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DETERMINATION OF MINOR ELEMENTS IN SOIL PROFILES
BY NEUTRON ACTIVATION ANALYSIS*

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Soil, a complex mixture of organic and inorganic constituents, is made up of underlying decomposed bedrock material and/or deposits that have been transported by glacial action. The composition of soil is, however, constantly changing as the result of the action of wind and rain, additions from vegetative growth, and from the activities of man such as farming or construction.

Within soil is contained a mixture of mineral particles ranging from microscopic to easily visible fragments; adhering to these particles may be nutrients, additional elements, or organic matter. These mineral particles may be clay or quartz with an admixture of other primary minerals differing markedly in size, shape, in chemical composition, in mineralogical nature, and in physical and chemical properties. The particular group or group of particles that dominates an individual soil largely determines the characteristics of that soil.⁽¹⁾ Thus as one samples the surface or the depth of a soil he finds variations -- some large some small -- in the concentrations of elements present.

A typical pattern of soil horizons is shown in Fig 1; in such a pattern the thickness of each horizon can vary from zero to several feet. Samples of various soil types and their horizons along with samples of known depth were collected and classified by the Ecology Division of Oak Ridge National Laboratory. The soil samples were collected from local soil over an area of several square miles.

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cause these various buried soil deposits to be raised up to the surface. The comparison of the elemental concentration of a questioned sample with the elemental concentration of a known sample taken from an excavated area would be most difficult, since the concentrations of the elements change with depth of sampling within one soil classification. This could become increasingly complex since on a particular farm for example, there may be more than half a dozen different kinds of soil present.⁽²⁾

The concentrations of minor elements in Sequoia sil and Muskingum loam horizons are shown in Table 3 and 4, respectively. The minor element data in Sequoia sil show the normal effects of eluviation as the elemental concentration increases with depth. However, in Table 4, the Muskingum loam data are erratic and do not show this type of pattern. Such a soil as this presents additional sampling problems when the horizon has been exposed recently by man since the minor element content varies considerably within the same horizon. Grid samples taken over such a soil produce wide deviations in data over a small area; this makes comparison with a questioned sample very difficult.

The comparison of the concentrations of the minor elements of A₁ horizons of several different soils is presented in Table 5. In these data there are similarities in the concentration of many elements with only a few showing large differences. However, when all the elemental concentrations are compared there are sufficient differences to separate and identify each soil.

In Figures 2 and 3 the distribution of the concentration of the elements Al, Co, Fe, K, Th, Sc, Ce and La are plotted versus the number in each concentration grouping. From these histograms one sees a distribution shifted toward the lower side with the higher concentrations showing a long tail. The data for Na and Mn result in a broad fluctuating distribution as seen in Figure 4.

Conclusions

The data in Tables 1-4 show there is a considerable difference in minor element concentrations in soil; this difference is a function of the depth or horizon where the samples were taken. Surface soil layers are easily removed by modern earth-moving equipment; this exposes the underlying soil of different horizons. Soil from such horizons is

In this study the minor elements in soil in abundances of a few percent or less were determined. Neutron activation analysis (NAA) was the technique used; in non-destructive NAA the samples were measured after irradiation by direct counting methods. In some instances chemical separation of particular nuclides was required, but in the interest of economy such procedures were kept to a minimum.

Irradiation of Samples

The soil samples were screened to remove organic debris and rocks prior to analysis. They were then dried at 110°C overnight, weighed, and placed in plastic vials for irradiation. Comparative standards for the longer lived radionuclides were prepared and irradiated along with the samples. After a one minute irradiation at the flux of 1×10^{12} n cm⁻² sec⁻¹, the samples were allowed to decay for 3 minutes and then counted for ²⁸Al. After decay for one hour the ⁵⁶Mn was measured. After 24 hours the ²⁴Na and ⁴²K were measured. After an additional irradiation of one week and decay times of one, two, and six weeks, the long lived induced radioactivities were measured. The elements As, Zn, Sb, Cs, Se, Rb, Cu, Ta, Cr, U, I, and Cl were chemically separated prior to the measurement of their radioactivities by standard radio-chemical procedures.

Results and Discussion

The distribution of the minor elements with respect to depth in the soil is shown in Tables 1 and 2. The elements Al, K and Fe are usually found in the micelle in compounds of kaolinite, illite, moscovite and other silicate clay minerals that may be partially substituted depending on ions available for exchange. It is interesting that the concentration of many of the minor elements increases with depth; this is probably an indication that they have been leached from the surface (eluviation) and carried to deeper regions of the soil. The sodium and manganese are high at the surface and decrease with depth. This could be attributed to a washing in effect, i.e. from the action of rainfall on added surface material such as debris or fertilizer. Several of the elements (La, Th, Se and Co) show no pattern in concentration changes with depth other than random variation. Such variations would seem to negate the comparison of a small forensic sample with soil from an area where it had been disturbed; construction or road building for example, would

probably often sampled for comparison of forensic samples: for example, such an area may be suspected as the source of soil found on a shoe or a vehicle. The difference in trace element concentration within a soil may be as great or greater than that between soils. Hence, there is a need for a statistical study of the minor element variation of all soil types over a large area as well as a study of differences within each soil. As shown in Table 2 chemical separation makes possible an increase in number of elements determined; this provides many more data points for soil comparison but increases the time and expense for such studies.

Samples from various depth and soil horizons show the expected changes in minor element concentrations due to the eluviation and illuviation action of the soil. In a soil depth profile if the concentration of minor elements increases with depth, the soil is probably undisturbed. If the concentration of minor elements is random or fluctuating the soil is probably fill. If concentrations are constant the area is probably graded. This information can be useful in determining the origin of soil samples.

Finally it should be noted that the presence of an abnormally high or abnormally low concentration of an element in the questioned soil is probably of more importance for an identification than knowledge of concentrations of many elements that vary over normal ranges.

REFERENCES

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TABLE 1

CONCENTRATION OF MINOR ELEMENTS
IN SOIL BY DEPTH

Depth in Soil, inches	ELEMENT CONCENTRATION										
	Al %	Fe %	K %	Na μg/g	Mn μg/g	La μg/g	Th μg/g	Sc μg/g	Ce μg/g	Zr μg/g	Co μg/g
0-1	3.45	3.15	1.96	611.	1625.	34.8	24.9	3.83	32.9	1740.	33.1
1-4	6.04	2.91	1.52	640.	1306.	36.6	31.4	4.75	57.2	1425.	35.0
4-7	8.41	4.11	1.54	628.	1053.	36.7	33.3	5.57	54.5	1063.	48.4
7-13	10.0	2.88	1.65	517.	974.	36.3	26.7	5.71	63.0	939.	35.4
13-19	10.0	4.19	2.29	455.	1295.	36.7	29.3	6.88	86.0	739.	107.0
19-24	7.70	4.29	2.84	417.	1970.	40.0	24.7	6.98	54.2	640.	17.7

TABLE 2
CONCENTRATION OF TRACE ELEMENTS
IN SOIL BY DEPTH

Depth in Soil Inches	ELEMENT CONCENTRATION ($\mu\text{g/g}$)												
	Cs	As	Zn	Sb	Se	Rb	Cu	Ta	Cr	U	Br	I	Cl
0-1	2.58	9.71	19.0	0.89	1.12	7.31	8.57	0.027	18.2	5.5	0.30	0.59	6.14
1-4	1.69	8.15	16.0	0.91	1.51	6.16	4.66	0.13	41.1	6.1	0.75	2.00	5.40
4-7	3.87	11.2	19.3	0.83	1.35	11.9	8.55	0.15	34.1	2.0	1.06	3.70	6.40
7-13	3.59	5.59	22.7	0.75	0.50	14.6	10.6	0.17	37.8	2.0	1.02	2.44	4.40
13-19	3.51	6.33	24.1	0.90	1.46	20.1	10.2	0.23	50.6	8.1	0.49	2.31	5.28
19-24	4.39	4.91	26.3	0.55	0.94	5.41	12.3	0.038	45.0	2.3	0.35	1.13	4.09

TABLE 3
CONCENTRATION OF MINOR ELEMENTS IN SEQUOIA SIL

Horizon	ELEMENTAL CONCENTRATION									
	Al %	Fe %	K %	Na μg/g	Mn μg/g	La μg/g	Th μg/g	Sc μg/g	Ce μg/g	Co μg/g
A ₁	1.77	3.36	0.35	428.	390.	36.9	32.0	8.54	334.	6.94
A ₂	2.73	8.64	0.42	370.	114.	41.6	48.7	13.9	340.	10.6
A ₂	3.62	9.10	0.59	477.	348.	52.6	46.8	13.0	341.	21.6
B ₁	4.35	10.7	0.86	423.	316.	56.1	43.7	15.1	225.	20.4
B ₁	4.16	7.97	0.55	373.	62.2	46.4	47.8	16.9	291.	17.1
B ₂	4.67	12.7	0.86	347.	179.	69.0	57.4	19.3	234.	38.4
B ₂	5.98	13.6	0.89	400.	66.4	70.7	51.7	27.1	251.	21.2
C	6.46	12.9	1.04	343.	66.5	70.5	54.6	25.6	322.	18.6
C	6.84	15.3	1.00	457.	60.5	62.3	58.0	26.2	195.	17.3

TABLE 4
CONCENTRATION OF MINOR ELEMENTS IN
MUSKINGUM LOAM

Horizon	ELEMENTAL CONCENTRATION									
	Al %	Fe %	K %	Na ug/g	Mn ug/g	La ug/g	Th ug/g	Sc ug/g	Ce ug/g	Co ug/g
A ₁	3.78	2.22	2.50	760.	1500.	49.2	39.1	9.44	316.	5.36
A ₂	3.78	4.11	7.38	1485.	720.	39.9	31.5	11.0	253.	27.6
A ₂	3.92	2.45	2.10	855.	512.	53.1	41.9	8.11	284.	4.26
A ₂	4.19	1.49	1.06	357.	101.	65.9	39.8	3.77	95.7	6.54
B	5.23	2.44	0.36	912.	85.9	84.3	39.2	5.84	92.7	9.12
B	4.83	2.71	5.73	1245.	25900.	50.9	21.4	4.77	67.8	17.4
C	5.86	2.46	2.70	832.	582.	34.7	42.5	11.6	294.	5.62
C	5.97	2.16	5.03	883.	43.5	83.9	40.9	7.13	92.6	6.08
C ₁₁	6.45	3.15	4.72	957.	106.	40.9	24.3	6.57	53.4	9.77
C ₁₂	5.64	2.94	4.62	932.	48.2	34.0	26.4	6.56	59.8	6.79

TABLE 5

CONCENTRATION OF MINOR ELEMENTS IN
A₁ HORIZON OF SEVERAL SOILS

Soils	Elemental Concentration									
	Al %	Fe %	K %	Na μg/g	Mn μg/g	La μg/g	Th μg/g	Sc μg/g	Ce μg/g	Co μg/g
Lehew Loam	3.42	1.09	2.19	597.	576.	57.3	15.6	2.11	63.1	6.19
Allen Loam	1.78	2.72	0.54	227.	30.6	33.9	24.6	7.19	145.	7.13
Muskingum Loam	3.67	2.22	2.50	760.	1500.	49.2	39.1	9.44	316.	5.36
Montavello Loam	6.36	12.1	1.57	140.	694.	62.6	54.0	26.2	292.	28.8
Leadville Sil	3.81	1.34	1.43	511.	947.	63.0	20.2	2.61	96.6	7.60
Letz Sil	3.60	3.16	0.90	187.	1240.	73.7	27.5	5.32	94.1	5.77
Prader Sil	2.82	1.93	1.86	6910.	731.	36.5	23.2	4.07	82.8	7.95
Emery Sil	3.40	3.34	1.06	670.	5340.	64.8	26.5	4.82	82.9	38.3
Fullerton Sil	3.60	5.00	1.03	541.	2030.	53.4	23.3	9.44	185.	26.2
Sequoia Sil	1.77	3.36	0.35	428.	390.	36.9	32.0	8.44	334.	6.94
Hartsell Sil	3.13	3.66	2.19	832.	160.	79.4	40.7	10.3	398.	14.5

Figure 1. Soil Horizon Profile.

Figure 2. Histogram of Concentrations of Th, Sc, La, Ce in 62 Soil Samples.

Figure 3. Histogram of Concentrations of Al, Co, K in 62 Soil Samples.

Figure 4. Histogram of Concentrations of Na and Mn in 62 Soil Samples.