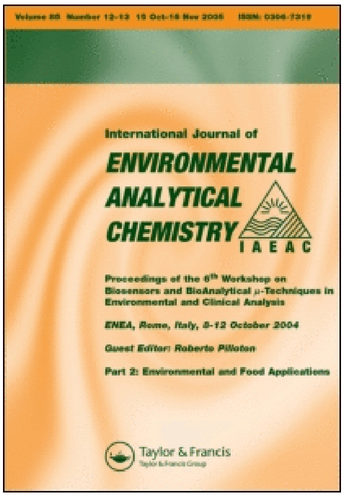

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CHARACTERIZATION OF PARTICLES ADSORBED ON PLANT SURFACES

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Conifer needles act as filter for aerosol particles. A substantial part of the needle deposit is irreversibly adsorbed and hence superficial leaf contamination increases with age of the leaves. The permanently adsorbed particles are mainly due to combustion products, contain high concentrations of trace elements and, due to their small size, are able to enter the interior of spruce needles. For chemical analysis of leaf material, it is strongly recommended that the leaves should be washed for a short time in chloroform in order to distinguish between superficially adsorbed and biomass incorporated, i.e. physiologically active, compounds.

KEY WORDS: Conifer needles, aerosol particles, adsorption, chemical analysis, forest damage.

INTRODUCTION

It is well known that plants act as filters for airborne dust. In particular, spruce trees with their large specific surface area have a very high collection efficiency for aerosol particles compared to other trees, which in turn are twenty-times higher than that of grass.[1] Norway Spruce is one of the most affected trees in the present forest decline in Europe[2] and hence, besides other causes such as attack by photooxidants and acidic precipitation, the fine fraction of aerosol particles containing high concentrations of inorganic and organic pollutants have been discussed as a further reason for the observed tree damage. In particular, in altitudes around 1000 m a.m.s.l. a maximal number of aerosol particles has been recently found in Germany, which is not yet explained.[3] Aerosol particles deposited on leaves have been observed by scanning electron microscopes (SEM)[4] and characterized qualitatively by electron probe microanalysis (EDX).[5] The dry deposited aerosol particles are considered to be washed off by rainfall and hence increase together with ions leached from the leaves, the elemental concentrations in the throughfall. Therefore, washing leaves in water for a short time is one method of estimating dry deposition on vegetation canopies.[6]

Recently, it was found that substantial amounts of particles can be released from the surface of spruce needles by short-time extraction with chloroform after washing the leaves with water.[7] This means that a certain part of the deposited aerosol particles is not removed by rainfall and hence irreversibly adsorbed on the hydrophobic epicuticular wax layer. The aim of this study was to analyse the elemental composition and to characterize the chemical structure of these particles which are not removed by rainwater.

EXPERIMENTALS

Spruce needles from the seventh whorl of small 12 year old and tall 90 year old *Picea abies* were washed in distilled water, dried and extracted with $CHCl_3$ for 15 s. The $CHCl_3$ extract contains the epicuticular wax,[8] and coagulated black particles which can be filtered.[7] The removed particles were thoroughly washed with $CHCl_3$ to remove the residual wax and analysed by X-ray diffractometry, X-ray photoelectron spectroscopy (XPS),[9] laser-assisted field desorption mass spectrometry[10] and, after acid digestion, by inductively coupled plasma—atomic emission spectroscopy (ICP-AES).[11] Using the regression equation of Dohrenbusch[12] the needle surface was estimated from the needle length. Needles were from the trees growing at the Kleiner Feldberg (Hessen, FRG) at 700 m a.m.s.l. and the annual mean aerosol concentration of the nearby forest measuring station, Königstein, was $30\,\mu g\,m^{-3}$.[13]

RESULTS AND DISCUSSION

The chloroform-removable particle-cover of spruce needles increase linearly with age of the needles from $0.10\,\mu g\,mm^{-2}$ (5 months) to $0.15\,\mu g\,mm^{-2}$ (30 months) for the small 12 year old trees and from $0.15\,\mu g\,mm^{-2}$ to $0.58\,\mu g\,mm^{-2}$ (30 months) for the tall 90-year old trees. The average standard deviation was estimated as $\pm 0.07\,\mu g\,mm^{-2}$. Hence, the needles of the old, damaged trees show a significant increase of the amount of needle cover. The young trees show no symptoms of damage and grow within the forest below the old trees. The needles of the young trees also show no significant increase of the needle deposit because they are exposed to forest air which has already been filtered by the canopy of the older trees.

The mean deposition velocity to a leaf surface v_g is defined as the quotient of contamination of leaf area to time-integrated aerosol particle concentration.[1] Using the deposit on 30 month old needles and the average particular concentration in ambient air, a value of $v_g = 0.02\,cm\,s^{-1}$ was estimated. This means that the average diameter of the deposited and permanently adsorbed particles is less

Table 1 Elemental composition of permanently adsorbed particles on spruce needles analysed by ICP-AES (underlined elements were analysed by laser-assisted field desorption mass spectrometry). For comparison the aerosol particle concentrations at the same location are shown (cf. Ref. 13).

Mg/g	*Needle deposit*	*Aerosol*	*Mg/g*	*Needle deposit*	*Aerosol*
Si	44.0		Cr	0.3	0.3
Al	9.1		Mn	0.3	0.2–1.4
Fe	3.3	3.2–31.6	Ba	0.2	
K	2.6		Cu	0.1	
Ca	1.6		As	0.01	
Mg	1.4		Ti	0.160	
Na	1.3		Rb	0.006	
Pb	0.4	1.0–6.2	Sr	0.005	
Ni	0.4	≦0.4	Li	0.005	
Zn	0.3	0.2–0.4	V	≦0.003	

than 4 μm.[1] Damaged spruce needles have in their epistomatal chamber prematurely aged wax plugs which show perforations with diameters ≦4 μm.[14] Hence, the deposited aerosol particles could also penetrate the epistomatal chamber and enter the interior of the spruce needles.

The chemical state of the needle deposit was assessed by XPS using the binding energy values (BE).[15] Semiquantitative XPS analysis (atomic percentages) indicated that the permanently adsorbed particles are mainly of organic origin consisting of 75.2% carbon (BE 285 eV, characteristic for C—C (80%), C—O (10%) and C=O bonds (10%)), 18.8% oxygen (BE 533 eV, characteristic of doubly bound O, e.g. SiO_2), 3.0% silicon (BE 103 eV, SiO_2 or silicates), 1.5% nitrogen (BE 400 eV, characteristic for PhN=NPh or phthalocyanine compounds, etc.), 1.0% aluminium (BE 74.5 eV, characteristic for boehmite or layered Al-silicates such as kaolinite), 0.19% phosphorous (BE 134 eV, characteristic for compounds such as KH_2PO_4, $NaPO_3$, etc.), 0.16% chlorine (BE 198 eV, inorganic and organic chlorides), 0.01% lead (BE 142 eV, characteristic for PbO) and traces of iron (BE 711 eV, Fe_2O_3, FeOOH) and manganese (BE 641 eV, MnOOH, Mn_2O_3, Mn_3O_4). Presumably the high amount of organic carbon (ignition loss at 450 °C, 63.4%) and the small size of the particulates causes the strong adsorption of these particles onto the hydrophobic epicuticular wax layer. X-ray diffractometry is in agreement with the XPS results showing the presence of quartz and kalifeldspar minerals and hence indicates that the needle cover also consists partially of soil material.

The quantitative elemental composition of the needle deposit determined by ICP-AES and laser-assisted field desorption mass spectrometry is shown in Table 1. The comparison with ambient aerosol concentrations shows that the elemental concentrations on the needle surface are lower for Fe, Pb and Mn. This is explained by the water soluble fraction of aerosol particles (40–95%)[13] which has been removed by rainfall and the washing with water. Silicon and aluminium reflect the presence of soil dust. The K/Fe-(weight) ratio of 0.8 and the presence of

Table 2 Estimation of the permanently adsorbed particle-deposit in a 90 year old Norway spruce forest. N: superficial deposit on two year old needles; F: superficial deposit on the whole forest.

	N $ng\,mm^{-2}$	*F* $g\,ha^{-1}$		*N* $ng\,mm^{-2}$	*F* $g\,ha^{-1}$
C	397	104 000	Mg, Na	0.7	180
O	99	25 000	Pb, Ni	0.2	55
Si	23	6 000	Zn, Cr, Mn	0.15	40
Al	4.8	1 260	P, Ba	0.10	30
Fe	1.7	460	Cl, Cu, Ti	0.05	15
K	1.4	360	As, Rb, Li, Sr	0.005	1
Ca, N	0.8	220			

lead indicate automotive soot as a further source of needle deposit.[16] The molar Fe/Mg-ratio of 2.4 and the presence of trace heavy metals are related to products of combustion (fly ash)[17] and other industrial processes.

As the amount of the needle deposit increases with age of the needles, the elemental concentrations increase as well.[18] Wentzel[19] estimated that in a 76 year old spruce forest with 26.6 ha ha^{-1} surface area, the needles account for 82% of this area. Using the estimates of the needle and the forest surfaces, the elemental deposits permanently adsorbed under natural conditions on plant surfaces are calculated and presented in Table 2. These are only approximate estimations, but they indicate the order of magnitude of amounts of superficially adsorbed elements which are not yet physiologically active.

CONCLUSION

The elemental analysis of needles is a widely used method for assessing the nutritional status of forest trees. In particular for comparative studies of leaves differing in age or in origin, it seems necessary to consider the elemental contamination of the leaf surface. This seems very important especially for micronutrients and trace elements. Thus, some authors have suggested washing leaf material for a short-time with chloroform prior to elemental analysis.[7,18,20–25] By analogy, for the analysis of physiologically active organic contaminants, the leaf surface should also be rinsed in advance with an organic solvent.[26,27] However, most reported data on elemental composition of leaf material has been gained on unwashed, i.e. superficially contaminated plant material.

Furthermore, it has been shown that the epicuticular wax layer of conifer needles is attacked by air pollution such as acid precipitation.[28] The impact of acids and oxidizing agents on the structure of the coniferous wax could be enhanced by the highly catalytic metal oxides found on and in the epicuticular wax layer. For these reasons, the distinction between superficially adsorbed and biomass incorporated elements should be generally taken into account in future.

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