogenization was carried out by quartering and pulverization procedures. Soil samples were solubilised by acid digestion adding 2 mL  $\text{HNO}_3$  70%, 2 mL HF 60% and 1 mL  $\text{H}_2\text{O}_2$  30% to 250 mg of powdered soil. Ultra-pure trace-grade reagents were used for soil preparation. The mixture was processed in Teflon bombs using a microwave lab station. The solution was filtered and diluted with

290 ultra-pure water to a final volume of 100 mL. A certified reference material and a blank  
291 of the employed reagents were included in each digestion batch.

292 The contents of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, V and Zn in soil samples expressed  
293 as dry weight basis (mg/kg dry weight), were determined by ICP-MS.

294 The accuracy of analytical determinations was checked using the NIST 2709 (San  
295 Joaquin soil) and NIST 2710 (Montana soil) certified reference materials of the  
296 National Institute of Standards and Technology. The recoveries were from 91% (Co) to  
297 106% (Sb). The precision was determined by five replicate analyses of each soil sample  
298 and expressed as percent relative standard deviation (% RSD). The analytical precision  
299 was within 8% for all the analyzed chemical elements.

300

### 301 ***2.7. Data interpretation and statistical analysis***

302 In order to evaluate the accumulation of heavy elements in transplanted lichens, the  
303 Exposed to Control (EC) ratio was utilized. The EC ratio is calculated as the ratio  
304 between the element concentration in lichen after its exposure in the study area and in  
305 non-exposed control lichen (Fрати et al., 2005). To assess the variations in accumulation  
306 or loss of heavy elements in transplanted thalli, an interpretative scale consisting of 5-  
307 class was used: severe loss  $EC=0.00-0.25$ , loss  $EC=0.25-0.75$ , normal  $EC=0.75-1.25$ ,  
308 accumulation  $EC=1.25-1.75$  and severe accumulation  $EC>1.75$ .

309 The Shapiro-Wilks W test was applied to verify the normal distribution of analytical  
310 data. Statistical differences between datasets were determined through the Student's t  
311 test for data normally distributed, and the Mann-Whitney U test for data not normally  
312 distributed, at the 5% significance level. Spearman's correlation test was used to  
313 identify the significant correlations among the concentrations of heavy elements and the  
314 values of physiological parameters in lichens.

315

## 316 **3. Results**

317

### 318 ***3.1. Heavy element accumulation in transplant lichens***

319 Table 1 reports the As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, V and Zn concentrations (as  
320 mg/kg dry weight) both in native specimens of *Evernia prunastri* collected from an  
321 uncontaminated habitat in the Province of Siena (control site) and in transplanted thalli  
322 after 4 months of exposure in the background, rural, fallout and landfill sites of the Cà  
323 Mascio MSWL area.

**Table 1**

Heavy element concentrations in transplanted lichens showed the following distribution patterns: i) the mean values of Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn concentrations decreased according to the features of the monitoring sites, as follows: landfill > fallout > rural > background; ii) As, Tl and V concentrations were rather homogeneous in all the selected sites.

Statistical analysis revealed that the Cd, Cr, Sb and Zn concentrations in landfill, fallout and rural transplants differ significantly with respect those in native lichens from control site ( $p < 0.05$ ; Tab. 1). Co, Cu and Pb concentrations in lichens from landfill and fallout sites and Ni concentrations in transplants from landfill sites differed significantly from those in control site. There were no significant differences between As, Tl and V concentrations in lichens exposed in landfill, fallout and rural sites and those in native lichens. For all the analyzed heavy elements, no statistically significant differences were found between concentrations in transplanted thalli from background sites and concentrations in native lichens from control site.

The lichen transplants located along a transect in the direction of prevailing winds showed an evident decrease in concentrations of several heavy elements (mainly Cr, Pb and Sb) within about 150 m of the perimeter of the landfill.

Based on the mean EC ratios, Cr, Pb, Sb and Zn showed severe accumulation ( $EC > 1.75$ ) in lichens exposed both in landfill and fallout sites (Fig. 2), and moderate accumulation ( $1.25 > EC > 1.75$ ) in transplants located in rural areas (except for Sb). For these heavy elements the highest EC ratios (1.96-11.6) pertained to lichens transplanted within a 100 m range of the Cà Mascio MSWL; the accumulation of Cr, Pb, Sb and Zn in the exposed lichens therefore decreased from landfill to rural sites.

Cd, Co, Cu and Ni accumulation in exposed lichens was generally severe in the landfill sites and moderate in fallout sites (Fig. 2). No accumulation of these heavy elements was detected in rural areas (except for Cd).

Analytical data indicated that As, Tl and V were not accumulated in lichens exposed in the monitoring sites of the study area. All heavy element concentrations (except Cu) determined in lichen transplants from background sites were similar to those of native control samples (EC from 0.75 to 1.25).

In summary, EC ratios indicated that Cr, Pb, Sb and Zn were the main airborne contaminants deriving from Cà Mascio MSWL emissions. Taking into account the EC

358 ratios in lichen transplants from landfill sites, the order of accumulation was the  
359 following:  $Sb \approx Cr > Pb > Zn > Cd \approx Cu > Co > Ni$ . The transplants in the landfill and  
360 fallout sites showed the highest levels of accumulation, whereas heavy element  
361 concentrations in lichens from rural and background sites were generally comparable to  
362 those measured in native lichens from an uncontaminated area of central Italy.

363

364

365

## Figure 2

### 366 *3.2. Physiological parameters of transplant lichens*

367 As shown in Figure 3a, the values of electrical conductivity in lichens exposed in the  
368 landfill and fallout sites were significantly higher ( $p < 0.05$ ) than those of native lichens  
369 in the control site. Conversely, there was no statistically significant difference between  
370 the electrical conductivity measured in transplants from rural and background sites and  
371 that measured in the control site, although the mean values of this parameter were  
372 slightly higher in exposed thalli.

373 The photosynthetic efficiency ( $F_V/F_M$ ) of transplanted lichens was lower than that of  
374 samples from the control site (Figure 3b). The lowest  $F_V/F_M$  ratios pertained to lichens  
375 exposed in the landfill and fallout sites, and statistically significant differences were  
376 found with respect to the values measured in the native control thalli ( $p < 0.05$ ).

377

378

## Figure 3

379

### 380 *3.3. Correlation among heavy element concentrations and physiological parameters* 381 *in lichen transplants*

382 Table 2 reports the Spearman correlation coefficients among heavy element  
383 concentrations and physiological parameters (electrical conductivity and  $F_V/F_M$ ) in  
384 lichens exposed in all the monitoring sites within the Cà Mascio MSWL area.

385

386

## Table 2

387

388 The most significant positive correlations ( $p < 0.001$ ) were found among the  
389 concentrations of heavy elements most accumulated by lichens, i.e. Cd, Cr, Cu, Pb, Sb  
390 and Zn. Electrical conductivity was positively correlated with the concentrations of  
391 these contaminants ( $p < 0.001$ ). Significant negative correlations ( $p < 0.01$ ) were found  
392 among photosynthetic efficiency and Cd, Cr, Cu, Pb, Sb and Zn concentrations. These

findings are consistent with the fact that higher electrical conductivity and lower photosynthetic efficiency values correspond to higher heavy element accumulation by lichens.

396

### 3.4. Heavy element contents in soils

Table 3 reports the As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, V and Zn contents (as mg/kg dry weight) in soil samples collected from the 17 sites where lichens were exposed. Heavy element contents in soil samples were compared to the respective local natural variability in soil (geochemical background) in order to evaluate the input of emissions from the Cà Mascio MSWL. For this purpose, the enrichment factor (EF) was calculated as  $EF = [C]_{\text{element}} / [C]_{\text{background}}$ , where  $[C]_{\text{element}}$  = element concentration in the soil sample and  $[C]_{\text{background}}$  = maximum value of the local geochemical background. Local geochemical background levels of heavy elements were assessed in soil samples collected from the background sites ( $n=4$ ) located far away from the Cà Mascio MSWL and other possible sources of contamination.

As shown in Table 3, heavy element contents in soils from the study area were rather homogeneous. Using the EF scale proposed by Sutherland (2000), no enrichment was found: EF values were usually less than 1, with mean values from 0.7 for Co, Cu and Pb 1.1 for As. These results suggest that heavy element contents in soils collected close to the landfill (landfill sites) and along a transect in the direction of prevailing winds (fallout sites) were within their respective local natural variability in soil. Therefore, the heavy element contents in soils from the study area must be considered geogenic, due to natural factors and processes such as the nature of the parent rock (clays and marly clays of the Argille azzurre formation), and the features of weathering and pedogenesis. Heavy element concentrations in soil samples were constantly below contamination thresholds for green public, private and residential areas set by the Italian guidelines (Italian Legislative Decree n° 152/2006; Tab. 4). Vanadium contents slightly above its contamination threshold (90 mg/kg) were found in 6 soil samples randomly distributed in the study area.

422

### Table 3

424

425

426

#### 4. Discussion

It is known that the chemical composition of lichens mainly depends on the availability of chemicals in the environment and that lichens respond to environmental changes (Bačkor and Loppi, 2009; Nimis et al., 2002). Lichens are able to head off and accumulate heavy elements from wet depositions and trapped airborne particles. This ability may be affected by environmental and climatic conditions as well as by the exposure time (Wolterbeek, 2002). Garty et al. (1993; 2001) demonstrated that thalli transplanted from uncontaminated to contaminated areas undergo changes, mainly due to the effects of contaminants. Moreover, several studies have shown that lichens transplanted close to contamination sources can uptake significant amounts of heavy elements within a few weeks or months (Bargagli, 1998; Conti et al., 2004; Paoli et al., 2011).

Chalvatzaki et al. (2010) recently pointed out that waste management techniques such as composting, unloading and sorting of waste and dust re-suspension, as well as meteorological conditions (wind direction and temperature) affect local concentrations of PM<sub>10</sub> in the surroundings of a municipal solid waste landfill. Furthermore, Koshy et al. (2009) reported that Cr, Ni, Pb and Zn were the main heavy elements in the particulate matter emitted from a MSWL in the UK. Likewise, Paoli et al. (2012) measured high Cd, Cr and Ni concentrations in *F. caperata* thalli collected near a MSWL in Italy.

Analytical data from this work indicated moderate to severe enrichments in heavy elements such as Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn, in lichens transplanted in the landfill and fallout sites. Conversely, lichens exposed in background sites showed no variations in heavy element concentrations with respect to the non-exposed control thalli. As, Tl and V were not accumulated in any of the lichens exposed in the monitoring sites. This finding suggested a geogenic source for the latter elements, in agreement with the results of a study carried out on soils around the largest MSWL in Europe (Malagrotta, Rome; Barbieri et al., 2014).

The highest EC ratios for Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn were measured in lichen transplants within the municipal solid waste landfill and along a transect in the direction of fallout. This evidence suggested that the airborne emissions from the Cà Mascio MSWL affected the heavy element concentrations in air, mainly Cr, Pb, Sb and Zn. This finding agrees with the results of Prechthai et al. (2008), who measured high Cd, Cr, Cu, Pb and Zn concentrations in municipal solid waste from a dumpsite in Thailand.



461 The main sources of these heavy elements were plastics, rubber, electronic equipment  
462 and non-ferrous metallic components (Prudent et al., 1996). In accordance with similar  
463 studies (Nannoni et al., 2015; Paoli et al., 2012; Protano et al., 2014), we did not find a  
464 specific heavy element acting as tracer of emissions from the Cà Mascio MSWL.

465 The moderate accumulation of Cu and Zn in lichens from the background sites attested  
466 to a wider distribution of these elements in the study area, probably in relation to the  
467 spraying of fertilizers and pesticides.

468 In agreement with Paoli et al., 2012; Protano et al., 2014, we conclude that airborne  
469 emissions from the Cà Mascio MSWL caused the accumulation of several heavy  
470 elements in lichens, mainly Cr, Pb, Sb and Zn. However, the landfill had a rather  
471 modest impact, as the highest concentrations and enrichments in heavy elements were  
472 found in lichens within about 150 m of the municipal solid waste landfill. Likewise,  
473 Paoli et al. (2012) revealed an increased deposition of some heavy elements limited to  
474 sites facing a municipal solid waste landfill in Italy.

475 Electrical conductivity is a good indicator of air contamination, as this parameter  
476 reveals the degree of damage to cell membranes in lichens (Munzi et al., 2009; Paoli et  
477 al., 2011; Pearson and Henriksson, 1981). This is because the plasma membrane is the  
478 first site of biological interaction with toxic substances, including heavy elements.

479 Electrical conductivity values from this study reveal that the damage to cell membranes  
480 of lichens exposed in the monitoring sites differs from that of lichens in control site.

481 The electrical conductivity of transplanted lichens varied as a function of site location:  
482 the highest values characterized the thalli exposed in the landfill and fallout sites,  
483 suggesting that the highest degree of cell membrane damage concerned the transplants  
484 within the Cà Mascio MSWL and the sector most affected by landfill emissions. These  
485 differences may be due to the higher heavy element concentrations in the landfill and  
486 fallout dispersion areas. Garty et al. (1998a) observed a similar difference in electrical  
487 conductivity between lichens exposed in industrial sites and urban centres and those  
488 exposed in rural sites.

489 The significant positive correlations between the concentrations of the main heavy-  
490 element contaminants in the study area (Cr, Pb, Sb and Zn) and the values of electrical  
491 conductivity in exposed lichens confirmed the hypothesis above. This is consistent with  
492 the results of other studies that found higher values of electrical conductivity in lichen  
493 transplants affected by heavy element accumulation (Adamo et al., 2003; Garty et al.,

2002; Garty et al., 1998b). Paoli and Loppi (2008) also observed that cell membrane damage in *E. prunastri* lichens was correlated with air quality.

Photosynthetic activity, expressed as  $F_V/F_M$ , has often been employed in biomonitoring studies as it is considered a general index of the health of lichens and can be used to assess their vitality. The photosynthetic activity of lichens in the field is influenced by several factors, including environmental conditions and anthropogenic disturbances (i.e., high levels of  $SO_2$ ,  $NO_x$  and heavy elements). The accumulation of certain air contaminants in lichen thalli is assumed to coincide with low  $F_V/F_M$  ratios. The  $F_V/F_M$  ratio of lichens growing in uncontaminated areas (healthy lichens) usually varies from 0.5 to 0.76 (Jensen and Kricke, 2002), and values lower than 0.5 reveal that lichens were exposed to stress. Several studies (i.e., Garty et al., 2000; Karakoti et al., 2014) reported low  $F_V/F_M$  ratios for lichens characterized by high heavy element concentrations.

The  $F_V/F_M$  ratios for lichens exposed in the landfill and fallout sites suggested that environmental conditions within and around the Cà Mascio MSWL caused a decrease in photosynthetic activity. However, the  $F_V/F_M$  ratios of transplanted lichens ranged from 0.51 to 0.66, in agreement with non-stressed conditions for lichens (Jensen and Kricke, 2002). As photosynthetic activity is considered a sensitive indicator of contamination stress, this finding suggested that airborne heavy element contamination due to landfill emissions was spatially limited in the study area and not sufficiently severe to determine significant changes in this physiological parameter.

Lastly, analytical data revealed that the selected heavy elements were not accumulated in soils surrounding the Cà Macio MSWL, despite the fact that the landfill site has been operating for 30 years. This finding could be ascribed to the fact that the contribution of heavy elements in soil due to fallout and re-suspension can be masked by run-off and leaching processes affecting the uppermost part of the soil profile (first 5 cm). Our results agree with those of Jain et al. (2005), who report that the concentrations of some heavy elements in soils sampled around a municipal solid waste landfill in Florida were below US regulatory thresholds. Likewise, Nannoni et al. (2015) and Amadi Akobundu and Nwankwoala (2013) did not detect accumulation of heavy elements in soils close to municipal waste dumpsites in Italy and Nigeria, respectively.

## 528    **5. Conclusions**

529    Analytical data indicated that airborne emissions from the Cà Mascio municipal solid  
530    waste landfill affected the Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn concentrations in *Evernia*  
531    *prunastri* lichens transplanted for 4 months within and around the landfill. Moderate to  
532    severe accumulation of these heavy elements was detected in lichens exposed within the  
533    landfill and along the direction of fallout. In these sites heavy element accumulation  
534    coupled with an increase in cell membrane damage and decrease in photosynthetic  
535    efficiency in lichens, was mainly due to the airborne particles generated by re-  
536    suspension and dispersal of waste materials.

537    Our results excluded that the Cà Mascio MSWL had a significant impact on heavy  
538    element levels in the study area. This statement is supported by the following evidences:  
539    (i) heavy elements accumulated only in the lichen transplants exposed within the  
540    landfill and along the direction of fallout up to about 150 m from the landfill; (ii)  
541    emissions from the solid waste caused weak stress symptoms only in lichens exposed in  
542    the landfill and fallout sites; (iii) sites far from the landfill (rural and background) were  
543    not affected by emissions from the MSWL. Moreover, in 30-years of waste  
544    management at the Cà Mascio landfill, there has been no accumulation of heavy  
545    elements in the surrounding soils, as concentrations were within the respective local  
546    geochemical background.

547    In conclusion, conditions in the area around the Cà Mascio MSWL are not remarkably  
548    stressful for lichens. Therefore, an appropriate landfilling management poses a  
549    relatively low risk of environmental contamination by heavy elements. Our research  
550    confirmed that lichens are very sensitive to even small changes in atmospheric  
551    concentrations of heavy elements.

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## 553    **References**

- 554    Acosta J.A., Faz A., Martínez-Martínez S., Arocena J.M., 2011. *Enrichment of metals in*  
555        *soils subjected to different land uses in a typical Mediterranean environment*  
556        *(Murcia City, southeast Spain)*. Applied Geochemistry 26, 405-414.
- 557    Adamo P., Giordano S., Vingiani S., Cobianchi R.C., Violante, P., 2003. *Trace element*  
558        *accumulation by moss and lichen exposed in bags in the city of Naples (Italy)*.  
559        Environmental Pollution 122, 91-103.
- 560    Amadi Akobundu N. and Nwankwoala H.O., 2013. *Evaluation of heavy metal in soils*  
561        *from Enyimba dumpsite in Aba, southeastern Nigeria using contamination factor*  
562        *and geo-accumulation index*. Energy and Environment Research 3, 125-134.
- 563    Augusto S., Pereira M.J., Soares A., Branquinho C., 2007. *The contribution of*  
564        *environmental biomonitoring with lichens to assess human exposure to dioxins*.  
565        International Journal of Hygiene and Environmental Health 210, 433-438.
- 566    Ayrault S., Clochiatti R., Carrot F., Daudin L., Bennett J.P., 2007. *Factors to consider*  
567        *for trace element deposition biomonitoring surveys with lichen transplants*.  
568        Science Total Environmental 372, 717-727.
- 569    Bačkor M. and Loppi S., 2009. *Interactions of lichens with heavy metals*. Biologia  
570        Plantarum 53, 214-222.
- 571    Baptista M.S., Vasconcelos M.T., Cabral J.P., Freitas M.C., Pacheco A.M., 2008.  
572        *Copper, nickel and lead in lichen and tree bark transplants over different periods*  
573        *of time*. Environmental Pollution 151, 408-413.
- 574    Barbieri M., Sappa G., Vitale S., Parisse B., Battistel M., 2014. *Soil control of trace*  
575        *metals concentrations in landfills: A case study of the largest landfill in Europe,*  
576        *Malagrotta, Rome*. Journal of Geochemical Exploration 143, 146-154.
- 577    Bargagli R., 1998. *Trace Elements in Terrestrial Plants: An Ecophysiological Approach*  
578        *to Biomonitoring and Biorecovery*, ed. Springer-Verlag, Heidelberg.
- 579    Bari A., Rosso A., Minciardi M.R., Troiani F., Piervittori R., 2001. *Analysis of heavy*  
580        *metals in atmospheric particulates in relation to their bioaccumulation in*  
581        *explanted Pseudevernia furfuracea thalli*. Environmental Monitoring Assessment  
582        69, 205-220.
- 583    Bennett J.P. and Wetmore C.M., 1999. *Changes in element contents of selected lichens*  
584        *over 11-years in northern Minnesota, USA*. Environmental and Experimental  
585        Botany 41, 75-82.

- 586 Bennett J.P. and Wetmore C.M., 2000. *16-Years trends in elements of lichens at*  
 587 *Theodore Roosevelt National Park, North Dakota*. Science Total Environment  
 588 263, 231-241.
- 589 Bergamaschi L., Rizzio E., Giaveri G., Loppi S., Gallorini M., 2007. *Comparison*  
 590 *between the accumulation capacity of four lichen species transplanted to an*  
 591 *urban site*. Environmental Pollution 148, 468-476.
- 592 Bettinelli M., Spezia S., Bizzarri G., 1996. *Trace element determination in lichens by*  
 593 *ICP-MS*. Atomic Spectroscopy 17, 133-141.
- 594 Biswas A.K., Kumar S., Babu S.S., Bhattacharya J.K., Chakrabarti T., 2010. *Studies on*  
 595 *environmental quality in and around municipal solid waste dumpsite*. Resource  
 596 Conservation and Recycling 55, 129-134.
- 597 Blasco M., Domeño C., Nerin C., 2008. *Lichens biomonitoring as feasible methodology*  
 598 *to assess air pollution in natural ecosystems: combined study of quantitative*  
 599 *PAHs analyses and lichen biodiversity in the Pyrenees Mountains*. Analytical and  
 600 Bioanalytical Chemistry 391, 759-771.
- 601 Bogner J. and Matthews E., 2003. *Global methane emissions from landfills: new*  
 602 *methodology and annual estimates 1980-1996*. Global Biogeochemical Cycles 17,  
 603 1-18.
- 604 Brown D.H., 1987. *The location of mineral elements in lichens: implications for*  
 605 *metabolism*, in: Peveling E. (Ed.), Progress and Problems in Lichenology in the  
 606 Eighties. Bibliotheca Lichenologica, Berlin, pp. 361-375.
- 607 Carreras H.A., Rodriguez J.H., Gonzalez C.M., Wannaz E.D., Ferreyra F.G., Perez  
 608 C.A., Pignata M.L., 2009. *Assessment of the relationship between total suspended*  
 609 *particles and the response of two biological indicators transplanted to an urban*  
 610 *area in central Argentina*. Atmospheric Environment 43, 2944-2949.
- 611 Chalvatzaki E., Kopanakis I., Kontaksakis M., Glytos T., Kalogerakis N., Lazaridis, M.,  
 612 2010. *Measurements of particulate matter concentrations at a landfill site (Crete,*  
 613 *Greece)*. Waste Management 30, 2058-2064.
- 614 Chrysikou L., Gemenetzi P., Kouras A., Manoli E., Terzi E., Samara C., 2008.  
 615 *Distribution of persistent organic pollutants, polycyclic aromatic hydrocarbons*  
 616 *and trace elements in soil and vegetation following a large scale landfill fire in*  
 617 *Northern Greece*. Environment International 34, 210-225.
- 618 Conti M.E. and Cecchetti G., 2001. *Biological monitoring: lichens as bioindicators of*  
 619 *air pollution assessment - a review*. Environmental Pollution 114, 471-492.

- 620 Conti M.E., Tudino M., Stripeikis J., Cecchetti G., 2004. *Heavy metal accumulation in*  
621 *the lichen Evernia prunastri transplanted at urban, rural and industrial sites in*  
622 *Central Italy*. Journal of Atmospheric Chemistry 49, 83-94.
- 623 Demiray A.D., Yolcubal I., Akyol N.H., Cobanoglu G., 2012. *Biomonitoring of*  
624 *airborne metals using the lichen Xanthoria parietina in Kocaeli province, Turkey*.  
625 Ecological Indicators 18, 632-643.
- 626 El-Fadel M., Findikakis A., Leckie J., 1997. *Environmental impacts of solid waste*  
627 *landfilling*. Environmental Management 50, 1-25.
- 628 European Union, 2008. *Directive 2008/98/EC of the European Parliament and of the*  
629 *Council of 19 November 2008 on waste and repealing certain directives*. Official  
630 Journal of the European Union 312, 3-30.
- 631 Fitz D.R. and Bumiller K., 2000. *Evaluation of watering to control dust in high winds*.  
632 Journal of Air and Waste Management Association 50, 570-577.
- 633 Frati L., Brunialti G., Loppi S., 2005. *Problems related to lichen transplants to monitor*  
634 *trace element deposition in repeated surveys: a case study from Central Italy*.  
635 Journal Atmospheric Chemistry 52, 221-230.
- 636 Garty J., 2001. *Biomonitoring atmospheric heavy metals with lichens: theory and*  
637 *application*. Critical Reviews in Plant Sciences 20, 309-371.
- 638 Garty J., Cohen Y., Kloog N., 1998a. *Airborne elements, cell membranes, and*  
639 *chlorophyll in transplanted lichens*. Journal of Environmental Quality 27, 973-  
640 979.
- 641 Garty J., Karary Y., Harel J., 1993. *The impact of air pollution on the integrity of cell*  
642 *membranes and chlorophyll in the lichen Ramalina duriaei (De Not.) Bagl.*  
643 *transplanted to industrial sites in Israel*. Archives of Environmental  
644 Contamination and Toxicology 24, 455-460.
- 645 Garty J., Kloog N., Cohen Y., 1998b. *Integrity of lichen cell membranes in relation to*  
646 *concentration of air borne elements*. Archives of Environmental Contamination  
647 and Toxicology 34, 136-144.
- 648 Garty J., Tamir O., Cohen Y., Lehr H., Goren A.I., 2002. *Changes in the potential*  
649 *quantum yield of photosystem ii and the integrity of cell membranes relative to the*  
650 *elemental content of the epilithic desert lichen Ramalina maciformis*.  
651 Environmental Toxicology and Chemistry 21, 848-858.
- 652 Garty J., Weissman L., Cohen Y., Karnieli A., Orlovsky L., 2001. *Transplanted lichens*  
653 *in and around the Mount Carmel National Park and the Haifa Bay industrial*

654        *region in Israel: physiological and chemical responses*. Environmental Research  
655        Section 85, 159-176

656        Garty J., Weissman L., Tamir O., Beer S., Cohen Y., Karnieli A., Orlovsky L., 2000.  
657        *Comparison of five physiological parameters to assess the vitality of the lichen*  
658        *Ramalina lacera exposed to air pollution*. Physiologia Plantarum 109, 410-418.

659        Giusti L., 2009. *A review of waste management practices and their impact on human*  
660        *health*. Waste Management 29, 2227-2239.

661        Godinho R.M., Wolterbeek H.Th., Verburg T., Freitas M.C., 2008. *Bioaccumulation*  
662        *behaviour of transplants of the lichen Flavoparmelia caperata in relation to total*  
663        *deposition at a polluted location in Portugal*. Environmental Pollution 151, 318-  
664        325.

665        Gupta D., Chatterjee J.M., Ghosh R., Mitra A.K., Roy S., Sarkar M., 2010.  
666        *Radioisotope-induced EDXRF investigation of elemental uptake in cauliflower*  
667        *grown at MSW-contaminated site*. X-ray Spectrometry 39, 364-371.

668        Guttova A., Lackovicova A., Pisut I., Pisut P., 2011. *Decrease in air pollution load in*  
669        *urban environment of Bratislava (Slovakia) inferred from accumulation of metal*  
670        *elements in lichens*. Environmental Monitoring and Assessment 182, 361-373.

671        ILD, 2003. *Italian Legislative Decree n° 36, January 13, 2003, Implementation of*  
672        *Directive 1999/31/EC on the waste landfill, Official Italian Gazette n° 59, March*  
673        *12, 2003 (in Italian)*.

674        ILD, 2006. *Italian Legislative Decree n° 152, April 3, 2006 and Subsequent*  
675        *Amendments, Environmental Regulations, Official Italian Gazette n° 88, April 14,*  
676        *2006 (in Italian)*.

677        Iwegbue C.M.A., Nwajei G.E., Ogala J.E., Overah C.L., 2010. *Determination of trace*  
678        *metal concentrations in soil profiles of municipal waste dumps in Nigeria*.  
679        Environmental Geochemistry and Health 32, 415-430.

680        Jain P., Kim H., Townsend T.G., 2005. *Heavy metal content in soil reclaimed from a*  
681        *municipal solid waste landfill*. Waste Management 25, 25-35.

682        Jensen M. and Kricke R., 2002. *Chlorophyll fluorescence measurements in the field:*  
683        *assessment of the vitality of large numbers of lichen thalli*, in: Nimis P.L.,  
684        Scheidegger C., Wolseley P.A. (Eds.), *Monitoring with Lichens - Monitoring*  
685        *Lichens*. Kluwer Academy Publishers, Berlin, pp. 327-332.

686        Karakoti N., Bajpai R., Upreti D.K., Mishra G.H., Srivastava A., Nayaka S., 2014.  
687        *Effect of metal content on chlorophyll fluorescence and chlorophyll degradation*

688        *in lichen Pyxine cokes (Sw.) Nyl.: a case study from Uttar Pradesh, India.*  
689        Environmental Earth Science 71, 2177-2183.

690    Koshy L., Jones T., Berube K., 2009. *Characterization and bioreactivity of respirable*  
691        *airborne particles from a municipal landfill.* Biomarkers 14, 49-53.

692    Krishna A.K. and Govil P.K., 2007. *Soil contamination due to heavy metals from an*  
693        *industrial area of Surat, Gujarat, Western India.* Environmental Monitoring and  
694        Assessment 124, 263-275.

695    Loppi S. and Frati L., 2006. *Lichen diversity and lichen transplants as monitors of air*  
696        *pollution in a rural area of central Italy.* Environmental Monitoring and  
697        Assessment 114, 361-375.

698    Loppi S., Giovannelli L., Pirintsos S.A., Putortì E., Corsini A., 1997. *Lichens as*  
699        *bioindicators of recent changes in air quality (Montecatini Terme, Italy).* Ecologia  
700        Mediterranea 23, 53-56.

701    Marques A.P., Freitas M.C., Wolterbeek H.T., Steinebach O.M., Verburg T., De Goeij  
702        J.J.M., 2005. *Cell-membrane damage and element leaching in transplanted*  
703        *Parmelia sulcata lichen related to ambient SO<sub>2</sub>, temperature, and precipitation.*  
704        Environmental Science and Technology 39, 2624-2630.

705    Maxwell K. and Johnson G.N., 2000. *Chlorophyll fluorescence - a practical guide.*  
706        Journal of Experimental Botany 51, 659-668.

707    McKersie B.D., Hucl P., Beversdorf W.D., 1982. *Solute leakage from susceptible and*  
708        *tolerant cultivars of Phaseolus vulgaris following ozone exposure.* Canadian  
709        Journal of Botany 60, 73-78.

710    Mikhailova I., 2002. *Transplanted lichens for bioaccumulation studies*, in: Nimis P.L.,  
711        Scheidegger C., Wolseley P.A. (Eds.), *Monitoring with Lichens - Monitoring*  
712        *Lichens.* Kluwer Academy Publishers, Berlin, pp. 301-304.

713    Munzi S., Pisani T., Loppi S., 2009. *The integrity of lichen cell membrane as a suitable*  
714        *parameter for monitoring biological effects of acute nitrogen pollution.*  
715        Ecotoxicology and Environmental Safety 72, 2009-2012.

716    Nannoni F., Mazzeo R., Protano G., Santolini R., 2015. *Bioaccumulation of heavy*  
717        *elements by Armadillidium vulgare (Crustacea, Isopoda) exposed to fallout of a*  
718        *municipal solid waste landfill.* Ecological Indicators 49, 24-31.

719    Nash T.H., 2008. *Introduction*, in: Nash T.H. (Ed.), *Lichen Biology.* Cambridge  
720        University Press, New York, pp. 1-8.



- 721 Ng O.H., Tan B.C., Obbard J.P., 2006. *Lichens as bioindicators of atmospheric heavy*  
722 *metal pollution in Singapore*. Environmental Monitoring and Assessment 123, 63-  
723 74.
- 724 Nimis P.L., Scheidegger C., Wolseley P.A., 2002. *Monitoring with lichens - Monitoring*  
725 *lichens*, ed. Kluwer Academic Publishers, Berlin.
- 726 Oztetik E. and Cicek A., 2011. *Effects of urban air pollutants on elemental*  
727 *accumulation and identification of oxidative stress biomarkers in the transplanted*  
728 *lichen Pseudovernia furfuracea*. Environmental Toxicology and Chemistry 30,  
729 1629-1636.
- 730 Pacheco A.M.G., Freitas M.C., Baptista M.S., Vasconcelos M.T.S.D., Cabral J.P., 2008.  
731 *Elemental levels in tree-bark and epiphytic-lichen transplants at a mixed*  
732 *environmental in mainland Portugal, and comparisons with an in situ lichen*.  
733 Environmental Pollution 151, 326-333.
- 734 Paoli L. and Loppi S., 2008. *A biological method to monitor early effects of the air*  
735 *pollution caused by the industrial exploitation of geothermal energy*.  
736 Environmental Pollution 155, 383-388.
- 737 Paoli L., Pisani T., Guttová A., Sardella G., Loppi S., 2011. *Physiological and chemical*  
738 *response of lichens transplanted in and around an industrial area of south Italy:*  
739 *Relationship with the lichen diversity*. Ecotoxicology and Environmental Safety  
740 74, 650-657.
- 741 Paoli L., Corsini A., Bigagli V., tannini J., Bruscoli C., Loppi S., 2012. *Long-term*  
742 *biological monitoring of environmental quality around a solid waste landfill*  
743 *assessed with lichens*. Environmental Pollution 161, 70-75.
- 744 Pearson L.C. and Henriksson, E., 1981. *Air-pollution damage to cell-membranes in*  
745 *lichens. 2. laboratory experiments*. Bryologist 84, 515-520.
- 746 Piccotto M., Bidussi M., Tretiach M., 2011. *Effects of the urban environmental*  
747 *conditions on the chlorophyll a fluorescence emission in transplants of three*  
748 *ecologically distinct lichens*. Environmental and Experimental Botany 73, 102-  
749 107.
- 750 Pirintsos S.A. and Loppi S., 2008. *Biomonitoring atmospheric pollution: the challenge*  
751 *of times in environmental policy on air quality*. Environmental Pollution 151, 269-  
752 271.

753 Prechthai T., Parkpian P., Visvanathan C., 2008. *Assessment of heavy metal*  
754 *contamination and its mobilization from municipal solid waste open dumping site.*  
755 *Journal of Hazardous Materials*, 156, 86-94.

756 Protano C., Guidotti M., Owczarek M., Fantozzi L., Blasi G., Vitali M., 2014.  
757 *Polycyclic aromatic hydrocarbons and metals in transplanted lichen*  
758 *(Pseudovernia furfuracea) at sites adjacent to a solid-waste landfill in central*  
759 *Italy.* *Archives of Environmental Contamination and Toxicology* 66, 471-481.

760 Prudent P., Domeizel M., Massiani C., 1996. *Chemical sequential extraction as*  
761 *decision-making tool: application to municipal solid waste and its individual*  
762 *constituents.* *Science Total Environmental* 178, 55-61.

763 Rajkumar N., Subramani T., Elango L., 2010. *Groundwater contamination due to*  
764 *municipal solid waste disposal – A GIS Based Study in Erode City.* *International*  
765 *Journal of Environmental Sciences* 1, 39-55.

766 Rizo O.D., Merlo M.H., Castillo F.E., Lopez J.A.O., 2012. *Assessment of metal*  
767 *pollution in soils from a former Havana (Cuba) solid waste open dump.* *Bulletin*  
768 *of Environmental Contamination and Toxicology* 88, 182-186.

769 Rodrigo A., Avila A., Gomez-Bolea A., 1999. *Trace metal contents in Parmelia*  
770 *caperata (L.) Ach. compared to bulk deposition, throughfall and leaf-wash fluxes*  
771 *in two holm oak forests in Montseny (NE Spain).* *Atmospheric Environment* 33,  
772 359-367.

773 Sloof J.E., 1995. *Lichens as quantitative biomonitors for atmospheric trace-element*  
774 *deposition, using transplants.* *Atmospheric Environment* 29, 11-20.

775 Sorbo S., Aprile G., Strumia S., Castaldo Cobianchi R., Leone A., Basile A., 2008.  
776 *Trace element accumulation in Pseudevernia furfuracea (L.) Zopf exposed in*  
777 *Italy's so called triangle of death.* *Science Total Environment* 407, 647-654.

778 Sutherland, R.A., 2000. *Bed sediment-associated trace metals in an urban stream,*  
779 *Oahu, Hawaii.* *Environmental Geology* 39, 611-627.

780 Vrijheid M., 2000. *Health effects of residence near hazardous waste landfill sites: a*  
781 *review of epidemiologic literature.* *Environment Health Perspectives* 108, 101-  
782 112.

783 Waheed S., Siddique N., Hamid Q., Chaudhry M.M., 2010. *Assessing soil pollution*  
784 *from a municipal waste dump in Islamabad, Pakistan: a study by INAA and AAS.*  
785 *Journal of Radioanalytical and Nuclear Chemistry* 285, 723-732.

- 786 Williamson B.J., Mikhailova I., Purvis O.W., Udachin V., 2004. *SEM–EDX analysis in*  
787 *the source apportionment of particulate matter on Hypogymnia physodes lichen*  
788 *transplants around the Cu smelter and former mining town of Karabash, South*  
789 *Urals, Russia*. Science Total Environment 322, 139-154.
- 790 Wolterbeek B., 2002. *Biomonitoring of trace element air pollution: principles,*  
791 *possibilities and perspectives*. Environmental Pollution 120, 11-21.
- 792 Zambrano A. and Nash T.H., 2000. *Lichen responses to short-term transplantation in*  
793 *Desierto de los Leones, Mexico City*. Environmental Pollution 107, 407-412.

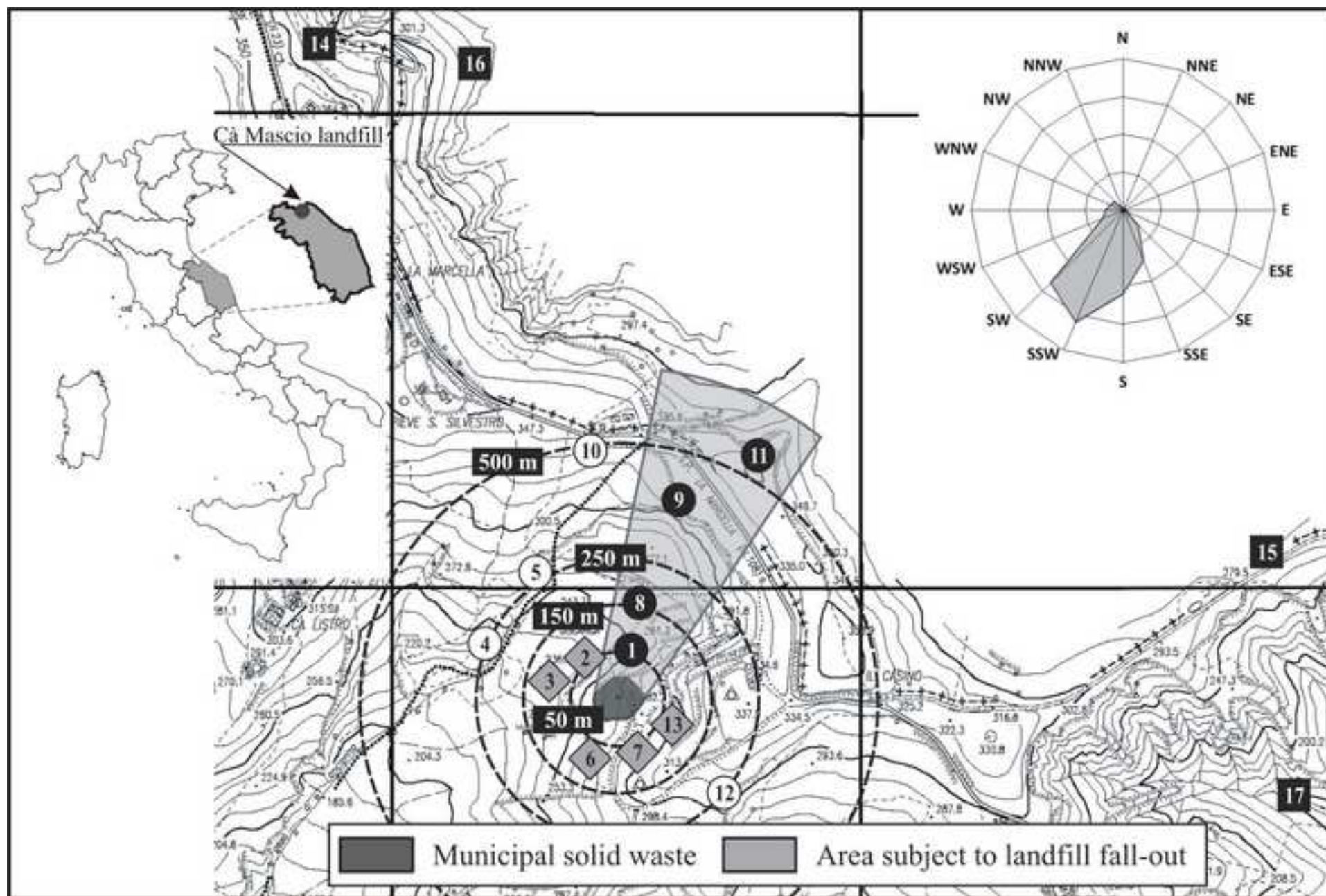
## FIGURE CAPTIONS

**Figure 1.** Map of the study area showing the direction of dominant winds and location of the monitoring sites: ♦ landfill, ● fallout, ○ rural and ■ background sites.

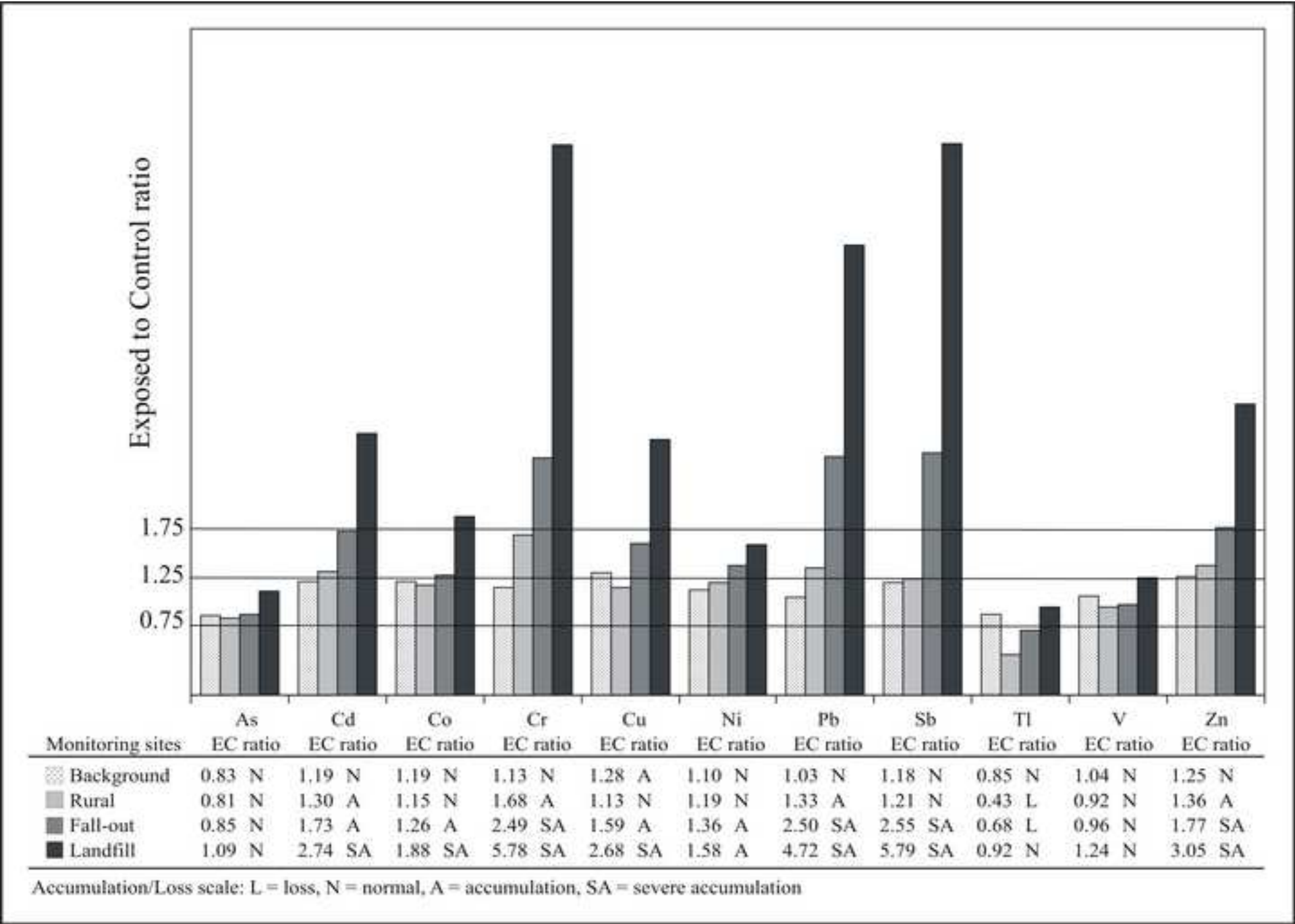
**Figure 2.** Mean values of EC ratio of lichens exposed in the monitoring sites (background, rural, fallout and landfill) of the study area and relative accumulation/loss scale.

**Figure 3.** Values (mean  $\pm$  standard deviation) of electrical conductivity (a) and photosynthetic efficiency (b) in *E. prunastri* lichens collected in the control site and transplanted in the monitoring sites (background, rural, fallout and landfill) of the Cà Mascio MSWL area. \* Significant differences of electrical conductivity and photosynthetic efficiency among background, rural, fallout and landfill lichens compared to control ones ( $p < 0.05$ ).

Figure\_1  
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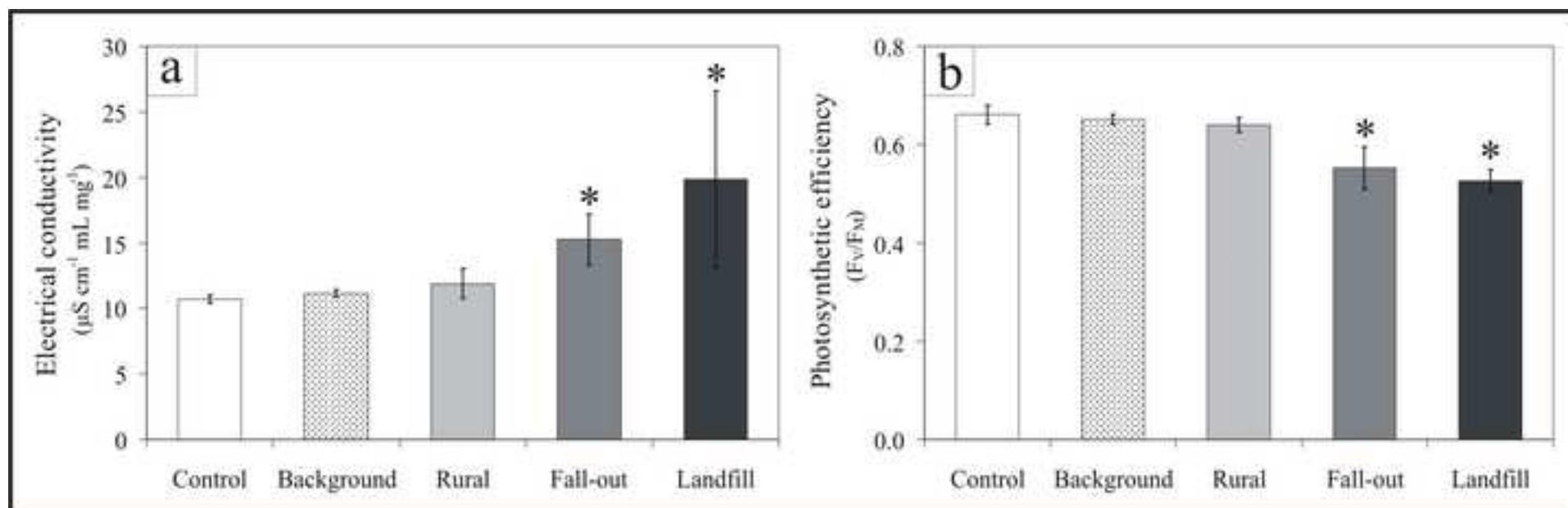


Figure\_2  
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Figure\_3

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1 **Table 1.** Concentrations and mean values of heavy elements (data in mg/kg ± standard deviation) in *E. prunastri* lichens collected in the control site  
2 and transplanted in the monitoring sites of the Cà Mascio MSWL area.  
3

Sites	As	Cd	Co	Cr	Cu	Ni	Pb	Sb	Tl	V	Zn
Control											
Native 1	0.21 ± 0.02	0.02 ± 0.004	0.2 ± 0.01	1.4 ± 0.06	3.2 ± 0.16	2.2 ± 0.07	1.4 ± 0.04	0.07 ± 0.02	0.003 ± 0.001	0.9 ± 0.04	14 ± 0.17
Native 2	0.21 ± 0.02	0.03 ± 0.003	0.18 ± 0.03	1.3 ± 0.02	2.9 ± 0.31	1.7 ± 0.11	1.2 ± 0.01	0.08 ± 0.01	0.008 ± 0.002	2 ± 0.09	19.3 ± 0.11
Native 3	0.29 ± 0.04	0.09 ± 0.008	0.17 ± 0.03	2.2 ± 0.09	4.4 ± 0.61	2.3 ± 0.05	3.1 ± 0.06	0.12 ± 0.03	0.007 ± 0.001	1.6 ± 0.06	20.6 ± 0.18
Native 4	0.24 ± 0.02	0.07 ± 0.009	0.31 ± 0.06	1.6 ± 0.08	4.3 ± 0.92	2.1 ± 0.09	3.3 ± 0.05	0.10 ± 0.01	0.003 ± 0.001	1.2 ± 0.03	14.8 ± 0.2
Mean	0.24 ± 0.04	0.05 ± 0.03	0.22 ± 0.06	1.6 ± 0.37	3.7 ± 0.77	2.1 ± 0.28	2.3 ± 1.1	0.09 ± 0.02	0.005 ± 0.003	1.4 ± 0.48	17.2 ± 3.3
Background											
MV-14	0.2 ± 0.01	0.06 ± 0.002	0.25 ± 0.01	1.8 ± 0.03	4.7 ± 0.05	2.1 ± 0.02	2.5 ± 0.04	0.09 ± 0.01	0.004 ± 0.001	1.5 ± 0.03	21 ± 0.38
MV-15	0.21 ± 0.01	0.05 ± 0.008	0.28 ± 0.02	1.9 ± 0.02	4.8 ± 0.06	2.4 ± 0.06	2.1 ± 0.05	0.11 ± 0.02	0.004 ± 0.001	1.4 ± 0.02	22 ± 0.29
MV-16	0.16 ± 0.02	0.03 ± 0.001	0.20 ± 0.01	1.5 ± 0.02	5.3 ± 0.07	1.8 ± 0.05	2.8 ± 0.03	0.13 ± 0.03	0.006 ± 0.002	1.4 ± 0.04	18.8 ± 0.21
MV-17	0.22 ± 0.02	0.08 ± 0.006	0.31 ± 0.02	2.2 ± 0.03	4.2 ± 0.03	2.7 ± 0.03	2 ± 0.04	0.09 ± 0.02	0.003 ± 0.001	1.5 ± 0.03	24.3 ± 0.28
Mean	0.2 ± 0.03	0.05 ± 0.02	0.26 ± 0.05	1.8 ± 0.31	4.7 ± 0.47	2.3 ± 0.39	2.3 ± 0.38	0.1 ± 0.02	0.004 ± 0.001	1.4 ± 0.08	21.5 ± 2.3
Rural											
MV-4	0.15 ± 0.01	0.05 ± 0.006	0.22 ± 0.03	2.2 ± 0.04	3.6 ± 0.04	3.0 ± 0.04	2.7 ± 0.03	0.09 ± 0.01	0.002 ± 0.001	1 ± 0.02	23 ± 0.24
MV-5	0.18 ± 0.02	0.05 ± 0.009	0.25 ± 0.01	3.2 ± 0.05	4.1 ± 0.07	2.1 ± 0.02	3 ± 0.04	0.1 ± 0.02	0.002 ± 0.001	1.3 ± 0.02	26.3 ± 0.31
MV-10	0.19 ± 0.01	0.07 ± 0.01	0.23 ± 0.02	2.3 ± 0.01	4.7 ± 0.02	2.5 ± 0.02	2.7 ± 0.03	0.12 ± 0.02	0.001 ± 0.001	1.1 ± 0.01	23.4 ± 0.1
MV-12	0.25 ± 0.03	0.07 ± 0.006	0.38 ± 0.07	3.3 ± 0.07	4.2 ± 0.05	2.2 ± 0.03	3.5 ± 0.06	0.11 ± 0.01	0.004 ± 0.002	1.7 ± 0.03	21.1 ± 0.25
Mean	0.19 ± 0.04	0.06 * ± 0.008	0.27 ± 0.07	2.8 * ± 0.57	4.2 ± 0.43	2.4 ± 0.41	3 ± 0.39	0.11 * ± 0.01	0.002 ± 0.001	1.3 ± 0.31	23.4 * ± 2.2
Fall-out											
MV-1	0.21 ± 0.03	0.09 ± 0.003	0.31 ± 0.01	8.5 ± 0.12	7.9 ± 0.1	2.4 ± 0.04	10.8 ± 0.08	0.58 ± 0.07	0.002 ± 0.001	1.3 ± 0.02	33.8 ± 0.5
MV-8	0.16 ± 0.01	0.06 ± 0.004	0.23 ± 0.04	2.9 ± 0.04	4.9 ± 0.54	2.1 ± 0.03	5.7 ± 0.12	0.2 ± 0.02	0.001 ± 0.001	0.95 ± 0.01	23.6 ± 0.12
MV-9	0.22 ± 0.01	0.09 ± 0.007	0.3 ± 0.02	3 ± 0.05	5.2 ± 0.52	3 ± 0.04	4.2 ± 0.07	0.15 ± 0.05	0.008 ± 0.002	1.7 ± 0.02	24.9 ± 0.17
MV-11	0.24 ± 0.04	0.1 ± 0.002	0.31 ± 0.05	5.5 ± 0.09	8.2 ± 0.68	2.5 ± 0.02	6.4 ± 0.07	0.32 ± 0.03	0.002 ± 0.001	1.5 ± 0.04	38.1 ± 0.22
Mean	0.2 ± 0.03	0.08 * ± 0.016	0.28 * ± 0.04	5 * ± 2.6	6.5 * ± 1.7	2.5 ± 0.37	6.8 * ± 2.8	0.31 * ± 0.19	0.003 ± 0.003	1.4 ± 0.32	30.1 * ± 7



Landfill												
MV-2	0.19 ± 0.01	0.07 ± 0.003	0.26 ± 0.01	4.9 ± 0.09	5.3 ± 0.05	3.5 ± 0.05	6.2 ± 0.09	0.24 ± 0.03	0.003 ± 0.001	1.2 ± 0.02	35.1 ± 0.43	
MV-3	0.2 ± 0.01	0.07 ± 0.006	0.27 ± 0.04	3.4 ± 0.03	5.1 ± 0.05	2.2 ± 0.02	4.7 ± 0.05	0.15 ± 0.01	0.002 ± 0.001	1.3 ± 0.01	35.2 ± 0.44	
MV-6	0.22 ± 0.02	0.24 ± 0.003	0.35 ± 0.01	9.3 ± 0.19	14.6 ± 0.14	3.8 ± 0.07	15.4 ± 0.11	0.59 ± 0.09	0.001 ± 0.001	1.1 ± 0.03	69.9 ± 0.67	
MV-7	0.31 ± 0.01	0.14 ± 0.007	0.53 ± 0.07	18.9 ± 0.16	15.1 ± 0.13	4.7 ± 0.06	16 ± 0.23	0.97 ± 0.12	0.005 ± 0.001	1.9 ± 0.03	78.7 ± 0.94	
MV-13	0.36 ± 0.02	0.09 ± 0.004	0.59 ± 0.02	7.1 ± 0.15	7.1 ± 0.06	3.3 ± 0.05	6.3 ± 0.05	0.28 ± 0.01	0.013 ± 0.003	3 ± 0.08	45.5 ± 0.57	
Mean	0.25 ± 0.08	0.12 * ± 0.07	0.4 * ± 0.15	8.7 * ± 6.1	9.4 * ± 5	3.5 * ± 0.9	9.7 * ± 5.5	0.44 * ± 0.34	0.005 ± 0.005	1.7 ± 0.79	52.9 * ± 20.3	

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\* Significant differences among the mean contents of heavy elements in background, rural, fall-out and landfill lichens compared to control ones ( $p < 0.05$ ).

5 **Table 2.** Spearman correlation coefficients among the heavy element concentrations and physiological parameters [electrical conductivity (EC) and  
6 photosynthetic efficiency ( $F_v/F_M$ )] in lichens exposed in the Cà Mascio MSWL area. Only significant values are reported.  
7

	As	Cd	Co	Cr	Cu	Ni	Pb	Sb	Tl	V	Zn	EC	$F_v/F_M$
As	1												
Cd	0.777 **	1											
Co	0.946 **	0.804 **	1										
Cr	n.s.	0.836 **	0.689 *	1									
Cu	n.s.	0.695 *	n.s.	0.667 *	1								
Ni	n.s.	0.618 *	n.s.	n.s.	n.s.	1							
Pb	n.s.	0.746 **	n.s.	0.917 **	0.821 **	n.s.	1						
Sb	n.s.	0.735 **	n.s.	0.840 **	0.921 **	n.s.	0.947 **	1					
Tl	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	1				
V	0.779 **	n.s.	0.667 *	n.s.	n.s.	n.s.	n.s.	n.s.	0.852 **	1			
Zn	n.s.	0.825 **	0.610 *	0.890 **	0.650 *	0.650 *	0.801 **	0.759 **	n.s.	n.s.	1		
EC	n.s.	0.817 **	0.641 *	0.847 **	0.684 *	n.s.	0.846 **	0.839 **	n.s.	n.s.	0.787 **	1	
$F_v/F_M$	n.s.	0.653 *	n.s.	0.719 *	0.632 *	n.s.	0.735 **	0.741 **	n.s.	n.s.	0.834 **	0.669 *	1

n.s. = not significant; \*  $p < 0.01$ ; \*\*  $p < 0.001$

9 **Table 3.** Content of heavy elements (data in mg/kg  $\pm$  standard deviation) in soil samples collected in the monitoring sites of the Cà Mascio  
10 MSWL area.  
11

Sites	As	Cd	Co	Cr	Cu	Ni	Pb	Sb	Tl	V	Zn
Background											
MV-14	6.7 $\pm$ 0.17	0.23 $\pm$ 0.02	14.2 $\pm$ 0.23	102 $\pm$ 1.3	28.7 $\pm$ 0.41	63.7 $\pm$ 0.72	16 $\pm$ 0.18	0.41 $\pm$ 0.02	0.41 $\pm$ 0.009	95.1 $\pm$ 1.2	90.5 $\pm$ 1.1
MV-15	6.2 $\pm$ 0.28	0.26 $\pm$ 0.02	13.1 $\pm$ 0.29	107 $\pm$ 1.7	35.6 $\pm$ 0.64	60.2 $\pm$ 0.75	19.6 $\pm$ 0.34	0.52 $\pm$ 0.04	0.44 $\pm$ 0.007	101 $\pm$ 2.3	98.1 $\pm$ 1.8
MV-16	6.9 $\pm$ 0.19	0.21 $\pm$ 0.04	13.9 $\pm$ 0.31	99.4 $\pm$ 2.1	38.7 $\pm$ 0.55	58.1 $\pm$ 0.65	14.3 $\pm$ 0.22	0.44 $\pm$ 0.03	0.39 $\pm$ 0.007	92.9 $\pm$ 1.8	92.2 $\pm$ 1.8
MV-17	6.3 $\pm$ 0.21	0.25 $\pm$ 0.03	12.7 $\pm$ 0.2	105 $\pm$ 3	30.1 $\pm$ 0.54	62.4 $\pm$ 0.97	18.5 $\pm$ 0.41	0.5 $\pm$ 0.05	0.42 $\pm$ 0.008	108 $\pm$ 2.7	97.5 $\pm$ 2
Rural											
MV-4	5.9 $\pm$ 0.1	0.19 $\pm$ 0.02	13.7 $\pm$ 0.4	96.3 $\pm$ 1.9	29.9 $\pm$ 0.46	60.9 $\pm$ 0.91	13.1 $\pm$ 0.06	0.49 $\pm$ 0.02	0.4 $\pm$ 0.006	93.5 $\pm$ 1.8	104 $\pm$ 1.2
MV-5	7.3 $\pm$ 0.25	0.2 $\pm$ 0.03	13 $\pm$ 0.16	87.8 $\pm$ 0.8	25.2 $\pm$ 0.4	55.9 $\pm$ 0.62	14.5 $\pm$ 0.22	0.44 $\pm$ 0.01	0.38 $\pm$ 0.012	80.8 $\pm$ 1.3	85.3 $\pm$ 0.69
MV-10	8.9 $\pm$ 0.1	0.24 $\pm$ 0.03	14.3 $\pm$ 0.37	106 $\pm$ 1.7	32.2 $\pm$ 0.29	62.6 $\pm$ 1.1	15.5 $\pm$ 0.12	0.49 $\pm$ 0.02	0.4 $\pm$ 0.011	85.4 $\pm$ 1.5	93.4 $\pm$ 2
MV-12	7.3 $\pm$ 0.11	0.15 $\pm$ 0.04	10.7 $\pm$ 0.3	69.4 $\pm$ 0.9	19.2 $\pm$ 0.46	43.1 $\pm$ 0.94	12.5 $\pm$ 0.16	0.32 $\pm$ 0.02	0.39 $\pm$ 0.008	49.3 $\pm$ 0.7	59 $\pm$ 0.63
Fall-out											
MV-1	7.4 $\pm$ 0.15	0.18 $\pm$ 0.02	13.1 $\pm$ 0.15	97.8 $\pm$ 1.1	29.4 $\pm$ 0.42	60 $\pm$ 0.47	13.5 $\pm$ 0.11	0.53 $\pm$ 0.01	0.36 $\pm$ 0.009	93.9 $\pm$ 1.2	94.3 $\pm$ 1.8
MV-8	8.8 $\pm$ 0.2	0.13 $\pm$ 0.02	12.9 $\pm$ 0.23	88.7 $\pm$ 0.9	25.5 $\pm$ 0.21	52.7 $\pm$ 0.69	11.6 $\pm$ 0.12	0.42 $\pm$ 0.02	0.4 $\pm$ 0.012	82.2 $\pm$ 0.8	83.6 $\pm$ 0.61
MV-9	7.5 $\pm$ 0.23	0.22 $\pm$ 0.01	13.2 $\pm$ 0.26	81.3 $\pm$ 1.1	23.8 $\pm$ 0.21	54.6 $\pm$ 0.91	15.8 $\pm$ 0.13	0.42 $\pm$ 0.01	0.37 $\pm$ 0.008	71.5 $\pm$ 1.2	76.9 $\pm$ 1.5
MV-11	7.2 $\pm$ 0.14	0.22 $\pm$ 0.01	13.6 $\pm$ 0.21	103 $\pm$ 0.7	28.7 $\pm$ 0.33	61.9 $\pm$ 0.75	16.7 $\pm$ 0.25	0.51 $\pm$ 0.02	0.4 $\pm$ 0.003	98.6 $\pm$ 1.2	95.2 $\pm$ 1.9
Landfill											
MV-2	7.1 $\pm$ 0.2	0.2 $\pm$ 0.02	13.9 $\pm$ 0.2	93.5 $\pm$ 1	25.7 $\pm$ 0.4	56.7 $\pm$ 0.62	15 $\pm$ 0.2	0.52 $\pm$ 0.01	0.38 $\pm$ 0.008	95.3 $\pm$ 1.1	95.8 $\pm$ 1.2
MV-3	7.1 $\pm$ 0.33	0.17 $\pm$ 0.05	11.3 $\pm$ 0.32	85.6 $\pm$ 0.9	22.5 $\pm$ 0.24	47 $\pm$ 0.84	11.1 $\pm$ 0.1	0.4 $\pm$ 0.02	0.32 $\pm$ 0.005	62.5 $\pm$ 1	73.8 $\pm$ 0.65
MV-6	7.9 $\pm$ 0.23	0.16 $\pm$ 0.01	13.7 $\pm$ 0.21	84 $\pm$ 1.1	25.6 $\pm$ 0.55	56.7 $\pm$ 0.74	14.2 $\pm$ 0.1	0.43 $\pm$ 0.02	0.41 $\pm$ 0.007	82.7 $\pm$ 1.2	83.6 $\pm$ 1.5
MV-7	7.5 $\pm$ 0.15	0.2 $\pm$ 0.03	12.9 $\pm$ 0.32	85.2 $\pm$ 1	27.4 $\pm$ 0.48	59.2 $\pm$ 1.2	13 $\pm$ 0.11	0.45 $\pm$ 0.02	0.36 $\pm$ 0.003	82.9 $\pm$ 1.4	87.6 $\pm$ 1.7
MV-13	7.9 $\pm$ 0.12	0.17 $\pm$ 0.03	12.6 $\pm$ 0.26	79.9 $\pm$ 1.4	23.3 $\pm$ 0.49	53.7 $\pm$ 1	12.6 $\pm$ 0.12	0.43 $\pm$ 0.02	0.37 $\pm$ 0.006	75.1 $\pm$ 1.1	79.9 $\pm$ 0.43
Contamination threshold in soils for public, private and residential green areas (Italian Legislative Decree n° 152/2006)											
	20	2	20	150	120	120	100	10	1	90	150