

Proton-Induced X-Ray Emission Analysis — A Promising Technique for Studying the Metal Content of Plants and Soils

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Summary. The ease of employing proton-induced X-ray emission analysis (PIXEA) to studies relating metal content of soils to metal uptake in plants was aptly demonstrated in an investigation concerning the effect of automotive pollution on the abundance of about 16 elements accumulated in ribwort plantain and its surrounding soil. Elemental concentrations were shown to be dependent on the age of the plant leaves, as well as the distance from the roadside.

Proton-induced X-ray emission analysis (PIXEA) is gradually becoming an effective technique for making rapid and economical multi-elemental analyses of a wide range of biological and environmental samples. A recent review of the breadth of applicability was given by Walter *et al.* [3]. We call attention here to an ideal application of this technique, that is, to study metal deposition from pollutant sources, and specifically, to study the relationship between the amount of metal present in soil taken from various locations and metal uptake in the plant, ribwort plantain, *Plantago lanceolata*. This brief report outlines some of the results of PIXEA determinations of 13 to 21 metals in about 80 specimens of ribwort plantain leaves, soil pellets, and acetic acid soil extracts.

As described in Ref. [3], our PIXEA system utilizes a 3.0 MeV beam of protons to irradiate a specimen, causing characteristic X-rays to be emitted immediately. Some of these X-rays impinge on a Si(Li) X-ray detector which emits pulses proportional to X-ray energy. This method of excitation coupled with the high resolution properties of Si(Li) detectors allows analyses from a hundred down to a few parts per million of all the elements from chlorine ($Z = 17$) through lead ($Z = 82$). The pulses from the detector are processed in a small,

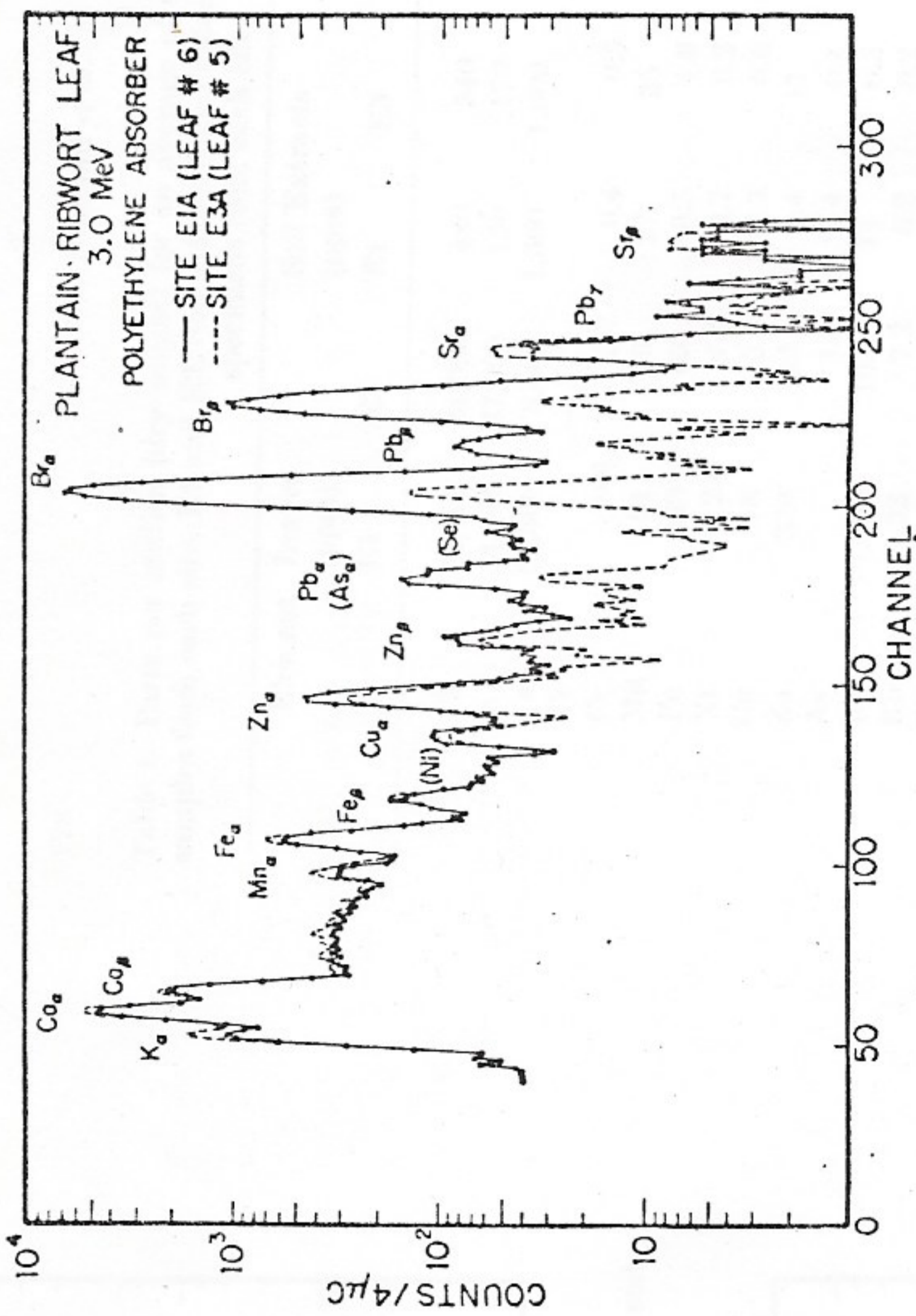


Fig. 1. Proton-induced X-ray emission spectra obtained from proton irradiation of leaf sections from sites E1 and E3. X-ray energy is proportional to channel number. (Polyethylene absorber over X-ray detector.)

on-line computer which provides spectra that display the number of pulses as a function of X-ray energy. The area under each peak can be related to the abundance of the element through a factor which incorporates the effects of X-ray emission, absorption, and detection efficiency for the various elements. Typical spectra are given in Figs. 1, 2, and 3 for specimens of leaves, whole soil, and soil extracts from two of the sites studied. These show the size of the characteristic X-ray peaks relative to the X-ray background level¹. Three different X-ray absorbers were employed across the face of the Si(Li) detector to enhance the signal-to-noise ratio for three regions of atomic weights: Mylar (S → Fe), polyethylene (Mn → Rb), and aluminum (As → Cd). Figs. 1 and 2 show spectra obtained with the polyethylene absorber and Fig. 3 gives spectra for the mylar and the aluminum absorbers. For most specimens, successive runs were made with each absorber.

Five sample sites were chosen. Site E1, the first of the two sample sites to be discussed here, is directly adjacent to an intersection of two roads in the center of Durham, N.C. with a very high traffic density. The other site to be considered here is E3 and is located 75 m back from E1 on a diagonal leading away from the traffic intersection and into an open lawn. A site intermediate to these was also chosen as well as two additional sites in an isolated forest area.

¹ Note that the manner chosen to display the data, i.e., log counts vs. energy, tends to visually enhance the background radiation level relative to the X-ray peaks.

Table 1. Parts per million (dry weight) for an average of at least nine leaves and six soil samples from each site, E1 and E3. Soil extract (ppm) values represent the average of three specimens from each site

Element	Leaves (ppm)		Soil Extracts (ppm)		Soil Pellets (ppm)	
	E1	E3	E1	E3	E1	E3
Cl	64,000	34,000	480	540	—	—
K	34,000	37,000	150	170	10,700	6,200
Ca	21,500	8,500	1,500	1,000	9,200	5,000
Ti	—	—	—	—	2,200	2,050
Cr	0.6	2.7	0.4	0.5	36	52
Mn	91	49	27	25	510	480
Fe	330	69	6.5	1.9	27,000	9,300
Ni	2.0	1.1	0.7	0.2	47	15
Cu	18	13	2.3	0.6	54	53
Zn	330	52	1.4	1.7	420	150
As	—	1.5	2.4	0.1	—	—
Br	7,900	105	14	0.3	160	28
Rb	32	7.3	0.2	0.2	42	49
Pb	440	8.7	370	0.9	2,900	210
Sr	110	46	4.5	6.5	180	72
Zr	—	—	—	—	310	560

Throughout sample collection and preparation, care was taken to avoid extraneous metal contamination of the samples. Three entire ribwort plantains along with soil in which they were growing were taken from each sample site. Immediately following sample collection, the plantain leaves were removed and merely washed and dried. All the soil samples were air dried and finely ground. One pellet was pressed from each set of the soil samples. Acetic acid extracts were prepared from all of the soil samples by shaking 10 g of each in 10 ml of 0.5 molar acetic acid for 1 hr. The solutions were then filtered until clear and 40 μ l of the filtrate deposited on a clean, thin film for proton irradiation. At least 3 systematically selected leaves from each of 15 plants, the soil pellets, and the extract deposits were analyzed using PIXEA. The X-ray spectral information was stored on magnetic tape and later was carefully analyzed with an interactive fitting program.

Results of the analyses for the two sites E1 and E3 are listed in Table 1. The data clearly confirm the expected presence of high metal content in roadside plants and soil [1, 2, 4, 5] and show that the lead level in plants, soil pellets, and soil extracts is significantly higher at the roadside site E1 than at the field site E3 (see Figs. 1, 2, and 3 and Table 1). In addition, the very strong drop off in Br concentration for all three sample types indicates another form of automotive pollution which may be accounted for by the additive $Pb(CH_3)_4Br$ in gasoline. The fall off in the levels of Fe, Zn and Sr was more rapid than the linear dependence exhibited by Pb and Br. This suggests that perhaps the Fe, Zn and Sr are not related to roadside pollution, but, on the other hand, one would expect a more rapid fall off for heavier particulate matter than for the lighter particulates (in which category Pb and Br reside). A previous study which employed radically different analysis

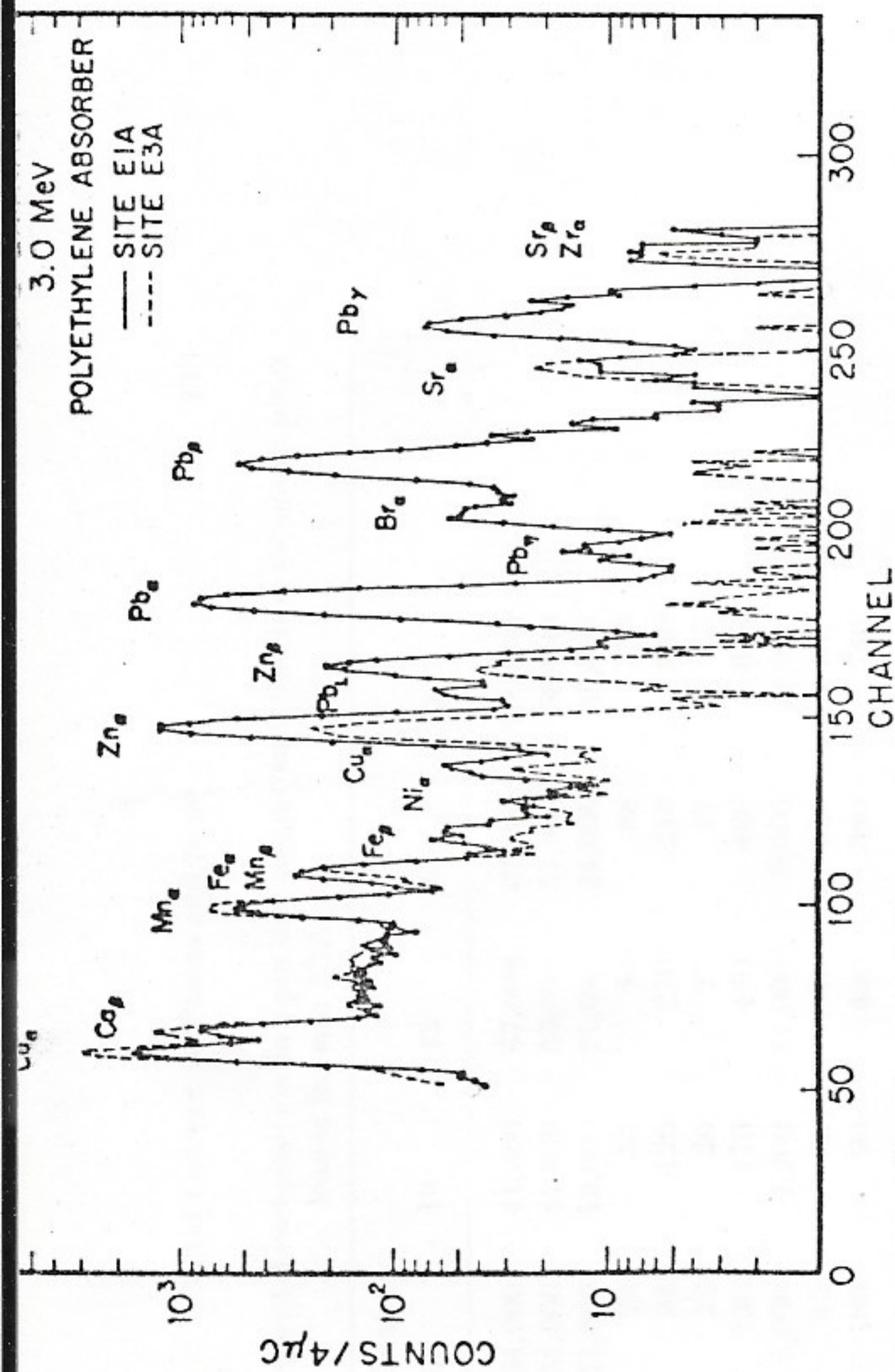


Fig. 2. Proton-induced X-ray emission spectra obtained from proton irradiation of soil extracts deposited on thin substrates. (Polyethylene absorber.)

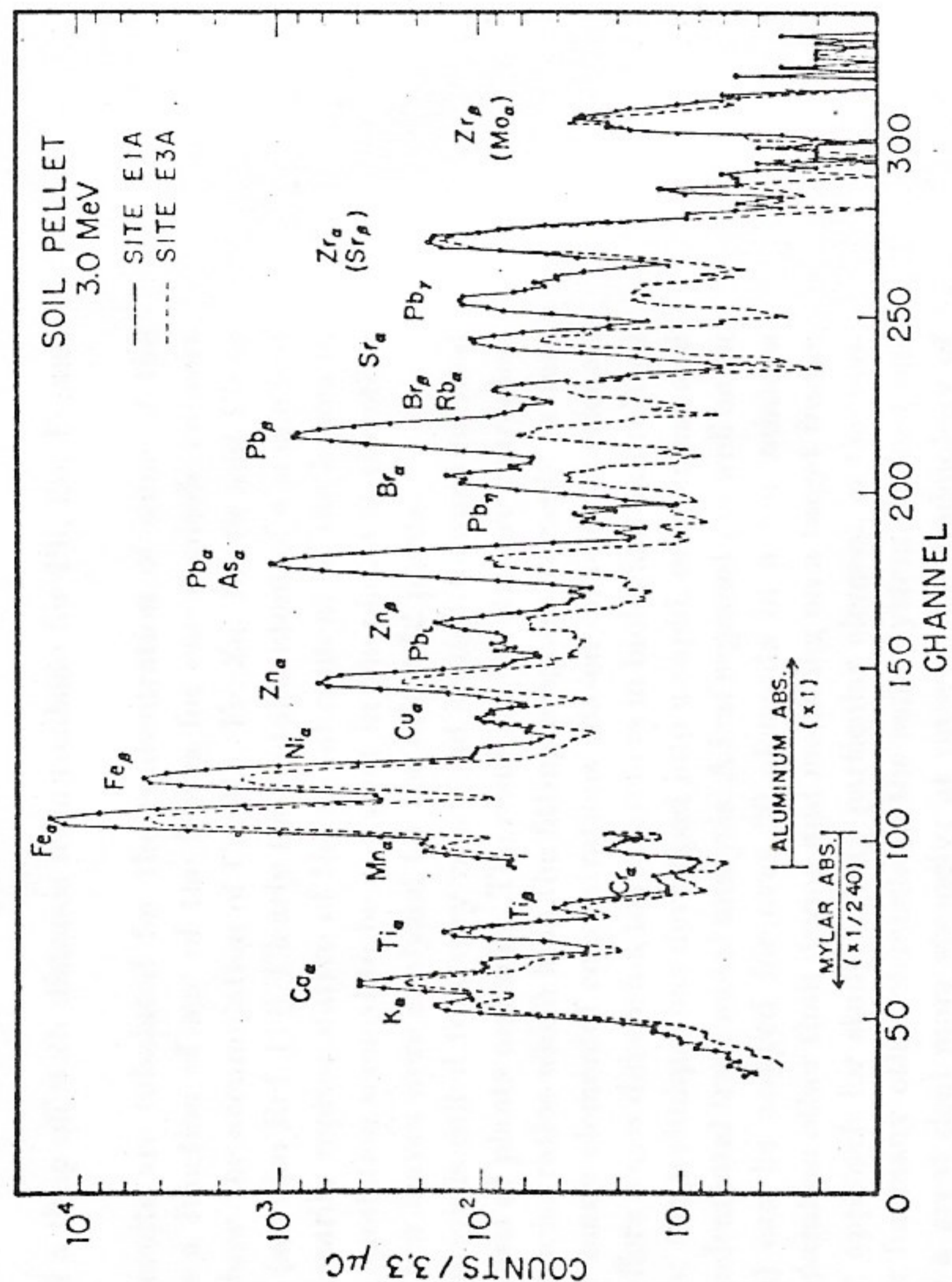


Fig. 3. Proton-induced X-ray emission spectra obtained from proton irradiation of self-supporting soil pellets. (Mylar or aluminum absorber.)

Table 2. Variation of elemental composition in ppm dry weight as a function of age of plant leaves for site B1A*

Element	Leaf no.	6	10	13	15	19
Cl		34,000	41,000	67,000	67,000	109,000
K		32,000	41,000	59,000	57,000	59,000
Ca		11,000	13,000	21,000	24,000	36,000
Mn	28	53	80	88	88	150
Fe	94	120	270	210	210	320
Cu	22	20	21	17	17	15
Zn	130	170	460	480	480	640
Br	5,900	7,200	11,000	9,000	9,000	12,000
Sr	45	66	70	120	120	101
Pb	180	90	430	380	380	740

* The leaf numbers listed indicate the position along the stem with the lowest number corresponding to the youngest leaf.

techniques also noted a drop off with distance from roadside for Pb, Zn, Fe and Sr [5].

In Table 2 the results are tabulated for the concentration of some of the observed elements as a function of age of the leaves for one roadside ribwort plantain. Our data show the accumulation of Ca, Mn, Fe, Zn, Br, Sr and Pb as the leaf age increases (see also Ref. [1]). Clearly the metal content of a single leaf of a plant is not necessarily representative of the metal content of the leaves in general². No such accumulation seemed to be apparent in the plants at the other sites although only a few leaves were analyzed for the other 12 plants.

In summary, attention is called to a very rapid and straightforward method for multielement analysis of plants and soils. The resulting spectra are characterized by high signal-to-noise ratios which help the fitting program to easily extract meaningful values for many elemental concentrations. Based on our experience, we feel that PIXEA offers a new dimension to researchers in biological and related environmental studies: the technique has developed into a rapid, economical and sensitive tool for multielemental trace metal analysis. A leaf segment (as well as an animal tissue section) can be assayed for over 20 elements in a few minutes without any prior preparation other than drying and mounting on a target frame. As a consequence the approach for studying any particular element in the ecosystem is very similar for many other elements in the same system. Indeed one could put the matter a great deal more strongly: at present, the technology of rapid and high accuracy, multielemental analyses are on the verge of many breakthroughs and all current studies of nutrient flow in ecosystems should ensure that the samples for the study are preserved so that complete elemental analysis can be performed as the techniques gain general acceptance.

² A more complete report of the present data along with additional data obtained from plants collected from the same region after a 6 month and a 10 month interval is planned for the future. Correlations between metal uptake and the presence of metals in the soil and in the soil extracts will be discussed there.

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