IODINE IN SOIL PROFILES IN RELATION TO IRON AND ALUMINIUM OXIDES AND ORGANIC MATTER

D. C. WHITEHEAD

(Grassland Research Institute, Hurley, Maidenhead, Berkshire, SL6 5LR)

Summary

The iodine content in successive 10 cm horizons of eighteen soil profiles from England and Wales was determined and correlated with contents of 'free' aluminium and iron oxides (oxalate-soluble) and organic matter.

The pattern of change in iodine content with depth varied considerably with soil type. In the rendzina soils, the content was relatively high in the surface 10 cm but declined markedly with depth. In the podsols, iodine was low at the surface but increased in the B horizon: in one of these soils an iron pan of about 1 cm thickness had an iodine content as high as 37.6 mg/kg. In two soils derived from Ordovician, and one from igneous, rock material, the iodine content was relatively high (up to 25 mg/kg) with maximum values at intermediate depths. In contrast, soils derived from river alluvium and from lowland clays generally had low iodine contents (< 6 mg/kg) which showed little variation with depth in the profile. In a peat soil the iodine content was relatively high in the horizons above 60 cm but was low (1.3 mg/kg) in the underlying clay.

In all 154 samples from the eighteen sites, iodine content was closely correlated with oxalate-soluble aluminium $(r = 0.834^{***})$ but not with oxalate-soluble iron (r = 0.35) or organic matter (r = 0.37). However, in the five most acidic soils, with pH below 4.8, the iodine content was more closely correlated with iron than with aluminium.

Introduction

THE distribution and behaviour of iodine in soils is currently of interest for two main reasons. First, iodine is an essential element for animals, and deficiencies are thought to occur widely in agricultural practice when supplementary iodine is not provided (Kubota and Allaway, 1972; Wilson, 1975). Secondly, the radioactive isotope 1^{29} I (half life 17 million years) is produced during the reprocessing of nuclear fuels (Bryant, 1970), and the fate of trace amounts that may be released to the atmosphere is uncertain: enhanced concentrations in the thyroid gland of animals have been reported near reprocessing plants in the USA (Matuszek *et al.*, 1974). Information on the naturally occurring stable isotope 1^{27} I assists in predicting the behaviour of the radioisotope in the environment: the amounts of 1^{27} I in soil will also influence the extent of uptake by plants of any added 1^{29} I. In these contexts it is important to have information on the amounts of iodine present at depth in soils and on the factors influencing the movement of iodine through soil profiles of different types.

While several authors (e.g. Vinogradov, 1950; Chilean Iodine Educational Bureau, 1956; Goldschmidt, 1958; Fuge, 1974) have stated that the content of iodine in soils is generally greatest at the surface and decreases with depth, information for British soils is lacking. The variation in iodine content with increasing depth has therefore been assessed in a range of soils from England and

IODINE IN SOIL PROFILES

Wales. Relationships between the contents of iodine and those of 'free' iron and aluminium oxides (oxalate-soluble) and of organic matter, have been examined, in view of previous evidence that these components were largely responsible for the retention of iodine in soils sampled to 10 or 15 cm depth (Whitehead 1973, a,b; 1974a). In order to examine further the possible importance of organic matter, iodine was also determined in five pairs of soils, sampled to 15 cm, one of each pair having a low, and the other a relatively high, content of organic matter. In addition, the proportions of the total iodine soluble in (a) 0.016 M KH₂ PO₄ and (b) hot water, have been determined.

Materials

Soil profiles were sampled at 18 sites in England and Wales selected to comprise a wide range of parent materials (Table 1). Two rendzinas (sites 1 and 2), two podsols (sites 3 and 4) and a peat (site 18) were included. Samples were taken from successive 10 cm horizons to a depth of at least 70 cm, except at one site where the depth of soil above rock material was less than this. With the two podsols, additional samples were taken from the pedologically distinct horizons. All the samples were collected from recently exposed vertical surfaces from which the superficial material was removed immediately before sampling. At the time of sampling, the majority of the sites were, or had recently been, in agricultural use, either under grass or cereal cultivation, but sites 3 and 4 were in pine forest and site 14 was moorland.

			Properties of $0-10$ cm horizon					
Site no.	County	Parent material	pН	Clay %	Organic C % C	Oxalate- soluble Al % Al	Oxalate- soluble Fe % Fe	
1	Oxon	Chalk	7.5	7.0	6.99	0.50	0.61	
2	Bucks	Chalk	7.4	8.8	4.45	0.13	0.34	
3	Surrey	River terrace gravel over sand	3.2	1.4	1.24	0.00	0.00	
4	Hants	Sand (Folkestone Beds)	3.0	4.0	3.00	0.02	0.13	
5	Berks	Thin colluvium over river gravel	6.8	10.8	2.12	0.07	0.53	
6	Berks	Thin colluvium over river gravel	7.4	25.4	5.87	0.11	0.86	
7	Derbys	Sand over river gravel	5.7	27.4	2.66	0.15	1.15	
8	Yorks	River terrace alluvium	5.8	25.7	5.14	0.21	0.93	
9	Gloucs	Clayey drift over Keuper marl	5.2	22.4	4.39	0.13	0.76	
10	Oxon	Thin colluvium over Oxford clay	7.2	15.3	6.24	0.11	0.90	
11	Bucks	Kimmeridge clay	7.1	36.1	3.7 9	0.11	1.28	
12	Gloucs	Clayey drift over Oolitic limestone	5.1	33.8	2.15	0.37	0.88	
13	Yorks	Sandstone	6.7	26.6	6.53	0.29	1.42	
14	Yorks	Mixed non-calcareous till	4.7	28.1	6.62	0.19	2.23	
15	Dyfed	Ordovician shale/sandstone	6.8	33.2	4.46	0.45	1.68	
16	Cumbria	Andesite/rhyolite (igneous)	5.1	25.0	5.87	0.42	1.45	
17	Cumbria		4.5	28.1	7.70	0.37	1.63	
18	Cumbria	Peat over alluvial clay	3.8	15.4	27.51	0.67	0.81	

TABLE 1

Soil parent material, and chemical properties of the 0-10 cm horizon, at each site*

*More detailed information on the location of the sites, on the soil series at some sites, and on the chemical properties of other soil horizons, is available from the author

The soils of contrasting organic matter content were obtained from sites where adjacent areas had been under either arable cultivation or grass for prolonged periods. Four pairs were obtained from commercial farms in East Anglia and the fifth from an experimental site at Hurley. On average, there was a twofold difference in organic carbon content between members of each pair, mean values being 1.35 and 2.58 per cent respectively for the arable and grassland soils. These soils were sampled to a depth of 15 cm.

All the samples were sieved through a 6 mm sieve to remove stones, dried below 30 °C and ground to pass a 2 mm sieve.

Methods

Total iodine content, and the proportions soluble in 0.016 M KH₂PO₄ and in hot water (100 °C), were determined by the procedures described previously (Whitehead, 1973*a*). Organic matter was determined as organic carbon by the modification of Tinsley's method developed by Kalembasa and Jenkinson (1973). 'Free' iron and aluminium oxides were estimated by extraction with acid oxalate solution (0.100 M oxalic acid + 0.175 M ammonium oxalate), 1.00 g oil being shaken in the dark for 16 h with 50 ml of reagent (Pritchard, 1964; Schwertmann, 1973), followed by centrifugation. Iron was determined in the extract by the colorimetric method of Krishna Murti *et al.* (1966). Aluminium was determined by atomic absorption spectrophotometry using a nitrous oxide—acetylene flame, the soil extracts in acid oxalate solution being mixed with a solution of potassium chloride to give a final concentration of 2000 mg K/l as recommended by Webber *et al.* (1974).

Clay and silt contents were determined using the hydrometer method, following treatment of the samples with hydrogen peroxide to destroy organic matter: the calcareous soils from sites 1 and 2 were, in addition, treated with HCl to remove calcium carbonate. Soil pH was determined, using a glass electrode, with a 1:2.5 suspension of soil in 0.01 M CaCl₂. All determinations, except those of clay and silt, were carried out in duplicate.

All the samples from the soil profiles were analysed for total iodine, 'free' iron and aluminium oxides, organic carbon and pH. Determinations of clay and silt were made on the 0-10 and 40-50 cm horizons only. The proportions of soil iodine soluble in $0.016 \text{ M KH}_2 \text{ PO}_4$ and in hot water were determined for those profiles in which total iodine contents were sufficiently high for the results to be meaningful (*viz.* sites 6, 8, 10, 12, 13, 15, 16, 17, 18). Details of the soil properties for the 0-10 cm horizons are given in Table 1.

With the surface soils of contrasting organic matter content, determinations were made of total iodine, of iodine soluble in KH_2PO_4 and in hot water, of organic carbon and pH.

Results and Discussion

The pattern of change in iodine content with depth varied considerably amongst the eighteen sites (Table 2). At three sites, comprising two rendzinas (1 and 2) and an acid soil developed on till (14), there was a marked and continuous decline with increasing depth. With the two podsols (3 and 4), iodine content was greatest at an intermediate depth in the profile, and was closely correlated with oxalate-soluble Fe (Table 3). The association between iodine and oxalate-soluble Fe was shown even more clearly by the pedologically distinct horizons of these two profiles. In

Site no.	0-10	10 - 20	20-30	30-40	40-50	50-60	60-70	70-80	80-90	90-100
1	22.6	19.4	7.6	1.1	1.2	0.9	0.4	0.4	0.4	
2	10.6	8.6	4.2	2.4	1.2	0.4	0.4	_	_	_
3	0.5	0.4	0.9	5.8	3.7	2.3	2.0	0.8	0.7	0.5
4	1.5	1.5	1.4	3.4	4.4	5.0	3.3	1.8	1.6	1.7
5	2.7	2.1	2.1	2.6	2.5	2.7	1.4	1.3	1.5	-
6	5.8	4.8	4.8	4.7	5.6	5.2	4.0	3.5	3.7	_
7	5.2	5.7	5.2	4.4	2.8	2.6	3.9	3.9	4.4	_
8	4.9	5.2	5.5	5.8	8.7	-	9.6	3.0	0.6	_
9	4.8	4.4	3.8	4.6	4.7	4.7	4.0	4.4	3.7	_
10	5.4	4.5	3.5	4.0	5.2	7.0	4.3	3.2	3.5	-
11	3.6	3.7	3.7	4.2	4.0	4.2	3.9	4.0	4.1	_
12	13.3	13.5	14.4	13.6	11.8	13.7	18.7	15.0	10.3	8.7
13	5.5	5.2	5.3	5.0	5.1	5.2	4.7	3.7	2.4	-
14	5.6	3.9	2.7	1.3	0.8	0.7	0.7	_	_	_
15	12.2	13.0	20.6	19.6	7.4	_	_	_	-	-
16	12.1	12.3	18.0	25.1	20.4	17.1	14.5	_	-	
17	8.3	10.5	13.2	15.7	15.8	16.1	16.0	16.5	16.3	8.6
18	19.5	16.3	21.4	16.5	11.6	9.2	4.8	1.3	_	-

 TABLE 2

 Iodine content of successive 10 cm horizons at each site; mg/kg of oven-dry soil

particular, at site 3, a distinct iron pan of about 1 cm thickness, within the 30-40 cm layer, had the high iodine content of 37.6 mg/kg, together with 4.6 per cent oxalate-soluble Fe, but only 2.1 per cent organic C and 0.38 per cent oxalate-soluble Al. The pedologically distinct horizons were less well defined at site 4, but its Bh (33-63 cm) horizon had contents of iodine (4.3 mg/kg) and oxalate-soluble Fe (0.64 per cent) considerably greater than those of the horizons above and below. In both podsols, iodine content was extremely low in the upper horizons, the values of 1.5 mg/kg or less being lower than those recorded in any of 70 surface soils from agricultural areas of England, Wales and Scotland (Whitehead, 1975). Low values for iodine in podsolic soils have also been reported from USSR by Vinogradov (1950). Other soils in which iodine content was at a maximum at intermediate depth included two on Ordovician (15, 17), and one on igneous (16), rock material (Table 2).

At seven sites changes with depth were relatively small but, at each of these, the content of iodine in the surface 10 cm was low ($\leq 6 \text{ mg/kg}$). These soils comprised three derived from river, or river terrace, alluvium (5, 6, 7), three derived from low-lying inland clay (9, 10, 11) and one derived from sandstone (13). The low iodine contents in the alluvial soils are consistent with reports from USA (Ergle, 1940), and from USSR (Vinogradov, 1950). Low iodine contents in soils with sandstone as parent material have also been reported from USA (Mitchell, 1941). One soil (8) developed on river terrace alluvium had higher contents of iodine than the other alluvial soils at depths between 20 and 70 cm (Table 2): it also had a considerably greater depth (about 70 cm) of clay-loam material overlying sandy gravel. The soil from site 12, developed on a clay (to silty clay) loam drift of about 150 cm depth over limestone, also had rather high iodine contents with a maximum value at 60–70 cm.

The relatively high iodine content in the peat horizons of site 18 was consistent

D. C. WHITEHEAD

TABLE 3

Correlation coefficients between contents of iodine and of (a) oxalate-soluble Al, (b) oxalate-soluble Fe, (c) oxalate-soluble Al + oxalate-soluble Fe (calculated on a gram atom basis) and (d) organic C

Site no.	(a)	(b)	(c)	(d)
1	0.993***	0.975***	0.990***	0.988***
2	0.926**	0.904**	0.919**	0.868**
3	0.926***	0.984***	0.968***	0.549*
4	0.831**	0.849**	0.924***	-0.029 n.s.
5	-0.752 n.s.	-0.719 n.s.	-0.757 n.s.	0.502 n.s.
6	0.239 n.s.	-0.875 n.s.	-0.860 n.s.	0.625*
7	0.830**	0.540 n.s.	0.678*	0.790**
8	0.637*	0.463 п.s.	0.618 n.s.	0.017 n.s.
9	0.063 n.s.	-0.507 n.s.	-0.419 n.s.	0.393 n.s.
10	-0.144 n.s.	-0.227 n.s.	-0.224 n.s.	0.258 n.s.
11	0.635*	0.041 n.s.	0.107 n.s.	-0.765 n.s.
12	0.569*	-0.432 n.s.	0.039 n.s.	0.132 n.s.
13	0.693*	0.635*	0.699*	0.503 n.s.
14	0.707*	0.910**	0.901**	0.984***
15	0.875*	0.396 n.s.	0.614 n.s.	0.099 n.s.
16	0.974***	0.042 n.s.	0.887**	-0.647 n.s.
17	0.462 n.s.	0.582*	0.841**	-0.482 n.s.
18	0.634*	0.803**	0.923***	0.734*
All sites	0.834***	0.355***	0.673***	0.370***

Significant at: *P < 0.05; **P < 0.01; ***P < 0.001; n.s. - not significant

with other reports for peat soils (Shee, 1940; Vinogradov, 1950; Whitehead, 1973*a*). However, although there is an apparent association between iodine and organic matter in peats, the profile at site 18 also had high values for oxalate-soluble Al; and, since the ratios between total I and oxalate-soluble Al were greater than in the majority of the other profiles, the sesquioxides may have been largely responsible for iodine retention. Closer correlations were obtained with oxalate-soluble Fe and oxalate-soluble Al + Fe than with organic C (Table 3).

In the correlations involving all 154 samples from the eighteen sites, iodine was much more closely related to oxalate-soluble Al than to oxalate-soluble Fe, but in the five soil profiles with pH below 4.8 in all horizons (sites 3, 4, 14, 17, 18), iodine was more closely correlated with Fe than with Al (Table 3): this clearly suggests that Fe has a greater effect than Al on iodine retention under strongly acid soil conditions.

The correlations presented in Table 3 show that, in most of the soil profiles, the content of organic matter was not a dominant influence on iodine content. Also, in none of the five pairs of surface soils of contrasting organic matter content did the soil with the higher organic matter content have an appreciably higher iodine content. Values for the arable and grassland members of each pair were 6.1 and 6.4 mg/kg; 4.4 and 3.9; 15.6 and 15.8; 16.0 and 16.7 and 3.2 and 2.9 mg/kg respectively. This finding contrasts with the results obtained in the investigation of 23 surface soils (Whitehead, 1973a) and in studies of iodide sorption (Whitehead 1973b, 1974). However, in the present investigation, the differences in organic

matter content between members of the pairs had arisen during the last 50 years or less, as a result of the soils being either under grass or cultivated annually. This is a much shorter time than the period of about 650 years that would be required for a doubling of iodine content, to 15 cm depth in the soil, from 5 to 10 mg/kg, on the assumptions (a) that atmospheric iodine reaches the soil entirely through rainfall, (b) that the average annual rainfall is 730 mm, (c) that the average iodine content of rain is $2 \mu g$ I/l (Goldschmidt, 1958; Chamberlain and Chadwick, 1966) and (d) that all the iodine is retained in the soil. This time factor may have obscured some influence of organic matter on the capacity of soils to retain iodine. The lack of association between iodine and organic matter also contrasts with the situation in marine and lake sediments: several investigations with these materials (see Fuge, 1974) have shown marked correlations with organic carbon, though contents of sesquioxides appear not to have been examined.

The proportion of the total iodine soluble in 0.016 M KH₂PO₄ varied from 0.5 to 18.8 per cent. The proportions were less than 3.5 per cent in all the horizons of the peat soil (18) and less than 4.8 per cent in all horizons of the soil from site 6. In the other soil profiles examined (8, 10, 12, 13, 15, 16, 17) the proportions were generally within the range 5–10 per cent for the upper horizons and increased to 8–18 per cent in the lower horizons. There were no appreciable differences between the pairs of contrasting organic matter content. In contrast to the trends with KH₂PO₄, the proportions of total iodine soluble in hot water were generally greatest in the uppermost horizon and, in this horizon, ranged between 14.7 and 33.3 per cent. In the peat soil (18), solubility in hot water decreased to < 3.5 per cent in the horizons below 30 cm but, in the other soils, it exceeded 10 per cent in all horizons.

Acknowledgements

I thank Dr. L. H. P. Jones for his interest; E. R. Drzymalski and M. K. Goss for technical assistance; and staff of the Soil Survey of England and Wales for information on soil parent material and the soil series at some sites.

REFERENCES

- BRYANT, P. M. 1970. Derivation of working limits for continuous release rates of ¹²⁹I to atmosphere. Health Phys. 19, 611-6.
- CHAMBERLAIN, A. C., and CHADWICK, R. C. 1966. Transport of iodine from atmosphere to ground. Tellus 18, 226-37.
- CHILEAN IODINE EDUCATIONAL BUREAU 1956. Geochemistry of Iodine, London.
- ERGLE, D. R. 1940. Iodine content of some Texas soils. Soil Sci. 49, 361-7.
- FUGE, R. 1974. In Handbook of Geochemistry (ed. K. H. Wedepohl), Iodine. Vol. II/4, 53 B-M. Berlin: Springer-Verlag.
- GOLDSCHMIDT, V. M. 1958. Geochemistry, pp. 602-20. Oxford: Clarendon Press.
- KALEMBASA, S. J., and JENKINSON, D. J. 1973. A comparative study of titrimetric and gravimetric methods for the determination of organic carbon in soil, J. Sci. Fd Agric. 24, 1085-90.
- KRISHNA MURTI, G. S. R., VOLK, V. V. and JACKSON, M. L. 1966. Colorimetric determination of iron of mixed valency by orthophenanthroline. Proc. Soil Sci. Soc. Am. 30, 663-6.
- KUBOTA, J. and ALLAWAY, W. H. 1972. In *Micronutrients in Agriculture* (ed. J. J. Mortvedt et al.), Geographic distribution of trace element problems, pp. 525-54. Soil Sci. Soc. Am., Madison, U.S.A.
- MATUSZEK, J. M., DALY, J. C., GOODYEAR, S., PAPERIELLO, C. J. and GABAY, J. J. 1974. In *Environmental surveillance around nuclear installations*, Environmental levels of iodine-129. Vol. II. Vienna: IAEA.

D. C. WHITEHEAD

- MITCHELL, J. H. 1941. Sources and distribution of iodine in South Carolina with special reference to types of soil and rocks. Soil Sci. 52, 365-71.
- PRITCHARD, D. T. 1964. Spectrophotometric determination of aluminium in soil. Analyst, Lond. 92, 103-6.
- SCHWERTMANN, U. 1973. Use of oxalate for Fe extraction from soils. Can. J. Soil Sci. 53, 244-6.
- SHEE, J. C. 1940. Soil and fresh-water iodine content in Ireland in relation to endemic goitre incidence. Scient. Proc. R. Dubl. Soc. New Series, 22, 307-14.
- VINOGRADOV, A. P. 1950. The geochemistry of rare and dispersed chemical elements in soils. (English Translation published by Consultants Bureau, New York).
- WEBBER, M. D. et al. 1974. A comparison among nine Canadian laboratories of dithionite, oxalate, and pyrophosphate-extractable Fe and Al in soils. Can. J. Soil Sci. 54, 293-8.
- WHITEHEAD, D. C. 1973a. Studies on iodine in British soils. J. Soil Sci. 24, 260-70.
- ----- 1973b. The sorption of iodide by soils as influenced by equilibrium conditions and soil properties. J. Sci. Fd. Agric. 24, 547-56.
- ---- 1974a. The sorption of iodide by soil components. Ibid. 25, 73-9.
- ----- 1975. Form and availability of iodine in soils. Annual Rep. Grassl. Res. Inst. 1974, 17.
- WILSON, J. G. 1975. Hypothyroidism in ruminants with special reference to foetal goitre. Vet. Rec. 97, 161-4.

(Received 3 March 1977)