A SPECTROGRAPHIC STUDY OF THE DISTRIBUTION OF TRACE ELEMENTS IN SOME PODZOLIC SOILS

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During soil development a partial redistribution of the inorganic elements occurs within the profile. Although the distribution of major elements has been determined in many different soil profiles, and comparative evaluations have been made of the weathering factors that contributed to it, similar determinations and evaluations have not been made for trace elements. Numerous workers have determined the content of a single trace element in a particular part of a soil profile (7) but few have determined the distribution of trace elements as a group throughout the profile (1, 4, 6, 9). The relationship between trace and major element distribution has similarly been studied largely on the single trace element basis.

Use of chemical instrumentation, in this report the emission spectrograph, facilities the study of a large number of elements at one time. This paper describes a study of the distribution of trace elements in relation to the major elements in specially selected profiles of some podzolic soils, and evaluates some of the weathering factors known to have been operative in them.

The nature of the parent material is a major factor in determining the quantities of trace elements present in a soil, but enrichment by plants (2), contamination by way of the air, and microbial activities (4) affect their distribution. Soil reaction, drainage, and permeability also influence trace element content and distribution in soils.

To control some major variables, sites were selected in glaciated areas where the composition of the drift was well established. Soils formed from drift from three kinds of parent materials—gray acid sandstone, carbonate rock, and red acid shale—were studied (table 1). Conformity of the lithology of the drift to that of the underlying bedrock was quite close, except for the older limestone drift which contained an admixture of gneissic rock. Soils formed from younger glacial materials and from corresponding older glacial deposits were studied. Comparisons were made between soils formed on glacial deposits of the same age but of different lithologies. Comparisons were also made between soils formed on glacial deposits with similar lithologies but different ages. All soils studied were deep and mature, and from areas where soil conditions were virgin.

In the younger Wisconsin drifts the lithologic composition of the material often plays a very important part in characterizing the soil. The nature of the parent material is usually directly or indirectly responsible for certain morphological features of the profile. Where the drift has undergone long-continued weather-

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Soils studied	for inor	ganic	content*

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Great Soil Group	Soil Type	Parent Material	Age of Drift
1. Podzol	Unnamed† sandy loam	Gray acid sandstone (Pocono)	Wiscon-
2. Podzol	Unnamed sandy loam	Gray acid sandstone (Pocono)	Kansan
3. Gray brown podzolic	Squires** silt loam	Calcareous material	Wiscon-
4. Red podzolic	Annandale** silt leam	Gneissic and carbonate rock	Kansan
5. Gray brown podzolic	Wethersfield loam	Red acid shale (Brunswick)	Wiscon-
6. Gray brown podzolic	Norton loam	Red acid shale (Brunswick)	Kansan

^{*} Locations: 1. Tobyhanna, Pa.; 2. Jim Thorpe, Pa.; 3. McAfee, N. J.; 4. Flanders, N. J.; 5. Mctuchen, N. J.; and 6. East Millstone, N. J.

ing, as in the Yarmouth and Sangamon interglacial stages, its original composition plays a comparatively minor role. The time-climate complex has altered and masked many inherited features in the old drift (8), but acquired features tend to be similar and original differences that once existed between drifts become less pronounced.

METHODS

Air-dried soil (20 pounds) was broken up with a wooden roller and put through a stainless steel sieve. It was successively quartered to give a 160-g, and a 50-g, portion. The 50-g, sample was oven-dried and used for total-soil analysis. The clay fraction was obtained by suspending the 160-g, portion in 8 liters of water that had been passed through a resin column; the suspension was adjusted to pH 8.5 with redistilled NH₄OH and particles of <0.002 mm, were separated by sedimentation. The clay fraction obtained was leached with 0.1 N HCl to remove sorbed cations.

The inorganic elements in the soil and clay fraction were determined spectrochemically by the method of Shimp et al. (5). Each sample was analyzed in duplicate after being dried at 110° C. A 2.0-g. sample was used for total soil and a 0.2-g. sample for the clay fraction. Co, Cr, Cu, Ga, Mn, Ni, Pb, Sn, V, and Zn were determined. Of the major constituents, only Al, Fe, Mg, and Ti were determined. Precision of these analyses was within the ±5-15 per cent range.

RESULTS

Contents of inorganic elements in the whole soil and in the clay fraction of each horizon of the six profiles are shown in table 2. To determine any changes in distribution of inorganic elements between the soils formed from the younger and

[†] Profile description by Tedrow (8).

^{**} Profile description by Krebs, R. D., Seven soil profiles in northern New Jersey, Ph.D. Thesis, Rutgers University, 1955.

older glacial deposits, a distribution ratio (table 3) was calculated for each element. This ratio was obtained by dividing the amount of each element in the A horizon of any soil by that in the C horizon. A value of less than 1 indicates that removal of the particular element from the A horizon has taken place; a value greater than 1 indicates accumulation.

Accumulation of the elements in the clay fraction was found by calculating a concentration ratio (table 4), that is by dividing the amount of element in the clay fraction of the A or B horizon by that in the entire soil of the C horizon. A value greater than 1 indicates that the particular element is in greater quantity in the A or B clay fraction than in the parent material.

PODZOLS ON WISCONSIN AND KANSAN DRIFTS

Total soil

All elements were partially removed from the A horizon with the exception of Ti in both profiles and Sn in the younger profile (A, B, table 2). The B and C horizons of each profile have virtually the same inorganic element content. The distribution ratios (table 3) show that Cr, Fe, Pb, Sn, and V were leached and Ti concentrated to a greater extent in the soil from the older Kansan drift than in that from the younger Wisconsin. This may have been due to a continuing trend with age, or to more intense leaching during pre-Wisconsin time. Ga, Ni, and Zn were leached from the A horizon to approximately the same extent in both soils. Al, Cu, Mg, and Mn were leached to a lesser extent from the soil formed on the older drifts than in that from the younger drifts.

Clay fraction

Except for Ti in both profiles, Cu in soil derived from Wisconsin drift, and Ga and Mn in soil from Kansan drift, the elements have not accumulated in the clay fraction of the A horizon to the extent that they have in the B (table 4). In the clay fraction of soil derived from Kansan age drift pronounced accumulation of Ti, Cu, and Ga occurred in the A horizon. This also applies to Ti, Cu, Sn, V, and Ga in the clay in the A horizon of the soil formed from Wisconsin drift. Comparison of the concentration ratios in the clay fraction of the A horizons of the two profiles reveals that the ratios for Cr, Cu, Fe, Ga, Pb, Su, and V are greater in the clay from the soil formed from Wisconsin drift than in that from Kansan drift. Ratios for Al, Ni, and Zn are virtually the same in both profiles, whereas those for Mg, Mn, and Ti are less in the younger clay fraction. The concentration ratios of the clay fraction of the A horizon and the distribution ratios of the soil indicate similar trends between the two soils for all elements except Cu and Ti.

All elements except Co are accumulated in the clay fraction of the B horizon of both podzol profiles (table 4). Al, Cr, Fe, Ga, Mg, Ni, Pb, Sn, and V are accumulated more in the clay of the soil of the Wisconsin age than in that of the

TABLE 2
Inorganic elements in soils

								; ; ;							
1: 0	1						0,4	Oven Dry Weight	ght						
1000	11011203	Fe.O.	Al ₂ O ₃	TiO	MgO	Cu	Ma	Zn	Ni	ပိ	Sa	Pb	Cr	Λ	C _a
					A. Podzol	zol soils	-Total	soit						į	
		250	26	2%	600	ppm.	ppm.	ppm.	ppm.	ppm-	ppm.	ppm.	ppm.	ppm.	ppn:
Podzol on Wis-	¥	0.76	0.74	0.50	0.05	₹1	20	16	ಣ	ND*	r.	∞0	17	11	2
consin drift	M	3.43	7.03	0.26	•	Ç)	67	63	13	-	9	24	48	38	ij
	Ö	2.86	6.84	0.30	0.34	13	88	89	14	က	'n	22	43	31	τĊ
Podzol on Kansan	₹	0.33	1.65	0.36	0.0	731	50	14	C3	*ON	77	9	12	О	က
drift	щ	1.92	6.65	0.28	0.18	∞	35	09	11	-	13	21	44	40	œ
	ပ	2.23	8.58	0.16	0.32	ō	17	61	15	~	∞ .	30	51	46	10
					B. Podzol	ol soils-	-Clay fr	fraction							
Podzol on Wis-	-4	00.9	15.84	1.85	0.41	135	80	86	15	ND*	20	#	101	133	27
consin drift	m	•		•	1.40	75	165	217	82	ಣ	200	75	177	174	30
	Ü	11.70			1.66	117	240	256	91	10	91	7.5	140	148	28
Podzol on Kansan	-4	-4		1.24	99.0	£-9	100	5	21	ND*	91	38	81	121	48
drift	m		•	•	_,	₹ 6	100	206	45	63	23	63	102	138	32
	Ç	•		0.49	•	26	17.5	206	51	io.	39	126	160	186	36
				C. Squ	Squires and	Annandale	tale soils-	s-Total	l soil						
Souires	¥	3.49	10.80	88.0	2.60	13	121	169	18	က	83	138	22	26	98
	m	•	11.60	0.81	1.97	18	118	500	53	7	۲۰	122	·	73	Çî.
	ပ		13.70	-	•	36	564	302	45	s.	rů.	109	∞	96	13
Annandale	~:	4.48	•	96.0	1.53	17	106	320	30	च्युः	14	155	58	20	16
	M	•	•		•	21	126	277	25	9	60	89	0E	65	21
	ပ	10.00	22.20	•	•	89	220	256	35	12	က	61	8	82	50

				D. Squires	₽	nd-Annandale soils	e soils	-Clay fraction	aetion						
Samiros		11.06	25.10	1 7	4.24	36	156	318	45	c.		30	83	119	53
	. α			•		20	296	405	#	12	رن د	29	10.8	137	င်- က
	۰ ۲	9				142	328	226	Ŧ	1~	, <u>.</u>	31	+ 6	152	31
Annandale	· •	,	70.00			99	120	271	181	-1 ⁴		40	£.	163	C]
	. cc	_				6.2	125	249	120	~†i	-	56	34	122	37
	٠ ٢	10.20	65.20	0.28	1.16	85	232	248	148	10		37	31	130	G#
				E. We	Wethersfield	and No	Norton soils	s-Total	l soil						1
Wothersfield	4	1 .	10.40		0.93	07	7 09#	102	17	-1 4	10	103	10	53	10
n center succe	; m	3.20		0.85	1.06	**	324	167	25	4	19	129	18	56	11
) C		17.60	•		98	324	146	21	က	12	101	21	56	0.
Norton) - -(•	•	0.30	30	520	86	38	ů	12	30	50	č.	s ·
	<u> </u>	•	12.50		4	20	330	122	1.7	-11	∞	101	10	69	13
	ا ا	6.28	19.40		•	7	350	218	45	10	б	116	33	85	#
				F. Wethersh	eld	and Norton	on soils	-Clay f	Clay fraction						
Wathorsfold		11 90	39.30	ı	3.30	115	420	352	103	10	48	63	134	147	31
niensnatha W	. r	11.70	•	65.0	. ,	97	450	297	84	-1 1	58	\$	134	135	34
	1 C	14.30	32.30	• •	•	110	320	273	92	12	50	64	167	172	32
Norton		13.10		+	2.90	69	500	110	121	10	08	++	167	193	33.5
			•	0.49	•	63	330	253	103	33	500	73	157	198	32
) 	14.70	34.20	0.55	2.90	88	021	231	\$	23	55	73	164	215	31
7 4 5 V			-												

* ND = Not detected.

TABLE 3

Distribution ratios* in the A horizon of the soils

Element	Wisconsin Age Podzoi	Kansan Age Podzoi	Squires	Annandale	Wethersfield	Norton
Fe	0.27	0.15	0.44	0.45	0.64	0.51
Al	0.11	0.19	0.79	0.82	0.59	0.54
Ti	1.97	2.25	1.19	0.89	1.24	0.86
Mg	0.06	0.13	1.09	3.40	0.56	0.59
Cu	0.28	0.38	0.36	0.25	0.41	0.73
Mn	0.23	0.49	0.46	0.48	1.42	1.33
Zn	0.24	0.23	0.56	1.25	0.70	0.39
Ni	0.18	0.14	0.40	0.94	0.81	0.84
Co	<1	<1	0.65	0.31	1.23	1.15
Sn	1.06	0.25	0.32	5,52	0.84	1.36
$\mathbf{P}\mathbf{b}$	0.36	0.20	1.27	2.54	1.02	0.26
Cr	0.39	0.23	2.67	3.59	0.48	0.61
V ·	0.35	0.19	0.58	0.85	0.95	0.67
Ga	0.35	0.28	0.65	0.80	1.03	0.58

* Distribution ratio = $\frac{\text{Amount in soil A horizon}}{\text{Amount in soil C horizon}}$

TABLE 4 Concentration ratios* in the A and B horizon clay fractions

Ele-	Wiscons Pod			in Age Izol	Squi	TCS	Annas	ndale	Wethe	rsfield	Nor	ton
ment	Λ	В	Λ	В	Λ	В	A	В	٨	B	A	В
Fe	2.41	5.10	1.79	4.30	1.40	1.46	1.02	1.11	2.35	2.31	2.08	2.32
Al	2.31	4.72	2.56	3.26	1.83	1.83	3.15	3.08	1.83	1.84	1.71	1.66
Ti	6.16	1.53	7.75	2.69	0.70	0.76	0.44	0.30	0.69	0.63	0.46	0.53
Mg	1.20	4.12	2.06	2.53	1.77	1.30	2.00	2.71	1.99	2.29	1.89	2.03
Cu	10.38	5.77	6.88	10.08	1.55	1.94	0.97	1.16	1.17	0.78	1.69	1.58
Mn	0.91	1.88	2.44	2.44	0.59	1.12	0.55	0.57	1.30	1.39	1.28	0.85
$\mathbf{Z}\mathbf{n}$	1.44	3.19	1.54	3.38	1.05	1.33	1.06	0.97	2.41	2.05	2.02	1.16
Ni	1.06	5.77	1.10	2.92	1.00	0.98	5.84	3.75	4.90	4.00	2.69	2.29
Co	'	1.00		1.56	1.73	2.37	0.34	1.20	3.00	1.21	2.26	2.85
Sn	4.00	10.00	2.11	3.03	0.10	0.36	0.32	0.28	4.00	4.83	9.41	5.88
Pb	2.00	3.41	1.27	2.07	0.28	0.26	0.66	0.43	0.62	0.83	0.38	0.65
\mathbf{Cr}	2.35	4.12	1.59	2.00	10.00	13.01	5.51	4.36	6.38	6.38	5.06	4.76
V	4.29	5.61	2.61	2.97	1.24	1.43] 1.99	1.49	2.62	2.41	2.35	2.41
Ga	5.87	6.52	4.90	3.27	2.19	2.50	2.15	1.90	3.13	3.43	2.25	2.25

* Concentration ratio = Amount in clay A (or B) horizon

Amount in soil C horizon

Kansan age. Ratios for Mn and Zn are similar for both clays, and less Cu and Ti accumulated in the clay fraction of the soil of Wisconsin age.

The types of clay minerals present in the two clay fractions are similar (8) so that differences in inorganic element content of the clay fraction are probably not due to variable amounts of these elements in different clay minerals.

SQUIRES AND ANNANDALE SOILS

Total soil

Of the two soils derived from calcareous material, Squires was formed from drift of Wisconsin age and Annandale² from that of Kansan age. The carbonate rock present in the drift originally was completely weathered away in the Annandale soil, whereas free carbonates persist in the lower horizons of the Squires soil. The distribution of Al, Cu, Fe, Ga, Pb, Ti, and V shows similar trends in the profiles of both soils; only that of Ni, Sn, and Zn is quite different (C, D, table 2). Despite these minor variations there are no outstanding differences in the distribution pattern of the elements. Distribution ratios (table 3) show that Cr, Mg, and Pb are not leached from the A horizon of either soil. In addition, Sn and Zn are not leached from the A horizon Annandale soil. Distribution ratios of Cr, Ga, Mg, Ni, Pb, Sn, V, and Zn are less in Squires than in Annandale. Al, Fe, Mn, and Ti are virtually the same in both soils but the distribution ratios for Cu and Co are lower in the Annandale.

Clay fraction

A very high content of Al is noted in the clay fraction of the Annandale soil (C, D, table 2). The Annandale clay minerals consisted principally of gibbsite and kaolinite. Mn, Pb, Sn, and Ti are notably reduced in concentration in the clay fractions of the A and B horizons of both soils and Co is reduced in the A horizon of the Annandale clay (table 4). Only Cr is notably accumulated in the clay fractions of both soils. In both Annandale and Squires a close similarity exists between the concentration ratios in the clay from the A and B horizons for all elements except Ni and Cr.

Comparison of the concentration ratios between the clay fractions of the A horizons shows that those for Al, Mg, Ni, Pb, Sn, and V are less in Squires than in Annandale. Ga, Mn, and Zn have virtually the same ratios in both clays, and Co, Cr, Cu, Fe, and Ti are lower in that of Annandale than that of Squires. Comparison of the concentration ratios of the elements in the clay fractions of the B horizons shows relationships virtually the same as those of the A horizon clays.

WETHERSFIELD AND NORTON SOILS

Total soil

Wethersfield and Norton soils were formed on glacial drift which was comprised mainly of the local acid red shale of Triassic age. This material is highly resistant to weathering (3), as the narrow range of values for the elements throughout the profiles for the soils as a whole and for their clay fractions indicates (E, F, table 2).

* Connor, Jane. Distribution of trace elements in the soil profile. Ph.D. Thesis, Rutgers University, 1956.

^{*}The profile contains some weathered limestone fragments and a gibbsite-kaolinite clay mineral suite, which is somewhat atypical of the Annandale series. For details see Krebs, R.D., Seven soil profiles in Northern New Jersey, Ph.D. Thesis, Rutgers University, 1955.

Distribution ratios (table 3) show no substantial increase of any element in the A horizon of either soil. The ratios for Al, Co, Fe, Mg, Mn, Cr, and Ni are virtually the same. Ga, Pb, Ti, V, and Zn are higher in the Wethersfield soil and Cu and Sn in the Norton.

Clay fraction

In the clay fraction of these soils (table 4) Ti and Pb are not accumulated, whereas Co, Cr, Ga, Ni, Sn, and V are accumulated in both clay fractions. Sn has a higher concentration ratio in the A horizon of the Norton clay; Al, Cu, Co, Mg, Mn, and V are virtually the same; but the ratios for Cr, Fe, Ga, Ni, Pb, Ti, and Zn are slightly higher in the Wethersfield clay. Co, Cu, and Sn have higher concentration ratios in the B horizon of the Norton clay; Al, Fe, Pb, Ti, and V are virtually the same, but Cr, Ga, Mg, Mn, Ni, and Zn are higher in the Wethersfield clay.

DISCUSSION AND CONCLUSIONS

Data from the six soil profiles show that parent materials high in trace elements tend to give rise to soils rich in these elements. The highly quartzose drift associated with the two podzol profiles is a poor source of trace elements. Not only are the total quantities low but intense leaching is indicated by the pronounced depletion in the surface horizons. The podzolic soils, however, from finer-textured materials that were not so siliceous nor so highly permeable, have a marked concentration of nearly all trace elements. This is evident from the quantities of trace elements present (table 2) and their distribution ratios (table 3). The gray-brown podzolic and red podolic soils had greater quantities of trace elements throughout their profiles and showed less leaching than the podzols.

The data show that the A horizons of all six profiles tend to be lower in their trace element content than the B or C horizons. This is most apparent in the podzols. But the red shale drift from which the gray-brown podzolic soils were formed is known to be resistant to weathering and soil formation. Many inherent lithologic characteristics of this material are well preserved in the soils formed from them, even though it has long been subjected to weathering and to soil-forming processes. In the soils formed on this drift there is less tendency to have large trace element differences between the horizons. Trace element differences between horizons of the two podzols and the gray-brown podzolic and red podzolic soils formed on carbonate rock, however, are quite outstanding.

Variation in trace element content of the soil due to the nature of the soil material is considerable. The clays extracted from various soil horizons show less variation in trace element content than the entire soils (table 2).

The climate-time complex was an important factor in the exhibited characteristics of the soils formed on pre-Wisconsin drift (8), but this was not found to be of major proportions in the trace element situation. Certain soils formed on deposits of pre-Wisconsin age evidence a stabilization of the trace elements in the older deposits affected by the Yarmouth and Sangamon interglacial stages. As was the case with the free iron oxide in the B horizon of these podzols (8), Al,

Cu, Ga, Mg, Mn, Ni, and Zn in the soil of the Kansan age drift may have been somewhat stabilized during interglacial times.

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