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Atmospheric elements deposition and evaluation of the anthropogenic part; the AAEF concept

Mickaël CATINON ^a, Sophie AYRAULT ^b, Omar BOUDOUMA ^c, Juliette ASTA ^a, Michel TISSUT ^a
and Patrick RAVANEL ^a

^a *Laboratoire LECA, UMR 5553, Equipe Perturbations Environnementales et Xénobiotiques, Univ. J. Fourier,
38041 Grenoble, France*

^b *Laboratoire des Sciences du Climat et de l'Environnement, UMR 8212, CEA-CNRS-UVSQ/IPSL, 91198 Gif-
sur-Yvette, France*

^c *Service du MEB, UFR928, Université Pierre et Marie Curie, 75252 ParisVI, France*

Michael.Catinon@e.ujf-grenoble.fr ; Sophie.Ayrault@lsce.cnrs-gif.fr ; boudouma@ccr.jussieu.fr ;
juliette.asta@ujf-grenoble.fr ; michel.tissut@ujf-grenoble.fr ; patrick.ravanel@ujf-grenoble.fr

Abstract

The atmospheric deposition on tree trunks is commonly used for evaluating air contamination on a large time scale . However, the deposits are mostly composed of organic matter (generally more than 80 %) and of minerals of geogenic origin. From the elemental composition of the whole deposit, measured by ICP-MS, a calculation was conceived which allows to separate the amounts of elements corresponding to organic matter, to geogenic compounds and, finally, to anthropogenic minerals. For this purpose, the weight of organic matter was obtained through incineration at 550 °C. The elements composition of organic matter was deduced from plant composition. The weight of geogenic compounds was evaluated from the Si, Al content. The formula of geogenic elemental composition took into account the composition of the local soil. This calculation was carried out on four different situations showing the contribution of the main anthropic atmospheric contaminants (Sb, Cd, Sn, Pb, Cu, V, Zn, W, Cr, Ni, Co, As).

1. Introduction

The analysis of atmospheric samples is currently the main process for controlling air quality. However, the analysis of the atmospheric deposit on the earth surface is also a very valuable information source for long term studies on atmospheric changes. The atmospheric deposition occurs on soil and on seas but sampling it in its pure state is extremely difficult. Consequently, in a quest for better conditions, it was shown that tree trunks were much better matrices, less contaminated by soil components, remaining alive for a long time, often over one century and being very common under our climatic conditions. From the seventies, numerous studies were carried out by several scientific teams all over the world in order to establish the chemical and especially elemental atmospheric

35 deposition on tree trunks [1-4]. These studies were a main contribution to the understanding of several
36 atmospheric contaminations for instance by heavy metals, Cd, Cr or Cu [5, 6]. They allowed to
37 compare non-polluted reference stations to heavily contaminated ones and to demonstrate whether the
38 concentration of the contaminants increased or decreased over time. It was, for instance, the case of Pb
39 which was seen to decrease after it was forbidden in 1994 as additive for gasoline [7].

40 More accurate studies concerning elements speciation and origins seemed then to be feasible on the
41 trunk deposits but they required a much better understanding of the deposition process and of the
42 evolution of the deposits on the bark, over time. For this purpose, several points were established:

43 1. A deposit, mostly of atmospheric origin exists on the tree bark surface. It can be isolated through
44 gentle washing with water [8].

45 2. It is mainly composed of organic matter either originating from the bark tissues, from plant or
46 animal fragments transported by wind or from beings living on the bark (algae, fungi, bacteria...) [8,
47 9].

48 3. As it is, the so-called "deposit" represents a revisiscent ecosystem in which biological activities and
49 growth depend on water supply [8].

50 4. The superficial bark tissue in dicotyledonae and gymnosperms is suber. It is constituted of cells
51 which die rapidly, the walls of which are impregnated with a lipophilic polymer named suberin [10].
52 This tissue can be isolated easily and is able to trap a large amount of atmospheric components [11].

53 5. The elemental compositions of the free deposit on the bark and of the suber tissue are not exactly
54 the same and change with a relative independence overtime.

55 6. In the two types of matrices, the constitutive elements may have three different origins: a) they may
56 be the elements contributing to the formation and activity of the living matter, mainly plant cell
57 constituents. This is the case of large amounts of Ca, K, N, S, P, Mg and oligoelements such as Fe, Cu,
58 Zn... b) they may be the elements contributing to the geogenic structures, such as CaCO₃ or primary
59 or secondary minerals (feldspars, clays, quartz...). Small particles of such minerals are transported
60 from the soil by the wind and represent one part of the atmospheric deposits. c) they may be the
61 elements having an anthropic origin, for instance from industrial activities or car traffic.

62 The purpose of the present report was to try to separate, through calculation, the amounts of the
63 different elements coming either from a biological origin or from a geogenic origin or from an
64 anthropic origin.

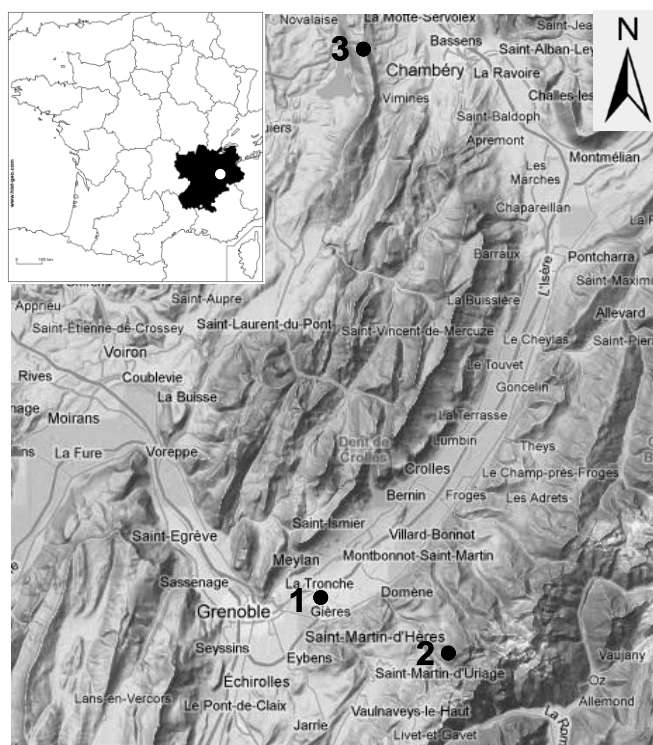
65 **2. Materials and methods**

66 **2.1 Sampling sites**

67 Three places were chosen for a comparative study. The three sampling sites were located in the
68 Rhone-Alpes region (France) near the city of Grenoble. The sites: 1- the Grenoble campus (Joseph
69 Fourier University, Saint Martin d'Hères, Isère, France, altitude 200 m); 2- the "Seiglières" peat bog

70 which is located in a wild, protected area on the North West side of the Belledonne range (altitude
71 1100 m); 3- the A₄₃ highway l'Épine tunnel with a length of 3200 m and with a traffic of 60,000
72 vehicles per day (Figure 1).

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88 **Figure 1: Scheme illustrating the location of the 3 studied sites. Site 1: Grenoble campus, site 2: Seiglières**
89 **peat-bog, site 3: l'Épine tunnel**

90 **2.2. Sampling methods**

91 In sites 1 and 2, the deposits on tree barks were collected from measured bark areas (2 to 10 dm²) by
92 repeatedly rinsing the bark surface with 10 ml distilled water per dm² with the help of a soft plastic
93 brush as described in [8]. The obtained suspension was centrifuged at 8000 rpm (corresponding to
94 9500 g). The pellet was dried and the supernatant was evaporated. The resulting dry matter weight
95 (DW) was measured. Following this procedure, the supernatant contained the elements issued from the
96 soluble and colloidal fractions of the superficial deposit. The pellet was composed of insoluble
97 particles. All dried samples were kept in the dark in closed Teflon flasks at room temperature.

98 On site 1, an alveolated wall protected from rain was shown to accumulate atmospheric dust. Dust
99 was collected using a vacuum cleaner and elemental composition was measured by ICP-MS.

100 On site 3, inside the tunnel, the walls have been washed and the deposit collected. The elemental
101 composition has been analyzed by ICP-MS.

102 **2.3. Total mineral content and organic matter content determination (Loss on ignition)**

103 An aliquot of each sample was heated at 550° C overnight under controlled conditions to minimise

104 mineral volatilization [12, 13]. The ashes were weighed and the ashes/DW ratios calculated. The
105 organic matter content corresponded to DW minus ashes weight.

106 **2.4. ICP-MS: determination of elemental contents**

107 The digestion step was conducted in PTFE closed flasks, on a digestion plate (Digiprep, SCP Science)
108 as previously described [11]. The acid mixture (10 M HNO₃, HF, HClO₄) was chosen to dissolve all
109 materials, whether of organic or mineral origins. Two mL of nitric acid were added to the samples in
110 the flasks, which were then heated for 24 h at 120 °C. After cooling, 2 mL of hydrofluoric acid were
111 added and the flasks were heated for 3 h at 120 °C. After cooling again, 1 mL of HClO₄ was added
112 and the flasks were heated for 3 h. Three successive additions of 10 M HNO₃ were performed. The
113 solutions were then heated to near dryness in opened flasks. The residual solutions after complete
114 digestion were brought to the appropriate volume with ultra-pure water. The elemental content was
115 analyzed by inductively coupled plasma–mass spectrometry ICP–MS (Xseries, Thermo Electron),
116 according to the procedure described by [14], modified by the use of a collision cell technique (CCT)
117 to reduce the isobaric interferences of the Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As. The data quality was
118 controlled with reference materials (lichen-336 and sediment-SL1, both from the International Atomic
119 Energy Agency, Vienna). The values obtained with this procedure agreed well with the certified
120 values as verified for each experiment.

121 **2.5. SEM–EDX: determination of particles content**

122 Samples were studied by scanning electron microscopy. Samples characterisation was performed
123 using a ZEISS SUPRA 55 VP Scanning Electron Microscope (3rd generation of GEMINI field
124 emission column), allowing spatial resolution down to 1.0 nm, coupled to an energy dispersive X-ray
125 microanalysis system (SAHARA Silicon Drift Detector with Spirit Software of PGT) allowing high
126 counting rate. Samples were studied using electronic imaging (secondary electrons [SE] and back
127 scattered electrons [BSE]), X-ray qualitative analysis and X-ray elemental mapping. Analytical
128 conditions were as below:

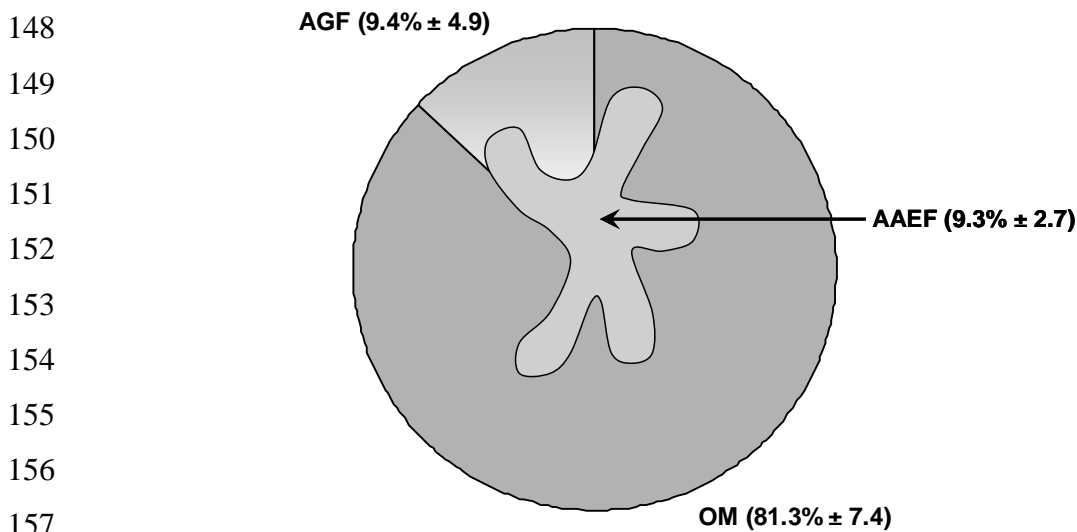
- 129 - Accelerating voltage: 15 kV.
- 130 - Working distance is about 7 mm (optimal distance for EDXanalysis).
- 131 - Samples were carbon coated to reduce charging effects.

132 **3. Results**

133 **3.1 Composition of the studied deposits**

134 Figure 2 illustrates the composition of the superficial deposit on the bark of 1 to 40-year-old ash-tree
135 stems of the Grenoble region (France). 81.3 % of the weight of dry matter is composed of organic
136 matter (OM) as shown by weight loss at 550°C. The estimation of the total weight of the atmospheric
137 geogenic fraction (AGF) is based on the mineral composition of the surrounding soil, sampled at a 50

138 cm depth, under the ploughing depth. It is supposed that the Si content of the organic matter can be
 139 neglected and that the main source of Si was geological. In country, urban or suburban atmospheres
 140 without specific industries (ceramics, steel industry, mining), the Si content of the anthropic fraction
 141 was also considered as negligible. In this context, the Si concentration in the sample allowed to deduce
 142 the amount of soil minerals to which it corresponded. In figure 1, this estimation gave 9.4% for the
 143 atmospheric geogenic fraction (AGF). In places where anthropic emission of Si occurs, the ratios
 144 between the main elements (Si, Ca, K, Al, Mg) in the bark samples change, as compared to the soil
 145 samples. The total weight of the atmospheric anthropic elements fraction (AAEF) expressed in % of
 146 the sample dry weight is obtained as follows: $AAEF\% = 100 - (OM+AGF)$. It reaches $9.3\% \pm 2.7$ in
 147 figure 2.



159 **Figure 2: Diagram showing the composition of the superficial deposit (mean ± SD, n=11) on the bark of**
 160 **ash-trees (*Fraxinus excelsior*) of 1 to 40-year-old sampled in the campus station. OM, organic matter;**
 161 **AGF, atmospheric geogenic fraction; AAEF, anthropic atmospheric elements fraction.**

162 **3.2 Estimation of the elements content of the organic matter fraction (OMF) and of the**
 163 **atmospheric geogenic fraction (AGF)**

164 The organic matter to be found in trunk deposits may have several different origins: through
 165 microscopic observation and diverse chemical analyses, one can deduce that the main components are:
 166 1. plant material, 2. humic substances. The other origins (microbes or invertebrates) seem to remain
 167 very low. Previous studies [15, 16] established a plant material global composition for elements, on a
 168 large number of species. Our own control on ash tree grown under an undisturbed atmosphere agreed
 169 with such a formula with few small changes affecting mainly Ca, K concentrations, probably
 170 depending on the transpiration rate (not shown). The use of Bargagli formula was chosen for OM in
 171 the 4 stations presented in this report.

172

173 Table 1. Composition formula for OM and AGF in 2 different studied sites

174

Element	OM	AGF (campus)	AGF (tunnel)
175 K	8000	19600	9500
Ca	6000	78500	2500
176 Mg	1500	15700	3600
Si	500	607200	369000
177 Mn	80	1100	510
Na	155	13000	4500
178 Fe	125	86000	16700
Al	50	165800	26000
Ti	12	10900	2700
179 Zn	57	200	44
Sr	30	290	45
180 Rb	30	79	79
Ba	30	670	180
181 Cu	12	67	4
Ni	1.8	73	22
182 Cr	1.8	127	62
Pb	0.5	65	16
V	0.55	65	48
183 Mo	0.8	1	1
Ce	0.55	65	65
184 W	0.22	5	5
Sn	0.14	7	7
185 La	0.24	40	40
Cs	0.22	7	7
186 Co	0.22	23	8
Zr	0.063	238	238
187 Sb	0.1	3	1
Ga	0.1	20	20
188 As	0.1	20	12
Hf	0.06	7	7
Cd	0.04	0.5	0.2
189 Sm	0.045	7	7
U	0.01	4	4

190

191 As shown in table 1, the mineral composition of the soil in the different sites was not the same and it
 192 was impossible to use a general formula of the superficial earth crust composition as previously
 193 published [17-19].

194 The SEM-EDX studies of the deposits show that a main part of the AGF is composed of solid particles
 195 which can be readily identified as clays, feldspars, quartz, CaCO₃... (Figure 3).

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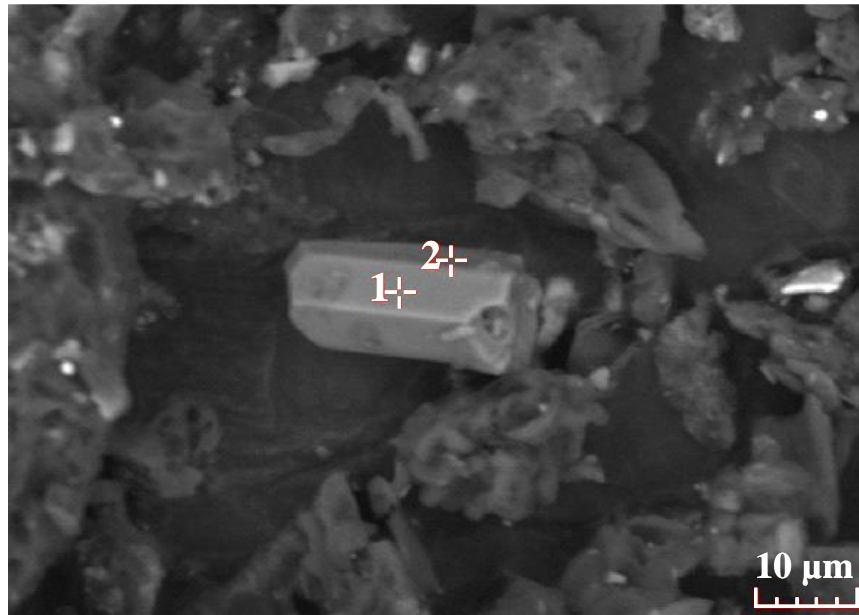
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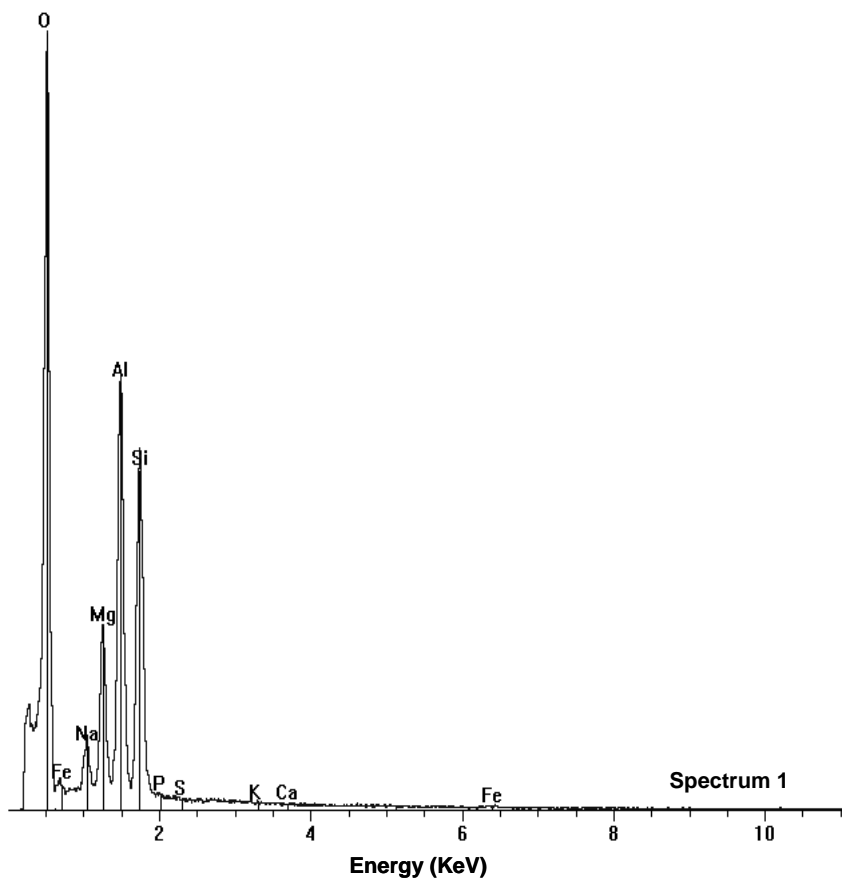
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227 **Figure 3: SEM-EDX picture (80 × 55 μm) of a superficial deposit on a washed bark of a 6-year-old ash**
228 **tree stem sampled in the Seiglières station. Two spots were chosen for chemical composition spectrum**
229 **analysis as shown for the particle. The spectrum corresponds to the spot n°1 on the picture.**
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231 The corresponding spectra issued from the X-ray emission contribute to complete the soil elemental
232 formula established through ICP-MS (Figure 4).

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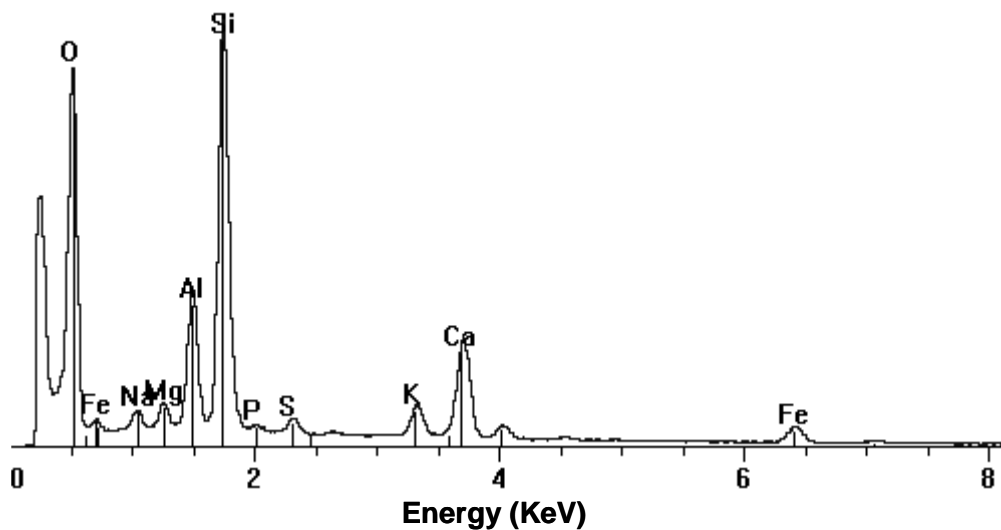


Figure 4: Global X-ray emission spectrums of the campus soil analysed by SEM-EDX

The choice of the surrounding sieved soil as reference formula for AGF is sustained by the fact that the main part of AGF is constituted of small particles coming from The neighbouring area. This use is appropriate in geologically homogeneous sites such as the Isère valley (Site 1) with a high rate of atmospheric emission probably due to agricultural practices (naked soils in early spring and ploughing). It might require supplementary care in places having a complex geology. In site 3, the AGF is mostly influenced by the composition of Hauterivian clay level.

3.3 An example of AAEF calculation: anthropogenic copper in a deposit

On 1 to 40-years-old ash tree stems, the copper content measured by ICP-MS is 102 mg.kg⁻¹ dry weight. Biological Cu reaches 12 mg.kg⁻¹ in OM which represents 81.3 % of the deposit. The biological Cu in the deposit is therefore $12 \times 0.813 = 9.8$ mg. Cu in the AGF reaches 67 mg.kg⁻¹ as shown by the soil formula. In the deposit, the AGF reaches 9.4 % of the weight. The geological Cu in the sample is equal to $67 \times 0.094 = 6.3$ mg. The "anthropic" Cu in the deposit is: $102 - (9.8 + 6.3) = 85.9$ mg. The Cu concentration in the AAEF is $(85.9 \times 100) / 9.4 = 914$ mg.kg⁻¹. The ratio between AAEF Cu content and sample whole Cu content is $(85.9 / 102) \times 100 = 84$ %.

3.4 The results of the AAEF study

Table 2 shows the values of the ratio between the amount of each element of anthropic origin and the whole amount of this element in the sample (in %). The elements which reach a high concentration either in OM or in the AGF or in the two undoubtedly show a low value for this ratio. A null value of this ratio, seen for K, Rb or Ti is probably not true. For an element such as Fe (AAEF = 27, 68, 14 and 4 % respectively in the four samples), the changes in the ratio value depends on the content of the AGF, which is submitted to important changes. Table 2 compares the values of the AAEF ratio for some elements in the 4 studied sites.

265 Table 2. A comparison of the AAEF ratio for the different studied sites, N.A: not analysed. Site 1a: campus ash
 266 trees, site 1b: campus alveolated wall, site 2: Seiglières peat-bog ash trees, site 3: highway tunnel walls.

267

Elements	Site 1a	Site 1b	Site 2	Site 3
Sb	93	97	80	96
Cd	92	99	89	95
Sn	89	N.A	N.A	91
Pb	87	96	84	97
Cu	84	92	67	96
V	83	N.A	71	33
Zn	81	96	26	92
W	72	N.A	N.D	58
Cr	72	78	51	80
Ni	72	84	61	49
Mo	68	N.A	N.A	94
Co	59	98	53	N.A
As	57	90	N.A	12
Ba	44	80	37	63
Mn	31	57	48	36
Na	30	N.A	N.A	37
Fe	27	68	14	4
Mg	25	45	10	2
Sr	12	76	N.A	84
Ca	8	79	27	66
K	0	22	0	3

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278 The lowest anthropic contribution on ash-tree was observed in the Seiglières station (alt 1100 m) in the
 279 mountain close to Grenoble. On the Grenoble campus, site 2 shows a heavy contamination for the 9
 280 elements considered (Sb, Cd, Pb, Cu, Zn, Cr, Ni, Co, As) with some specific features (high Co and As
 281 concentrations). The fact that site 2 was protected from rain was to be taken into account. However,
 282 SEM-EDX study (not shown) demonstrated that this site was submitted to a specific industrial
 283 contamination. In the A₄₃ tunnel, the level of anthropic contamination was high with a noticeable
 284 typology: anthropic V, W, Ni, As were specifically at a low level.

285 4. Discussion and conclusion

286 As seen in table 2, the AAEF calculation allows to see several interesting differences between sites,
 287 which seem to depend clearly on atmospheric activities. We can expect that a more extensive use of
 288 this method will increase its accuracy and reliability. Furthermore, it may induce some diversification
 289 in the reference formula for OM, possibly depending on the composition of the local flora.

290 If crossed with observation methods such as SEM-EDX, this method may contribute to give a much
 291 better insight of the type of contamination of a sample.

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