

QUANTITATIVE MONITORING OF AIRBORNE LEAD POLLUTION BY A FOLIOSE LICHEN

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Abstract. The potential use of lichens as quantitative monitors of airborne heavy metal pollution has been demonstrated by measurements of Po^{210} , Pb, Cd, Zn, and V levels in sequential growth of the foliose lichen *Pseudoparmelia baltimorensis* from three localities in the greater Washington, D.C. area. Samples were dated using the growth rate measured by Lawrey and Hale (1977). Po^{210} , Pb, and V increase with age in a given colony. Higher levels of Pb, V, Cd, and Zn are present in samples from the two more polluted sites. The retention of heavy metals is consistent with trapping by an ion exchange mechanism. Since Po^{210} is the daughter product of *in situ* decay of Pb^{210} , accumulated from atmospheric fallout of known rate, its levels can be used to calculate trapping efficiencies of Pb and retrospective fallout rates. These rates are similar to published data from rural and urban areas.

1. Introduction

Lichens have been used widely in Europe as indicators of heavy metal deposition (e.g., Folkesson, 1979; Pilegaard, 1978; Yule and Lloyd, 1984). Lichens accumulate heavy metals in their thalli either on the outer surfaces of the walls of fungal hyphae or within the walls themselves. Most of the previous work on the accumulation of heavy metals by lichens has focused on pollution from smelters or foundries but a few studies looked at urban heavy metal releases presumably from automobiles, at least for Pb (Anderson *et al.*, 1978; Lawrey and Hale, 1979, 1981; Saeki *et al.*, 1975; Kasim *et al.*, 1982).

Previous studies using lichens have been qualitative or semi-quantitative (see Richardson and Nieboer, 1981). Their use as quantitative monitors would directly give retrospective fallouts of heavy metals. Quantitative biological monitoring using lichens would have several advantages to conventional air sampling now in use (Martin and Coughtrey, 1982).

We report here preliminary work towards the use of the foliose lichen *Pseudoparmelia baltimorensis* as a quantitative monitor of airborne heavy metal pollution. The strategy was to use colonies dated by the known growth rate of this species and to measure Po^{210} along with Pb and other heavy metals on sequential growth. The levels of Po^{210} , decay product of the *in situ* Pb^{210} accumulated from atmospheric fallout (itself the decay

product of Rn^{222} , derived from U^{238} decay in the crust), can be predicted for a trapping efficiency of 100% since the Pb^{210} fallout rate is known. Thus from measurements of Po^{210} the trapping efficiencies as a function of age could be determined and the fallout rates of Pb could be inferred.

To our knowledge, no previous study of Po^{210} and Pb levels has been made on the sequential growth of a single lichen colony. Persson (1970) and Persson *et al.* (1974) did report Pb^{210} and Pb levels in a fruticose species, and inferred Pb^{210} deposition rates and residence times of Pb .

2. Methods

Lawrey and Hale (1977) found that *Pseudoparmelia baltimorensis*, a common species growing on rocks, had an annual growth rate of 5.09 ± 0.25 mm yr⁻¹, while juvenile colonies (less than 1.5 cm in diameter) had a lower rate of 2.63 ± 0.31 mm yr⁻¹. Thus we collected mature colonies of this species in the Washington, D.C. area in this study with confidence in their ages from growth rates. Samples were collected in the field, transported to the laboratory in brown paper bags, washed in deionized water and oven dried for 24 hr at 65 °C. After drying they are cleaned of dirt, and ground in a mortar to pass through a 0.5 mm sieve to insure homogeneity of aliquots. Two blank samples for each digestion group are also prepared. Samples are digested using aqua regia (concentrated HNO_3 , HCl) on a hot plate for 8 hr. Samples are filtered after digestion through ashless filter paper adjusting the volume with deionized water. The dried residues were weighed to correct for the presence of insoluble constituents in the lichens. Standard solutions were prepared every day. Lead, Cd, and other metals are analyzed by atomic absorption spectrophotometry (Perkin-Elmer Model 3030). Vaporization of sample solutions with matrix modifier in a graphite Lvov platform was used for all elements except Zn, since it results in negligible interference. Zinc was analyzed by the flame method because of high blanks using the former technique.

Po^{210} rather than Pb^{210} was measured because the former is an alpha emitter which is easily determined by a alpha spectrometry. We measured Po^{210} levels from lichen aliquots; the Po^{210} was plated on silver foil and counted according to the methodology of Flynn (1968) and Bacon (1976) as modified by Stieff *et al.* (1981) and Stieff (1981). The reproducibility of the Po^{210} measurement is 4% (1 sigma), determined from analysis of 6 aliquots of lichen.

3. Results and Discussion

Before presenting the results and their implications, the physical and mathematical basis of using the Po^{210} measurements will be discussed. Pb^{210} fallout rates are well established; the levels in the lichen are determined by fallout accumulation and radioactive decay, which is described by the following differential equation:

$$\frac{dy}{dt} = -\lambda y + \alpha$$

whose solution is:

$$y = \frac{\alpha}{\lambda} (1 - e^{-\lambda t})$$

where:

y = Pb^{210} level (atoms cm^{-2})

t = time (yr)

λ = decay constant of Pb^{210}

α = flux rate, atoms $\text{cm}^{-2} \text{yr}^{-1}$ (is about 169×10^5 atoms $\text{cm}^{-2} \text{yr}^{-1}$ or 1.0 ± 0.2 dpm $\text{cm}^{-2} \text{yr}^{-1}$ for eastern U.S.; see Benninger, 1978).

Substituting values for time we obtain the values in Table I.

TABLE I
 Pb^{210} ($x (\lambda/\alpha)$) as a function of t

t (yr)	$1 - e^{-\lambda t}$
1	0.031
2	0.060
5	0.14
10	0.27
20	0.46
50	0.79
100	0.95
200	0.998

Note that measurable differences in Pb^{210} levels result, with a steady state reached in about 100 yr. E.g., $t = 10$ yr: activity is 8.8 dpm cm^{-2} lichen.

The level of Po^{210} (half-life of 138 days), daughter of Pb^{210} (with short-lived intermediate Bi^{210}) is given by the solution of the differential equation:

$$\frac{dy_1}{dt} = \lambda y - \lambda_1 y_1,$$

where y_1 is the level of Po^{210} (atoms cm^{-2}) with decay constant λ_1 . The solution is:

$$y_1 = \alpha \left(\frac{1}{\lambda_1} - \frac{1}{(\lambda_1 - \lambda)} e^{-\lambda t} + \frac{\lambda}{\lambda_1(\lambda_1 - \lambda)} e^{-\lambda_1 t} \right).$$

Unless otherwise noted, it is assumed that all the Po^{210} results from decay *in situ* of Pb^{210} in the lichen. Benninger (1978) gives an activity ratio of $\text{Po}^{210}/\text{Pb}^{210}$ of 0.04 from atmospheric fallout. For a sector of age t_1 to t_2 from a single foliose lichen colony, y_1 is obtained by integrating the above expression from t_2 to t_1 and dividing by $t_2 - t_1$.

Two colonies of *P. baltimorensis* from Great Falls, Md., collected within 10 m of each other and about 10 yr of age, were divided into three sectors and analyzed for Po^{210} .

TABLE II
 Po^{210} concentrations in 2 Great Falls, Md. lichens

Approximate age (yr)	Measured Po^{210}	Predicted Po^{210}	Trapping efficiency
Counts $g^{-1} hr^{-1}$			
L1			
outer 0 to 2.6	2067 ± 91	5105	0.40 ± 0.02
middle 2.6 to 7.6	2632 ± 103	25,311	0.10 ± 0.004
inner 7.6 to 10.6	4420 ± 133	45,014	0.10 ± 0.003
L2			
outer 0 to 2.9	2679 ± 104	5901	0.45 ± 0.02
middle 2.9 to 9.8	3560 ± 119	31,555	0.11 ± 0.004
inner 9.8 to 12.9	4870 ± 140	55,008	0.09 ± 0.003

The results are given in Table II. The ages of each sector were calculated from Lawrey and Hale's (1977) growth rate. From a measurement of the diameter of the two colonies 0.010 ± 0.001 g of lichen corresponds to 1 cm^2 area. The predicted Po^{210} levels, assuming a 100% trapping efficiency and 0.01 g cm^{-2} are given in Table II. Thus, approximate trapping efficiencies can be computed using the predicted Po^{210} corresponding to the range of ages for the given sector (Table II). The measured Po^{210} in L2 are somewhat higher than L1, which is consistent with their inferred ages. There is good

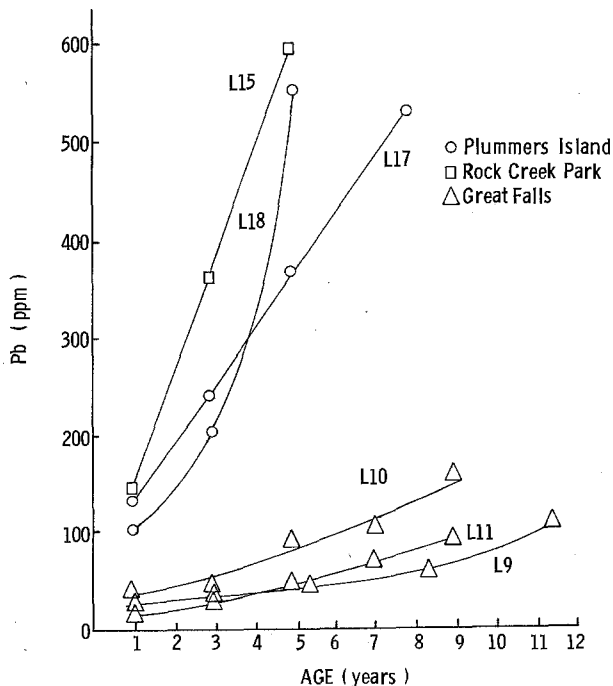


Fig. 1. Pb vs age.

agreement as well between trapping efficiencies (T.E.) of the two colonies; the outer sector (> 3 yr old) has a T.E. of 0.425 ± 0.014 , while the older sections have a T.E. of 0.099 ± 0.002 . The possible causes of the drop of T.E. with age will be discussed later.

These preliminary experiments were followed up on colonies of *P. baltimorensis* collected from Great Falls, Md. and the more polluted locations in Rock Creek Park, Washington, D.C. and Plummers Island, Md. (underneath Route 495) from May 1984 to January 1985.

The results are shown in Table III and Figures 1, 2, and 3. The ages were calculated as above using measured widths of nearly circular colonies as far as possible. The predicted Po^{210} values were calculated assuming a T.E. of 100%, a Pb^{210} flux of $1.0 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ and an assumed 0.01 g cm^{-2} . L13 and 14 were collected from a pure quartz outcrop. Their levels of Po^{210} are comparable to the other samples indicating that retention of substrate Pb^{210} or Po^{210} is negligible since quartz has very low levels of *U*. The ages for L13 and L14 are quite uncertain since the colonies were irregular in shape. The levels of Po^{210} , Pb, and V in each colony increase monotonically with age except for L18/4. We suspected during collection that the latter sample is

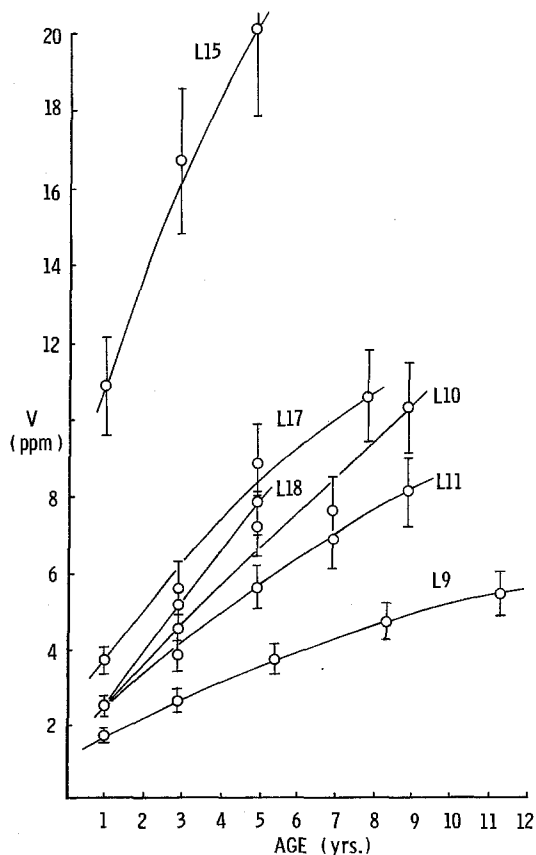


Fig. 2. V vs age.

TABLE III
Analytical results

Sample #	Age (mean) (yr)	Po ²¹⁰ measured alphas g ⁻¹ hr ⁻¹	Po ²¹⁰ predicted alphas g ⁻¹ hr ⁻¹	Trapping efficiency (cum.)	Pb (ppm)	Pb/Po ²¹⁰ measured	Cd (ppm)	V (ppm)	Pb/V	Zn (ppm)
Great Falls, Md. metagraywacke substrate										
L9/1	0-1.9 (1.0)	636 ± 22	3312	0.19	22 ± 2	0.0346 ± 0.0038	0.05 ± 0.01	1.7 ± 0.2	13 ± 3	38 ± 7
L9/2	1.9-3.9 (2.9)	1026 ± 39	13608	0.075	34 ± 2	0.0331 ± 0.0022	0.15 ± 0.26	2.6 ± 0.3	13 ± 4	47 ± 11
L9/3	3.9-6.9 (5.4)	1114 ± 26	26909	0.041	45 ± 5	0.0404 ± 0.0042	0.09 ± 0.02	3.7 ± 0.4	12 ± 2	56 ± 5
L9/4	6.9-9.8 (8.35)	2035 ± 31	41597	0.049	57 ± 1	0.0280 ± 0.0008	0.22 ± 0.01	4.7 ± 0.5	12 ± 1	44 ± 3
L9/5	9.8-12.8 (11.3)	2116 ± 35	54720	0.039	107 ± 2	0.0506 ± 0.0012	0.33 ± 0.03	5.4 ± 0.6	20 ± 2	49 ± 5
L10/1	0-1.9 (1.0)	2114 ± 44	3312	0.64	41 ± 2	0.0194 ± 0.0009	0.46 ± 0.04	2.5 ± 0.3	16 ± 2	46 ± 7
L10/2	1.9-3.9 (2.9)	3182 ± 45	13608	0.23	47 ± 2	0.0148 ± 0.0007	0.07 ± 0.02	4.5 ± 0.5	10 ± 1	102 ± 5
L10/3	3.9-5.9 (4.9)	3750 ± 66	24282	0.15	92 ± 2	0.0245 ± 0.0007	0.03 ± 0.01	7.2 ± 0.8	13 ± 1	103 ± 10
L10/4	5.9-7.9 (6.9)	5464 ± 113	34672	0.16	98 ± 4	0.0179 ± 0.0009	-	7.6 ± 0.9	13 ± 2	98 ± 17
L10/5	7.9-9.8 (8.85)	5712 ± 127	43920	0.13	151 ± 5	0.0264 ± 0.0010	0.17 ± 0.04	10.3 ± 1.2	15 ± 2	93 ± 25
L11/1	0-1.9 (1.0)	1417 ± 31	3312	0.43	14 ± 1	0.00988 ± 0.0007	0.05 ± 0.01	2.5 ± 0.3	5.6 ± 0.8	45 ± 5
L11/2	1.9-3.9 (2.9)	2474 ± 49	13608	0.18	29 ± 2	0.0117 ± 0.0010	0.02 ± 0.01	3.8 ± 0.4	7.6 ± 1.0	63 ± 7
L11/3	3.9-5.9 (4.9)	3600 ± 56	24282	0.15	41 ± 2	0.0114 ± 0.0005	0.11 ± 0.03	5.6 ± 0.6	7.3 ± 0.9	81 ± 6
L11/4	5.9-7.9 (6.9)	4522 ± 90	34672	0.13	66 ± 2	0.0146 ± 0.0006	0.13 ± 0.03	6.9 ± 0.8	9.6 ± 1.1	-
L11/5	7.9-9.8 (8.85) foil crinkled (low count)				89 ± 2	-	0.03 ± 0.01	8.1 ± 0.9	11 ± 1	85 ± 8
Quartz substrate										
L13/1	0-3.7	? 3039 ± 44	(8043)	(0.38)	88 ± 1	0.0290 ± 0.0006	0.26 ± 0.02	5.8 ± 0.7	15 ± 2	92 ± 4
L13/2	3.7-6.5	? 4159 ± 68	(25402)	(0.16)	94 ± 2	0.0226 ± 0.0006	0.37 ± 0.04	9.9 ± 1.2	9.5 ± 1.2	98 ± 8
L14/1	0-5.9	? 1890 ± 30	(13928)	(0.14)	29 ± 2	0.0153 ± 0.0012	0.13 ± 0.02	4.3 ± 0.5	6.7 ± 0.9	70 ± 4
L14/2	5.9-11.4	? 3445 ± 48	(42832)	(0.080)	47 ± 1	0.0136 ± 0.0003	0.23 ± 0.04	7.8 ± 0.9	6.0 ± 0.7	101 ± 5

Table III (continued)

Sample #	Age (mean) (yr)	Po ²¹⁰ measured alphas g ⁻¹ hr ⁻¹	Po ²¹⁰ predicted alphas g ⁻¹ hr ⁻¹	Trapping efficiency (cum.)	Pb (ppm)	Pb/Po ²¹⁰ measured	Cd (ppm)	V (ppm)	Pb/V	Zn (ppm)
Rock Creek Park D.C. metagraywacke substrate										
L15/1	0-1.9 (1.0)	2939 ± 58	3312	0.89	135 ± 2	0.0459 ± 0.0012	0.15 ± 0.03	10.9 ± 1.3	12.4 ± 1.5	106 ± 9
L15/2	1.9-3.9 (2.9)	7005 ± 85	13608	0.52	368 ± 2	0.0525 ± 0.0007	0.28 ± 0.05	16.7 ± 1.9	22.0 ± 2.5	139 ± 8
L15/3	3.9-5.9 (4.9)	8354 ± 112	24282	0.34	594 ± 4	0.0711 ± 0.0011	0.95 ± 0.09	20.1 ± 2.3	29.6 ± 3.4	147 ± 13
L16/1	0-1.9 (1.0)?	3280 ± 4.6	3312	0.99	85 ± 2	0.0259 ± 0.0008	0.08 ± 0.01	11.9 ± 1.4	7.1 ± 0.9	106 ± 5
L16/2	1.9-3.9 (2.9)?	5209 ± 74	13608	0.38	132 ± 4	0.0253 ± 0.0008	0.35 ± 0.04	16.8 ± 2.0	7.9 ± 1.0	150 ± 10
L16/3	3.9-5.9 (4.9)?	6275 ± 91	24282	0.26	217 ± 3	0.0346 ± 0.0007	0.32 ± 0.05	19.7 ± 2.3	11.0 ± 1.3	160 ± 12
Plummers Island, MD metagraywacke substrate										
L17/1	0-1.9 (1.0)	658 ± 25	3312	0.20	143 ± 1	0.2173 ± 0.0085	0.50 ± 0.04	3.7 ± 0.4	39 ± 4	117 ± 7
L17/2	1.9-3.9 (2.9)	2174 ± 53	13608	0.16	242 ± 5	0.1113 ± 0.0035	0.78 ± 0.07	5.6 ± 0.7	43 ± 5	139 ± 12
L17/3	3.9-5.9 (4.9)	3331 ± 79	24282	0.14	370 ± 3	0.1111 ± 0.0045	1.65 ± 0.10	8.9 ± 1.0	42 ± 5	171 ± 17
L17/4	5.9-9.7 (7.8)	4107 ± 128	38948	0.11	533 ± 8	0.1298 ± 0.0045	1.18 ± 0.22	10.6 ± 1.2	50 ± 4	192 ± 44
L18/1	0-1.9 (1.0)	1427 ± 36	3312	0.43	102 ± 2	0.0715 ± 0.0024	0.52 ± 0.06	2.5 ± 0.3	41 ± 5	91 ± 7
L18/2	1.9-3.9 (2.9)	2549 ± 50	13608	0.19	201 ± 4	0.0789 ± 0.0021	0.67 ± 0.05	5.1 ± 0.6	39 ± 5	109 ± 8
L18/3	3.9-5.9 (4.9)	4633 ± 80	24282	0.19	549 ± 7	0.1185 ± 0.0025	1.09 ± 0.11	7.9 ± 0.9	69 ± 8	155 ± 12
L18/4	5.9-10.7?	2610 ± 121	-	-	179 ± 11	0.0686 ± 0.0051	0.75 ± 0.15	4.2 ± 0.5	43 ± 6	150 ± 56

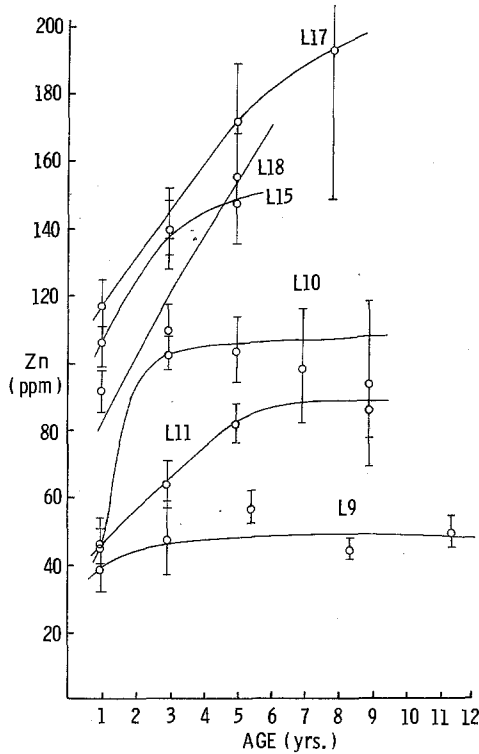


Fig. 3. Zn vs age.

actually younger than indicated by its presence in the interior of the colony since it was lighter in color than thalli to its periphery. This is supported by the low Po^{210} , Pb, and V levels. The results show considerable variability in trapping efficiencies from colony to colony. This may be caused by differences in foliage cover, tilting from the horizontal and other factors that could affect the amount of rain water in contact with lichen surfaces for a given time.

These results are in marked contrast to those of Hale and Lawrey (1985) on the same species from Plummers and Bear Island (Great Falls) Md. They sampled growth from 1 to 3 yr old. Their results indicate a leveling out of Pb concentrations after 1 yr. Samples from central parts of the thalli (10 to 20 yr old) contained similar levels to the 2 and 3 yr old growth. A plausible reason for the apparent leveling out of Pb concentrations is that composite samples from several colonies were analyzed for each age. If trapping efficiencies were variable from colony to colony this could have covered up any systematic increase in Pb concentration with age, since the relative contribution of each colony to each composite was not constant. Thus, if the composite sample of 10 to 20 yr old growth had a greater proportion of a low trapping efficiency component than the younger composite this could explain the leveling out.

Cadmium levels do not show a clear dependence on age, but an age effect may be hidden by the high uncertainties in the computed concentrations because of high and

variable blank levels (19 to 89% of total signals). Blank levels for Pb are much lower (1 to 9%), for Zn 9 to 60% (average 18%) and for V negligible. Significant matrix interference was only found for V analysis; the results were corrected for this effect by the method of standard addition.

Higher levels of Pb, V, Cd, and Zn in samples of similar age are clearly present from the more polluted sites of Rock Creek Park and Plummers Island. Zinc, however, appears to level out with age, at least for the colonies from Great Falls. This difference in behavior of Pb and Zn is consistent with experimental evidence indicating Pb is firmly bound to extracellular sites, while a significant part of the Zn is loosely held in soluble sites in the lichen thallus (Brown, 1976). Apparently, a similar mechanism involving ion exchange is involved in the strong retention of atmospheric Pb by an organic fraction in soil (Lewis, 1977). The drop in cumulative trapping efficiencies ('T.E.') with age (Table III) could at first sight be the result of loss of Pb, but we prefer as an alternative explanation the gradual saturation of ion-exchange sites with a constant partition coefficient of Pb between rain water and the lichen thallus. This would be consistent with a longer residence time for Pb in the foliose species studied than the fruticose species (2 to 4 yr) studied by Persson *et al.* (1974). The ion exchange model predicts decreasing T.E.'s with age, as well as cumulative T.E.'s that are greater than incremental T.E.'s (see appendix for details). Figure 4 illustrates the case for a constant flux of Pb; the T.E. for Pb^{210} would be identical. For a variable flux of Pb, higher in the past, the number of available sites for exchange in the lichen would be reduced faster resulting in a more rapid decrease in T.E. These qualitative relationships are consistent with the computed T.E.'s. We cannot rule out the possibility that the drop in observed T.E.'s is a result of Pb and Pb^{210} loss but attempts at modeling the Pb levels as a function of

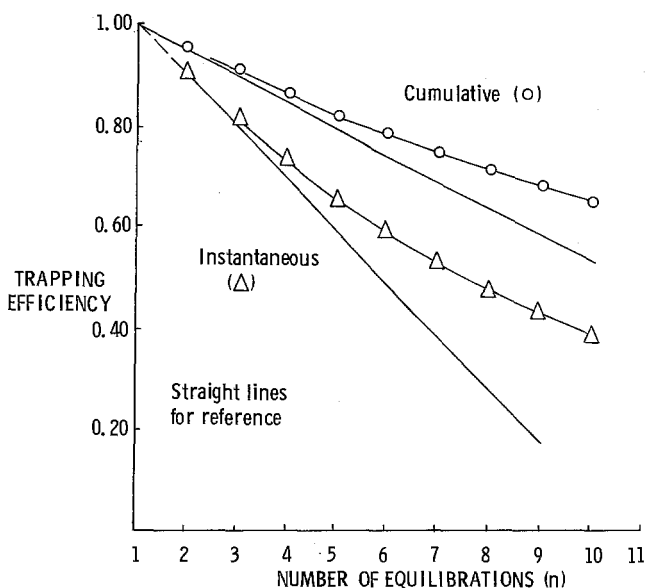


Fig. 4. Trapping efficiency versus number of equilibrations (ion exchange model).

age with various kinetic laws were not successful in duplicating the observed data, again supporting a residence time longer than the ages of the colonies studied. In any case the proposed determination of Pb^{210} and Po^{210} will help clarify this question; if the measured Pb^{210}/Po^{210} ratios agree with the theoretical ratios on lichen colonies dated by known growth rates this would support quantitative retention of Pb.

What follows is an outline of the approach to modeling the data to obtain estimates of retrospective Pb fallouts (Table IV). Ignoring the T.E.'s is justified only in the case

TABLE IV
Sample calculations used in modelling

Age (mean) (yr)	Incremental trapping efficiency	$Pb_{\text{incremental}}$ (ppm)	Pb T.E. = 100%	$\frac{Pb_t}{Pb_{t=1 \text{ yr}}}$
L9				
1	0.192 ± 0.007	22 ± 2	115 ± 11	1
2.9	0.038 ± 0.004	12 ± 3	431 ± 86	3.75 ± 0.83
5.4	0.0066 ± 0.0035	11 ± 5	2098 ± 1167	18.2 ± 10.3
8.35	0.063 ± 0.003	12 ± 5	2178 ± 1167	18.9 ± 10.3
11.3	0.0062 ± 0.0035	50 ± 2	$10,243 \pm 4708$	89 ± 42
L10				
1	0.638 ± 0.013	41 ± 2	64 ± 4	1
2.9	0.104 ± 0.006	6 ± 3	122 ± 29	1.91 ± 0.47
4.9	0.053 ± 0.007	45 ± 3	971 ± 129	15.2 ± 2.2
6.9	0.165 ± 0.013	6 ± 4	1007 ± 131	15.7 ± 2.3
8.85	0.027 ± 0.018	53 ± 6	2970 ± 1333	46 ± 21
L11				
1	0.43 ± 0.01	14 ± 1	33 ± 2	1
2.9	0.103 ± 0.006	15 ± 2	179 ± 21	5.42 ± 0.72
4.9	0.105 ± 0.007	12 ± 3	293 ± 37	8.88 ± 1.24
6.9	0.089 ± 0.010	25 ± 3	574 ± 59	17.4 ± 2.1
L15				
1	0.887 ± 0.018	135 ± 2	152 ± 4	1
2.9	0.395 ± 0.010	233 ± 3	742 ± 17	4.88 ± 0.17
4.9	0.126 ± 0.013	226 ± 4	2536 ± 189	16.7 ± 1.3
L18				
1	0.43 ± 0.01	102 ± 2	237 ± 7	1
2.9	0.109 ± 0.006	99 ± 4	1145 ± 62	4.83 ± 0.30
4.9	0.195 ± 0.009	348 ± 8	2930 ± 85	12.4 ± 0.5

of constant T.E. for the lifetime of an entire colony since a change in T.E. leads to a change in the Pb/Po^{210} ratio (the same principle applies to loss models). The inclusion of this effect in modeling does not change the fallout estimates significantly. Incremental rather than cumulative T.E.'s were used in modelling since there is much less variation in T.E. over short time intervals. Thus, these computed incremental T.E.'s approximate an effective constant T.E. over the short time interval considered ($t_2 - t_1$).

Incremental Trapping Efficiency is calculated as follows:

$$\text{T.E. for increment in Pb accumulated by lichen sector of age } t_2 \text{ over age } t_1 = \left[\frac{(\text{Po}^{210} t_2 - \text{Po}^{210} t_1)_{\text{measured}}}{(\text{Po}^{210} t_2 - \text{Po}^{210} t_1)_{\text{theoretical}}} \right]$$

where the theoretical Po^{210} is for T.E. = 100%.

Hypothetical Pb concentrations for T.E. = 100% can then be calculated using the computed incremental T.E. The hypothetical concentration for any age t is the sum of the increment in Pb concentration and the concentration computed for the previous age.

Then the hypothetical Pb concentration for T.E. = 100% of lichen sector of age t_2 , Pb T.E. = 100% is

$$\frac{\text{Pb } t_2 - \text{Pb } t_1}{\text{Incremental T.E. } t_2} + \text{Pb}_{\text{T.E.} = 100\% t_1}$$

Then the ratios of Pb T.E. = 100% t /Pb T.E. = 100% $t = 1$ yr were calculated and plotted versus age (Figure 5). The theoretical curves calculated are for different ratios of Flux $\text{Pb}_{t=10 \text{ yr}}/\text{Flux } \text{Pb}_{t=1 \text{ yr}}$ assuming a linear variation of the Pb flux (fallout rate) with time. The flux ratios for each lichen sector of a given age were then estimated and fluxes computed by the method outlined below. The details of calculating the theoretical curves are also discussed below. This approach neglects the direct airborne Po^{210} flux into the lichen; as already noted Benninger (1978) gives an activity ratio of $\text{Po}^{210}/\text{Pb}^{210}$ of 0.04 for atmospheric fallout. Others (Moore *et al.*, 1976) report even higher ratios. In any case, for direct Po^{210} flux ≤ 0.10 Pb^{210} flux the estimated Pb fluxes are not significantly changed.

The details of modeling are as follows:

Any variation of the Pb fallout rate (F) is assumed to be a linear function of age (t), higher in the past:

$$F = mt + \beta_0; \tag{1}$$

β_0 is of course F_{now} . Since F is $d\text{Pb}_T/dt$ Equation (1) can be integrated to get Pb_T , the Pb concentration at time t , for T.E. of 100%:

$$\text{Pb}_T = (m/2)t^2 + \beta_0 t. \tag{2}$$

The computation of m and β_0 remains to define F_t for each lichen colony.

β_0 as a $f(m)$ was calculated as given below.

From the estimate of F_{10}/F_1 for each lichen sector (see Figure 5) β_0 as a $f(m)$ was then easily computed:

$$\beta_0 = \frac{m \left(10 - \frac{F_{10}}{F_1} \right)}{\frac{F_{10}}{F_1} - 1} \quad \text{since} \quad \frac{F_{10}}{F_1} = \frac{10m + \beta_0}{m + \beta_0}. \tag{3}$$

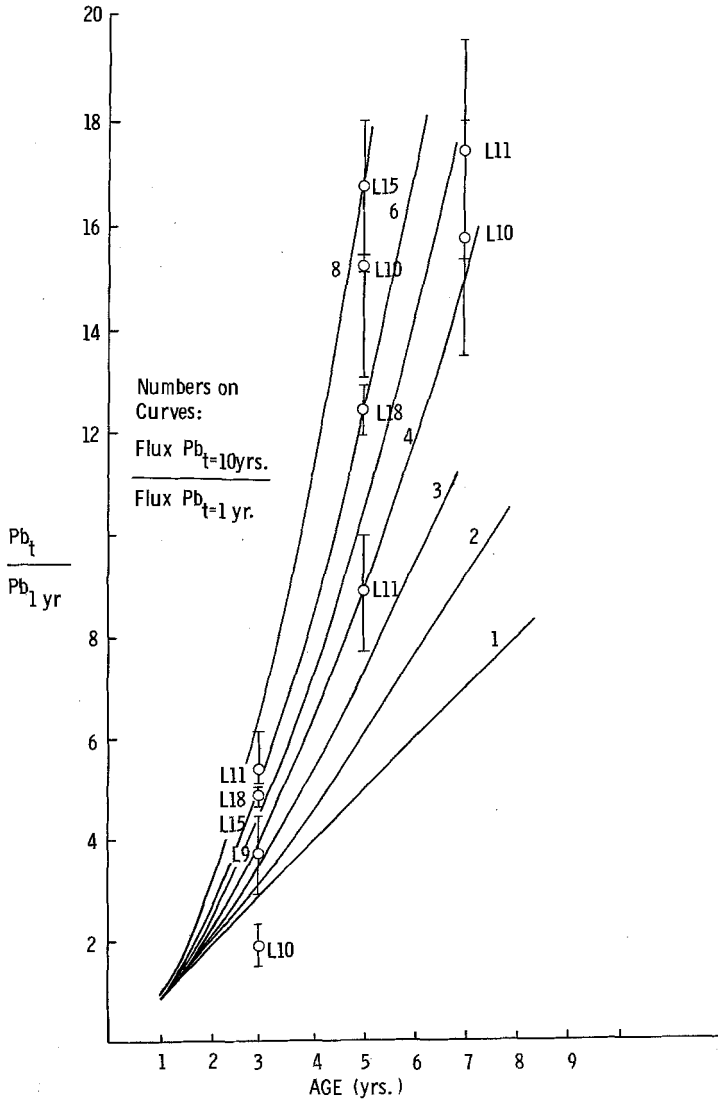


Fig. 5. $(\text{Pb}_t/\text{Pb}_{1\text{yr}})$ vs age.

m was then computed from Pb_T and Equation (2). The flux at any time t can now be computed from Equation (1). The theoretical curves corresponding to different F_{10}/F_1 ratios in Figure 5 were calculated using Equation (2) to get $\text{Pb}_t/\text{Pb}_{1\text{yr}}$ ratios, eliminating an unknown using Equation (3).

The computed values are summarized in Table V. The data for L17 were not modeled because the Po^{210} level in L17/1 is anomalously low: we do not understand why. Another anomaly appears in the different $\text{Pb}/\text{Po}^{210}$ values for L15 and 16 even though they were collected from the same boulder. The L16 colony was markedly elliptical in

TABLE V
Lead fallout estimates ($F_i^?$)

	F_{1983}	F_{1979}	$\frac{F_{1979}}{F_{1983}}$
	$(\mu\text{g cm}^{-2} \text{yr}^{-1})^a$		
Rock Creek Park, D.C.			
L15	2.0 ± 1.0	10.0 ± 0.2	5.0 ± 2.5
Plummers Island, MD.			
L18	3.2 ± 1.2	10.5 ± 0.3	3.3 ± 1.2
Great Falls, MD.			
L9	1.3 ± 0.2	— ^b	
L11	0.48 ± 0.05	0.9 ± 0.1	1.9 ± 0.3

^a Assumes $1 \text{ cm}^2 = 0.01 \text{ g}$ lichen.

^b Uncertainty too high for meaningful estimate.

Time of collection: May, June, 1984.

Average F_{1979}/F_{1983} of L15, L18 (polluted areas): 3.6 ± 1.1 ,

F_{1979}/F_{1983} from national gasoline Pb use: 2.5 (unpublished NEPA data).

shape so the age values may be incorrect (all other colonies were nearly circular except for L13 and 14 as already mentioned).

The computed differences in F_{1983} from Great Falls colonies may be real. The values for L9 and 11 may reflect a pollution plume from a nearby road 1 km from L9 and 1.4 km from L11 (the site is 5 km from Interstate 495). Both polluted locales give significantly higher fallout rates in the past than the Great Falls site. The computed values of F_{1983} and F_{1979} are plausible, within the range given in the literature for urban and rural areas (see National Research Council, 1980, p. 154) urban values range from 2.5 to 800, rural from 0.6 to $3.4 \mu\text{g cm}^{-2} \text{yr}^{-1}$. Most of these data were obtained in the 1960s and 1970s. Note that the estimates of the Pb fallout ratio F_{1979}/F_{1983} from the polluted locales agree within experimental error with the ratio computed from national gasoline Pb use for those years; the ratio for the Washington, D.C. area is probably higher because of faster substitution of new cars burning unleaded gasoline.

There is a significant body of research which supports the use of Pb^{210} as a tracer for Pb from automobile exhausts and other pollutant sources (e.g., Chow *et al.*, 1973; Lewis, 1977). However, Martell and Poet (1982) found preferential uptake of Pb^{210} and Po^{210} on tobacco leaves, with a different behavior expected for stable Pb. We do not believe this is a model for the retention of Pb^{210} by lichens, particularly the variety studied, which appears to trap Pb by ion exchange (Nieboer *et al.*, 1978.) Further, as Lewis (1977) pointed out, one should expect homogenization of normal Pb^{210} fallout and stable Pb in rain. Even if there are differences in, for example, depositional velocities of Pb^{210} and stable Pb, chemical homogenization should be expected in the lichen; hence, it is irrelevant to the model proposed here using known fallout rates of Pb^{210} to infer the trapping efficiency of stable Pb.

The scatter in the data in Figure 5 may result from the following factors:

- (1) Uncertainty in ages; in the future we plan to measure Pb^{210} and Po^{210} on each

TABLE VI
 Pb^{210}/Po^{210} as a function of age

Age (yr)	Pb^{210}/Po^{210} (activity ratio)
1	1.817
2	1.349
5	1.113
20	1.020

sample. The ratio of Pb^{210}/Po^{210} is a function of age (see Table VI). Thus age could well be determined independently of any knowledge of growth rates. Growth rates could be determined retrospectively; this would be of great interest to lichenologists. In addition, there may be significant variation in the thickness of lichens with age. While we found agreement between L1 and 2 within 10% this needs to be checked for each colony.

(2) Variation in Pb^{210} flux with time: Benninger (1978) determined a 20% fluctuation over a 3 yr sampling period. Another source of scatter may be the fallout of excess Po^{210} from coal-burning power plants, plant exudates, volcanic emissions and other sources (see Moore *et al.*, 1976; Lambert *et al.*, 1979; Kuroda *et al.*, 1984). Measurements of Pb^{210}/Po^{210} on dated air filters from D.C. would help determine whether excess Po^{210} is a problem.

(3) Incomplete retention of Pb once trapped. Could the drop in the apparent trapping efficiency with age really be from a loss of Pb and Po^{210} ? Preliminary modeling does not support this explanation but more data are needed to consider this possibility.

(4) Departure of Pb fallout rates from a linear function of age. Historic records of gasoline Pb consumption and traffic densities need to be analyzed to clarify this possibility.

The variation of Pb/V ratios with age (Table III) implies that the fallout of Pb decreased to the present faster than V assuming equal T.E. for Pb and V; this effect is most marked more than 8 yr ago. The observed Pb/V ratios from Rock Creek Park, especially L15, are quite similar to that ratio obtained (17.6 ± 1.6) from air filters in the summer of 1976 by Kowalczyk *et al.* (1982).

Nuclear emulsion studies on selected lichen samples are now underway. These studies should give some insight into the mode of collection and retention of Pb^{210} and by inference Pb and other heavy metals. Preliminary results indicate a homogeneous distribution of Pb^{210} supporting retention by an ion-exchange mechanism since multiple alpha tracks are not seen to come from point sources (particulate trapping).

4. Conclusions

The analysis of dated sectors of *P. baltimorensis* for Po^{210} , Pb, and V demonstrated the accumulation of airborne Pb^{210} , Pb, and V with time, with higher levels of Pb, V, and Zn in lichens from more polluted locations. These results can be modeled to obtain

plausible retrospective airborne fallout rates for Pb by using measured Pb and Po^{210} concentrations in each sector.

The observed scatter in the data from linear models of Pb fluxes as a function of time needs, to be understood better; 'What are the factors responsible for the scatter?', 'Are more complicated models indicated?' (e.g., non-linear variation of fluxes with time, residence times less than the age), 'Are differences in inferred fluxes real?' 'Can measurement of Pb^{210}/Po^{210} ratios be used to date lichen growth?'

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Appendix

Modeling Pb accumulation in foliose lichen by ion exchange mechanism:

Let $D = C_w/C_L$ where D is partition coefficient of Pb (or Pb^{210}),

C_w = concentration of Pb in water in equilibrium with lichen,

C_L = concentration of Pb in lichen.

Assuming a constant fallout rate of Pb it can be shown that

$$C_L = \frac{m_i}{w_1 D} (1 - \phi^n)$$

where n is number of separate equilibrations of lichen with rain (n is proportional to age).

m_i = initial mass of Pb in rain,

w_1 = mass of water in contact with lichen thallus,

w_2 = mass of lichen.

$$\phi = 1 - \frac{w_1^2 D}{w_1^2 D + w_1 w_2}$$

Note that ϕ is always < 1 since second term is always < 1 but > 0 .

Now the instantaneous T.E. is

$$\frac{m_n/w_2}{m_i/w_2} = \frac{m_n}{m_i} = \frac{w_2}{w_1 D} (\phi^{n-1} - \phi^n).$$

The cumulative T.E. is

$$\frac{C_L}{n(m_i/w_2)} = \frac{1}{n} (1 - \phi^n) \left(\frac{w_2}{w_1 D} \right).$$

For example, for $\phi = 0.9$ (assumes $w_1 = w_2 = 0.01$ g, $D = 0.1$) the results in Figure 4 are obtained. It can be shown that the cumulative T.E. (A) is always $>$ instantaneous T.E. (B); i.e.,

$$\frac{A}{B} = \frac{1 - \phi^n}{n(\phi^{n-1} - \phi^n)} > 1 \quad \text{for } 0 < \phi < 1.$$

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