

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

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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⁻²) 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 1st
75 Daughter Directive addresses NO_x, SO₂, PM₁₀ and lead. An atmospheric limit value for lead,
76 expressed as an average over a calendar year, is set at 0.5 µg m⁻³ 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 10th 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 m³. 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 km² 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⁻²). 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 m³-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-HNO₃ (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 ± 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 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 (mg kg^{-1} aqua regia
212 extractable) of Torino urban soils as 191 and 209 mg kg^{-1} respectively. Chromium (mean $<150 \text{ mg}$

213 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 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 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 mg kg^{-1} (Ingwersen and Streck, 2005). In ambient air, it is mostly
222 found in the fine particle fraction PM_{2.5} and ambient air levels at rural sites generally do not
223 exceed 0.4 ng m^{-3} . Urban background levels range from 0.2 to 2.5 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 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 mg kg^{-1} . For plants it is a nonessential metal and is known to be easily absorbed reaching
230 concentrations of 50 mg kg^{-1} (Kabata-Pendias, 2001). Antimony in our soils seems relatively
231 undispersed (mean 1 mg kg^{-1}) and peak concentrations (up to 15 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 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 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 PM_{2.5}. Ambient air concentrations of

239 arsenic at rural sites generally do not exceed 1.5 ng m^{-3} , with lowest values of 0.2 ng m^{-3} . Urban
240 background levels show a range of 0.5 to 3 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 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 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 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 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 mg kg^{-1} . In the present study the average concentration is 71
267 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 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 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 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 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 mg g^{-1} (Pereira et al., 2005). Total gaseous Hg in
287 Europe varies between less than 2 ng m^{-3} (background locations) to 35 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⁻²
330 y⁻². 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

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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 PM_{10} as modelled (example of 2001 December 19th-22nd). The
468 contour map shows the sorted landfill component only. Grey-tone scale from $<1\text{ }\mu\text{g m}^{-3}$ (white) to
469 $500\text{ }\mu\text{g m}^{-3}$ (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 kg^{-1} soil.

478

479 Fig. 3b. Distribution of Factor II, Sb and As (cumulative mg 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 ¹), soil surveys of the first 10 centimetres (9 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⁻¹.

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⁻¹), according to the European
499 codification.

500

501 Table 2b

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

505

506 Table 3

507 Descriptive statistics of soil HM concentrations in the first 10 cm (mg HM kg⁻¹ soil).

508

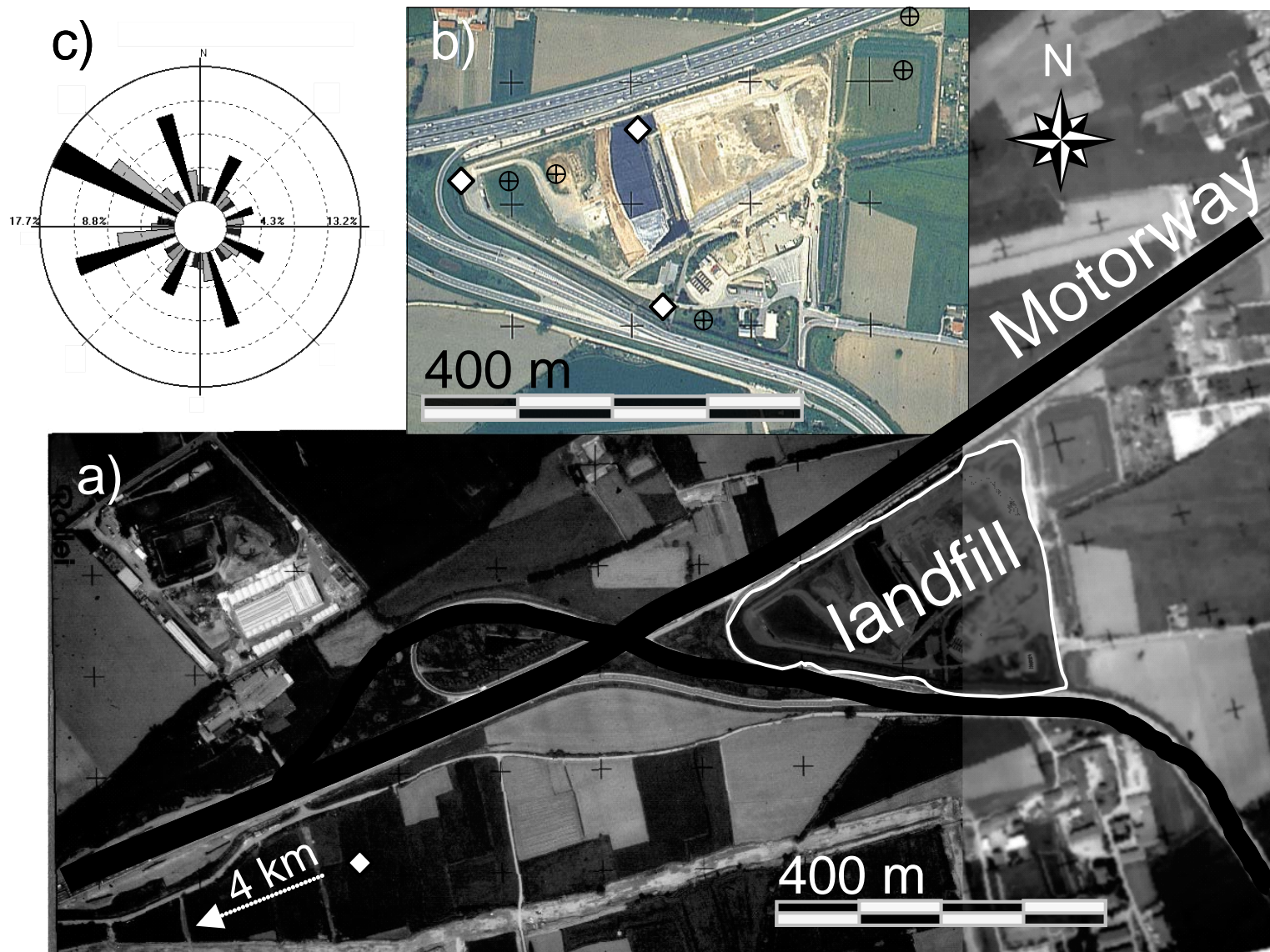
509 Table 4

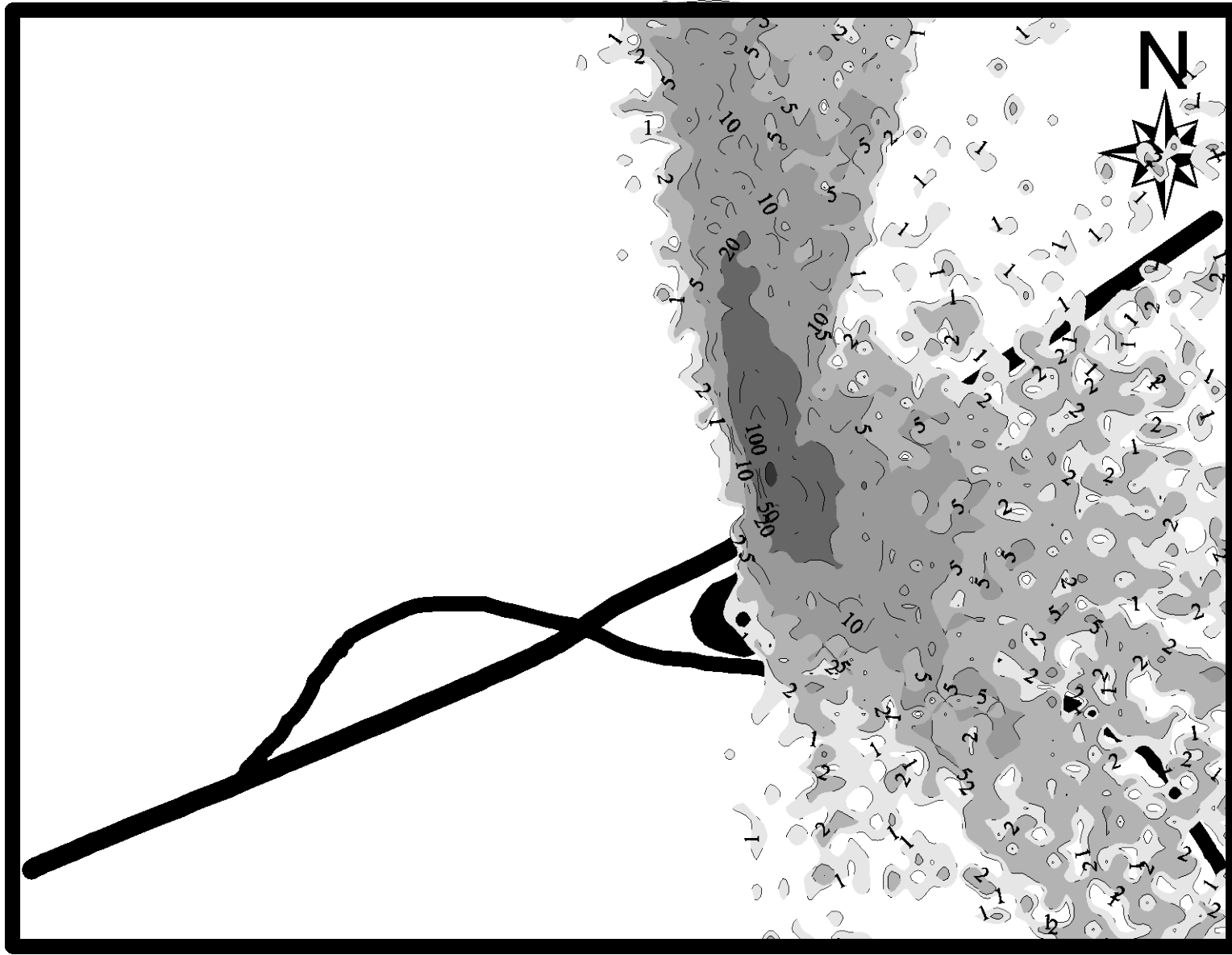
510 Statistics of Factor Analysis (percent).

511

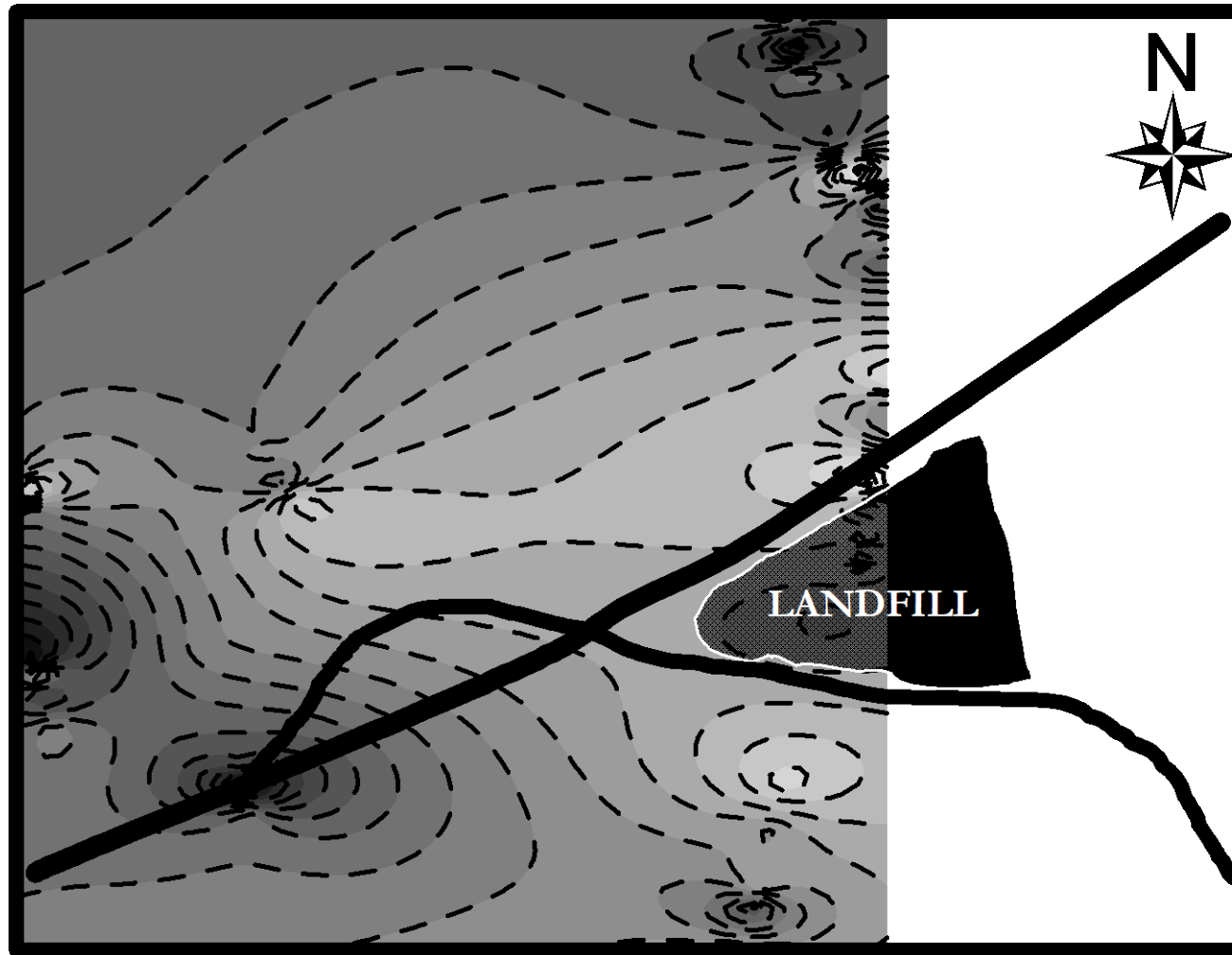
512 Table 5

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

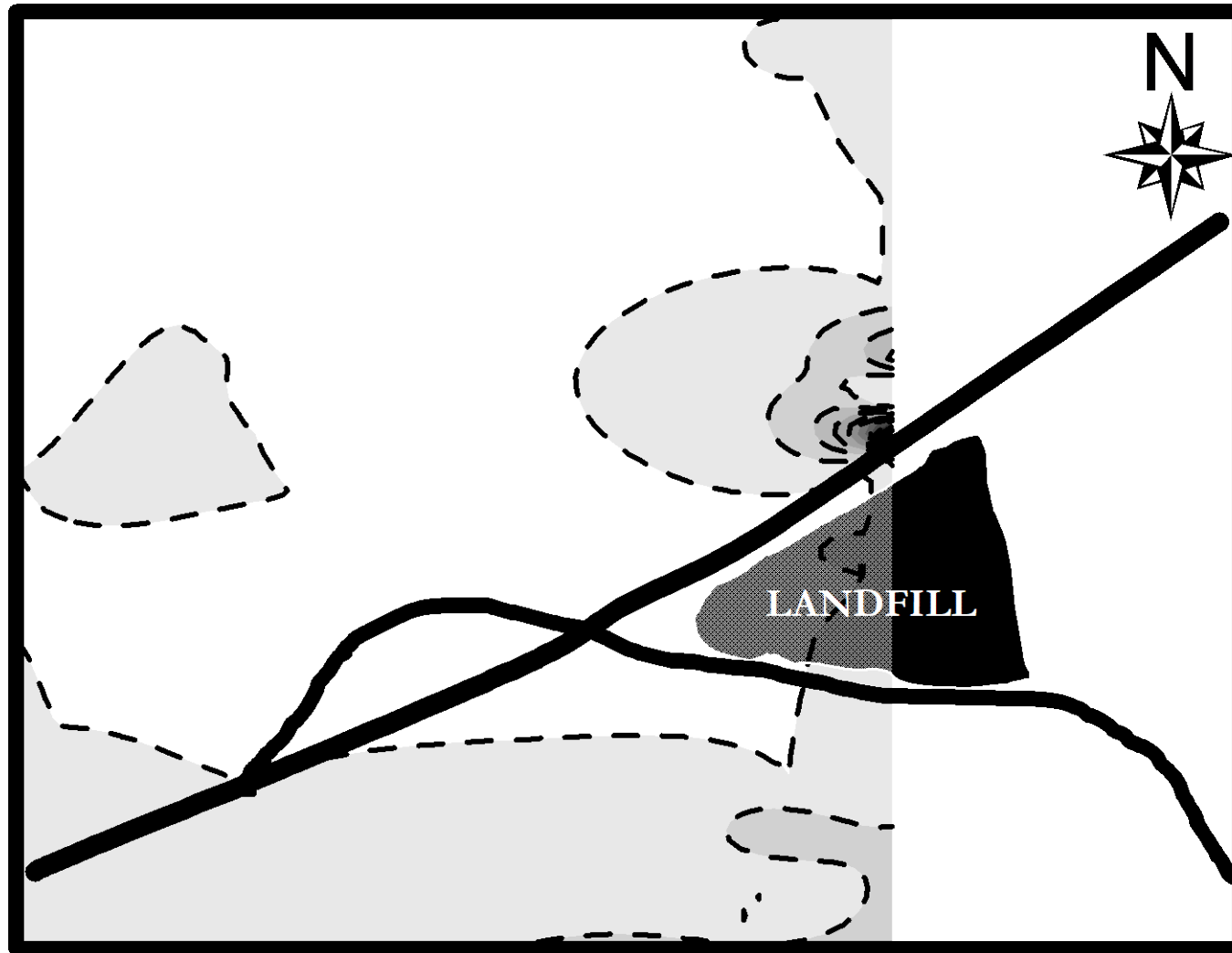




521 Fig. 3a
522

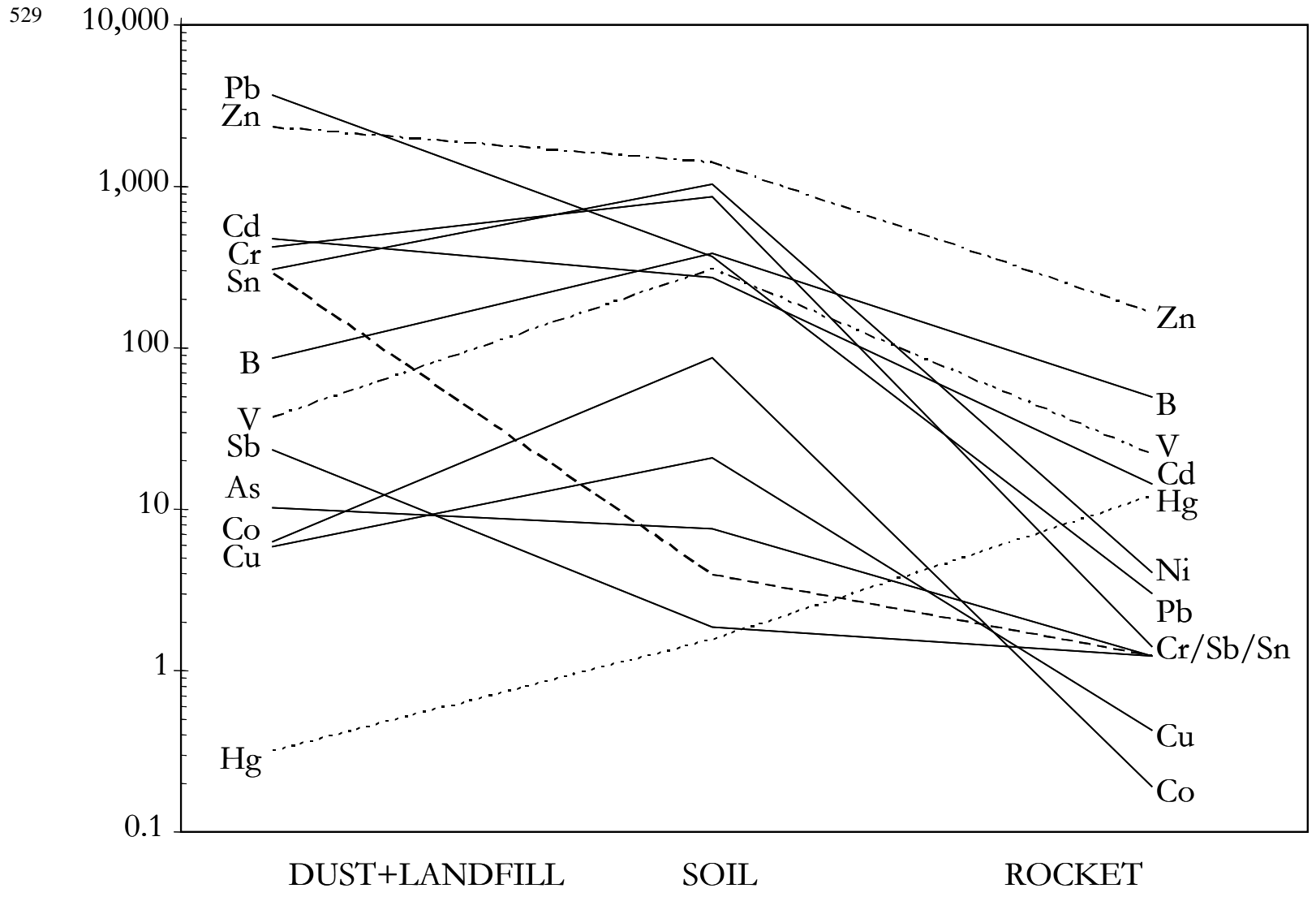


523
524



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 ^a	100/380	35/210	85/530	140/720	36/190
Slovenia ^b	100/150/380	50/70/210	85/100/530	200/300/720	60/100/300
Portugal ^c	200/300	75/110	300/450	300/450	100/200
Spain ^d	250-400 /250-400	80-500 /100-300	250-450 /400-500	300-600 /500-1000	150-300 /300-500
United Kingdom ^e	600-1000	70	500-2000	300	130

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

536

537 Table 2a

Classes of wastes	Quantity	E.U. code
lead metallurgy (1 st and 2 nd 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 nd , 3 rd 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> _{<i>t</i>₀}
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