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► **To cite this version:**

Riccardo Scalenghe, G. Fasciani. Soil Heavy Metals Patterns in Torino Olympic Winter Games Venue (E.U.). Soil and Sediment Contamination, 2008. hal-01577545

**HAL Id: hal-01577545**

**<https://hal.science/hal-01577545>**

Submitted on 26 Aug 2017

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1 **Soil Heavy Metals Patterns in Torino Olympic Winter Games Venue (E.U.)**

2  
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12  
13 *Keywords:* Italy; Fluvisol; landfill; motorways; *Eruca sativa* Mill.

14

15 **Abstract**

16 The city of Torino (45°N, 7°E NW Italy) has a long history of heavy industry. Additional  
17 sources of potential pollutants originate from transport such as car emissions. We selected an  
18 area potentially at high risk of contamination: it is sandwiched between roads, the circular  
19 Turin highway and the motorway which connects to France, and a landfill where special and  
20 hazardous solid wastes from industry are disposed of. Our main aim was i) to discriminate  
21 between these sources of heavy metals (HM) and ii) to assess a simplified HM transfer  
22 scenario. We started with air diffusion models (inputs were meteo and chemistry of the  
23 particulate), then we described topsoils (12 samples km<sup>-2</sup>) and we sampled, reallocated  
24 undisturbed, and cultivated an Ap soil horizon, being the soil *ceteris paribus*. The topsoils  
25 description discriminated Factor I, related to the vehicular load and soil parent material  
26 (mainly Cd, Co, Cr, Ni, V, and Zn), and Factor II, HM univocally dispersible from the landfill  
27 (Sb and As). The ecosystem response is resilience: soil tends to buffer loadings of most HM.  
28 In the case of mercury, lead, and arsenic our findings indicate that their transfer to the food  
29 chain may be massive.

30

## 31 **1. Introduction**

32 The number of potentially contaminated sites in the European Union is estimated to be  
33 approximately 3.5 millions (CEC, 2006). The stretches of motorway that cross the Alpine arc  
34 amounted to less than 100 km in 1963 and reached 4,000 km in 1993, according to the International  
35 Union for the Conservation of Nature (IUCN). The Alps are currently the most endangered  
36 mountain chain in the world. One example of increasing pressure which must be balanced with  
37 socioeconomic results is Torino (“Turin”) in Italy. Torino is surrounded by 400 kilometers of  
38 mountains as part of the European western Alps, from the Maritime Alps to Monte Rosa. The  
39 Torino metropolitan area (approximately 1.7 million inhabitants against a total population of 2.3  
40 million people in the province) is fifty percent mountainous. From a social point of view, the city is  
41 losing inhabitants, while the metropolitan area is growing. In other words, Torino is no longer used  
42 only by its residents and commuters for living and working but also by those who live and work  
43 elsewhere but use its services. The Alpine valleys of the province are the actual destination of  
44 metropolitan life, with built-up areas spread out and congested road traffic. Torino hosted the 2006  
45 Olympic Winter Games, which produced positive lasting effects in terms of economic growth  
46 (tourism) and negative in terms of environmental impacts (pollution). For instance, the quality of  
47 the air of Torino has been monitored for the past 25 years and the results demonstrate that a large  
48 percentage of the pollution produced is attributable to city traffic. In the last quarter of a century the  
49 individual mobility has increased by about eighty per cent over the Torino area; today over three  
50 million individual journeys are made daily. A program for the reduction of air pollution, developed  
51 between 1993 and 1998, has produced remarkable results for air quality in the city. Over the period  
52 of the last five years, carbon monoxide, nitric oxide, and suspended dust have been reduced by one  
53 third. Sulphur dioxide has practically disappeared while particulate emissions increased (2.8 Mg  
54  $\text{PM}_{10} \text{ km}^{-2} \text{ y}^{-1}$  in 2003; APAT, 2006). Urban traffic could often be the main source of heavy metals  
55 (e.g. from Belgrade, Crnkovi et al., 2006 or Newark, Joselow et al., 1978 to Karak, El-Hasan et al.,  
56 2006). In the city of Torino many industrial areas are still active and concerned with the production

57 of heavy metals (HM)-rich dusts which are primarily collected in one important hazardous waste  
58 site.

59

### 60 *1.1 Waste legislation in the European Union*

61 The only international convention covering waste issues is the Basel Convention. The convention  
62 regulates the import and export of hazardous waste to and from the parties of the convention. Every  
63 year the parties are required to submit a report (e.g., the quantities of hazardous waste imported and  
64 exported) to the Secretariat of the Basel Convention. The Basel Convention is implemented in the  
65 EU with the Regulation EEC/259/93 (OOPEC, 2002).

66 Early phases of Community waste legislation focused on clearly identified problems such as  
67 hazardous waste shipments, PCB disposal, and waste from the titanium dioxide industry. Later  
68 amendments of the Treaty, particularly the Single European Act in 1987 and the Maastricht Treaty  
69 five years later (OOPEC, 1992) introduced a more general objective of protecting and improving  
70 the quality of the environment.

71 EU has introduced its own legislation covering heavy metals in the form of EU Directives. The  
72 Framework Directive 96/62/EC set out a common strategy to define and set objectives for ambient  
73 air quality. Directive 1999/30/EC was the first of three so called “Daughter Directives” that  
74 specified limit values for various substances identified in the Framework Directive. This 1<sup>st</sup>  
75 Daughter Directive addresses NO<sub>x</sub>, SO<sub>2</sub>, PM<sub>10</sub> and lead. An atmospheric limit value for lead,  
76 expressed as an average over a calendar year, is set at 0.5 µg m<sup>-3</sup> to have been achieved by January  
77 2005 (or January 2010 in the immediate vicinity of specific point sources). Following two further  
78 Daughter Directives (covering benzene, carbon monoxide and ozone), the Commission has  
79 prepared a fourth Daughter Directive on heavy metals. The directive covers the remaining  
80 substances identified in the Framework Directive, namely arsenic, cadmium, mercury, nickel and  
81 polycyclic aromatic hydrocarbons (OOPEC, 2002). At present, a revision of the Integrated  
82 Pollution Prevention and Control, IPPC, (Council Directive 96/61/EC, OJ L 257) is envisaged

83 (CEC, 2006) and the strengthening of soil protection and contamination prevention elements shall  
84 be considered. European target HM loadings for soils are still under discussion and the variability  
85 between individual partner countries is high (Table 1).

86

87 The present study aims to discriminate the sources of heavy metals in a complex urban/rural area in  
88 which different HM sources occur and to infer final loadings from a simplified transfer scenario.

89

## 90 **2. Materials & Methods**

### 91 *2.1 Site description*

92 On February 10<sup>th</sup> 2006, the lighted torch inaugurated the XX Olympic Winter Games in Torino.  
93 Overall investments for the infrastructure of Torino 2006 amounted to 2,478 million USD, of which  
94 1,415 million USD were earmarked for major works (competition venues, training venues, villages,  
95 roads), 272 for associated works (TOROC, 2006).

96 Before the impact of the winter games on the city, we studied a complex area (Fig. 1) located on the  
97 Torino border district (45°N, 7°E NW Italy), a floodplain collecting the ultramafic rock outcrops  
98 from the Susa Valley, in between two high-traffic roads: the circular Turin highway and the  
99 motorway which connects the city to Lyon (France) through the Frejus mountain tunnel. A landfill  
100 is the fourth element of potential HM diffusion.

101 The soil heavy metal patterns (as parent material sources mainly) have been well described over a  
102 regional basis by Facchinelli et al. (2001) while a discussion on the motorway system appears in  
103 Campo et al. (1996).

104 The landfill is currently defined, for Italian legislation, as a 'controlled II-Class type C landfill'  
105 where special and hazardous solid wastes from industry are disposed of. The landfill is equipped  
106 with two HDPE liners and a clay layer to guarantee impermeability of the system. A drainage  
107 system consisting of pipes and pumps provides for leachate collection. The main kinds of waste  
108 disposed of are dust and asbestos fibers (disposed of in sealed bags), biological washing sludges

109 and physico-chemical inorganic washing sludges. The overall volume of the empty pit is  
110 approximately 600,000 m<sup>3</sup>. The wastes belong to the following classes: electrical and electronic  
111 devices and equipment, electric and electronic wastes, also containing precious metals,  
112 contaminated soils and crushed stones from demolition sites, and waste sands. Based on the  
113 European Waste Catalogue classification (CEC, 2000), the quantities of waste collected are  
114 reported in the Table 2a. The waste contains large amounts of heavy metals and the total inputs, as  
115 averaged data and recalculated over the surface, occupied by the landfill are given in Table 2b.

116

## 117 2.2 Soils

118 The city of Torino was built and spread on an alluvial plain, which has been formed by the rivers  
119 Po, Sangone, Stura di Lanzo and Dora Baltea. The watershed of these rivers contains a mixture of  
120 very diverse rocks that have contributed to the chemical composition of the deriving soils. In  
121 particular, serpentinites are present that might have increased Cr and Ni contents in the alluvial  
122 deposits (Biasioli et al., 2006). A 9 km<sup>2</sup> cultivated area situated close to the river Dora Baltea (with  
123 the landfill as its centroid) was studied. Soils belong mainly to Fluvisol, Cambisol, Albeluvisol  
124 groups (IUSS Working Group WRB, 2006). The quantitative methods developed for this analysis  
125 are based on 110 soil samples (11.6 samples km<sup>-2</sup>). Only Ap horizons (medium thickness 0–10 cm)  
126 were collected on the basis of a regular grid pattern.

127

128 Within the range of 200-metres from the centroid of the landfill a homogeneous benchmark  
129 environment was simulated by five 0.5 m<sup>3</sup>-mesocosms (8 replicates each) filled with Ap horizons  
130 from a Haplic Eutric Fluvisol, collected as an undisturbed block using a bottomless box. After  
131 collection the soil block was placed into a plastic box equipped with a bottom collector for drainage  
132 waters.

133 Each mesocosm was cultivated with a fast growing horticultural crop: rocket, *Eruca sativa* Miller  
134 which is most typically used as a flavouring for salads and a garnish and is one of the most diffuse

135 horticultural crops in Italy. Using rocket provided a simple way of testing potential bioavailability  
136 and subsequent transfer into the food chain with popular and widely cultivated, fast growing plant  
137 (3-4 cycles per year). The mesocosms were cultivated over three years, without removing the roots  
138 and adding new seeds and fertilizers, and the leaves were collected three times during each growing  
139 season.

140

### 141 *2.3 HM air diffusion model*

142 The system of monitoring of air quality was projected coupling and integrating existing models.  
143 The integrated system, collecting wet and dry deposition, enables to sort the activity of the landfill  
144 from those deriving from neighborhood sources, on a daily basis. Four automatic stations measure  
145 daily both meteorological with ultrasonic anemometer, collecting air temperature data from each  
146 vectorial wind component, and wet and dry depositions, which were analyzed in laboratory for  
147 HMs after digestion. Input data included meteorological data and chemical data of the particulate.  
148 In this paper two models have been used: i) the *Minerve* meteorological model and ii) the *Spray* 1.1  
149 diffusion model. *Minerve* is a mathematical model aimed to pattern locally and tri-dimensionally air  
150 temperature and wind direction with specific attention to air turbulence. This model of total  
151 emission from was validated by running previous tests over the period 1994-96 (LIFE Project  
152 94/IT/A32/IT00147/PIE, at <http://ec.europa.eu/environment/life/project/Projects/index.cfm>). *Spray*  
153 1.1 is a Lagrangian model of particle dispersion; it simulates transport and dispersion of species  
154 chemically inert under complex environments (wind calm, and orography) characterized by spatio-  
155 temporal anisotropy of the meteorological variables (wind shear and breeze induced by soil  
156 roughness). The dispersion and the meteorological models were coupled and implemented with  
157 algorithms based on Stokes law.

158

### 159 *2.4 Analytical procedures*

160 Soil samples were dried, sieved and then digested. The leaves were washed (leacheates were

161 analyzed and compared to the deposimeter loads) and ground before being analyzed. All samples  
162 (three replicates) were dried at 398 K, sieved at 2 mm, and microwave digested using a mixture of  
163 HCl-HNO<sub>3</sub> (3:5) acids. Solutions were analyzed spectrophotometrically (ICP-Varian Liberty 100).  
164 Standard Reference Material (SRM) used for verification analytical procedures were NBS 1567a  
165 and NIST 1573a (Environmental Protection Agency, Test Method for Evaluating Solid Waste  
166 Physical/Chemical Method, SW-846 – Method for determination of metals 6020A). SRM was used  
167 to verify the accuracy of the plant material analyses. However, even though the soil samples  
168 (without replicates) exceeded 2,500 (this number of observations meets the criteria of Italian  
169 legislation), we did not verify the accuracy of the soil analyses since there were no commercially  
170 available SRM for *aqua regia* similar to the soils of this study. They are, in fact, totally comparable  
171 to the concentrations reported in the same area by Biasioli et al. (2006). Twenty percent of analyses  
172 were replicated to ensure the consistency of analytical results. Reproducibility of results was  
173 verified by establishing method detection limits for each analysis according to procedures outlined  
174 by EPA. All quality controls were reproduced with a minimum precision of 10%; the recovery in  
175 the SRM ranged between 99 and 102%.

176 Spatial data have been modeled using univariate and multivariate geostatistics, some parameters  
177 adjusted to accommodate the Poisson-distributed nature of data. HM spatial patterns were tested by  
178 analysis of variance of fitted semivariogram model parameters such as field observations and  
179 laboratory results, and by comparing interpolation maps. In our study, block Kriging was applied to  
180 estimate HM at unsampled locations and the accuracy of Kriging was based on cross-validation.  
181 The spatial structure of the HM in the soil was determined through fitted variograms in a two-step  
182 procedure: (i) computation of experimental variograms, and (ii) fitting them to theoretical models  
183 cross-validated. Each variogram lag distance class contained an average of 150 data pairs with a  
184 minimum of 50 pairs. Model fitting for the variograms was selected based on sample variograms,  
185 and on the statistical results obtained from cross-validation.

186

### 187 3. Results & Discussion

#### 188 3.1 HM air diffusion model

189 Metal-rich particles are scattered over the whole area (data not shown) but after sorting the  
190 motorway-component from the landfill component as individual sources (Fig. 2), it appears that the  
191 spatial distribution of particles concentrated more than  $5 \mu\text{g m}^{-3}$  and could potentially exceed 250-m  
192 from the landfill centroid only along the N-S axis.

193

#### 194 3.2 HM soil diffusion pattern

195 Topsoils (0-20 cm) from Torino and the surrounding rural fields were taken from the area delimited  
196 by those rivers that might have contributed to the deposition of alluvial materials where the city is  
197 located. The measured pH in urban soils was mostly neutral-alkaline with a mean value of 7.2  
198 (Biasioli et al., 2006). The median pH of the studied area is  $7.3 \pm 0.2$ .

199 The descriptive statistics of element distribution in the  $<2$  mm soil fractions is provided in Table 3:  
200 Al, Fe and Mn (parent material core fingerprint), are unevenly distributed over the area. The last  
201 two patterns clearly indicate the presence of a former “iron oxide landfill”. These three elements are  
202 from moderately to highly correlated:  $r^2$  0.52, 0.63 and 0.89 ( $p < 0.05$  Al vs Fe, Al vs Mn and Fe vs  
203 Mn, respectively). Despite these correlations, the distributions are different: Al is leptokurtic, Fe is  
204 mesokurtic while Mn is platykurtic.

205 The weathering of ultramafic rocks produces soils abundant in magnesium and iron and rich in Zn,  
206 Ni and Cr (e.g. Shallari et al., 1998). In our case, Zn (mean  $220 \text{ mg kg}^{-1}$ ; comparable with the  
207 findings of Biasioli et al., 2006) over the whole area is concentrated in two areas 250 m WSW of  
208 the landfill, on both the motorway and the northern side of the motorway. The Zn distribution is  
209 leptokurtic. Cr, Ni and Zn, as inherited by the parent material, are highly correlated:  $r^2$  .67 and .70  
210 ( $p < 0.05$  Cr vs Ni, and Zn vs Ni respectively).

211 Biasioli et al. (2006) measured mean topsoil Cr and Ni concentrations ( $\text{mg kg}^{-1}$  aqua regia  
212 extractable) of Torino urban soils as 191 and  $209 \text{ mg kg}^{-1}$  respectively. Chromium (mean  $<150 \text{ mg}$

213  $\text{kg}^{-1}$ ) is spatially concentrated in areas 350 m NW of the landfill. Its distribution is leptokurtic.  
214 Nickel (mean  $<100 \text{ mg kg}^{-1}$ ) over the whole area, is unevenly distributed and concentrations  
215 between 150 and  $200 \text{ mg kg}^{-1}$  are found west of the landfill (300 meters) mainly N of the motorway.  
216 The distribution is highly leptokurtic. In different environments, Nicholson et al. (1999) calculated  
217 that atmospheric deposition of Zn and Ni to be between 32-45% of the total annual inputs of these  
218 metals to soils.

219 Cadmium is strongly associated with Zn geochemistry and the average content in soils lies between  
220  $0.06$  and  $1.1 \text{ mg kg}^{-1}$  (Kabata-Pendias and Pendias, 1992; Banat et al., 2007) while in plants it could  
221 range between  $0.09$  and  $0.29 \text{ mg kg}^{-1}$  (Ingwersen and Streck, 2005). In ambient air, it is mostly  
222 found in the fine particle fraction  $\text{PM}_{2.5}$  and ambient air levels at rural sites generally do not  
223 exceed  $0.4 \text{ ng m}^{-3}$ . Urban background levels range from  $0.2$  to  $2.5 \text{ ng m}^{-3}$  (CEC, 2003) and  
224 accumulate at atmospheric deposition rates of around  $2 \text{ g ha}^{-1} \text{ y}^{-1}$  ( $1.9$  in the UK, Alloway, 1999). In  
225 the present study, Cd is concentrated in soils with mean of  $6 \text{ mg kg}^{-1}$  and relatively scattered over  
226 the surveyed area, without peak concentration clearly related to a single source and with a  
227 leptokurtic distribution.

228 Antimony in the Earth crust is not abundant, and its concentration in soils spans between  $0.3$  and  $10$   
229  $\text{mg kg}^{-1}$ . For plants it is a nonessential metal and is known to be easily absorbed reaching  
230 concentrations of  $50 \text{ mg kg}^{-1}$  (Kabata-Pendias, 2001). Antimony in our soils seems relatively  
231 undispersed (mean  $1 \text{ mg kg}^{-1}$ ) and peak concentrations (up to  $15 \text{ mg kg}^{-1}$ ) occur within 50 meters of  
232 the landfill perimeter.

233 Arsenic is a metalloid that forms a variety of inorganic and organic compounds. It is distributed  
234 rather uniformly in major types of rocks and concentrations range from  $0.5$  to  $2.5 \text{ mg kg}^{-1}$  (Kabata-  
235 Pendias and Pendias, 1992). Arsenic is a constituent of most plants but little is known about its  
236 biochemical role. As-phytotoxicity is presumed but critical values vary between species and  
237 experiments ( $20$  to  $100 \text{ mg kg}^{-1}$ , e.g., Macnicol and Beckett, 1985, or Kitagishi and Yamane, 1981).  
238 In ambient air it is mostly found in the fine particle fraction  $\text{PM}_{2.5}$ . Ambient air concentrations of

239 arsenic at rural sites generally do not exceed  $1.5 \text{ ng m}^{-3}$ , with lowest values of  $0.2 \text{ ng m}^{-3}$ . Urban  
240 background levels show a range of  $0.5$  to  $3 \text{ ng m}^{-3}$  (CEC, 2003). Arsenic, in our study area, is  
241 concentrated (mean  $<0.5 \text{ mg kg}^{-1}$ ) nearby the landfill ( $<50$  meters) and is virtually non-dispersed in  
242 the first 350 meters area W but concentrations start to increase unevenly after this threshold  
243 distance. Arsenic and Sb distributions are highly correlated  $r^2 0.83$  ( $p < 0.05$ ). Both of them are  
244 highly leptokurtic distributed, indicating that there are higher frequencies of values near the means  
245 and there are peaked distributions with thick tails.

246 Berillium exists in relatively small quantities, comprising less than  $10 \text{ mg kg}^{-1}$  of the major rock  
247 types and its abundance in surface soils has not yet been investigated to a large scale, Kabata-  
248 Pendias and Pendias (1992) reported a range of  $0.27$ - $3.52 \text{ mg kg}^{-1}$ . At the studied site, Be (average  
249 soil content  $<0.01 \text{ mg kg}^{-1}$ ) is virtually non-dispersed and normal distributed.

250 Boron is not uniformly distributed in the crust of the Earth and its adsorption on Fe and Al oxides is  
251 believed to be an important mechanism governing the solubility in soils (Gupta, 1993) where the  
252 range of concentrations span between one and hundreds of part per million, and is similar in plants  
253 (Kabata-Pendias, 2001). Over the whole study area (mean  $73 \text{ mg B kg}^{-1}$  soil) B is concentrated in  
254 two areas 400 m west of the landfill, both on the southern and northern side of the motorway. The  
255 distribution is leptokurtic.

256 Cobalt is abundant in ultramafic rocks. Its soil concentration reflects the parent material and ranges  
257 from  $0.1$  to hundreds of part per million. In plants, it is more common to observe deficiency than  
258 toxicity and mean concentrations range from  $0.01$  to  $200 \text{ mg Co kg}^{-1}$  soil (Kabata-Pendias, 2001).  
259 Cobalt at the studied site (mean  $20 \text{ mg kg}^{-1}$ ) over the whole area is concentrated in two peak 350 m  
260 WSW of the landfill, on both the motorway and the northern side of the motorway. The distribution  
261 is platykurtic indicating that most of the values share about the same frequency of occurrence and  
262 the distribution curve is plateau-like.

263 Lead, which is a target element as a linear-diffusive pollutant, follows the general pattern of the  
264 motorway (e.g., Massadeh et al., 2004, calculated enrichment factors to extrapolate the degree of

265 urban pollution). Biasioli et al. (2006) measured an average Pb concentration of the Torino  
266 surrounding agricultural soils of  $149 \text{ mg kg}^{-1}$ . In the present study the average concentration is  $71$   
267  $\text{mg kg}^{-1}$  and the distribution is highly leptokurtic.

268 Copper in the Earth's crust is most abundant in mafic rocks and is of great importance in agronomic  
269 practice. At the studied site, Cu the mean concentration was  $55 \text{ mg kg}^{-1}$ , which is half of the  
270 average concentration reported by Biasioli et al., 2006, and two times the concentration reported by  
271 Kumar et al., 2005. Copper levels in the studied area was concentrated on the southern side of the  
272 motorway and was relatively scarce in the near the landfill. The Cu distribution is platykurtic.

273 Tin, present in relatively small amounts, follows the As pattern of distribution. While this  
274 concentration of Sn may have important effects on human health it is not toxic for rocket plants,  
275 Gough et al. (1979) reported the common range in plants to be  $20$  to  $30 \text{ mg kg}^{-1}$ . The Sn distribution  
276 is highly leptokurtic.

277 Vanadium is generally concentrated in mafic rocks and, due to weathering passes into the soils.  
278 Average worldwide soil ranges from tens to hundreds parts per million: in the United States, a  
279 geometric mean concentration of  $58 \text{ mg kg}^{-1}$  (Shacklette and Boerngen, 1984). In plants, the  
280 evidence that it is essential for their growth is not yet conclusive and there are no reports indicating  
281 V phytotoxicity under field conditions (Gough et al., 1979). Vanadium follows the Pb general  
282 pattern and in our study area it is concentrated on the southern side of the motorway (averaged  
283 concentration of  $60 \text{ mg kg}^{-1}$ ) with a mesokurtic distribution.

284 Mercury concentrations in all types of rocks is fairly low and does not exceed concentrations of  
285 parts per billion (Kabata-Pendias and Pendias, 1992). In highly contaminated soils of the Estarreja  
286 Channel, Ria de Aveiro, Hg does not exceed  $0.2 \text{ mg g}^{-1}$  (Pereira et al., 2005). Total gaseous Hg in  
287 Europe varies between less than  $2 \text{ ng m}^{-3}$  (background locations) to  $35 \text{ ng m}^{-3}$  at heavily impacted  
288 locations (CEC, 2003). In the present study, average concentrations of mercury were  $<0.5 \text{ mg kg}^{-1}$ .

289 With ordinary statistics no diffusion pattern was apparent, although geostatistically a strong

290 relationship with wind and soil concentration following the W direction is apparent. The  
291 distribution at our site study is mesokurtic.

292

293 The principal component analysis, PCA, enables a reduction in data and description of a given  
294 multidimensional system by means of a small number of new variables. According to Morrison  
295 (1967), principal components should account for approximately three quarters of the total variance  
296 and relevant components are those whose eigenvalue is higher than 1 (Kaiser, 1974). In our case,  
297 PCA was carried out by an orthogonal rotation and scores for selected factors were computed by  
298 regression (Table 4). According to Kaiser, our KMO value permits use of the factor model. Two  
299 factors accounted for a large proportion (75.47%) of the overall variance. Respectively Factor I is  
300 closely related to B, Cd, Co, Cr, Ni, Cu, V, Zn, Al, Fe and Mn, and Factor II to Sb and As. They  
301 were correlated with the original variables and could therefore be assumed as independent grouping  
302 factors. The factor loadings on the original variables after Varimax rotation and factor score  
303 coefficient matrix are not shown.

304 Roads introduce a variety of toxic pollutants to the surrounding environments and are a source of  
305 chronic, seasonal and accidental pollution. Lead from gasoline was a common contaminant  
306 associated with roads, but other HM also included Ni, Cu (part of clutch lining), Zn (additive to  
307 tires), Cd (Bellinger et al., 1982) and V, which is present in carbon containing deposits such as  
308 crude oil, coal, and oil shale and is usually recovered as a oil by- or co-product (Lide, 2006). The  
309 contour maps of the Factors distribution (Figs. 3a and 3b) are plotted overlapping this zone. Factor I  
310 (Fig. 3a), formed by metals abundant in the parent material (Cr, Ni, Al, Fe and Mn) and metals  
311 related to the vehicular load (Cd and V), describes the landfill-undirect component. Its spatial  
312 distribution is according to the soil types distribution and does not directly reflect depositional  
313 scenarios. Factor II, formed by metals univocally dispersed from the landfill, is the landfill-direct  
314 component. The spatial distribution roughly follows depositional scenarios but is concentrated  
315 within 250-m N from the landfill centroid.

316 *3.3 Ecosystem feedback: a simplified scenario*

317 Jennings et al. (2002), in Cleveland, discovered that public areas commonly have heavy metal  
318 contamination significantly above background levels suggesting that redevelopment initiatives  
319 should control urban exposure to heavy metal contamination.

320 In the Torino area, our finding confirms that where the metal loading was high, the accumulation in  
321 fast growing plant leaves (Table 5) was high as well, both in terms of maxima and median  
322 concentrations. Particles deposited during the growing seasons were not removed by rains or wind  
323 and large concentrations of Sb, As, Hg and Pb were observed. The observed concentrations of  
324 arsenic may have important effects on human health, but are not toxic for rocket plants which  
325 concentrate it in the leaves (Kabata-Pendias and Pendias, 1992).

326 We sampled and analyzed soils prior to the landfill activity (year 2000), cultivated rocket in  
327 mesocosm isolated (soils and percolates were analysed after each cropping), and collected leaves  
328 monthly (2 years) and depositions daily (3 years). All the sampling was made on a volume basis.  
329 For these reasons, we extrapolated results converting all the metal concentrations in grams HM m<sup>-2</sup>  
330 y<sup>-2</sup>. The ecosystem response, in terms of median (over the whole area) heavy metal concentrations  
331 is resilience (Fig. 4). However, the HM transfer to the food chain is massive in the areas of  
332 deposition of metals-rich particles and the spatial correlation between HM soil pseudototals and the  
333 concentration detected in leaves cultivated in the mesocosms (where the soil is the same at the time  
334 zero of cultivation) at the same location is high:  $r = 0.964$ ,  $p < 0.005$ .

335 Even if the decrease in HM concentration was noticeable, i.e. lead, the concentrations in leaves of  
336 some metal (arsenic, principally) are above the threshold for human health risks and horticultural  
337 crops are distributed everywhere, largely at the urban/rural interface areas. Additionally, the  
338 concentrations of mercury increase ten times from the potential anthropogenic sources to the leaves.

339

340

341 **4. Conclusions**

342 The study revealed a considerable loading of the topsoils with metals and the PCA allows a  
343 reduction in data and description of the given multidimensional system through a small number of  
344 new variables. In this case, sorting out single impact factors enables us to find that even elevated  
345 anthropic contamination is identifiable.

346 The ecosystem response: for most HM soil tends to buffer loadings but the HM transfer to the food  
347 chain is massive and the correlation between heavy metals potentially dispersible and the  
348 concentration detected in leaves is high ( $r = 0.964$ ,  $p < 0.005$ ). Even if the decrease in HM  
349 concentration in soils was noticeable, i.e. lead, the concentrations in leaves of some elements  
350 (antimony and arsenic above all) are higher than the attention threshold for human health risks.  
351 Furthermore, as the horticultural crops are diffused everywhere, largely in urban/rural interface  
352 areas, particular attention must be paid to the concentrations of mercury, which increase ten times  
353 from the source to the leaves.

354

355 **Acknowledgements**

356 We are indebted to Ermanno Zanini for his overall supervision at this first stage of the project and  
357 Bruno Biasiol, Marco Menegaldo and Silvia Stanchi for their field and laboratory assistance, and  
358 Pat Di Bin who made an important editorial work.

359 A great 'Grazie!' to Franco Ajmone Marsan and Renzo Barberis for their enlightening advice on  
360 the paper. Special thanks to Anthony C Edwards and Richard Scalenghe, without their fundamental  
361 insights this manuscript would not exist.

362

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458

459 FIGURES CAPTION

460 Fig. 1. The study area ( $45^{\circ}06'20''\text{N } 7^{\circ}36'29''$ , centroid). The landfill is the isosceles triangle (base  
461 360 m, legs 460 m) indicated by the shaded area while the motorway system is in black. Details of  
462 the landfill in box-picture (b), while in box-picture (c) the area rose-wind describes direction and  
463 intensity of winds from  $0.25\text{-}0.50 \text{ m s}^{-1}$  (open bars) to  $1.50\text{-}2.50 \text{ m s}^{-1}$  (filled bars), following a  
464 grey-tone scale. Diamonds (boxes a and b) indicate the locations of four automatic stations while  
465 circles (box b) indicate the 8 replicates-mesocosm position.

466

467 Fig. 2. Distribution of particles  $\text{PM}_{10}$  as modelled (example of 2001 December 19<sup>th</sup>-22<sup>nd</sup>). The  
468 contour map shows the sorted landfill component only. Grey-tone scale from  $<1 \mu\text{g m}^{-3}$  (white) to  
469  $500 \mu\text{g m}^{-3}$  (black).

470

471 Fig. 3a. Distribution of Factor I (B, Cd, Co, Cr, Ni, Cu, V, Zn, Al, Fe and Mn) in grey-tone scale  
472 [average 60229, range 41223 (white)-81240 (black), kurtosis 0.4, skewness 0.1], where the landfill  
473 is indicated by the grey-shaded area while the motorway system is in black. Contour map from  
474 block Kriging with Gaussian variogram (nugget 257.3). The white portion of the figures occurs as  
475 the experimental variogram's nugget over the whole area was too high, probably due to sampling  
476 errors which caused short scale variability. We did not compute those values in both contour maps.  
477 Data expressed as cumulative mg HM  $\text{kg}^{-1}$  soil.

478

479 Fig. 3b. Distribution of Factor II, Sb and As (cumulative mg  $\text{kg}^{-1}$ ), in grey-tone scale [average 1,  
480 range 0 (white) -24 (black), kurtosis 40, skewness 6], where the landfill is indicated by the grey-  
481 shaded area while the motorway system is in black. Contour map from block Kriging with spheric  
482 variogram (nugget 1.8).

483

484 Fig. 4. HM potential loadings extrapolated as median values over three years time ( $\text{mg kg}^{-1} \text{y}^{-1}$ )  
485 coming from wet and dry depositions collected (three depositometers in Fig. 1b, data in  $\text{mg kg}^{-1} \text{day}^{-1}$ )  
486 <sup>1</sup>), soil surveys of the first 10 centimetres ( $9 \text{ km}^2$  area in Fig. 1a, a regular grid with the landfill as  
487 its centroid,  $11.6 \text{ samples km}^{-2}$ ,  $n = 110$ , data in  $\text{mg kg}^{-1} \text{y}^{-1}$ ), rocket leaves collected every three  
488 months (eight mesocosm in Fig. 1b, data in  $\text{mg kg}^{-1} \text{month}^{-1}$ ).  
489

490 TABLES CAPTION

491 Table 1

492 Maximum acceptable soil concentration limits for heavy metals in various European countries  
493 (modified from Madrid et al., 2006). Data in mg HM kg<sup>-1</sup>.

494

495 Table 2a

496 The European Union defines waste as an object the holder discards, intends to discard or is required  
497 to discard is waste under the Waste Framework Directive (European Directive 75/442/EC as  
498 amended). Here are listed the wastes collected in 2000 (in ton y<sup>-1</sup>), according to the European  
499 codification.

500

501 Table 2b

502 HM loadings: averaged data over the landfill surface (g HM m<sup>-2</sup> y<sup>-1</sup>). HM loadings were  
503 extrapolated as median values over a period of three years (mg kg<sup>-1</sup> y<sup>-1</sup>) coming from wet and dry  
504 depositions collected (three deposimeters in Fig. 1b, data in mg kg<sup>-1</sup> day<sup>-1</sup>).

505

506 Table 3

507 Descriptive statistics of soil HM concentrations in the first 10 cm (mg HM kg<sup>-1</sup> soil).

508

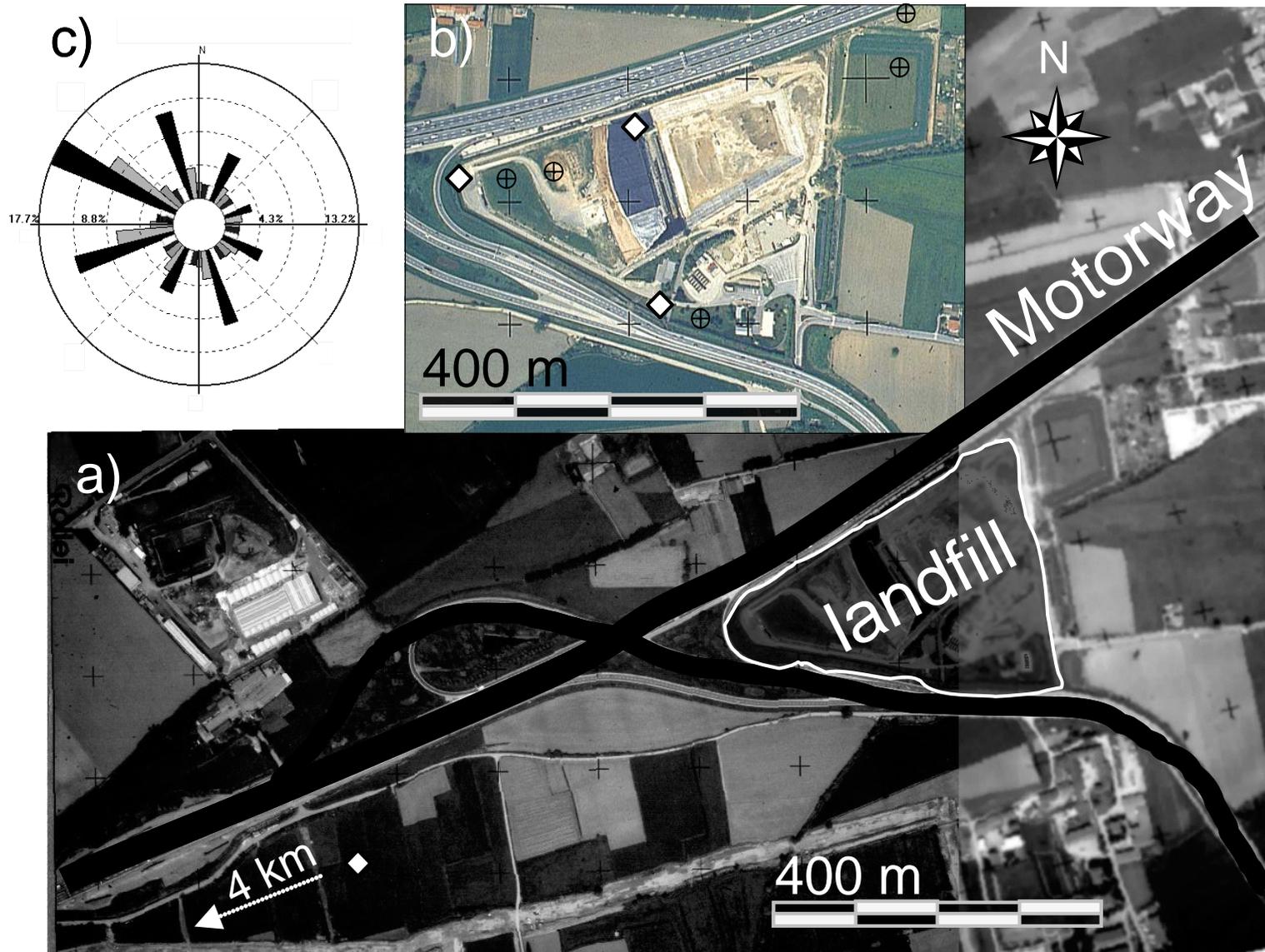
509 Table 4

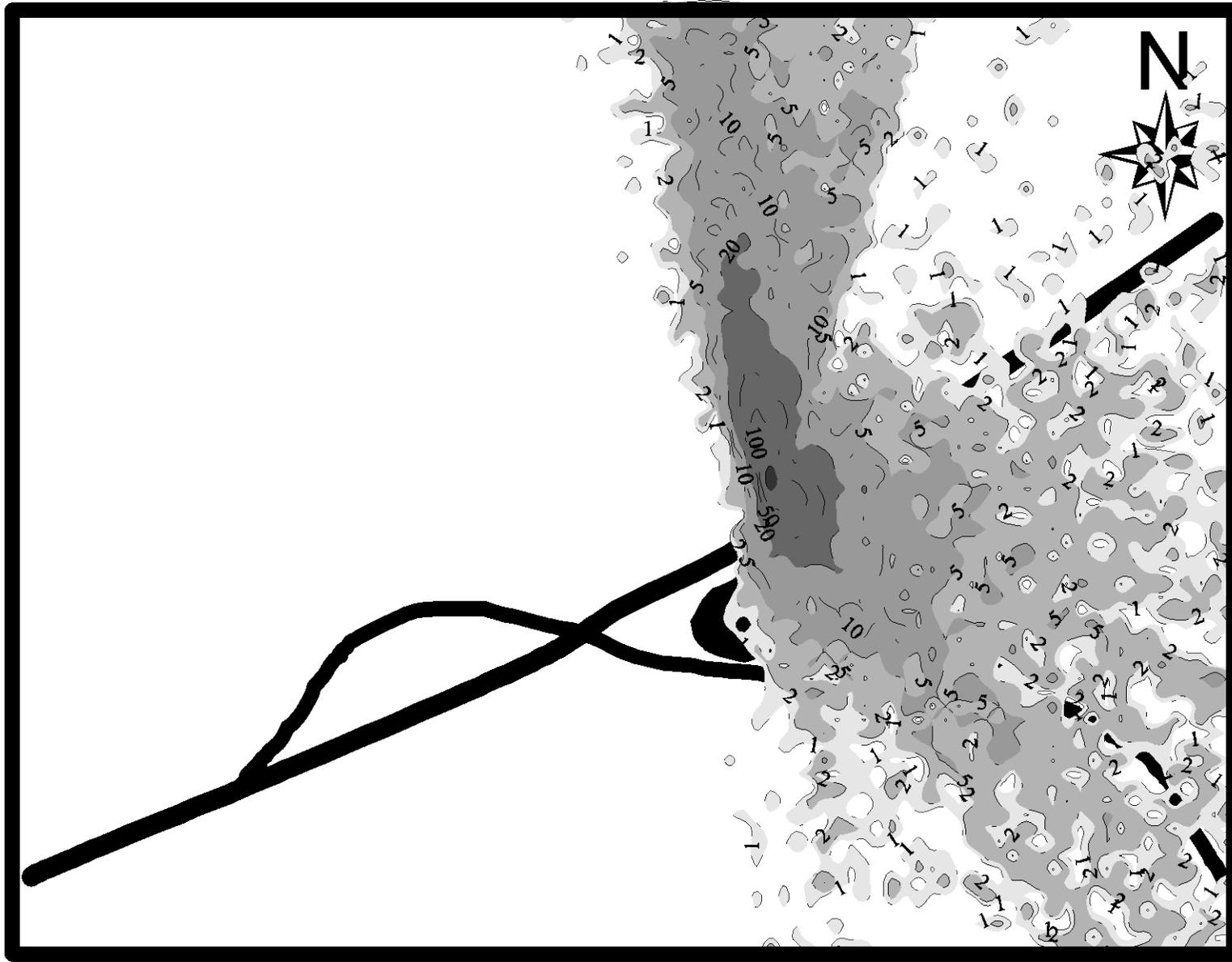
510 Statistics of Factor Analysis (percent).

511

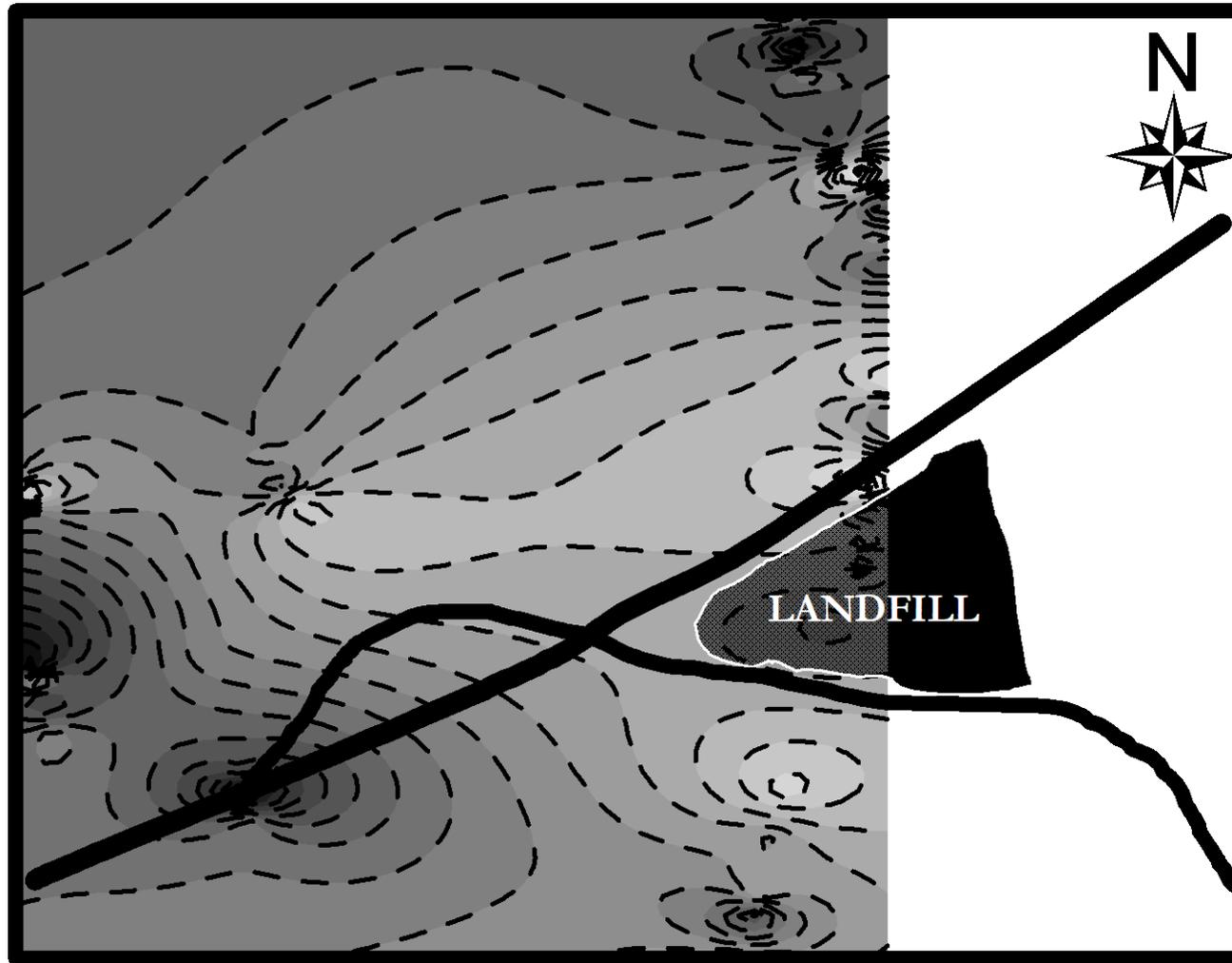
512 Table 5

513 Heavy metal concentrations in rocket leaves (mg HM kg<sup>-1</sup> dry matter). Descriptive statistics based  
514 on twelve observations over a three year period. In italics median concentration in rocket leaves  
515 (*MEDIAN<sub>t0</sub>*) when the landfill was not operative (four observations, year 2000).

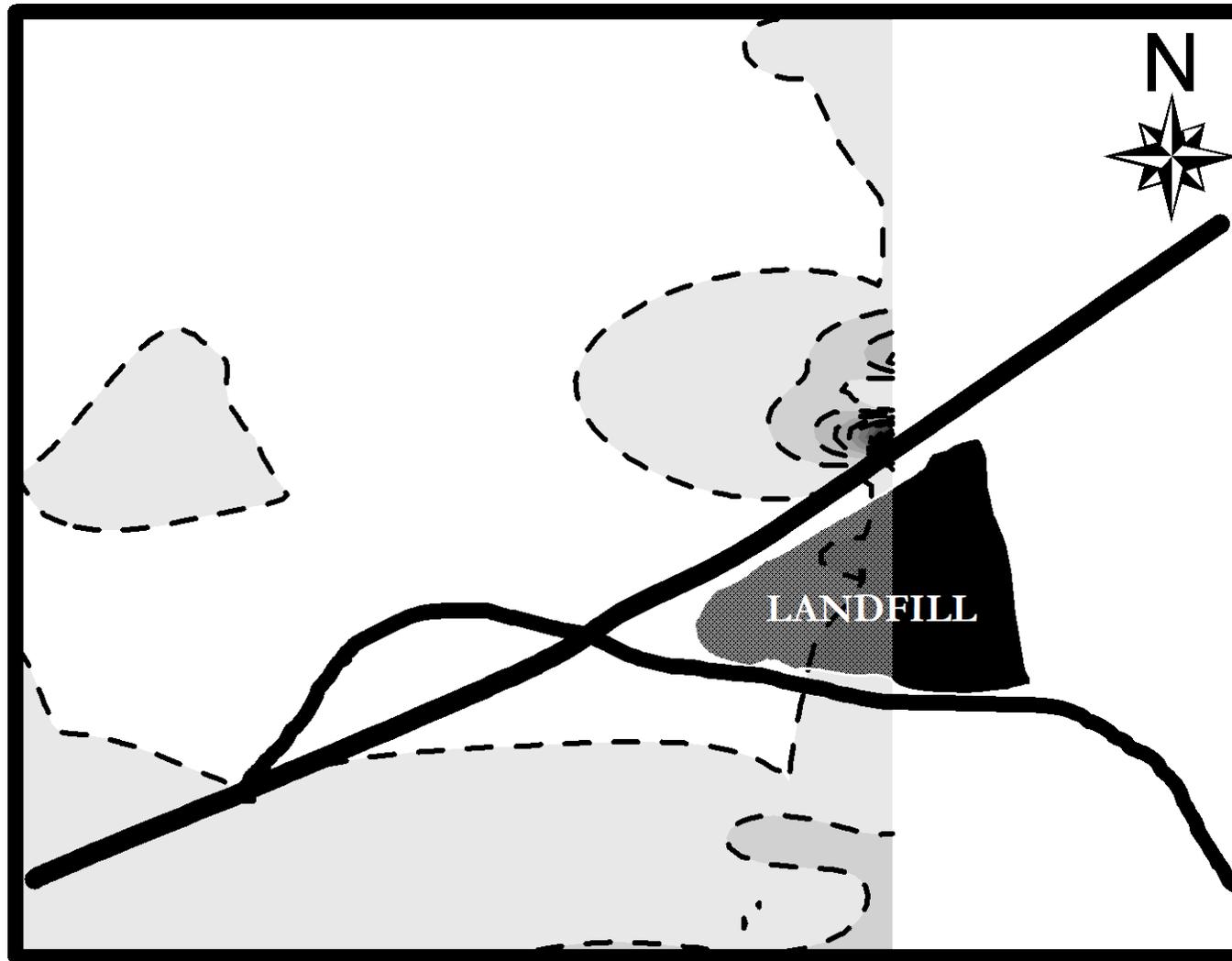




521 Fig. 3a  
522

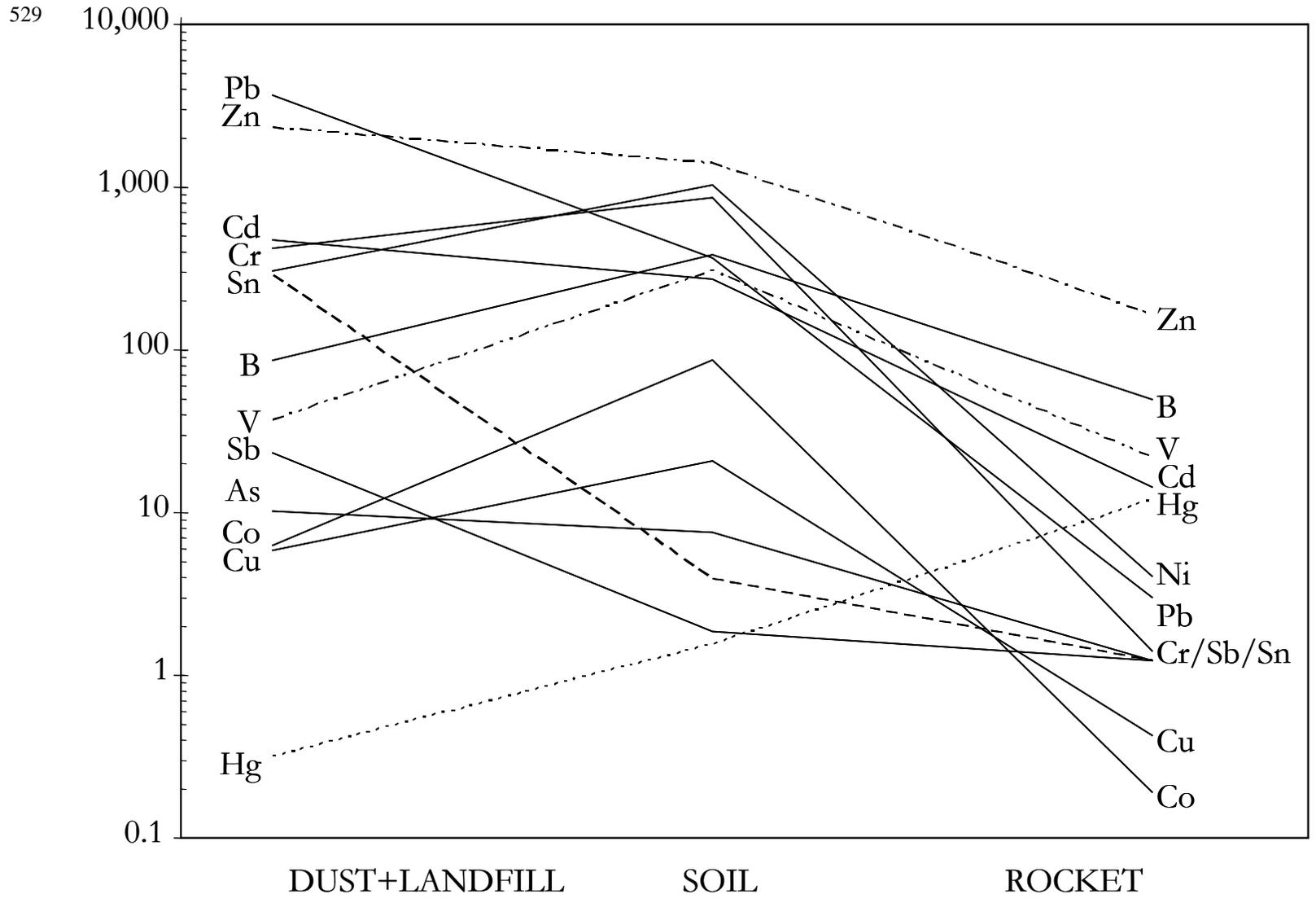


523  
524



525 Fig. 3b  
526  
527

528 Fig. 4.



530 Table 1

Country	Cr	Ni	Pb	Zn	Cu
Italy	150	120	100	150	120
Sweden	120	35	80	350	100
Netherlands <sup>a</sup>	100/380	35/210	85/530	140/720	36/190
Slovenia <sup>b</sup>	100/150/380	50/70/210	85/100/530	200/300/720	60/100/300
Portugal <sup>c</sup>	200/300	75/110	300/450	300/450	100/200
Spain <sup>d</sup>	250-400 /250-400	80-500 /100-300	250-450 /400-500	300-600 /500-1000	150-300 /300-500
United Kingdom <sup>e</sup>	600-1000	70	500-2000	300	130

531 <sup>a</sup> “Target” and “intervention” values,532 <sup>b</sup> “Limit”, “warning” and “critical” values,533 <sup>c</sup> Different values are given for pH below and above 7,534 <sup>d</sup> “Research required” values. Ranges instead of single values are given,535 <sup>e</sup> “Threshold” values.

536

537 Table 2a

Classes of wastes	Quantity	E.U. code
lead metallurgy (1 <sup>st</sup> and 2 <sup>nd</sup> smelting)	16,633	100401
chemical treatment metals surface (non-Fe metallurgy)	21	110104
wastewater treatment (industrial wastes)	18	190804
contaminated soils (with hazardous substances)	1,499	170501
ceramic product with hazardous substances	99	101299
from industrial treatments (2 <sup>nd</sup> , 3 <sup>rd</sup> wastes)	1,594	190301

538

539 Table 2b

	Parent material		Road dust		Landfill	
Sb	1	±0.2	1	±1	46	± 5
As	0.8	±0.1	0.2	±0.2	24	± 0.8
Be	0.9	±0.021	n.d.		0.00	± 0.001
B	0.4	±0.02	1.3	±1.10	0.0	± 0.01
Cd	0.1	±0.11	0.03	±0.01	18	± 0.50
Co	51	±17.0	0.3	±0.20	12	± 0.90
Cr	111	±76	5	±3	716	± 34
Ni	863	±93	6	±4	463	± 38
Pb	354	±306	4	±1	4,703	±112
Cu	32	±12	5	±2	715	± 82
Sn	11	±4.5	0.6	±0.1	551	± 47.0
V	54	±9	1	±1	77	± 6
Zn	632	±331	16	±8	2,901	±203
Hg	0.001	±0.005	0.032	±0.045	0.600	± 0.001
Al	633	±881	345	±209	11,870	±654
Fe	994	±1,153	589	±377	24,849	±965
Mn	573	±374	14	±9	2,350	±274

540

541

542 Table 3  
543  
544

	mean	SD	Max	kurtosis
Sb	1	2	15	26
As	<0.5	1	10	54
Be	<0.05	0	0	0
B	73	27	119	1
Cd	6	1	8	3
Co	20	2	24	-1
Cr	146	34	255	2
Ni	175	56	480	17
Pb	71	121	905	45
Cu	55	8	70	-1
Sn	<0.1	3	18	28
V	60	16	90	0
Zn	222	116	690	5
Hg	<0.5	0	2	0
Al	24953	5813	41200	1
Fe	33272	3257	38800	0
Mn	1213	146	1515	-1

545  
546

547 Table 4  
548

Factor	Eigenvalue	Total variance	Cumulative variance
1	10.28	64.25	64.25
2	1.79	11.22	75.47

549  
550

551 Table 5  
552

	min	Max	median	<i>MEDIAN</i> <sub><i>t</i><sub>0</sub></sub>
Sb	0.16	2.82	1.63	<i>0.10</i>
As	0.33	11.90	4.60	<i>0.31</i>
Be	<0.05	<0.05	<0.05	<0.05
B	12	25	18	<i>12</i>
Cd	0.41	0.65	0.54	<i>0.40</i>
Co	0.15	0.49	0.31	<i>0.38</i>
Cr	1.9	4.0	3.2	<i>0.6</i>
Ni	0.1	4.9	4.3	<i>1.4</i>
Pb	6.5	16.3	10.7	<i>1.1</i>
Cu	3.8	6.2	4.9	<i>4.2</i>
Sn	0.4	20.9	12.2	<i>0.4</i>
V	0.0	90.0	60.0	<i>6.0</i>
Zn	2.2	109.0	90.0	<i>35.0</i>
Hg	<0.5	4.5	1.1	<0.5
Al	108	899	237	<i>40</i>
Fe	284	783	476	<i>100</i>
Mn	13	35	21	<i>22</i>

553