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Multianalytical determination of trace elements in atmospheric biomonitors by k_0-INAA, ICP-MS and AAS

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Abstract

Elemental contents of atmospheric biomonitors—epiphytic lichens and tree bark, exposed in continuous and discontinuous modes—have been assessed through k_0-standardised instrumental neutron activation analysis (k_0-INAA) (two different institutions), inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS). Certified reference materials—ISE-921 (river clay), NIST-1547 (peach leaves), ICHTJ-INCT-TL-1 (tea leaves; TL-1 hereinafter) and IAEA-336 (lichen material), and nonparametric statistics—rank-order correlations (Spearman R_S) and enhanced-sign tests (Wilcoxon T)—were used for analytical control and data comparison, respectively. In general, quality of procedures was deemed good, except for k_0-INAA in determining Br, Cu and Na, all likely affected by high counting statistics, and/or contamination issues (the latter). Results for Cu, Ni, Pb and Sr (by both ICP-MS and AAS) revealed that, despite an outstanding correlation (asymptotic $p = 0.000$), they could be viewed as statistically equal for Cu only: AAS tended to yield higher values for Pb and Ni, and lower ones for Sr. The comparison between ICP-MS and k_0-INAA data from TUDelft, for Al, Ca, Cu, Mg, Mn, Na, Ti and V, showed an excellent correlation (as above) and random (relative) magnitude for Cu, Mg, Mn and Ti only: ICP-MS tended to yield higher values for Al, Na and V, and lower ones for Ca, whereas between k_0-INAA data from TUDelft and ITN, for Br, Ca and Na, resulted in systematically higher [Br] and [Ca] variates from TUDelft, even if all corresponding data sets were found to correlate at stringent significance levels. In a few cases, though—Ca, Sr in lichens; Pb in bark—matrix effects did appear to interfere in the outcome of matched-pairs, signed-rank tests, since random hierarchy of variates could be asserted just when lichen and bark data sets were processed separately.

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1. Introduction

In its most pragmatic sense, biological monitoring boils down to an intensive assessment of a certain attribute in both space and time, with a significant reduction in total sampling costs. Tracking such an attribute from the change(s) thereby imparted to some organisms—or parts of them—may result in relevant information on a full-scale range, from any characteristic of the biosphere at large down to some specific aspect at the habitat level. This is the conceptual, comprehensive scope; still, when it comes to botanical specimens in terrestrial environments, one invariably thinks of monitoring airborne contaminants at ground level [1].

The use of vegetable organisms for atmospheric monitoring really started getting widespread attention after the work with mosses in the late 1960s [2,3], even if there is an

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overwhelming literature dealing with plant species and airborne contaminants that goes back to the mid-19th century [4]. Since then, and apart from mosses, most studies and surveys have been conducted with lichens [5–10]. Despite a much lower proportion relative to lower epiphytes, work with vascular plants has shown that tree bark could be successfully used in atmospheric monitoring as well [11–13], even if specific issues might be seen to limit barks as biomonitors [14,15]. However, bark features some well-known assets too—greater availability and accessibility, easier identification and sampling, (much) lower ecological impact, to name just a few—let alone a few others that are seldom referred to, such as an ability for isotopic discrimination or elemental enrichment, at least for certain elements of interest [16,17].

The downside of biomonitoring—or, at least, its major drawback—is, of course, an inherently high variability of all biological data. Everything that may help to abate the uncertainty of final results should be sought, and that includes an adequate choice of one analytical routine, or, preferably if at all possible, a multianalytical approach when assessing an elemental pool. The point is, analytical accuracy notwithstanding, distinct techniques ask for different sample-preparation procedures and rely on dissimilar signal-producing methodologies, which can lead to some divergence in their operational outputs.

The present study brings into focus tree-bark and lichen-thalli data from *Parmelia caperata* (L.) Ach. (syn. *Flavoparmelia caperata* (L.) Hale) and *Platanus hybrida* Brot. (syn. *Platanus acerifolia* (Ait.) Willd.), respectively, which were exposed simultaneously at three locations of mainland Portugal, and then searched for elemental contents by means of k_0-standardised, instrumental neutron activation analysis (k_0-INAA), inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) [18–21]. Their results for Al, Br, Ca, Cu, Mg, Mn, Na, Ni, Pb, Sr, Ti and V are assessed and discussed herein, as part of an ongoing research on the suitability (and interchangeability) of analytical techniques for determining specific elements in air-monitoring matrices [22,23], since an intrinsic accuracy may not necessarily imply an equal (optimal) performance in every real situation [24].

2. Materials and methods

2.1. Field exposure and sample preparation

The starting material for transplants has been picked up in a low-pollution area of northern Portugal (Baião), where *Parmelia caperata* thalli were collected from pine trees at ca. 1.5 m above ground, and *Platanus hybrida* bark samples from corresponding trunks at an approximate height. All lichen thalli were kept with their bark substrate. The samples, weighing between 200 and 900 mg (bark) and from 150 to 450 mg (lichens), were then transferred to testing facilities at three coastal cities—Viana do Castelo (north), Lisboa (centre) and Sines (south-west)—where

Table 1
Elemental concentrations (mg kg^{-1}, unless otherwise specified) in reference materials by INAA (ITN[a]; TUDelft[b]), ICP-MS (Netherlands Institute of Applied Geoscience—National Geological Survey) and AAS (University of Porto), and their comparison with the corresponding certified values (n = number of replicates)

Reference material	Analytical method	Elemental data										
TL-1	INAA	Na[a]	Na[b]	Mg [%][b]	Al [%][b]	Ca[a][%]	Ca[b][%]	V[b]	Mn[b][%]	Cu[b]	Br[a]	Br[b]
	Exp. mean (n)	24.5 (*7*)	<110	0.251 (*9*)	0.236 (*9*)	0.571 (*7*)	0.632 (*9*)	2.17 (*9*)	0.1631 (*9*)	30.6 (*7*)	10.4 (*7*)	15.6 (*7*)
	Unc. (95%)	5.7	—	0.028	0.013	0.079	0.055	0.28	0.0054	9.5	1.0	2.9
	Cert. value	24.7	24.7	0.224	0.229	0.582	0.582	1.97	0.157	20.4	12.3	12.3
	Unc. (95%)	3.2	3.2	0.008	0.014	0.052	0.052	0.18	0.005	0.8	1.0	1.0
NIST-1547	INAA	Na[a]	Na[b]	Mg[b][%]	Al[b]	Ca[a][%]	Ca[b][%]	**V[b]**	Mn[b]	Cu[b]		
	Exp. mean (n)	35.6 (*8*)	39.1 (*9*)	0.459 (*9*)	272.8 (*9*)	1.25 (*8*)	1.652 (*9*)	0.400 (*9*)	99.8 (*9*)	<5		
	Unc. (95%)	11.8	6.1	0.018	9.8	0.91	0.058	0.076	2.3	—		
	Cert. value	24	24	0.432	249	1.56	1.56	0.37	98	3.7		
	Unc. (95%)	2	2	0.008	8	0.02	0.02	0.03	3	0.2		
ISE-921	ICP-MS	Na [%]	Mg [%]	Ca [%]	Ti [%]	V	Mn [%]	Ni	Cu	Sr	Pb	
	Exp. mean (n)	0.557 (*6*)	1.12 (*6*)	3.59 (*6*)	0.3570 (*6*)	89.9 (*6*)	0.116 (*6*)	40 (*6*)	91 (*6*)	162 (*6*)	166 (*6*)	
	Unc. (95%)	0.075	0.11	0.38	0.0074	8.9	0.0115	3.8	11	10	11	
	Cert. value	0.5570	1.12	4.31	0.3690	90	0.1188	43	95	164	167	
	Unc. (95%)	n.a.	n.a.	n.a.	0.0050	5	0.0045	4	5	8	9	
IAEA-336	AAS	Na [%]	Mg [%]	Ca [%]	Ti [%]	V	Mn [%]	Ni	Cu	Sr	Pb	
	Exp. mean (n)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.8 (*31*)	5.0 (*27*)	8.9 (*32*)	
	Unc. (95%)	—	—	—	—	—	—	—	0.2	0.6	0.6	
	Cert. value	—	—	—	—	—	—	—	3.6	4.9	9.3	
	Unc. (95%)	—	—	—	—	—	—	—	0.5	0.6	1.1	

n.a., not available; n.d., not determined.