The Lichenologist **37**(4): 329–344 (2005)
doi:10.1017/S0024282905015288 *Printed in the United Kingdom*

Investigating biogeochemical signatures in the lichen *Parmelia sulcata* at Burnham Beeches, Buckinghamshire, England

O. William PURVIS, P. James CHIMONIDES, Teresa E. JEFFRIES, Gary C. JONES, Helen READ and Baruch SPIRO

Abstract: Biogeochemical signatures were compared in 'living' and 'dead' *Parmelia sulcata* samples with their oak bark substratum. Eighteen elements reached maximum concentrations in 'dead' lichens, at lower concentrations than reported from industrial regions. High N concentrations in 'dead' lichens confirm exceedances of critical levels established for deciduous woodlands, supported by alien algae and 'nitrophytic' lichen colonization. Negative $\delta^{15}N$ values recorded in lichen samples indicate N originated mainly from ammonia. Less negative $\delta^{15}N$ values in healthy samples near busy roads suggest local NO_x accumulation by *Parmelia*. Higher $\delta^{15}N$ values in bark may result from different processes. Twenty-eight elements reach higher concentrations in healthy lichens near roads carrying higher traffic volumes. Thirteen elements correlate positively with lichen $\delta^{15}N$, suggesting that $\delta^{15}N$ is a powerful indicator of the balance between agricultural and vehicular N influx. Maximum Ca and Sr concentrations recorded in bark and their spatial distribution suggest a local geological origin. High concentrations of Ga, Ba, Pb and Ni bark contents testify to a previous pollution legacy, including that from petrol which carried higher lead concentrations than today. Mn concentrations are higher than reported from other studies and show no clear relationship with local roads. Mn is known to limit lichen diversity and health in coniferous forests in US and Germany, but not yet in deciduous woodlands. Current atmospheric conditions and the former pollution legacy must be understood to conserve epiphytes and for biomonitoring.

Key words: conservation, lichen, management, manganese, nitrogen, pollution

Introduction

Rapid changes in atmospheric pollutant concentrations have occurred across Europe following a reduction in SO_2 emissions (NEGTAP 2001). Road traffic, along with other high temperature combustion processes, contribute a major part of NO_x. Ammonia, although largely a product of intensive farming, also arises from vehicular emissions. Several studies suggest NO_x and other gaseous traffic emissions influence lichen health, diversity and abundance (Glenn *et al.* 1995; Angold 1997; Fuentes & Rowe 1998; Purvis *et al.* 2001; DEFRA 2002; Batty *et al.* 2003; Gombert *et al.* 2003; Purvis *et al.* 2003; Bell *et al.* 2004; Davies 2004; Davies *et al.* 2004; Gombert *et al.* 2004). Other emissions include ammonia (3-way catalytic converters), nitrous acid, carbon monoxide, carbon dioxide, volatile aromatic compounds, polycyclic aromatic hydrocarbons, particulates and metals (Bignal *et al.* 2004). Road size and proximity influenced N concentrations in *Physcia adscendens* (Gombert *et al.* 2003). Cadmium, Zn, Cu, Fe, Ni, Sb, Mn, Ba found in windscreen wash, emitted from car exhausts, the abrasion of tyres, friction linings (e.g. brake and clutch disks), and engine parts as well as re-suspended materials may all be accumulated by lichens (Garty *et al.* 1996; Owczarek *et al.* 1999; Garty 2001). Agro-chemicals used in neighbouring farmland may further influence lichen metal

O. W. Purvis (corresponding author), P. J. Chimonides, T. E. Jeffries, G. C. Jones and B. Spiro: The Natural History Museum, Cromwell Road, London SW7 5BD, UK.
H. Read: The Corporation of London, Burnham Beeches Office, Hawthorn Lane, Farnham Common, Slough SL2 3TE, UK.

concentrations along roads (Cuny *et al.* 2001). Roadsides provide important habitats for lichens, some normally associated with mine sites. *Stereocaulon* spp. colonized polluted roadside verges during the period of high Pb emissions and *Vezdaea leprosa* occurs alongside motorway crash barriers in Germany and the UK (Ernst 1995; Gilbert 2000). The present study compares for the first time the relationship between $\delta^{15}N$ and other elements in lichen samples and bark substratum, and assesses their relationship with lichen health. $\delta^{15}N$ and other element concentrations are also compared in 'healthy' and 'dead' samples taken from trees subjected to relatively high and low exposure to traffic.

Study Area

Burnham Beeches (Fig. 1) is a National Nature Reserve of European conservation importance (Natura 2000 site), designated for its ancient Beech forests with *Ilex* and *Taxus* rich in epiphytes (mosses and lichens). Remnants of a wood pasture system with abundant *Quercus*, the site is sensitively managed to conserve its many veteran trees (Barnard *et al.* 2005). It lies adjacent to Slough in Buckinghamshire, a largely rural county. The area is surrounded by 3 major motorways (M40, M25 and M4). The study site is bordered to the south by a busy rural road, Hawthorn Lane (*c.* 1500 traffic movements a day). An important trunk road, the A355 (*c.* 14 000 traffic movements a day) is close to the east. Minor roads within Burnham Beeches carry less traffic and some were closed shortly after sampling; Victory Cross has a busy car park (site 3) and lies *c.* 100 m from the A355. Farmland (grazing pasture) lies to the south beyond which are some gravel workings. Heavy industry has largely gone from Slough Trading Estates but in December 2000 it still had one Part A1 process [Slough Heat and Power (SHP)], one part A(2) and 36 part B authorized processes registered according to the Pollution Prevention and Control (England and Wales) Regulations 2000. The power station has been operating since the early 1920s, originally coal fired, more recently multi-fuelled utilizing pollution abatement technologies. Two Part A processes, ICI plc in Central Slough and a waste incinerator lie 11 km east, towards Heathrow. Several metal industries (part B processes) are in the area, some of which have closed in recent years. Burnham Beeches was used as a major vehicle depot during World War II and contained a prisoner of war camp (Read 2003; Barnard *et al.* 2005); 100 000 vehicles were on-site prior to D-Day landings. These together with clean-up operations may have caused local soil contamination.

The site is geologically complex consisting of acid gravels with pockets of clay and sand overlying chalk which almost reaches the surface in a few places. Several brick kilns formerly existed in the south-west of the area. A link between above and below ground beech tree health at Burnham Beeches was established where certain conditions of soil chemistry correlated with fewer mycorrhizal roots and poor crown condition (Power & Ashmore 1996). Mean SO_2 levels halved between 1994 and 1999 (8·25 to 3·76 ppb) whilst black smoke increased between 1994 and 1996 and subsequently fell, a pattern mirrored by mean annual NO_2 levels (Purvis *et al.* 2003). Unlike in London (Bell *et al.* 2004) both NO_2 and SO_2 values within Burnham Beeches are currently within the current limits for Vegetation Objectives, although not applicable on economic grounds in urban areas (Purvis *et al.* 2001). The European Habitats Directive requires that Member States prevent harm and deterioration to Special Areas of Conservation and the UK government is committed to achieve favourable conditions on 95% of Sites of Special Scientific Interest (SSSIs) in England by 2010 (Sutton *et al.* 2004). Pollution is one of many threats to the structure and integrity of such sites.

Photographic quadrat monitoring of *Parmelia sulcata* assemblages and dust monitoring commenced at Burnham Beeches 15 years ago adjacent to a gravel working (Fig. 1) (Purvis 1989; Purvis *et al.*

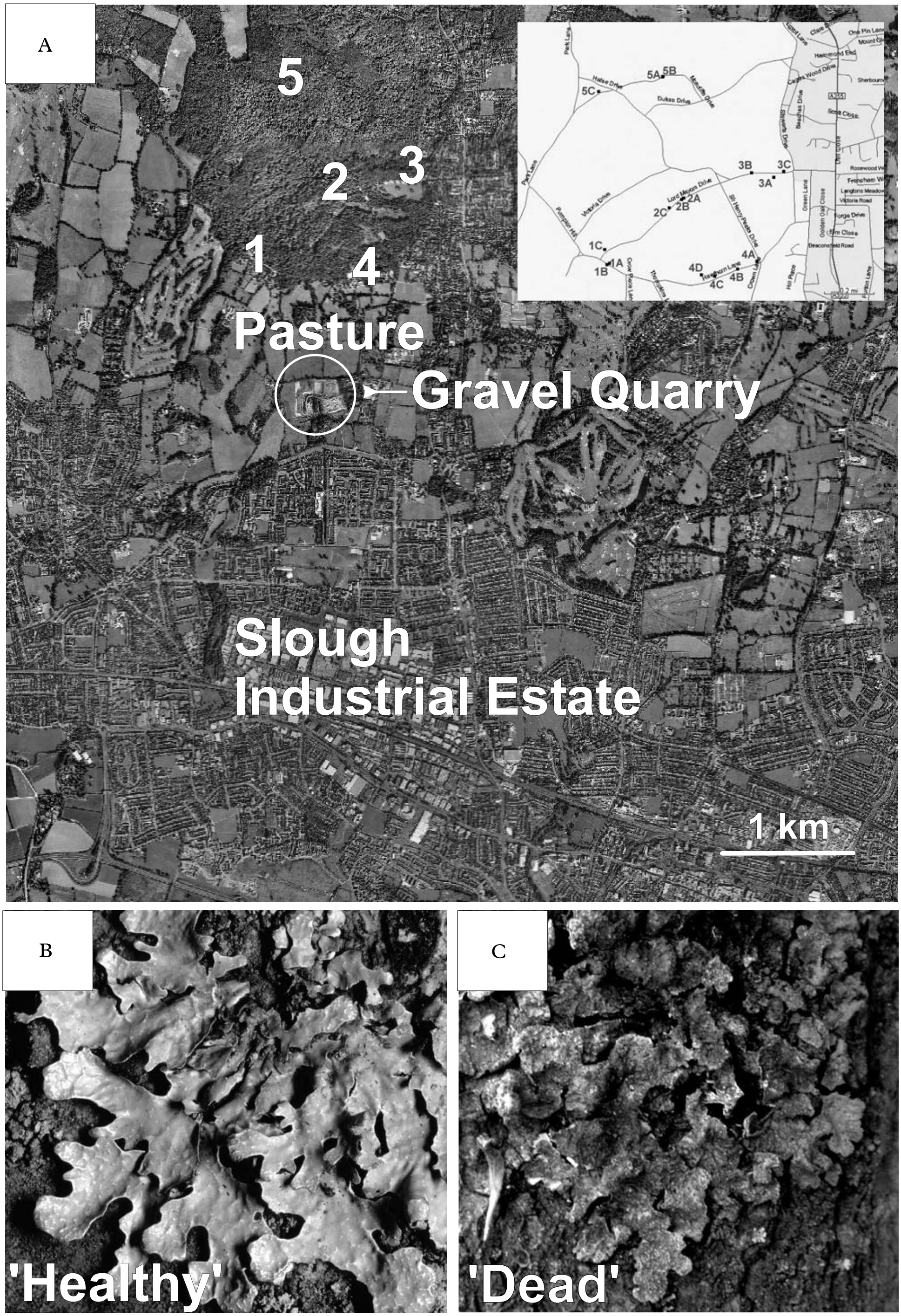

FIG. 1. A, aerial photograph showing Burnham Beeches sampling sites (1–5), inset shows individual sampling trees and relationship with with roads, sites 1, 3 & 4='high exposure' to traffic, sites 2 & 5='low exposure' to traffic; B & C, *Parmelia sulcata*.

https://doi.org/10.1017/S0024282905015288 Published online by Cambridge University Press

2001, 2002, 2003); acid-barked trees near limestone quarries develop a lichen flora typical of calcareous rocks, the 'alkaline dust effect' (Gilbert 1976). *Parmelia sulcata* is widely employed as a biomonitor of metal contamination (Herzig 1993; Sloof 1995; Frigoli & Quartieri 1999; Reis *et al.* 1999; Chibowski & Reszka 2001; Garty 2001; Bargagli & Mikhailova 2002; Costa *et al.* 2002; Pandey *et al.* 2002; Marques *et al.* 2004). An impact on the health of *P. sulcata* and *Hypogymnia physodes* was recorded during episodic high exhaust emissions and unusual weather conditions at Burnham Beeches suggesting particles and nitrogen from vehicles were responsible (Purvis *et al.* 2003). Higher lichen $\delta^{34}S$ values in *P. sulcata* compared with bark suggested derivation from coal and that bark reflected deposition over a longer time and earlier period when S had a low $\delta^{34}S$ (Purvis *et al.* 2003). Today *P. sulcata* colonizes twigs and branches rather than trunks suggesting bark and stem flow chemistry may limit growth.

Oxidized and reduced forms of N pollution may have different natural isotopic signatures, oxidized forms being enriched in $\delta^{15}N$ relative to reduced forms. In mosses, a significant correlation between exposure to traffic and $\delta^{15}N$, coupled with a correlation between Zn and Pb and traffic exposure suggested that $\delta^{15}N$ may distinguish between NO_x and NH_y (Pearson *et al.* 2000).

Methods

Chemical analysis

Between 20 and 30 g of 'healthy' and 'dead' *P. sulcata* (Fig. 1B & C) and their bark substratum were sampled on ± horizontal branches in the canopy from an elevated access platform at 5 stations (3 replicate trees at each site, apart from site 4 with 4 replicate trees), within easy reach of roads and tracks on 6 and 13 June 2000. A central location was chosen in Burnham Beeches and 4 outer regions (Fig. 1A). Sites 1, 3, 4 corresponded to 'high exposure' and 2, 5 to 'low exposure' to traffic sites (see 'study area' for traffic volumes). High exposure sites were more exposed to pollutants on account of the greater shelter afforded by roadside vegetation that hampers pollutant dispersion. Historical samples from the Natural History Museum lichen herbarium were also investigated. All samples were hand-cleaned under a microscope and the outer 1 cm (for healthy lichens) selected to standardize the exposure period. Approximately 6 g of material representing samples from over 30 individual thalli were pooled. Digestion was carried out using a HNO_3/H_2O_2 digest [method 'B' (Bettinelli *et al.* 1996)], the resultant solution filtered and analysed for 37 elements using inductively-coupled plasma atomic emission spectrometry (ICP-AES), and ICP mass spectrometry (ICP-MS). Both instruments were calibrated using mixtures of single element standard solutions traceable to NIST and checked using solutions of standard international reference materials. ICP-MS also used internal standardization while ICP-AES used a drift standard, to compensate for any instrumental sensitivity and sample introduction variations during analysis. Samples were analysed for sulphur (Spiro *et al.* 2002) and nitrogen stable isotope composition in triplicate, in a continuous flow GV Instruments Isoprime mass spectrometer. Results are expressed as $\delta^{15}N$ (air) with overall analytical reproducibility of ± 0·2 per ml. $\delta^{15}N$ is expressed relative to its natural abundance in the atmosphere (> 0·3663 atom %) and is expressed in parts per thousand, according to the following equation:

$$\delta^{15}N(‰) = [(^{15}N{:}^{14}N\ sample/^{15}N{:}^{14}N\ standard) - 1) \times 1000$$

Statistical analyses

Linear correlations for element pairs and isotope ratios were examined in 'healthy' and 'dead' *P. sulcata*, and 'bark' samples; summary statistics were calculated and compared with published data and historical samples from the Natural History Museum lichen herbarium. Multivariate analysis was carried out using Principal Components Analysis (PCA), non-metric MultiDimensional Scaling (MDS) and Cluster Analysis (CA) using PRIMER 6. Data were transformed (normalized, square root, or $\log_{10}$) to reduce the effects of scale and range in measurements. ANOSIM, an analogue of multivariate analysis of variance (MANOVA) was performed to compare signatures in 'high exposure' and 'low exposure' to traffic areas.

Results and Discussion

Eighteen elements reached maximum concentrations in dead *Parmelia* compared with all sample types. In order of decreasing concentrations, six elements reached >1000 ppm: N (2·97%), S (0·249%), P (0·229%), Fe (0·225%), Al (0·135%); Zn>100 ppm; Ti and Cu>10 ppm; As>1 ppm; seven elements (Se, Cd, Co, Li, Sb, Tl, Th)>100 ppb; Cs and Be>10 ppb (Table 1). Fifteen elements (Ca, K, Mg, Mn, Ba, Pb, Sr, B, Bi, Ni, V, Ga, Mo, Ge, W) reached maximum concentrations in bark and four elements (Na, Rb, Sn and U) maximum concentrations in living thalli. Twenty-eight elements (N, S, Al, P, Mg, Na, K, Ca, V, Fe, Co, Ni, Cu, Zn, Ga, Sr, Cd, Sn, As, Ba, Pb, Li, Ge, Mo, Sb, W, Tl, Th) reached higher average concentrations in 'healthy' lichens in 'high exposure to traffic' sites (Fig. 2). Signatures in *P. sulcata* from 'high exposure' and 'low exposure' to traffic sites in 'healthy' ($R=0{\cdot}689$, $P<0{\cdot}2\%$) and 'dead' ($R=0{\cdot}544$, $P<0{\cdot}1\%$) are distinct (Fig. 2). Summary $\delta^{15}N$ statistics are shown (Table 1) and correlation coefficients with S, N and metals (Table 2). The high number (13) of correlations between $\delta^{15}N$ and elements in 'healthy' compared with 'dead' and 'bark' partly reflect vehicle emissions. Dissolution and subsequent adsorption by lichen biomass result in numerous correlations with S and N in dead thalli (Table 2). Lower concentrations for certain elements (e.g. Rb) in 'high exposure' to traffic sites may reflect displacement by competing cations.

Cluster Analysis revealed distinctive patterns of element associations reflecting similar concentrations within groups across the study site. Different element associations in the three sample types reflect different chemical forms and binding affinity. Groups are arranged in increasing order of similarity (i.e. most dissimilar first) based on healthy lichens (Fig. 3).

(i) Outlier 'A'. K is associated with Ca in 'healthy' (maximum concentration), but only Ca in 'dead' lichens and 'bark'.
(ii) Outlier 'B'. Se in 'healthy' lichens and 'bark'. Se may substitute for S in biological systems and is closely associated with S in 'group C' in dead samples.
(iii) 'Group C' containing S, P and Na (maximum concentration). Sn (maximum concentration and highest CV, Table 1, suggests coarse particulates, (Garty 2001). Other elements, reach higher concentrations in dead lichens. Dead lichens and 'bark' have low K concentrations compared with healthy samples.
(iv) Group 'D'. Healthy samples characterized by highest Rb concentration. Ba is correlated with S ($R=0.639$, $P<0{\cdot}01$) suggesting sulphate. Loss of Ba and Pb from this group in dead and 'bark' samples suggest mobilization and fixation in organic form.
(v) Group 'E'. Same elements (sub ppm) in all sample types suggesting lithological origin.
(vi) 'Group F'. In 'dead' and 'bark' samples. Characterized by Ba, Na and Pb, also Zn in 'dead' samples.

Accumulation

Higher accumulation in dead lichens and bark reflect a longer accumulation period, soil contamination, a legacy of emissions arising downwind from former heavy industry on Slough Estates and the effects of transboundary pollution. Foliar leaching of metals (e.g. Mn, Cs, Rb, Ba and Zn) strongly absorbed from the soil by certain species enhance metal levels in epiphytic lichens and mosses (Ceburnis & Steinnes 2000). Rhizines on the *Parmelia* lower surface may trap particles washed down the tree-trunk leading to higher trace element concentrations in the inner, older parts of thalli (Bargagli *et al.* 1987; Brown *et al.* 1994). Lichens may accumulate elements after death. Cations bound to exchange sites are displaced by cations with a higher binding affinity and the greater availability of cation exchange sites in damaged material may lead to enhanced accumulation (Purvis *et al.* 2004; Spiro *et al.* 2004). Calcium reached highest concentrations of all metals (8460 ppm) in dead lichens and bark (29 300 ppm) in the north and shows no clear relationship with roads suggesting a geological influence. Sodium concentrations are higher in 'high exposure' to traffic areas in all sample types suggesting accumulation from salt application during winter (Backstrom *et al.* 2004). Higher Pb, Ga, Ba, Mn, and Ni bark concentrations (Table 1) reflect a legacy of pollution. Lead is of decreasing importance following the phasing out of leaded petrol (Garty *et al.* 1996); resuspension of Pb-rich particles

TABLE 1. *Summary statistics, element concentrations and* $\delta^{15}N$ *in 'healthy' and 'dead'* Parmelia sulcata*, and 'bark' samples from Burnham Beeches compared with polluted, (Herzig 1993) and historical samples (Natural History Museum lichen herbarium). Elements arranged according to decreasing concentrations in healthy samples*

Concentration (ppm)	$\delta^{15}N$	%N	%S	Ca	K	P	Mg	Fe	Al	Mn	Na	Zn
Healthy (*n*=16)												
mean	−8·80	1·63	0·14	3284	4171	1471	779	702	412	157	108	64
max	−6·57	2·01	0·21	5750	5380	1890	1330	1340	780	300	**230**	95
min	−10·76	1·26	0·10	2230	3160	980	510	360	220	66	60	50
SD	1·25	0·25	0·25	943	706	302	209	278	166	72	46	12
CV	−0·14	0·15	0·18	0·29	0·17	0·21	0·27	0·40	0·40	0·46	0·42	0·19
Dead (*n*=12)												
mean	−8·04	2·34	0·20	5358	2538	1889	984	1313	712	303	102	70
max	−5·55	**2·97**	**0·25**	8460	3530	**2290**	1540	**2250**	1350	490	150	**105**
min	−9·98	1·80	0·17	3370	1800	1370	640	470	270	130	70	40
SD	1·30	0·35	0·24	1581	510	294	303	571	299	138	25	18
CV	−0·16	0·15	0·12	0·30	0·20	0·16	0·31	0·43	0·42	0·46	0·25	0·26
Bark (*n*=15)												
mean	−3·42	0·83	0·10	13233	1360	443	728	597	413	343	104	30
max	−0·87	1·18	0·13	**29300**	3580	640	**2000**	1020	630	**1210**	190	50
min	−7·89	0·56	0·07	4910	550	260	370	230	160	115	50	12
SD	2·06	0·19	0·18	6557	820	130	386	218	136	278	34	11
CV	−0·60	0·23	0·19	0·50	0·60	0·29	0·53	0·37	0·33	0·81	0·33	0·38
Historical (NHM)		1·37	0·07	980	1970	1060	1080	140	190	20	460	35
Herzig 1993 (polluted)		3·11	0·18	9511	3166	1503	1030	1780	1009	38·1	286	98
SD		0·43	0·04	4239	516	642	179	225	119	14·6	21	10·5

TABLE 1. *Continued*

Concentration (ppm)	Pb	Ba	Ti	Cu	Sr	Rb	V	B	Ni	Sn	Ga
Healthy (n=16)											
mean	30	22	15	13	7	5·34	4	2·27	1·83	1·01	1·09
max	48	34	35	19	11	**7·52**	5	6·60	7·00	**5·98**	1·50
min	22	15	5	8	4	1·81	3	<0·12	0·87	0·42	0·69
SD	7	5	9	3	2	1·63	1	2·35	1·45	1·33	0·22
CV	0·23	0·24	0·59	0·24	0·29	0·30	0·21	1·03	0·79	1·31	0·20
Dead (n=12)											
mean	62	45	24	20	12	3·46	7	2·56	2·97	0·98	2·30
max	96	85	**48**	27	19	5·19	9	6·82	4·60	2·27	4·10
min	27	33	9	14	8	1·62	3	<0·12	1·60	0·52	1·60
SD	19	15	12	5	4	1·06	2	1·79	0·93	0·50	0·68
CV	0·31	0·33	0·49	0·23	0·30	0·31	0·25	0·70	0·31	0·51	0·30
Bark (n=15)											
mean	59	96	14·3	13	34	1·70	5	6·90	3·3	0·97	5·0
max	**135**	142	35·8	20	**69**	3·40	**12**	**26·51**	12·9	3·94	7·4
min	11	61	6·7	8	13	0·47	1	1·58	1·3	0·45	3·0
SD	40	27	8·2	4	19	0·76	3	5·68	2·6	0·82	1·4
CV	0·68	0·28	0·57	0·29	0·55	0·45	0·73	0·82	0·80	0·85	0·28
Historical (NHM)	14	7	5·9	9	13	0·589	0·44	<0·12	2·4	0·81	0·36
Herzig 1993 (polluted)	71·1			22·8			14·6	8·7	7·0	6·0	
SD	32·7			9·5			6·4	3	2·3	3·6	

TABLE 1. *Continued*

Concentration (ppb)	As	Se	Cd	Co	Li	Ge	Mo	Sb	Cs	W	TI	Bi	Th	U	Be
Healthy (*n*=16)															
mean	881	466	299	252	128	22	227	211	19	68	25	<14·1	113	22	<5
max	1650	530	420	450	269	38	450	407	36	186	31	<14·1	188	74	<5
min	480	<214	210	120	<11·9	<12·3	89	92	<1·2	<12·5	<3	<14·1	<11·9	11	<5
SD	281	38	57	103	95	10	93	93	10	80	5		33	15	
CV	0·32	0·08	0·19	0·41	0·74	0·46	0·41	0·44	0·52	1·17	0·20		0·29	0·68	
Dead (*n*=12)															
mean	1483	643	458	483	177	56	343	458	50	54	81	77	133	31	12
max	**3780**	760	870	800	497	89	484	**996**	74	152	**133**	142	**242**	49	**19**
min	420	<214	340	220	<11·9	<12·3	142	120	21	<12·5	<3	<14·1	<11·9	16	<5
SD	857	61	138	188	148	21	101	220	14	45	51	56	46	10	6
CV	0·58	0·09	0·30	0·39	0·84	0·38	0·30	0·48	0·28	0·83	0·63	0·72	0·34	0·33	0·48
Bark (*n*=15)															
mean	358	445	471	329	80	95	202	281	12	102	47	8395	114	18	<5
max	790	560	820	480	300	**397**	595	748	17	**227**	121	**18664**	193	**48**	<5
min	150	<214	240	150	15	<12·3	74	64	<1·2	<12·5	<3	<14·1	<11·9	11	<5
SD	169	151	156	104	81	105	129	218	7	77	39	9250	44	9	
CV	0·47	0·34	0·33	0·31	1·01	1·10	0·64	0·77	0·61	0·75	0·84	1·10	0·39	0·48	
Historical	1290	820	630	85	<11·9	12	77	<13·6	<1·2	<12·5	<3	<14·1	<11·9	15	<0.05
Herzig 1993 (polluted)	781		673				1014				5·4				
SD	228		235				221				3				

Bold=maximum and underlined=minimum concentrations.

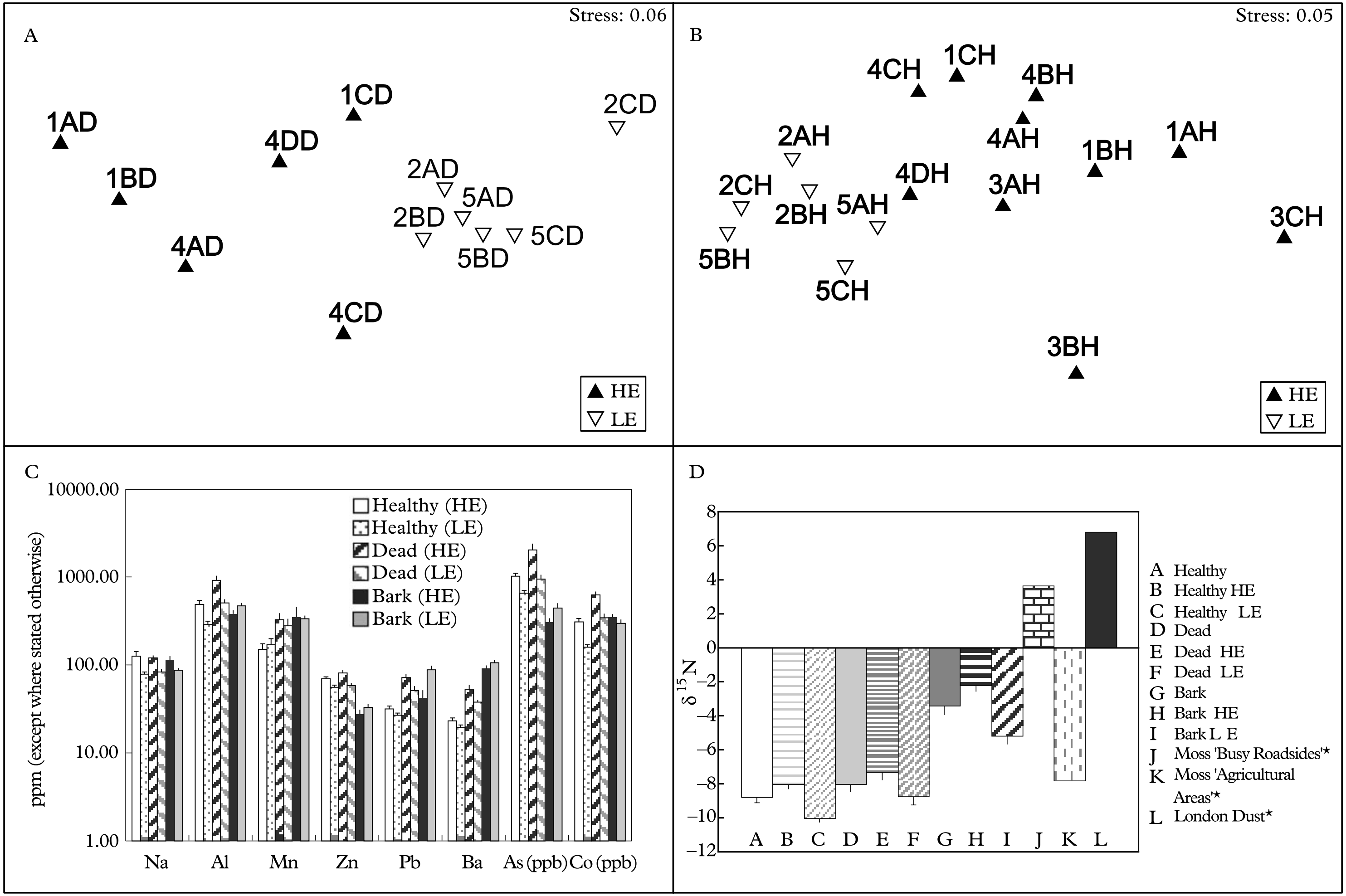

FIG. 2. Element concentration data for *Parmelia sulcata* and tree bark at Burnham Beeches. A & B ordination diagrams (ANOSIM), normalized, euclidean distance, sampling trees coded according to 'high exposure to traffic' (HE) and 'low exposure to traffic' (LE) (see Fig. 1). A, 'dead' lichens; B, 'healthy' lichen; C, selected element concentrations in Burnham samples from 'high exposure' and 'low exposure' to traffic areas (see inset, Fig. 1); D, $\delta^{15}N$ in Burnham samples and in moss species either collected at the side of a major road with heavy traffic or on a farm roof or wall near to cattle or poultry pens and London dust samples (Pearson *et al.* 2000). Error bars = standard error.

TABLE 2. *Top 15 most highly correlated elements with* $\delta^{15}N$ *in 'healthy'* P. sulcata *(i.e. suggesting at least partly emitted by vehicle exhausts) and their relationship with N and S in 'healthy', 'dead' and 'bark' samples*

	Healthy (n=16)			Dead (n=12)			Bark (n=15)		
	N	δ^{15}N	S	N	δ^{15}N	S	N	δ^{15}N	S
K	0·398	0·861***	0·611*	0·439	0·576	0·544	0·219	0·234	− 0·201
P	0·426	0·826***	0·574*	0·321	0·663*	0·486	0·731**	− 0·114	0·522*
Cu	0·364	0·753***	0·813***	0·680*	0·466	0·722**	0·585*	− 0·187	0·599*
Mg	0·347	0·753***	0·757***	0·733**	0·641*	0·797**	0·299	0·137	− 0·077
Sb	0·293	0·747***	0·652**	0·573	0·302	0·591*	0·505	− 0·241	0·777***
ppb Co	0·368	0·703**	0·707**	0·808**	0·611*	0·935***	0·327	0·320	0·231
Zn	0·443	0·680**	0·884***	0·772**	0·287	0·808**	0·816***	− 0·441	0·693**
Th	0·051	0·671**	0·459	0·833***	0·309	0·917***	− 0·142	0·331	0·023
S (tot)	0·654**	0·610*		0·890***	0·496		0·803***	− 0·551	
Al	0·395	0·599*	0·773***	0·866***	0·541	0·962***	0·400	− 0·213	0·773***
Fe	0·305	0·596*	0·794***	0·842***	0·578*	0·932***	0·210	0·144	0·587*
ppb As	0·094	0·593*	0·414	0·336	0·092	0·330	0·402	− 0·107	0·781***
Pb	0·577*	0·564*	0·651**	0·651*	0·420	0·728**	0·419	− 0·313	0·743**
ppb Sn	0·432	0·467	0·245	0·395	0·334	0·487	0·257	− 0·140	0·442
Li	0·222	0·465	0·431	0·828***	0·673*	0·944***	− 0·135	0·407	− 0·066
Total (P<0·001)	0	5	5	5	0	10	2	0	4
Total (P<0·01)	1	3	5	6	7v	5	2	0	5
Total (P<0·05)	1	5	3	5	0	1	1	0	7

*P<0·05, **P<0·01, ***P<0·001.

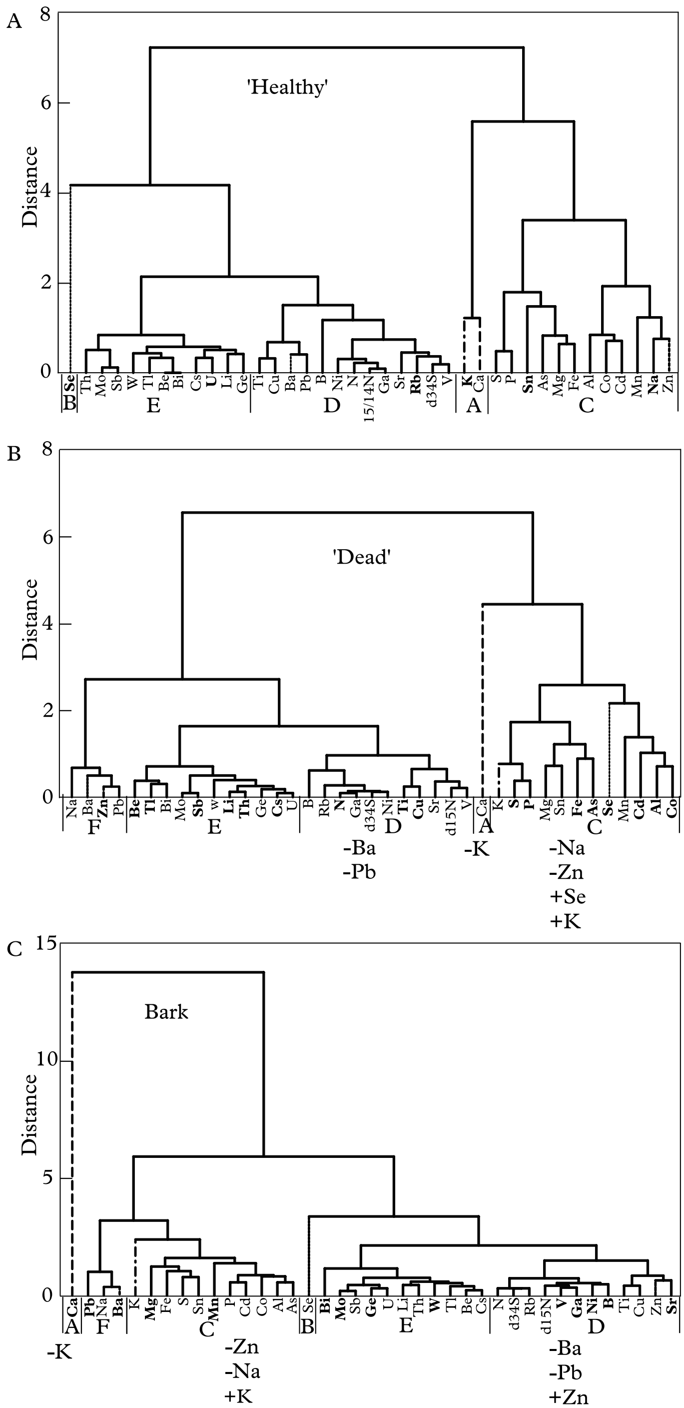

FIG. 3. Cluster diagrams (MDS) showing element associations in Burnham samples. A, 'healthy' *Parmelia sulcata*; B, 'dead' *P. sulcata*; C, bark substratum. Elements in **bold**=maximum concentrations. Elements below indicate 'loss' or 'gain' compared to 'healthy' samples.

https://doi.org/10.1017/S0024282905015288 Published online by Cambridge University Press

from surface soils remains a problem (Nobel *et al.* 2004). Introduction of alternative fuel with new anti-knock agents and modern catalysts has led to a new suite of potential contaminants from catalytic converters whose environmental impact remains to be determined (Nobel *et al.* 2004). Levels generally show an exponential decay with distance from the road; particulates also contribute to transboundary pollution (Weiss *et al.* 1999; Steinnes *et al.* 2003).

Isotopic signatures

Negative $\delta^{15}N$ measurements at Burnham Beeches contrast with the mainly positive $\delta^{15}N$ (+6 to −1%) values recorded in moss samples and London dusts along motorways and busy roads, but are very similar to values recorded in mosses sampled near poultry or cattle pens in rural areas (Pearson *et al.* 2000; Solga *et al.* 2005) (Fig. 2D). This suggests that background levels of NH_3 are dominant rather than NO_x, as ammonia emitted from agricultural practices has a very negative $\delta^{15}N$ because the ammonia volatilized is preferentially enriched with lighter ^{14}N (Heaton *et al.* 1997). The most negative $\delta^{15}N$ recorded at Burnham was furthest from pastureland (site 5, Fig. 1A) and Hawthorn Lane where a less negative $\delta^{15}N$ suggests slight NO_x accumulation. In 'healthy' lichens highly significant positive correlations between less negative $\delta^{15}N$ values and Co, Sb, Pb, Cu, Fe, Zn, S, Al etc (Table 2), elements known to be associated with vehicles, further suggests lichen N is derived, at least in part, from traffic emissions (NO_x). However, it is necessary to characterize both the source signal and fractionation occurring between source and sink (Handley & Scrimgeour 1997). Changes in $\delta^{15}N$ can result from various processes such as loss of ammonia nitrogen where the isotopically lighter ammonia is more readily lost, or from biochemical processes such as denitrification or from internal transport and recycling within thalli (Ellis *et al.* 2003; Ellis *et al.* 2004).

Toxicity

Low K concentrations recorded in dead compared with living lichens suggest membrane damage and electrolyte loss (Garty 2001). Conversely, element correlations together with S and N in 'dead' samples suggest enhanced binding with organic substances (Table 2). Several studies report higher concentrations of potentially phytotoxic elements in *P. sulcata* in industrial regions than those recorded in the present study without noting any adverse health effects (Herzig 1993; Fig. 1C). Significantly higher N concentrations (up to 3%), were recorded in 'dead' than living lichens (Table 1). Road size and proximity influenced the N concentration in the lichen *Physcia adscendens*, but not *Hypogymnia physodes* (Gombert *et al.* 2003). The link between atmospheric N deposition and tissue nitrogen concentrations in mosses is well established (Pitcairn *et al.* 2001). UNECE (United Nations Economic Commission for Europe) empirical critical load ranges are based on observed changes in abundance of particularly sensitive plant species, or on changes in overall vegetation composition (NEGTAP 2001). Nitrogen deposition at Burnham Beeches is estimated as 37·0 kg $N\,ha^{-1}y^{-1}$ (where N deposition $=NO_x+NH_y$, including both wet+dry deposition) (APIS 2005). Five exceedances of critical loads based on different ecosystem/habitat classes are indicated at Burnham Beeches, including the empirical critical load for temperate and boreal forests (lichens and algae) of 10–15 kg N/ha/year (APIS 2005). An exceedance of critical loads is supported at Burnham Beeches by colonization of dead *Parmelia* by alien algae and nitrophytic *Physcia* spp. (Fig. 1C).

Manganese is the sole element recorded in significantly higher concentrations in *P. sulcata* at Burnham Beeches than from other studies including busy roads, near incinerators and other industrial regions (Bargagli *et al.* 1987; Herzig 1993; Bennett 1995; Garty *et al.* 1996; Nimis *et al.* 2000; Loppi & Pirintsos 2003). Few studies have investigated metal effects on lichen diversity/vitality in the field in the absence of major SO_2 gaseous emissions (Branquinho 2001). Impoverishment of floras was noted near abandoned copper and zinc contaminated brass mills in Sweden (Folkeson & Anderssonbringmark 1988), declines in fruticose lichens observed in response to fugitive dust emissions from waste heaps at a Portuguese copper mine (Branquinho *et al.* 1999; Branquinho 2001) and improvements in lichen diversity and abundance noted following a decline in element concentrations in *Parmelia caperata* in central Italy (Loppi *et al.* 1998). Over 15 publications by Hauck and co-workers suggest soil-derived Mn species may harm lichens, including *Hypogymnia physodes*, in coniferous forests in regions remote from pollution sources in Germany (Hauck *et al.* 2001; Hauck *et al.* 2002*a*, *b*; Hauck & Runge 2002; Hauck 2003) and the US (Schmull *et al.* 2002; Schmull & Hauck 2003). At Burnham Beeches spatial distribution and lack of element correlations with Mn suggest accumulation is not primarily due to local traffic. A significant inverse relationship between Mn and Ca ('healthy' lichens $R=-0{\cdot}661$, $P<0{\cdot}01$) may be due to competitive exclusion (Mengel & Kirby 1982). Manganese, an abundant element in the earth's crust can exist in air as suspended particulate matter derived from industrial emissions or the erosion of soils. About 80% of the Mn emitted into the atmosphere is associated with particles with a mass median equivalent diameter of less than 5 µm, *c.* 50% with particles less than 2 µm and contributes to transboundary pollution (Lee *et al.* 1972). Mn-containing particles are removed from the atmosphere mainly by gravitational settling or by rain (USEPA 1984). Manganese measured in Greenland snow core samples confirm a large fraction of transboundary pollution originates from rock and soil dust, the relative significance of anthropogenic inputs remains unclear (Veysseyre *et al.* 1998). Manganese concentrations in *Parmelia caperata* were attributed to transboundary pollution in Italy (Loppi & Pirintsos 2003). Some mosses accumulate much higher Mn concentrations than expected compared with deposition data, calling into question their value as monitors of deposition for this element (Steinnes 1995; Ceburnis & Steinnes 2000; Leblond 2004). Manganese hyperaccumulating higher plants are known (Xue *et al.* 2004). Manganese is accumulated by roots, deposited in bark and leached from trees by precipitation up to 4400 × compared to source concentrations (Levia & Herwitz 2000), resulting in enhanced stemflow concentrations and decreased lichen cover (Hauck *et al.* 2002).

Implications

Trees are efficient scavengers of metals deposited in wet and dry deposition which may lead to increased soil metal levels which may be recycled by plants. Total analyses may mask subtle information regarding impacts of elements on lichens, especially where particulates are trapped by rhizines (Brown *et al.* 1994). Particles are not necessarily inert and may be solubilized releasing toxic elements which can interfere with cellular processes (Branquinho 2001). Synergistic effects of pollutants, tree health, bark substratum, soils and climate require investigation both at Burnham and other localities to understand lichen and bryophyte recolonization and may assist in developing critical loads/critical levels within the UNECE Convention on Transboundary Air Pollution (CLRTAP). This is important to develop lichens (and mosses) as sensitive biomonitors and to conserve sensitive flora and fauna, including invertebrates which depend on them for shelter and nutrition.

The authors dedicate this paper to Oliver Gilbert for stimulating OWP's interest in lichens whilst an undergraduate at Sheffield University and for his esteemed friendship ever since. We are grateful for funding from the Corporation of London, MinUrals, an European Union INCO-Copernicus 2 contract (ICA2-CT-2000-10011), and a Natural Environment Research Council (Isotope Geochemical Science Facility) facilities grant.

References

Angold, P. G. (1997) The impact of a road upon adjacent heathland vegetation: effects on plant species composition. *Journal of Applied Ecology* **34:** 409–417.

APIS (2005) The Air Pollution Information System (APIS) http://www.apis.ac.uk

Backstrom, M., Karlsson, S., Backman, L., Folkeson, L. & Lind, B. (2004) Mobilisation of heavy metals by deicing salts in a roadside environment. *Water Research* **38:** 720–732.

Bargagli, R., Iosco, F. P. & D'Amato, M. L. (1987) Zonation of trace metal accumulation in three species of epiphytic lichens belonging to the genus *Parmelia*. *Cryptogamie Bryologie et Lichenologie* **8:** 331–337.

Bargagli, R. & Mikhailova, I. (2002) Accumulation of inorganic contaminants. In *Monitoring with Lichens—Monitoring Lichens* (P. L. Nimis, C. Scheidegger & P. A. Wolseley, eds): 65–84. Dordrecht: Kluwer Academic.

Barnard, A., Hartup, M. & Read, H. (2005) Burnham Beeches management plan. April 2005–March 2010, Corporation of London.

Batty, K., Bates, J. W. & Bell, J. N. B. (2003) A transplant experiment on the factors preventing lichen colonization of oak bark in southeast England under declining SO_2 pollution. *Canadian Journal of Botany* **81:** 439–451.

Bell, J. N. B., Davies, L. & Honour, S. (2004) Air Pollution research in London. In *Urban Air Pollution, Bioindication and Environmental Awareness* (A. Klumpp, W. Ansel & G. Klumpp, eds): 3–16. Göttingen: Cuvillier.

Bennett, J. P. (1995) Abnormal chemical element concentrations in lichens of Isle Royale National Park. *Environmental and Experimental Botany* **35:** 259–277.

Bettinelli, M., Spezia, S. & Bizzarri, G. (1996) Trace element determination in lichens by ICP-MS. *Atomic Spectroscopy* **17:** 133–141.

Bignal, K., Ashmore, M. R. & Power, S. A. (2004) *The ecological effects of diffuse air pollution from road transport*. English Nature Research Reports: 580. Peterborough.

Branquinho, C. (2001) Lichens. In *Metals in the Environment: Analysis by Biodiversity* (M. N. V. Prasad, eds): 117–115. New York: Marcel Dekker.

Branquinho, C., Catarino, F., Brown, D. H., Pereira, M. J. & Soares, A. (1999) Improving the use of lichens as biomonitors of atmospheric metal pollution. *Science of the Total Environment* **232:** 67–77.

Brown, D. H., Avalos, A., Miller, J. E. & Bargagli, R. (1994) Interactions of lichens with their mineral environment. *Cryptogamic Botany* **4:** 135–142.

Ceburnis, D. & Steinnes, E. (2000) Conifer needles as biomonitors of atmospheric heavy metal deposition: comparison with mosses and precipitation, role of the canopy. *Atmospheric Environment* **34:** 4265–4271.

Chibowski, S. & Reszka, M. (2001) Investigation of Lublin town environment contamination by radionuclides and heavy metals with application of Parmeliaceae lichens. *Journal of Radioanalytical and Nuclear Chemistry* **247:** 443–446.

Costa, C. J., Marques, A. P., Freitas, M. C., Reis, M. A. & Oliveira, O. R. (2002) A comparative study for results obtained using biomonitors and PM10 collectors in Sado Estuary. *Environmental Pollution* **120:** 97–106.

Cuny, D., Van Haluwyn, C. & Pesch, R. (2001) Biomonitoring of trace elements in air and soil compartments along the major motorways in France. *Water Air and Soil Pollution* **125:** 273–289.

Davies, L. (2004) *A study of the lichens of London under contemporary atmospheric conditions*. Ph.D. thesis. Imperial College, University of London.

Davies, L., Purvis, O. W. & James, P. W. (2004) A study of epiphytes in London under a climate of low sulphur dioxide. In *Lichens in a Changing Pollution Environment. English Nature Research Report No 525* (P. Lambley & P. A. Wolseley, eds): 21–26. Peterborough: English Nature.

DEFRA (2002) *Effects of NO_x and NH_3 on lichen communities and urban ecosystems. A pilot study.* Air Pollution Research in London (A.P.R.I.L.) network. London, Imperial College and Natural History Museum: http://www.airquality.co.uk/archive/reports/cat10/DEFRA_LICHEN_NOX_NH3_final.pdf.

Ellis, C. J., Crittenden, P. D. & Scrimgeour, C. M. (2004) Soil as a potential source of nitrogen for mat-forming lichens. *Canadian Journal of Botany* **82:** 145–149.

Ellis, C. J., Crittenden, P. D., Scrimgeour, C. M. & Ashcroft, C. (2003) The natural abundance of ^{15}N in mat-forming lichens. *Oecologia* **136:** 115–123.

Ernst, G. (1995) *Vezdaea leprosa*—Spezialist am Strassenrand. *Herzogia* **11:** 175–188.

Folkeson, L. & Anderssonbringmark, E. (1988) Impoverishment of vegetation in a coniferous forest polluted by copper and zinc. *Canadian Journal of Botany* **66:** 417–428.

Frigoli, G. & Quartieri, M. (1999) Biomonitoring of atmospheric deposition of heavy metals by means of the lichen *Parmelia sulcata* in an urbanized area. *Annali Di Chimica* **89:** 711–719.

Fuentes, J. M. C. & Rowe, J. G. (1998) The effect of air pollution from nitrogen dioxide (NO_2) on epiphytic lichens in Seville, Spain. *Aerobiologia* **14:** 241–247.

Garty, J. (2001) Biomonitoring atmospheric heavy metals with lichens: theory and application. *Critical Reviews in Plant Sciences* **20:** 309–371.

Garty, J., Kauppi, M. & Kauppi, A. (1996) Accumulation of airborne elements from vehicles in transplanted lichens in urban sites. *Journal of Environmental Quality* **25:** 265–272.

Gilbert, O. L. (1976) An alkaline dust effect on epiphytic lichens. *Lichenologist* **8:** 173–178.

Gilbert, O. L. (2000) *Lichens*. London: Harper Collins.

Glenn, M. G., Gomez-Bolea, A. & Lobello, R. (1995) Metal content and community structure of cryptogam bioindicators in relation to vehicular traffic in Montseny Biosphere Reserve. *Lichenologist* **27:** 291.

https://doi.org/10.1017/S0024282905015288 Published online by Cambridge University Press

Gombert, S., Asta, J. & Seaward, M. R. D. (2003) Correlation between the nitrogen concentration of two epiphytic lichens and the traffic density in an urban area. *Environmental Pollution* **123:** 281–290.

Gombert, S., Asta, J. & Seaward, M. R. D. (2004) Assessment of lichen diversity by index of atmospheric purity (IAP), index of human impact (IHI) and other environmental factors in an urban area (Grenoble, southeast France). *Science of the Total Environment* **324:** 183–199.

Handley, L. L. & Scrimgeour, C. M. (1997) *Terrestrial Plant Ecology and ^{15}N Natural Abundance: the Present Limits to Interpretation for Uncultivated Systems with Original Data from a Scottish Old Field*. London: Academic Press Ltd.

Hauck, M. (2003) Epiphytic lichen diversity and forest dieback: the role of chemical site factors. *Bryologist* **106:** 257–269.

Hauck, M. & Runge, M. (2002) Stemflow chemistry and epiphytic lichen diversity in dieback- affected spruce forest of the Harz Mountains, Germany. *Flora* **197:** 250–261.

Hauck, M., Hesse, V. & Runge, M. (2002*a*) The significance of stemflow chemistry for epiphytic lichen diversity in a dieback-affected spruce forest on Mt Brocken, northern Germany. *Lichenologist* **34:** 415–427.

Hauck, M., Hesse, V. & Runge, M. (2002*b*) Correlations between the Mn/Ca ratio in stemflow and epiphytic lichen abundance in a dieback-affected spruce forest of the Harz Mountains, Germany. *Flora* **197:** 361–369.

Hauck, M., Jung, R. & Runge, M. (2001) Relevance of element content of bark for the distribution of epiphytic lichens in a montane spruce forest affected by forest dieback. *Environmental Pollution* **112:** 221–227.

Heaton, T. H. E., Spiro, B., Madeline, S. & Robertson, C. (1997) Potential canopy influences on the isotopic composition of nitrogen and sulphur in atmospheric deposition. *Oecologia* **109:** 600–607.

Herzig, R. (1993) Multi-residue analysis with passive biomonitoring: a new approach for volatile multi-element contents, heavy metals and polycyclic aromatic hydrocarbons with lichens in Switzerland and the principality of Liechtenstein. In *Plants as Biomonitors. Indicators for Heavy Metals in the Terrestrial Environment* (B. Markert, eds): 285–328. Weinheim: VCH.

Leblond, S. (2004) Étude pluridisciplinaire du transfert des métaux de l'atmosphère vers les mousses. Laboratoire Interuniversitaire des Systèmes Atmosphériques—Université Paris 7/Paris 12 et Muséum National d'Histoire Naturelle. Paris.

Lee, R. E., Goranson, S. S., Enrione, R. E. & Morgan, G. B. (1972) NASN cascade impactor network. Part II: Size distribution of trace metal components. *Environmental Science & Technology* **6:** 1025–1030.

Levia, D. F. & Herwitz, S. R. (2000) Physical properties of water in relation to stemflow leachate dynamics: implications for nutrient cycling. *Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere* **30:** 662–666.

Loppi, S. & Pirintsos, S. A. (2003) Epiphytic lichens as sentinels for heavy metal pollution at forest ecosystems (central Italy). *Environmental Pollution* **121:** 327–332.

Loppi, S., Putorti, E., Signorini, C., Fommei, S., Pirintsos, S. A. & De Dominicis, V. (1998) A retrospective study using epiphytic lichens as biomonitors of air quality: 1980 and 1996 (Tuscany, central Italy). *Acta Oecologica-International Journal of Ecology* **19:** 405–408.

Marques, A. P., Freitas, M. C., Reis, M. A., Wolterbeek, H. T., Verburg, T. & De Goeij, J. J. M. (2004) Lichen-transplant biomonitoring in the assessment of dispersion of atmospheric trace-element pollutants: effects of orientation towards the wind direction. *Journal of Atmospheric Chemistry* **49:** 211–222.

Mengel, K. & Kirby, E. A. (1982) *Principles of Plant Nutrition*. Worblaufen, Switzerland: International Potash Institute.

NEGTAP (2001) *Transboundary Air Pollution: Acidification, Eutrophication and Ground-Level Ozone in the UK*. London: Department for Environment, Food and Rural Affairs.

Nimis, P. L., Lazzarin, G., Lazzarin, A. & Skert, N. (2000) Biomonitoring of trace elements with lichens in Veneto (NE Italy). *Science Of The Total Environment* **255:** 97–111.

Nobel, W., Kostka-Rick, R., Honnen, W. & Blum, T. (2004) Biomonitoring of ambient air pollutants from automobile traffic near a highway. In *Urban Air Pollution, Bioindication and Environmental Awareness* (A. Klupp, W. Ansel & G. Klumpp, eds): 123–135. Göttingen.

Owczarek, M., Spadoni, M., De Marco, A. & De Simone, C. (1999) Lichens as indicators of air pollution in urban and rural sites of Rieti (Central Italy). *Fresenius Environmental Bulletin* **8:** 288–295.

Pandey, V., Upreti, D. K., Pathak, R. & Pal, A. (2002) Heavy metal accumulation in lichens from the Hetauda Industrial area Narayani zone Makwanpur district, Nepal. *Environmental Monitoring and Assessment* **73:** 221–228.

Pearson, J., Wells, D. M., Seller, K. J., Bennett, A., Soares, A., Woodall, J. & Ingrouille, M. J. (2000) Traffic exposure increases natural ^{15}N and heavy metal concentrations in mosses. *New Phytologist* **147:** 317–326.

Pitcairn, C. E. R., Leith, I. D., Fowler, D., Hargreaves, K. J., Moghaddam, M., Kennedy, V. H. & Granat, L. (2001) Foliar nitrogen as an indicator of nitrogen deposition and critical loads exceedance on a European scale. *Water Air and Soil Pollution* **130:** 1037–1042.

Power, S. A. & Ashmore, M. R. (1996) Nutrient relations and root mycorrhizal status of healthy and declining beech (*Fagus sylvatica* L) in southern Britain. *Water Air and Soil Pollution* **86:** 317–333.

https://doi.org/10.1017/S0024282905015288 Published online by Cambridge University Press

Purvis, O. W. (1989) *The lichens of Burnham Beeches and the impact of the proposed quarry workings on its lichen communities*. Report for Corporation of London. London: British Museum (Natural History).

Purvis, O. W., Bamber, R. N., Chimonides, J., Erotokritou, L., Jones, G., Jeffries, T. & Din, V. (2001) *Burnham Beeches lichen monitoring phase 2. Year 3*. Report for Corporation of London, The Natural History Museum: pp. 124.

Purvis, O. W., Erotokritou, L., Wolseley, P. A., Williamson, B. & Read, H. (2002) A photographic quadrat recording method employing image analysis of lichens as an indicator of environmental change. In *Monitoring with Lichens—Monitoring Lichens* (P. L. Nimis, C. Scheidegger & P. A. Wolseley, eds): 337–341. Dordrecht: Kluwer Academic.

Purvis, O. W., Chimonides, J., Din, V., Erotokritou, L., Jeffries, T., Jones, G. C., Louwhoff, S., Read, H. & Spiro, B. (2003) Which factors are responsible for the changing lichen floras of London? *Science of the Total Environment* **310:** 179–189.

Purvis, O. W., Chimonides, P. J., Jones, G. C., Mikhailova, I. N., Spiro, B., Weiss, D. J. & Williamson, B. J. (2004) Lichen biomonitoring near Karabash Smelter Town, Ural Mountains, Russia, one of the most polluted areas in the world. *Proceedings of the Royal Society of London Series B-Biological Sciences* **271:** 221–226.

Read, H. J. (2003) *Burnham Beeches during World War II. A compilation of recollections and information gathered from civilians and military personnel stationed in the Beeches and from Corporation of London records*. London: Corporation of London.

Reis, M. A., Alves, L. C., Freitas, M. C., van Os, B. & Wolterbeek, H. T. (1999) Lichens (*Parmelia sulcata*) time response model to environmental elemental availability. *Science of the Total Environment* **232:** 105–115.

Schmull, M. & Hauck, M. (2003) Element microdistribution in the bark of *Abies balsamea* and *Picea rubens* and its impact on epiphytic lichen abundance on Whiteface Mountain, New York. *Flora* **198:** 293–303.

Schmull, M., Hauck, M., Vann, D. R., Johnson, A. H. & Runge, M. (2002) Site factors determining epiphytic lichen distribution in a dieback-affected spruce-fir forest on Whiteface Mountain, New York: stemflow chemistry. *Canadian Journal of Botany* **80:** 1131–1140.

Sloof, J. E. (1995) Lichens as quantitative biomonitors for atmospheric trace-element deposition, using transplants. *Atmospheric Environment* **29:** 11–20.

Solga, A., Burkhardt, J., Zechmeister, H. G. & Frahm, J. P. (2005) Nitrogen content, ^{15}N natural abundance and biomass of two pleurocarpous mosses *Pleurozium schreberi* (Brid.) Mitt. and *Scleropodium purum* (Hedw.) Limpr. in relation to atmospheric nitrogen deposition. *Environmental Pollution* **134:** 465–473.

Spiro, B., Morrisson, J. & Purvis, O. W. (2002) Sulphur isotopes in lichens as indicators of sources. In *Monitoring with Lichens—Monitoring Lichens* (P. L. Nimis, C. Scheidegger & P. Wolseley, eds): 311–315. Dordrecht: Kluwer.

Spiro, B., Weiss, D. J., Purvis, O. W., Mikhailova, I., Williamson, B. J., Coles, B. J. & Udachin, V. (2004) Lead isotopes in lichen transplants around a Cu smelter in Russia determined by MC-ICP-MS reveal transient records of multiple sources. *Environmental Science & Technology* **38:** 6522–6528.

Steinnes, E. (1995) A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals. *Science of the Total Environment* **161:** 243–249.

Steinnes, E., Berg, T. & Sjobakk, T. E. (2003) Temporal trends in long-range atmospheric transport of heavy metals to Norway. *Journal de Physique 1V* **107:** 1271–1273.

Sutton, M. A., Pitcairn, C. E. R. & Whitfield, C. P. (2004) *Bioindicator and biomonitoring methods for assessing the effects of atmospheric nitrogen on statutory nature conservation sites.* JNCC Report 230. Peterborough: JNCC.

USEPA (1984) Health Assessment Document for Manganese. Final Report. Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, Cincinnati, OH. EPA/600/8-83/013F.

Veysseyre, A., van de Velde, K., Ferrari, C. & Boutron, C. (1998) Searching for manganese pollution from MMT anti-knock gasoline additives in snow from central Greenland. *Science of the Total Environment* **221:** 149–158.

Weiss, D., Shotyk, W., Kramers, J. D. & Gloor, M. (1999) *Sphagnum* mosses as archives of recent and past atmospheric lead deposition in Switzerland. *Atmospheric Environment* **33:** 3751–3763.

Xue, S. G., Chen, Y. X., Reeves, R. D., Baker, A. J. M., Lin, Q. & Fernando, D. R. (2004) Manganese uptake and accumulation by the hyperaccumulator plant *Phytolacca acinosa* Roxb. (*Phytolaccaceae*). *Environmental Pollution* **131:** 393–399.

Accepted for publication 16 *May* 2005