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Accumulating pollutants in conifer needles on an Atlantic island – A case study with *Pinus canariensis* on Tenerife, Canary Islands

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Pollutant concentrations in pine needles indicate moderate local impact of sulphur, particulate matter, and sea sprays at lower elevation plots in Tenerife.

Abstract

Concentrations of potential pollutant elements Na, Cl, and S were investigated in needles of *Pinus canariensis* grown at 55 field plots in Tenerife. Microelement concentrations (including heavy metals) were measured at a subset of 18 plots. Na and Cl concentrations were high at low elevations (up to 8 mg g^{-1} Cl and 5.5 mg g^{-1} Na). Na/Cl ratio close to standard seawater indicated sea spray influence up to 1200 m a.s.l. Only at few plots, sulphur concentrations indicated possible pollutant impact. Cluster and correlation analyses identified a related group of V, As, Cr, Fe, Mo, Ni, Cu, Pb, and Al, possibly related to traffic exhaust aggregated with soil particles. Mainly north-eastern, lower elevated plots were exposed to those immissions, but metal concentrations were generally low compared to data from other studies. In conclusion, seawater and soil particles explained most of the element distribution pattern in pine needles in Tenerife, but strong indications for some effect of local sources of air pollutants were detected.

Keywords: Bioindication; Sulphur; Chloride; Heavy metal; Pine needles

1. Introduction

Element concentrations in conifer needles are widely accepted bioindicators for the impact of airborne pollutants (Arndt et al., 1987; Guderian, 2001; Lombardo et al., 2001; Poykio and Torvela, 2001; Rautio and Huttunen, 2003). In the Austrian Federal Law, for example, threshold values for spruce and pine needle concentrations of sulphur, chloride, and fluoride are listed depending on the needle age class (Austrian Federal Law, 1984). For example, sulphur concentrations of more than 1.2 mg g^{-1} needle dry weight in current year's needles and more than 1.5 mg g^{-1} in 1-year-old pine needles are indicative of field plots impacted by sulphur air pollution.

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On the European scale, needle concentrations of nutrients and pollutants are included in the monitoring programme of the ICP Forest (De Vries et al., 2000). In this programme, correlation analysis corroborated close relation between sulphur deposition and needle sulphur concentrations in conifer needles, particularly in pine needles (De Vries et al., 2000). Foliar element concentrations are classified in three ranges, based on criteria established by the Forest Foliar Coordinating Center for major elements (Stefan et al., 1997).

Conifer needles are not only best suited accumulators of major elements present in higher concentrations, but are also used for trace elements found in small concentrations, which are, nevertheless, of environmental importance. Heavy metal concentrations in needles have been reported as indicators of industrial pollution and traffic exhaust impact. A survey of Poland used *Pinus sylvestris* as a monitor plant and reported pollution maps for Zn, Pb, Cd, Cu, As in addition to needle S concentrations (Dmuchowski and Bytnerowicz, 1995). Some studies included pine species in bioindication in the vicinity of heavily polluted sites (Reimann et al., 2001). Metal pollution by traffic exhausts was investigated in detail by Monaci et al. (2000) who studied evergreen oak leaves (albeit not conifers) in an urban environment.

However, most of these studies were performed in temperate (Dmuchowski and Bytnerowicz, 1995; Guderian, 2001) or boreal (Manninen and Huttunen, 2000; Reimann et al., 2001) climate regions. Only a smaller number of studies were conducted in Mediterranean conditions (Monaci et al., 2000; Raddi, 1992), and they are only rarely on pines. In the ICP forest programme, Mediterranean pine species *Pinus halepensis* and *Pinus pinaster* are included, but data are restricted to the European continent (De Vries et al., 2000). In spite of its local importance in a region which is part of the European Union, *Pinus canariensis* is not included. This species is endemic to the Canary Islands where it mainly forms pure stands under widely different ecological conditions (Blanco et al., 1989). The distribution limit in Tenerife ranges from about 500 to more than 2500 m above sea level on the south facing slopes of the island and from 800 to 2200 m on the northern slopes. The southern pine forests are exposed to very dry, partly semi-arid climates whereas the northern pine forests experience frequent fog impacts and, consequently, more humid conditions. At the high elevation plots, the trees have to cope with regular winter frosts. These pine forests (“pinares”) are essential for the local forestry and contribute strongly to the water balance of the islands by filtration of “horizontal precipitation” (from clouds and fog) and by providing protection from erosion. Furthermore, *P. canariensis* is of potential importance for forestry in Mediterranean climate. It has been successfully used as a commercial forest tree mainly in regions of Morocco and South Africa, and to some extent also in Australia, Southern America, and New Zealand (Stephan, 1995), and as an ornament e.g. in Southern California. In addition to an earlier small scale study at one particular elevational profile at the southern slope of the island (Tausz et al., 1998), mineral nutrients of *P. canariensis* needles were investigated in an extended survey in Tenerife (Tausz et al., 2004). However, concentrations of potential pollutants have not been reported for this species.

Small scale bioindication studies often pointed out the close connection between geomorphology and pollutant impact. Studies in narrow Alpine valleys near smaller industrial pollution sources (e.g. Tausz et al., 1994) contrasted the large scale studies of predominantly flat land (Dmuchowski and Bytnerowicz, 1995). As addressed in a recent investigation on organochlorine pesticides (Villa et al., 2003), the situation in Tenerife, a relatively isolated island rising to nearly 4000 m above sea level, exposed to regular trade winds and hosting heavy traffic and considerable industry, may be very different. The objective of the present work was a survey of potential pollutant elements in foliage of *P. canariensis* to test whether anthropogenic or natural, local or distant sources of these elements can be indicated.

2. Materials and methods

2.1. Plant material and study area

Sampling procedure was based on the ICP Forests protocols (De Vries et al., 2000). Fifty-five plots were selected in the pine forest regions of Tenerife (Fig. 1). Microelement analysis (e.g. heavy metals) were done on a subset of sites (Fig. 7). Three *P. canariensis* trees per plot were sampled in August 1998. Sampling trees were dominant or, at open stands, of an average stand height. Twigs were pruned from the light exposed portions of crowns at 5 m height with pole pruners. Fully developed needles of the youngest (current year’s needles) and previous season’s (1-year-old) flush were collected and oven-dried at 80 °C. The needles were ground in a laboratory mill (Analysenmühle A10, Janke and Kunkel, Germany) and the powder stored over silica gel until extraction. Aliquots of each tree per plot were combined to one mixed sample per plot for each age class separately.

For a subset of samples ($n = 18$), a sub-sample of needles were washed in distilled water prior to analysis to evaluate external adhesion of substances.

2.2. Sulphur and chloride determination

Total S was determined after combustion in O_2 atmosphere over H_2O_2. Resulting extracts were subjected to isocratic HPLC analysis on an anion exchange column

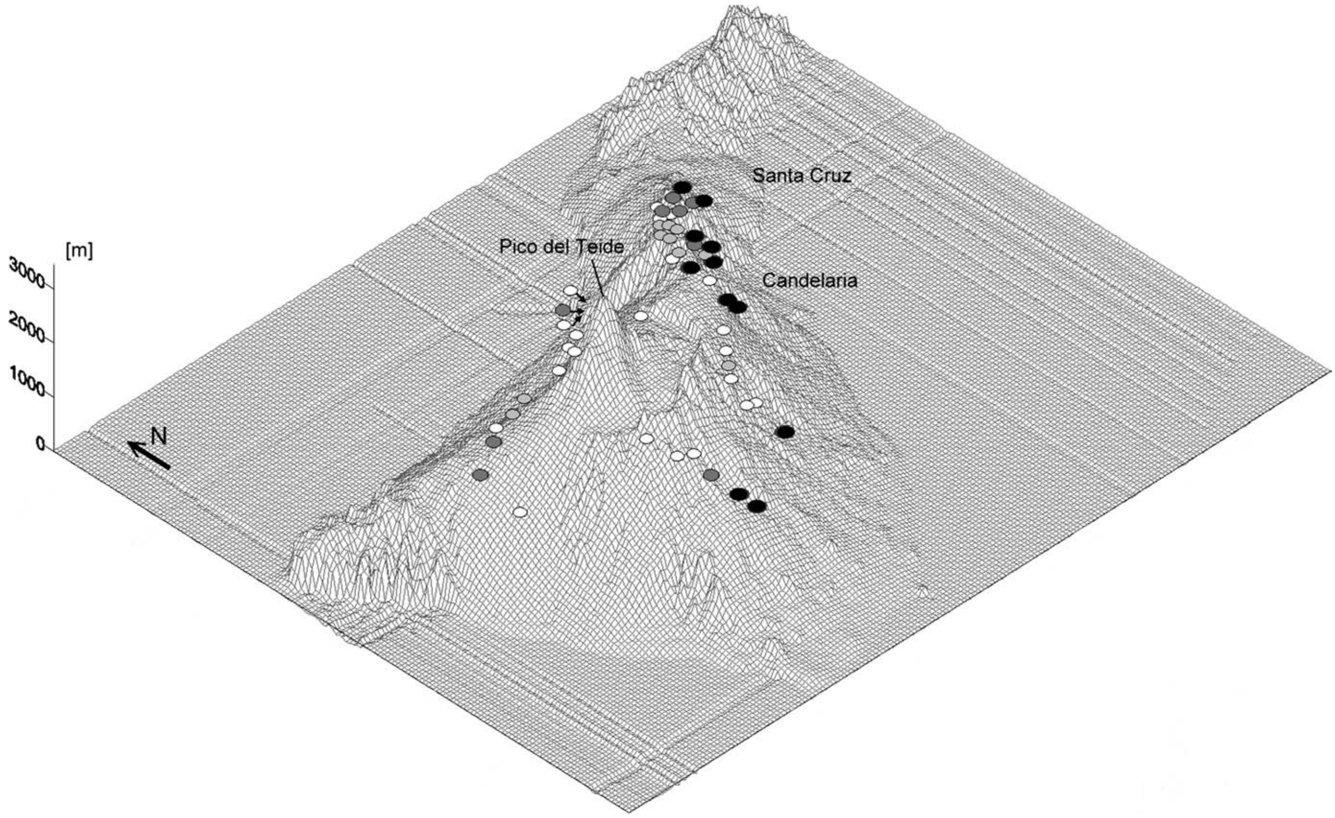

Fig. 1. Distribution of Cl concentrations in 1-year-old *Pinus canariensis* needles in Tenerife. Arrows: plots would be behind the Pico del Teide from the present viewpoint. ○ <0.60 mg Cl g^{-1} needle DW, ◍ $0.60 \leq x < 1.10$ mg g^{-1}, ◉ $1.10 \leq x < 1.60$ mg g^{-1}, ● ≥ 1.60 mg g^{-1}.

(Metrosep Anion Dual 1 3 × 150 mm, pre-column ODS-2 3 × 40 mm, Metrohm, Herisau, Switzerland). Solvent was phthalic acid (8 mmol l^{-1}) with acetonitrile (2% v/v) at pH 4.0. At a flow rate of 0.5 ml min^{-1} elution time of sulphate was 15 min, that of chloride was 5 min. Quantification was done after conductivity detection (ESA conductivity meter). Calibration was controlled by co-analysis of certified standard materials (Spruce needles Nr. 70, Standard Reference Material 101, EC Bureau of Reference).

2.3. Sodium determination

The extracts were prepared by wet digestion in H_2SO_4 and HNO_3. A mixture of 2.5 ml 65% (w/w) HNO_3 and 6 ml H_2SO_4 (96–98% w/w) were used for 500 mg sample powder. Extraction was carried out in a digestor (Digestor 430, Büchi, Switzerland) until extracts were clear and colourless. The extract was adjusted to 50 ml with double distilled water (Urbach et al., 1976). Sodium was determined by atomic absorption spectroscopy (AAS 5 FL, Zeiss, Germany).

2.4. Microelement analyses

For the determinations of the microelements ~300 mg of sample powder were weighed to 0.1 mg into the 12-mL quartz digestion vessels of the microwave assisted heating autoclave UltraCLAVE 2 (EMLS, Leutkirch, Germany). After addition of 5.0 mL subboiled nitric acid, the vessels were closed with Teflon cups, placed in the quartz rack and the rack was mounted in the UltraCLAVE 2. Thereafter, the system was loaded with Argon to a final pressure of 40 bar. The heating programme was ramped to 250 °C within 40 min and then the temperature was kept at 250 °C for 30 min. After cooling the samples were quantitatively transferred into 50 mL polyethylene tubes.

An Agilent 4500 inductively coupled plasma mass spectrometer (Agilent, Waldbronn, Germany), equipped with a Babington-type nebulizer was used for the determination of the micronutrients. Quantification was performed with external calibration curves in the appropriate concentration ranges. For quality control NIST SRM 1575 Pine Needles (National Institute of Standards and Technology, Gaithersburg, USA) were mineralized and analysed in the same way.

2.5. Statistics

Differences between needle age classes were judged by Wilcoxon's two sample test. Correlations between element concentrations were evaluated by Pearson's r correlation coefficient.

Table 1
Medians and quartiles of potential pollutant macroelement concentrations (mg g^{-1} needle dry weight) in *P. canariensis* needles from 55 plots in Tenerife

Element	Current year's needles			1-year-old needles			Threshold[a]
	25 Percentile	Median	75 Percentile	25 Percentile	Median	75 Percentile	
S	0.75	0.88	0.99	0.96	1.13	1.34	>1.20[b], >1.50[c]
Cl	0.44	0.69	1.26	0.44	0.70	1.49	>1.10[b,c]
Na	0.07	0.12	0.24	0.44	0.77	1.34	–

[a] Concentrations larger than thresholds indicate air pollution impact (Austrian Federal Law, 1984; Huttunen et al., 1985).

[b] Current year's needles.

[c] 1-year-old needles.

To evaluate patterns in the data set (microelement data), cluster analysis techniques were applied. Sample plots were clustered on element concentrations after standardization of the input variables using Ward's algorithm and the Euclidian distances. Results were the same, when the unweighted paired group average (UPGA) method was used. Element concentrations were tested for significant differences between clusters by Mann–Whitney's *U*-test.

Similarities in patterns between different elements are commonly judged by multivariate statistical techniques based on correlation analysis, such as factor analysis. Since the present data set is too small to allow reliable factorization, evaluation was done by cluster analysis. Elements were clustered using Ward's algorithm and the Euclidian distances on the normalized data set, results were corroborated by the UPGA method (StatSoft, 2003).

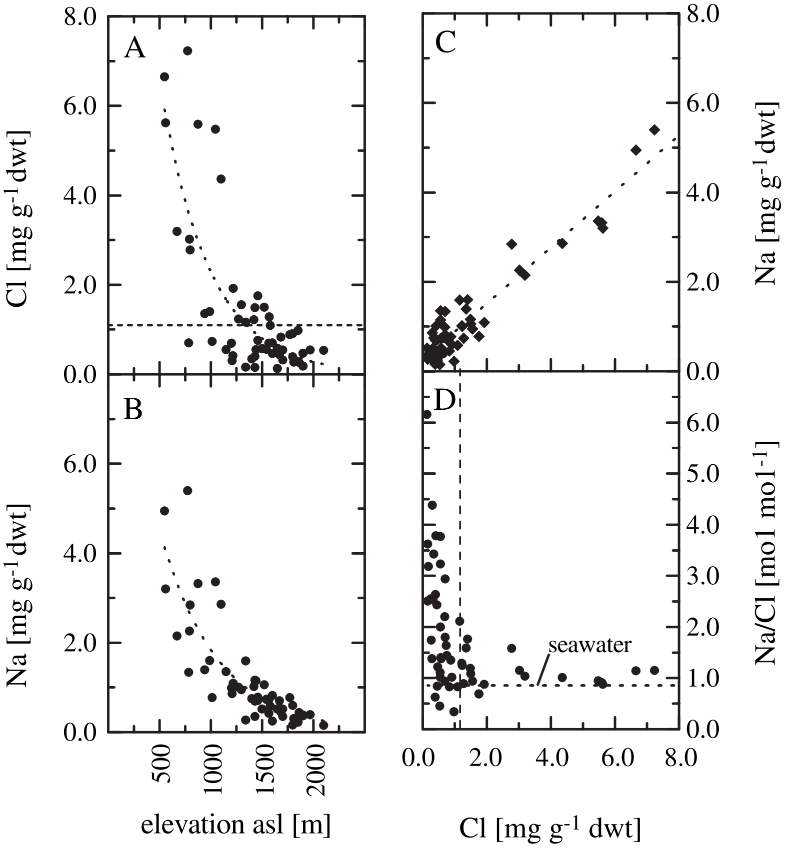

Fig. 2. Relations between Na and Cl concentrations in 1-year-old needles of *Pinus canariensis* at 55 plots in Tenerife. (A) Chloride concentrations vs elevation. Fitted by exponential decay function; horizontal line indicates Cl threshold value in pine according to Austrian Federal Law (1984). (B) Sodium concentrations vs elevation. Fitted by exponential decay function. (C) Na vs Cl concentrations. Fitted by linear fit. (D) Na/Cl ratio vs Cl concentrations. Horizontal line indicates Na/Cl ratio of standard seawater, vertical line indicates Cl threshold value in pine according to Austrian Federal Law (1984).

3. Results

3.1. Sodium, chloride, and sulphur

Macroelements Na and Cl were significantly higher in 1-year-old needles compared to current ones (Table 1). Within needle age classes, both elements were closely intercorrelated (in youngest needle age class: $r = 0.82$, $p < 0.001$; in 1-year-old needles: $r = 0.95$, $p < 0.001$), and both elements were negatively correlated with elevation of the plots. Correlation coefficients with elevation were $r = -0.57$ ($p < 0.001$) and -0.79 ($p < 0.001$) for Na in current and 1-year-old needles, and $r = -0.48$ ($p < 0.001$) and -0.69 ($p < 0.001$) for Cl (Fig. 1). Twenty plots could be classified in the highest Cl class according to Austrian Federal Law (1984). Highest values were found at plots in the north- and south-eastern slope of the island, located in the closest distance to the sea (Figs. 1 and 2). When needles were washed to remove external ions, Na and Cl concentrations were up to 9% lower. However, these differences were not significant ($p > 0.01$), indicating that only low amounts of Na and Cl were present at needle surfaces. In samples with high Cl concentrations, the Na/Cl ratios were close to standard seawater composition, which indicated a sea spray as the main chloride source.

Sulphur concentrations were higher in the 1-year-old needles than in the current year flush (Table 1). At 9 plots, S concentrations in 1-year-old needles were higher than the threshold values suggested for S polluted pines (Austrian Federal Law, 1984; Stefan et al., 1997). This was only true at 1 plot for the current year's needles. All these plots were at the eastern slope of the island, predominately at the north-eastern part (Fig. 3). Sulphur values were negatively correlated with elevation for the 1-year-old needles ($r = -0.66$, $p < 0.001$), but not for the current season's needles ($r = -0.07$, not significant). Sulphur concentrations in 1-year-old needles were also correlated with Na ($r = 0.45$, $p = 0.001$) and Cl ($r = 0.41$, $p = 0.002$), but not in the current year needles. Needle washing decreased S concentrations by about 7%, but differences to unwashed needles were not significant. According to most sampling protocols (De Vries et al., 2000), all further evaluations are based on data of unwashed needles.

3.2. Microelements

Microelement concentrations are shown in Table 2. All the investigated elements were closely correlated between current and previous year's needles, and significant differences between needle age classes were not found.

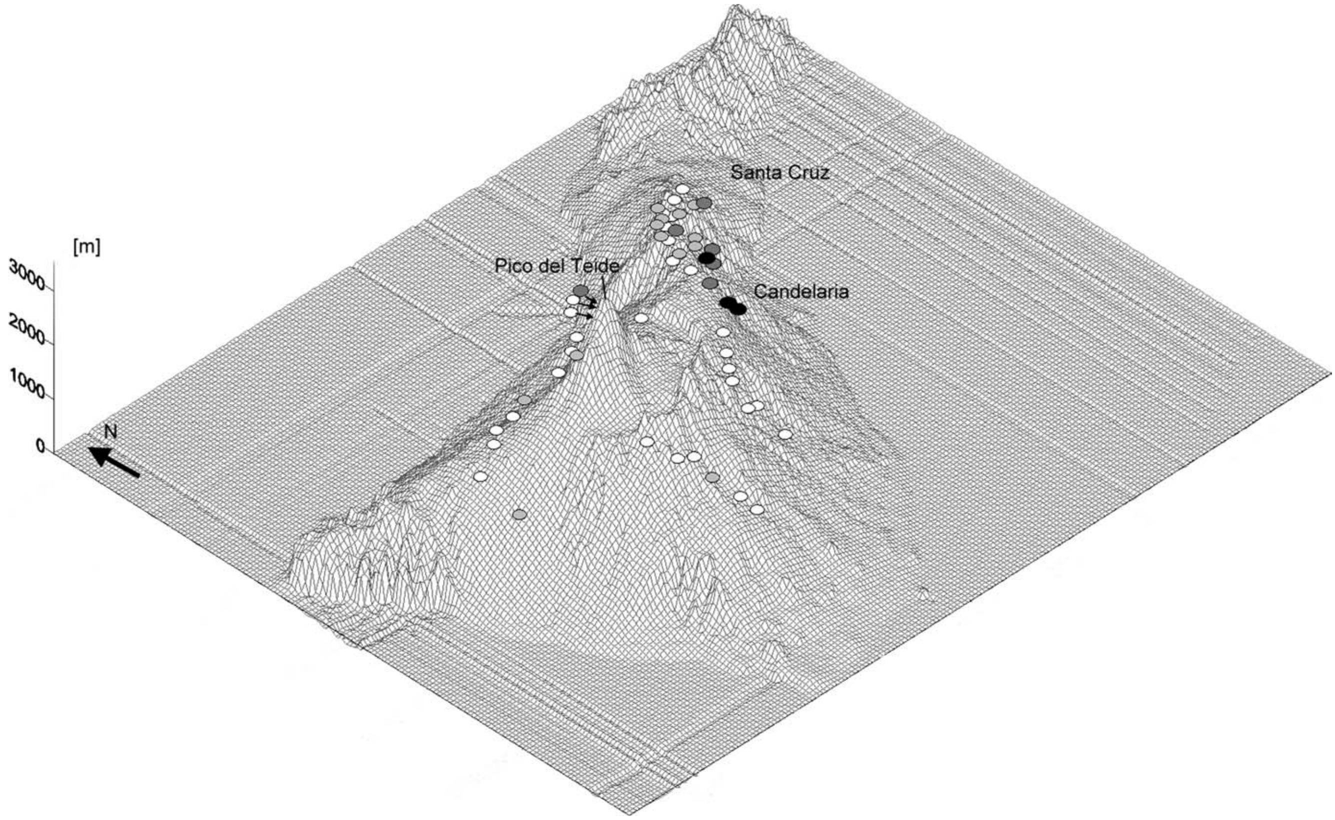

Fig. 3. S concentrations in 1-year-old *Pinus canariensis* needles in Tenerife. Arrows: plots would be behind the Pico del Teide from the present viewpoint. ○ <1.20 mg S g^{-1} needle DW, ◍ $1.20 \le x < 1.50$ mg g^{-1}, ◉ $1.50 \le x < 1.80$ mg S g^{-1} needle DW, ● ≥ 1.80 mg S g^{-1} DW.

Table 2
Medians and quartiles of trace element concentrations in *Pinus canariensis* needles from 18 plots in Tenerife

Element	Current year's needles			1-year-old needles			Threshold[a]
	25 Percentile	Median	75 Percentile	25 Percentile	Median	75 Percentile	
Al (μg g^{-1} dry weight)	594.0	786.5	862.6	601.0	772.7	847.3	
B (μg g^{-1} dry weight)	14.2	19.5	30.1	13.9	19.1	30.9	
Fe (μg g^{-1} dry weight)	443.2	557.4	719.4	442.6	563.3	683.8	200[b]
Mn (μg g^{-1} dry weight)	99.5	229.1	317.7	99.9	224.8	313.0	800[b]
Sr (μg g^{-1} dry weight)	21.3	33.9	43.9	21.3	31.0	42.3	
Zn (μg g^{-1} dry weight)	20.4	32.5	38.9	20.5	32.4	39.2	70[b,c]
Ag (ng g^{-1} dry weight)	9	11	13	9	12	14	
As (ng g^{-1} dry weight)	69	107	157	62	104	131	300[c]
Ba (ng g^{-1} dry weight)	3735	5817	6950	3643	5664	6653	
Cd (ng g^{-1} dry weight)	15	31	39	15	29	39	500[c]
Co (ng g^{-1} dry weight)	226	481	605	265	468	584	
Cr (ng g^{-1} dry weight)	2134	2679	3132	2182	2773	3087	
Cu (ng g^{-1} dry weight)	1928	2467	3042	1842	2398	2862	10 000[c]
Hg (ng g^{-1} dry weight)	26	37	49	24	35	48	
Li (ng g^{-1} dry weight)	276	489	680	272	471	659	
Mo (ng g^{-1} dry weight)	35	91	153	36	90	135	
Ni (ng g^{-1} dry weight)	1114	1676	2058	1166	1692	1921	
Pb (ng g^{-1} dry weight)	286	393	574	284	373	540	10 000[c]
Rb (ng g^{-1} dry weight)	2956	4764	5672	2910	4387	5645	
Se (ng g^{-1} dry weight)	231	259	293	198	243	286	
Sn (ng g^{-1} dry weight)	17	25	30	17	23	31	
V (ng g^{-1} dry weight)	899	1482	2121	902	1414	1949	

[a] For 1-year-old needles. Values greater than threshold are regarded indicative of pollution uptake.
[b] Stefan et al. (1997).
[c] Dmuchowski and Bytnerowicz (1995).

Compared to values reported in industrially polluted areas, concentrations of potential pollutants were rather low. For example, Dmuchowski and Bytnerowicz (1995) classified pine needle concentrations of below 0.3 mg g^{-1} As, below 5 mg g^{-1} Cu, below 10 mg g^{-1} Pb, below 0.5 mg g^{-1} Cd, and below 70 mg g^{-1} Zn in the lowest (unpolluted) of four pollution zones within a study in Poland. These values were hardly exceeded in the present study (Table 2).

Correlation analysis indicated groups of trace elements showing similar distribution patterns among investigated plots (Table 3). Significant bivariate correlations between trace element concentrations were found within the group of V, As, Cr, Fe, Mo, Ni, Cu, Pb, and Al. Furthermore, Zn and Cd were significantly correlated (Table 3). This grouping was corroborated by a cluster analysis resulting in a clustering of V, As, Cr, Fe, Mo, Ni, Cu, Pb, and Al in one cluster, and Cd and Zn in another, as well as Na and Cl in one more (Fig. 4). These results point toward common origins of the elements clustered together.

3.3. Element patterns at different plots

The subset of those 18 plots, where trace elements were analysed, was subjected to a cluster analysis according to the similarity patterns in element distribution. This resulted in three clusters (Fig. 5). One cluster consisted only of one plot. Separating variables, i.e. those showing significant differences ($p < 0.01$) between clusters were V, Mn, Fe, Ni, As, Pb, and Zn in both needles age classes, and Cr in current year's needles only. Needles of trees in cluster 1 contained higher amounts of most of these elements, except for lower values in Mn and Zn (Fig. 6). Samples from the one plot clearly separated from all others (in cluster 2) contained highest concentrations of V, Fe, Ni, As, Pb, and Zn, and lowest of Mn (Fig. 5). In Fig. 7, location of these plots on the island is shown. Members of cluster 1 are predominately situated at the eastern slope, mainly at lower elevated plots.

4. Discussion

A relatively isolated island, Tenerife is exposed to the regular (humid and cool) trade winds coming from the northeast. A frequent temperature inversion at about 1500 m a.s.l. prevents the ascending of the oncoming air masses and creates the "mar de nubes" (ocean of clouds) at about 800–1000 m a.s.l. The southern slopes are shielded from the direct trade winds by the mountain range, which makes them drier and warmer (Villa et al., 2003). Sparser vegetation cover on the southern slopes may facilitate the distribution of airborne compounds by more local winds.

Table 3
Correlation matrix of trace elements in current and 1-year-old *Pinus canariensis* needles ($n = 18$)

	B	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Mo	Cd	Ba
Current year's needles														
Al	0.56													
V	0.41	**0.81**												
Cr	0.48	**0.80**	**0.85**											
Mn	−0.12	−0.48	−0.52	−0.40										
Fe	0.55	**0.94**	**0.93**	**0.88**	−0.51									
Ni	0.49	**0.80**	**0.96**	**0.95**	−0.48	**0.92**								
Cu	0.22	0.55	**0.60**	**0.63**	−0.59	**0.60**	**0.65**							
Zn	0.08	0.02	−0.27	0.14	0.47	−0.11	−0.11	−0.20						
As	0.51	**0.71**	**0.80**	**0.78**	−0.43	**0.77**	**0.85**	**0.77**	−0.06					
Se	−0.11	−0.20	−0.02	−0.18	0.03	−0.12	−0.09	−0.25	−0.11	−0.06				
Mo	0.40	**0.63**	**0.70**	**0.69**	−0.29	**0.74**	**0.81**	0.48	0.24	**0.64**	0.00			
Cd	−0.04	−0.22	−0.40	−0.08	0.48	−0.27	−0.24	−0.20	**0.68**	−0.24	−0.11	−0.09		
Ba	−0.12	−0.21	−0.02	−0.12	0.19	−0.01	−0.03	0.18	0.26	−0.02	0.14	−0.01	0.02	
Pb	0.35	0.59	**0.86**	**0.73**	−0.46	**0.71**	**0.87**	**0.70**	−0.25	**0.87**	0.07	**0.60**	−0.33	0.03
1-year-old needles														
Al	0.53													
V	0.43	**0.79**												
Cr	0.48	**0.77**	**0.84**											
Mn	−0.17	−0.47	−0.53	−0.39										
Fe	0.54	**0.93**	**0.93**	**0.87**	−0.52									
Ni	0.48	**0.77**	**0.96**	**0.94**	−0.48	**0.91**								
Cu	0.13	0.49	0.58	**0.59**	**−0.61**	0.56	**0.62**							
Zn	0.04	0.02	−0.28	0.12	0.47	−0.14	−0.13	−0.22						
As	0.48	**0.67**	**0.83**	**0.78**	−0.48	**0.76**	**0.87**	**0.66**	−0.05					
Se	−0.25	−0.27	−0.11	−0.23	0.09	−0.20	−0.17	−0.36	0.02	−0.11				
Mo	0.41	**0.60**	**0.71**	**0.90**	−0.29	**0.74**	**0.82**	0.45	0.21	**0.68**	−0.03			
Cd	−0.13	−0.25	−0.40	−0.08	0.50	−0.28	−0.25	−0.22	**0.67**	−0.30	−0.02	−0.09		
Ba	−0.20	−0.27	−0.04	−0.15	0.16	−0.04	−0.06	0.18	−0.29	−0.11	0.12	−0.03	0.03	
Pb	0.32	0.51	**0.84**	**0.70**	−0.47	**0.67**	**0.84**	**0.65**	−0.26	**0.89**	−0.02	**0.59**	−0.35	0.01

Significant correlation coefficients are marked in bold ($p < 0.01$).

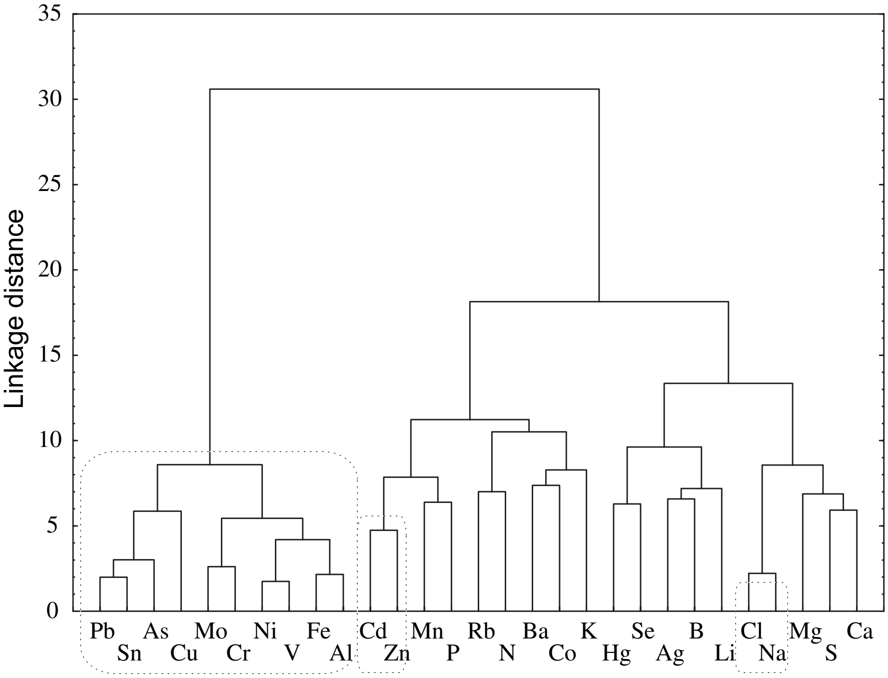

Fig. 4. Cluster analysis results on element concentrations in *Pinus canariensis* needles. In addition to elements reported in Tables 1 and 2, major nutrient elements (reported in Tausz et al., 2004) were included in this analysis. Elements were clustered according to similarities in their distribution on 36 samples (18 plots). Together with correlation analysis results (Table 3), encircled groupings of elements point toward common sources of the elements contained in one group.

The use of conifer needles as biomonitors for accumulating atmospheric pollutants is a widely accepted tool in bioindication (Arndt et al., 1987; Guderian, 2001) and implemented in several national laws and European scale monitoring programs (De Vries et al., 2000).

Sodium and chloride values are closely correlated to each other and significantly higher at lower elevated plots. This points clearly toward a common origin of these elements, most probably from sea salt, which reaches plots as high as 1000 m probably in the form of spray or mist (Fig. 2). In seawater, Na/Cl ratio is equal to 0.858 mol mol^{-1}. Assuming sea sprays are the main source, this ratio should be close in needles, at least in those exhibiting high concentrations. Present data show

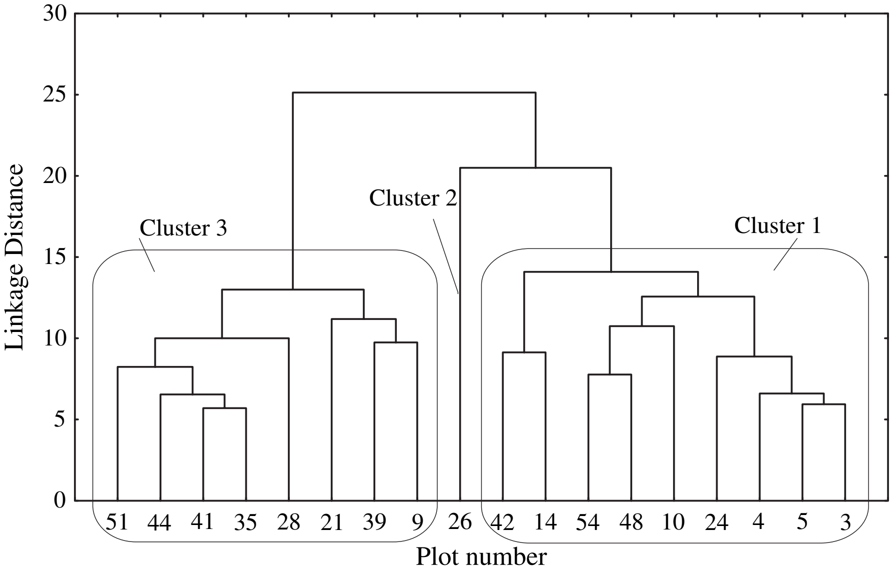

Fig. 5. Tree plot of cluster analysis results. Sample plots were clustered according to their similarities in needle element concentration patterns. For location of plots, see Fig. 7.

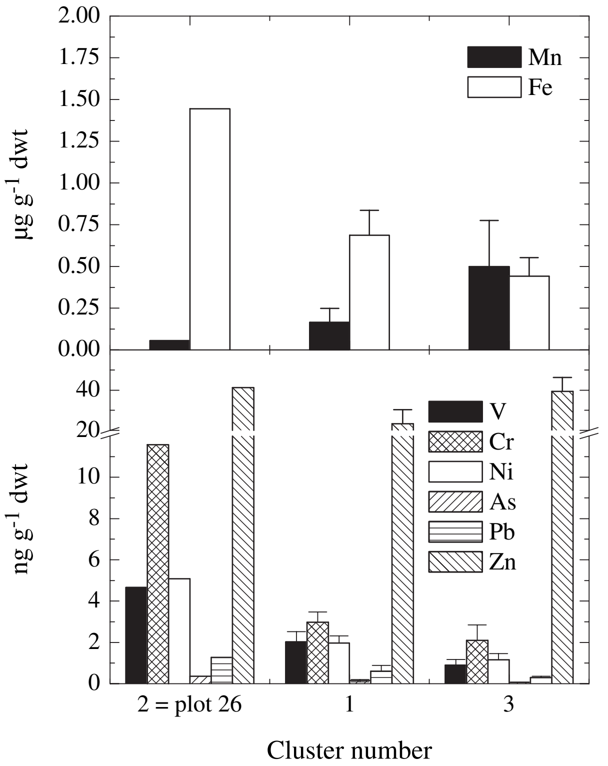

Fig. 6. Characterisation of clusters of sample plots shown in Fig. 5. Only element concentrations in 1-year old needles significantly different between clusters 1 and 3 are shown (cluster 2 consists only of one plot and was not included in statistical test for differences). Means and SD.

that this is true for the plots with high Na and Cl ion concentrations, at Cl concentrations of more than 1 mg g^{-1}. At lower Cl values, Na/Cl ratios vary more and reach higher values (Fig. 2D). Similar results were observed in bulk deposition measurements in Central European countries where the influence of sea salt on Na and Cl deposition is likely to be low (De Vries et al., 2000). Chloride concentrations in needles are frequently used as indicators of acidic pollution impacts and threshold values are legally accepted in air quality standards (Austrian Federal Law, 1984). In the present study, there is no need to assume another important source for chloride apart from seawater, because samples with high Cl values also show Na/Cl ratios close to seawater (Fig. 2D).

Sulphur concentrations in the needles vary widely within the investigated areas, at some plots even exceeding threshold values legally accepted in other pine species. In general, S concentrations seem higher at plots of lower elevation, which would point to sea spray impact as a possible source. On the other hand, correlation of S to Na and Cl is weak. Furthermore, according to standard seawater composition (2.7 g L^{-1} SO_4^{2-} and 19.4 g L^{-1} Cl^-; Larcher, 1995), the ratio of S over Cl is about 0.05 mol mol^{-1}. Under the assumption that all Cl in the needles comes from seawater, a maximum of 0.25 mg g^{-1} S would origin from the same source. If this amount of S was subtracted from the total needle concentration, two of the three plots exceeding 1.8 mg S g^{-1} needle weight would still exceed this threshold, and the third would still be close (data not shown in detail). Hence, an additional source for sulphur is required to explain the highest concentrations in the north-eastern area (Fig. 3). Sulphur as an important nutrient is taken up as sulphate from the soil, but this uptake is well regulated and will not lead to high foliar S concentrations. Since Tenerife is a vulcanic island, even natural sources of sulphurous gases may be taken into account, but there is no spatial relation of plots with high foliar S to potential natural sources. Plots with highest foliar S concentrations are in closest vicinity to the urban area of Santa Cruz, where some industries (among others, a refinery) are located, and to an oil-fuelled thermal power plant near Candelaria (Fig. 3). This indicates that SO_2 from such industrial sources could be involved. The regular north-eastern trade winds and local vertical air movements would lead to the transportation of air from Santa Cruz and Candelaria towards the plots in question (Fig. 3).

Pine needles are well suited for the biomonitoring of trace elements, e.g. heavy metals (Dmuchowski and Bytnerowicz, 1996; Čeburnis and Steinnes, 2000; Reimann et al., 2001; Rautio and Huttunen, 2003), although the accumulation of these elements is much lower than in mosses (Čeburnis and Steinnes, 2000). The analysis of similarities in the distribution of trace elements allows the recognition of potential sources. In large databases, factor analysis is the method mainly used to investigate relations among many elements and elude source apportionment. In the present study, cluster analysis and correlation matrices were used instead, because data quantity was too small for factor analysis. Results point toward close connections among V, As, Cr, Fe, Mo, Ni, Cu, Pb, and Al on one hand, and Cd and Zn on the other (Fig. 4). Čeburnis and Steinnes (2000) reported comparable results in spruce needles in Lithuania, where significant correlations were found between V, As, Cr, and Pb, whereas Zn, Cd, and Mn were not related to this group. Correlations among different elements on evergreen oak foliage were studied in detail to identify deposition sources in urban environments (Monaci and Bargagli, 1997; Monaci et al., 2000). However, since in the present study most elements were also correlated to aluminium (one of the principal elements of earth crust and of limited physiological significance in plants) the common source of these depositions may be soil particles translocated by winds or particulate matter dispersed by traffic. However, soil particles may adsorb exhaust particles from emission sources which would lead to the present apportionment pattern. In a study on evergreen oaks, Ba and Zn were suggested as tracers for motor vehicle emissions (Monaci

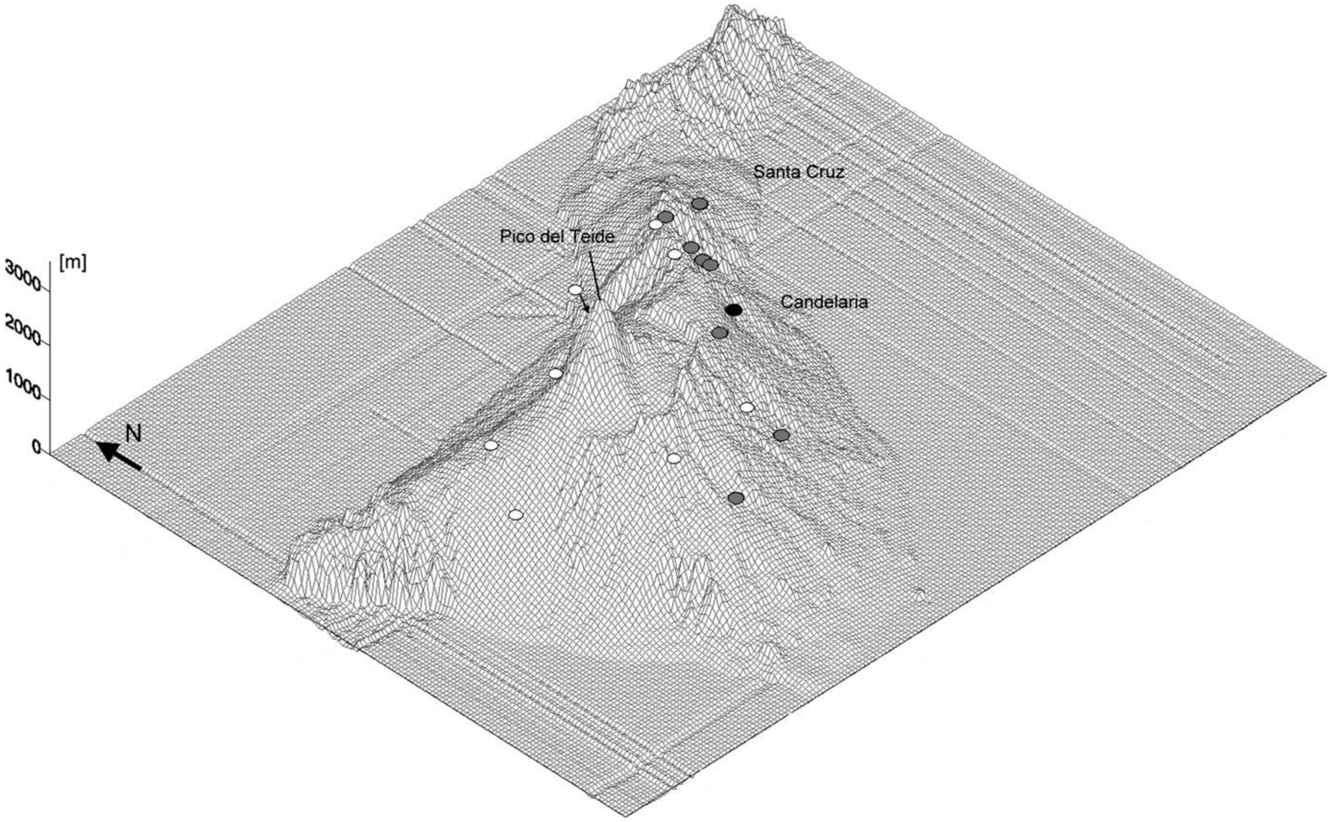

Fig. 7. Distribution of 18 plots where microelement analyses were performed. Signatures indicate cluster membership according to Fig. 6. Arrow: plot is behind the Pico del Teide from the present viewpoint. ◍ members of cluster 1, ● member of cluster 2, ○ members of cluster 3. For cluster characterisation, see Figs. 5 and 6.

et al., 2000). In the present data set, both elements were unrelated to the group of metals discussed above.

When plots were grouped according to similarities in their element profiles, two main groups significantly separated by several metal concentrations (Fig. 5) were extracted. The plots with higher concentrations of V, As, Cr, Fe, Mo, Ni, Cu, Pb, and Al are located at the eastern border of the *Pinus* distribution range in Tenerife, which is also close to the main freeway of the island. Soil particles could aggregate with exhaust solids from traffic as indicated by the presence of V. Since V is a widespread trace element in marine algae (Wallnöfer and Engelhardt, 1995), it is also abundant in crude oil (and fossil fuel) originating from marine organisms. Soil matter could be easily distributed by the wind, because at the south-eastern slope of the island vegetation cover is scarce.

Needles from only one plot (but for both investigated needle age classes) showed an exceptional profile, exhibiting highest concentrations of heavy metals. Only at this plot (Fig. 7), concentrations of heavy metals Cu and Ni were as high as described for pines at polluted sites (Giertych et al., 1999), but even there, concentrations of Cd, Pb, Zn would be classified in the lowest (less polluted), and As in the second lowest of five categories reported by Dmuchowski and Bytnerowicz (1996).

5. Conclusions

In conclusion, our investigations indicate two main sources of atmospheric deposition of potential pollutant elements: seawater and dust particles. Seawater influence can be traced by elevated, correlated Na and Cl concentrations at plots up to about 1200 m a.s.l. around the island. Dust impact was characterized by a pattern of microelements (metals) related to aluminium, a signature that occurs mainly at the eastern to southern slope of the island. In this case, a conglomeration of soil particles with exhaust elements could not be ruled out. Only at small areas, additional impact of atmospheric sulphur, possibly regionally caused by the burning of fossil fuels in the industrial area in the northeast (around Santa Cruz and Candelaria), could be indicated. In general, all foliar element concentrations (except sulphur at some plots) were relatively low, and would be classified in the lowest (unpolluted) classes according to most classification systems (Dmuchowski and Bytnerowicz, 1996).

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