THE INFLUENCE OF ORGANIC MATTER, CHALK, AND SESQUIOXIDES ON THE SOLUBILITY OF IODIDE, ELEMENTAL IODINE, AND IODATE INCUBATED WITH SOIL

D. C. WHITEHEAD

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

Summary

Iodine in each of the forms iodide, elemental iodine, and iodate was added, at a rate of 5 mg/kg to a sandy loam and to mixtures of the soil with composted grass roots, chalk and sesquixoides, and its solubility determined after various periods of incubation.

With iodide, solubility in both o·oɪ M $CaCl_2$ and ɪ·o M NH_4 acetate (pH 4·8) declined rapidly over the period o to 3 days and subsequently reached approximate equilibrium levels of 2·8 per cent solubility in $CaCl_2$ and 7·8 per cent in NH_4 acetate, these values being the means of samples incubated for 48, 103, and 160 days. The partial (5 per cent) replacement of the soil by composted grass roots had no appreciable effect on the solubility of added iodine, while chalk, incorporated at a rate of 5 per cent, depressed the solubility of iodide in $CaCl_2$ to ɪ·8 per cent but caused a slight increase in solubility in NH_4 acetate. The incorporation of 2 per cent hydrated ferric oxide or of 2 per cent hydrated aluminium oxide reduced the solubility of iodide in $CaCl_2$ to o·ɪ and o·3 per cent, and in NH_4 acetate to 3·8 and 5·7 per cent respectively. Elemental iodine was similar to iodide in its solubility in the two extractants and in its response to the various soil treatments. Iodate, however, differed considerably from the other two forms of iodine. With soil alone, and with the soil/chalk mixture, its decline in solubility with increasing incubation time was relatively slow, although after 160 days its solubility was similar to that of iodide and elemental iodine. The incorporation of composted grass roots caused a rapid reduction in iodate solubility, suggesting that the organic matter accelerated the reduction of iodate to elemental iodine or iodide. With the treatments involving the incorporation of ferric and aluminium oxides, there appeared to be considerable sorption of iodate during the 16 h extraction period and the effects of these materials on iodate solubility during incubation were therefore difficult to assess.

Introduction

LITTLE is known of the factors which govern the content of iodine in soils and its availability for uptake by plants (Martin, 1966), although these factors are of importance in several contexts. Firstly, iodine is an essential nutrient element for animals that is deficient in many areas of the world (Underwood, 1966). Secondly, the herbicide ioxynil (3, 5-diiodo-4-hydroxybenzonitrile) decomposes in soil to release iodide (Zaki, *et al.*, 1967), and inorganic iodides also have been considered for use as herbicides (Mynett and Wain, 1971). Thirdly, a knowledge of the behaviour of iodine in soil/plant systems is important in understanding the fate of ^{131}I that may be released to the atmosphere as a result of accidents to nuclear reactors.

Under natural conditions, the atmosphere is an important source of the iodine in soils. Atmospheric iodine occurs partly in the forms of

iodide and elemental iodine (Goldschmidt, 1958), partly as methyl iodide which is relatively unstable (Lovelock *et al.*, 1973), partly as organic iodine compounds in dust arising from marine algae and plankton (Dean, 1963), and probably to a small extent as iodate since this form is dominant in at least some ocean waters (Liss *et al.*, 1973) and would therefore occur in sea spray. Inputs of both iodide and iodate can also arise from agricultural practices. Thus iodine, probably as iodide, is present in some phosphate fertilizers (Whitehead, 1973*a*). Iodide is also released by the decomposition of plant residues and animal excreta, while iodate occurs in Chilean nitrate fertilizer (Goldschmidt, 1958). Although the content of iodine in plants can be increased substantially by the application of iodine compounds to the soil (Chilean Iodine Educational Bureau, 1950; Calderbank, 1963) the percentage recovery of iodine is generally low. Thus calculations (using assumed average crop yields) from the data cited by the Chilean Iodine Educational Bureau for experiments in which iodate, contained in Chilean nitrate fertilizer, was applied to various crops indicate that the recovery of iodine was always less than 0·5 per cent. Low recoveries (0·05 and 0·19 per cent) were also obtained from iodide added, at a rate of 50 mg/kg to pots of two soils sown with perennial ryegrass (Whitehead, 1973*b*). These results suggest that iodine, added either as iodide or iodate, is to a large extent retained by soils, at least by surface soils of humid temperate regions, and this conclusion is supported, for iodide, by recent sorption studies (Whitehead, 1973*c*).

In the present investigation, assessments have been made of the solubility, in two extractants, of iodide, elemental iodine, and iodate added to a sandy loam soil and to mixtures of the soil with organic matter, chalk, ferric oxide, and aluminium oxide. These materials were chosen because organic matter and the sesquioxides have been shown to sorb iodide (Whitehead, 1974) and because calcium carbonate has been reported to depress the availability of iodine to plants (Chilean Iodine Educational Bureau, 1956). Each form of iodine was added at a rate of 5 mg/kg and the samples incubated for periods of time varying from nil to 160 days. The reagents selected for the assessment of solubility were 0·01 M $CaCl_2$ and 1·0 M NH_4 acetate adjusted to pH 4·8. Calcium chloride was chosen to extract the most soluble fraction of inorganic iodine, previous work having shown it to extract between 0·6 and 3·0 per cent of the total iodine of a range of soils (Whitehead, 1973*a*). It was preferred to water as it prevented deflocculation of soil clay material. Ammonium acetate was chosen as a second extractant because it has been used to assess 'available' iron (Cox and Kamprath, 1972), a soil constituent with which iodine may be associated (Whitehead, 1973*a*).

Materials and Methods

Soil

The soil was a sandy loam of the Sonning series from Reading University Farm, Sonning, Berkshire. The sample, obtained from a depth of 0–15 cm, was sieved through a 6 mm sieve and stored in a moist condition in a refrigerator. Its iodine content, determined as described

by Whitehead (1973*a*) was 2·2 mg/kg D.M. The results of determinations of organic matter (Clement and Williams, 1964), 'free' ferric oxide (Jackson, 1958) and 'free' aluminium oxide (Pritchard, 1964) are given in Table 1. The soil had a pH of 6·3 in 0·01 M $CaCl_2$.

TABLE 1

Experimental soil treatments with percentage contents of organic matter, chalk, 'free' ferric oxide, and 'free' aluminium oxide on a D.M. basis

Treatment	% O.M.*	% Chalk	% 'Free' Fe_2O_3	% 'Free' Al_2O_3
1. Soil alone	1·53	0·0	1·0	< 0·1
2. Soil with 5% D.M. replacement by composted roots	4·65	0·0	1·0	< 0·1
3. Soil with 5% D.M. replacement by chalk	1·45	5·0	1·0	< 0·1
4. Soil with 2% D.M. replacement by Fe_2O_3	1·50	0·0	3·0	< 0·1
5. Soil with 2% D.M. replacement by Al_2O_3	1·50	0·0	1·0	2·1

* % organic carbon × 1·72.

Materials representing soil components

The source of organic matter was a compost prepared from roots obtained from an area of permanent pasture. The roots were washed, so far as possible, free from soil, cut into approximately 2 cm lengths and allowed to decompose under moist but aerobic conditions for 24 weeks before being passed through a 2 mm sieve. The compost had a dry matter content of 27 per cent and, of this, 64 per cent was organic matter. Iodine content was 2·4 mg/kg D.M.

The chalk, crushed to pass a 4 mm sieve and used undried, had an iodine content of 0·5 mg/kg D.M.

The iron and aluminium oxides were precipitated by the addition of NH_4OH to solutions of $Fe(NO_3)_3$ and $AlCl_3$ as described by Jones (1957): they were then washed several times with deionized water, dialysed against deionized water until free of nitrate or chloride, filtered and partially dried to a crumbly moist condition in a forced draught oven at 21 °C.

Experimental treatments and methods

The five soil treatments are indicated in Table 1. The table also includes values for the contents of organic matter, chalk, 'free' ferric oxide and 'free' aluminium oxide in each treatment.

Samples of moist soil and component materials, calculated to amount to a total of 10 g dry matter, were weighed into 65 ml polystyrene capsules, and mixed. They were then treated with 2 ml of a solution containing 25 mg I/l in the form of potassium iodide, elemental iodine, or potassium iodate and incubated in the dark at laboratory temperature for periods of time ranging from 0 to 160 days. At approximately weekly intervals the capsules were opened and held briefly in a stream

of air. Duplicate samples were prepared for each treatment and incuba-
tion time, and control samples incubated with 2 ml water instead of
iodine solution were included in each batch. At the end of the incuba-
tion period the samples were treated with a volume of either 0·01 M
$CaCl_2$ or 1·0 M NH_4 acetate (pH 4·8) adjusted to give a total liquid
volume of 50 ml, After shaking for 16 h on an end-over-end shaker the
mixtures were centrifuged and filtered. The concentration of inorganic
iodine in the extracts was determined by an automated colorimetric
procedure based on that described by Riley and Gochman (1964) for
the estimation of iodine in blood. Since only inorganic iodine was to be
determined the digestor unit was excluded from the system and 6 N
H_2SO_4 was used in place of concentrated H_2SO_4 and the $HNO_3/HClO_4$
mixture. Reagent tube sizes were selected to give satisfactory readings
with a range of standard solutions. In calculating the percentage
solubility of the added iodine for each treatment and extractant,
allowance was made for the iodine extracted from the appropriate
control samples. In addition, a set of samples, which had been incubated
for 103 days, was extracted with boiling 2 N NaOH to determine total
iodine content and hence the recovery of added iodine.

Results and discussion

The results presented in Figs. 1 and 2 and Table 2 are expressed in
terms of the percentage solubility of added iodine. There appeared to
be no appreciable loss of gaseous iodine to the atmosphere, since the
determination of total iodine on the batch of samples of each treatment
incubated for 103 days indicated that the recovery of added iodine
consistently exceeded 90 per cent and was not influenced by the form
of iodine.

With all treatments, the percentage solubility of the added iodine in
both extractants had declined to less than 50 per cent within 7 days and
to less than 25 per cent within 48 days. The reduction in solubility was
particularly marked with iodide and elemental iodine which, within
3 days, showed less than 12 per cent solubility in $CaCl_2$ (Figs. 1a, 1b)
and less than 20 per cent in NH_4 acetate (Figs. 2a, 2b). Iodate on the
other hand was consistently more soluble after incubation with all
treatments except soil+composted roots, and showed a less rapid
decline in solubility than iodide and elemental iodine (Figs. 1c, 2c).

In general, the solubility of all three forms of iodine was, as expected,
greater in NH_4 acetate than in $CaCl_2$. However, with the samples
extracted immediately after the addition of the iodine solution, solubility
was greater in $CaCl_2$ than NH_4 acetate in all instances except iodate in
treatments 4 and 5. With the samples extracted without incubation, the
solubility values were governed by the extent of sorption during the
16 h extraction period; and the sorption of iodide from solution, by soil,
compost, ferric oxide and aluminium oxide has been shown to be
greater at a pH of about 4·8, as given by NH_4 acetate, than at approxi-
mately 6·3, as given by $CaCl_2$ (Whitehead, 1973c, 1974). Percentage
solubility for other incubation times could also have been influenced
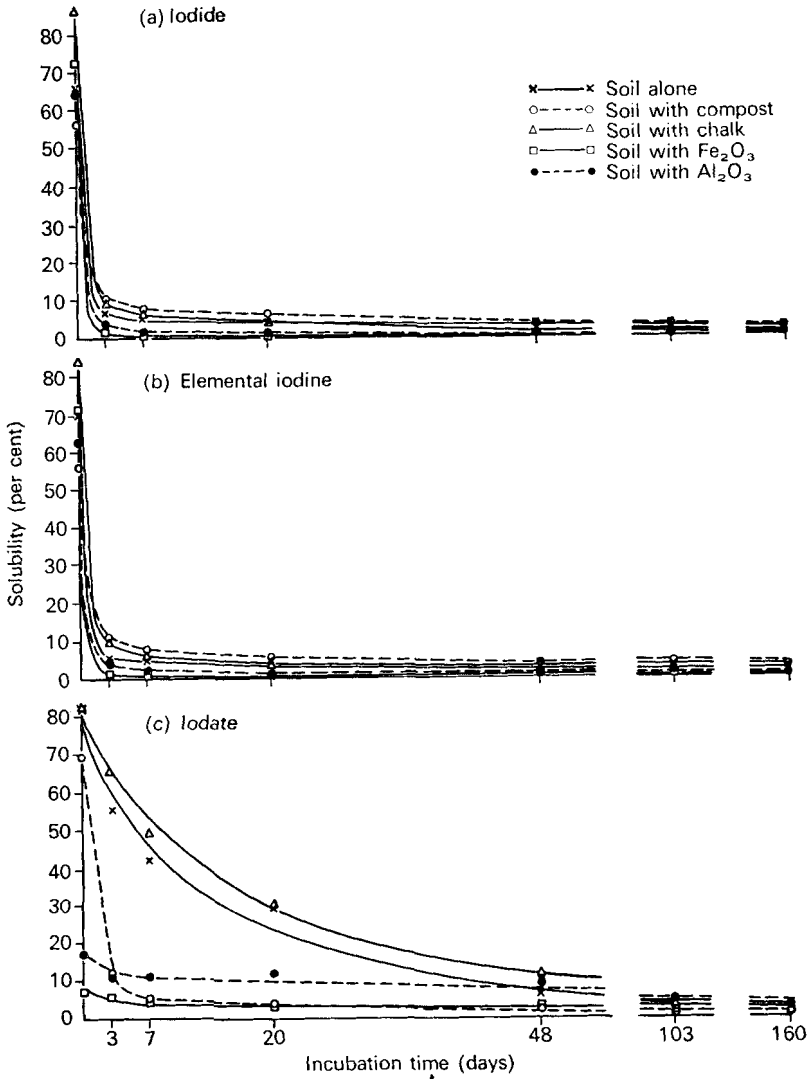by sorption during the extraction period, but since most treatments

FIG. 1. Percentage solubility in 0·01 M CaCl₂ of (a) iodide, (b) elemental iodine, and (c) iodate, added at a rate of 5 mg/kg to a sandy loam soil and to mixtures of the soil with composted grass roots, chalk, hydrated ferric oxide, and hydrated aluminium oxide. (Each point represents mean of duplicate values.)

showed a large decrease in solubility during the first 3 days of incubation, this effect is likely to have been relatively small.

After the first 20 days of incubation, the solubility of iodide and elemental iodine changed only slightly, though the solubility of iodate continued to decline in some treatments (Figs. 1 and 2). Since the solubility values in CaCl₂ at 48, 103, and 160 days were close to zero,
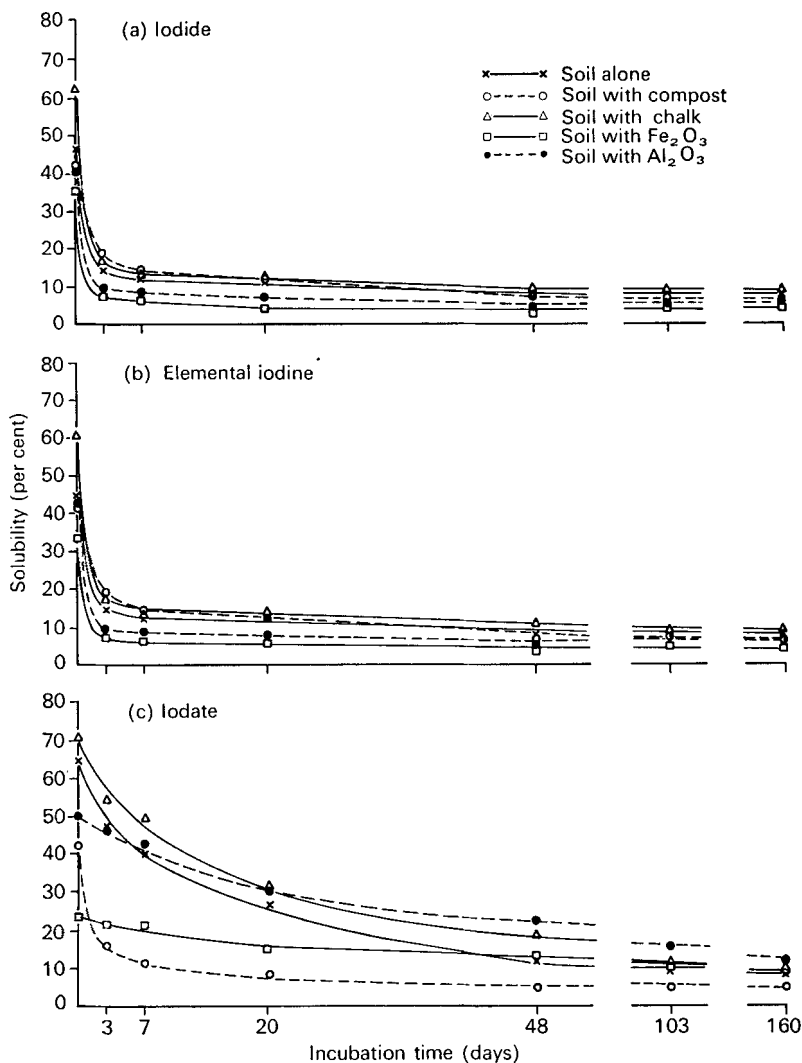
FIG. 2. Percentage solubility in 1·0 M NH$_4$ acetate (pH 4·8) of (a) iodide, (b) elemental iodine, and (c) iodate, added at a rate of 5 mg/kg to a sandy loam soil and to mixtures of the soil with composted grass roots, chalk, hydrated ferric oxide, and hydrated aluminium oxide. (Each point represents mean of duplicate values.)

they are not easily distinguished in Fig. 1 and are therefore presented in Table 2.

The lowest solubilities of both iodide and iodine, for incubation times of 48, 103, and 160 days, were given by treatment 4 (ferric oxide), the differences from treatment 5 (aluminium oxide) being significant (P < 0·05) in NH$_4$ acetate though not in CaCl$_2$. The solubility values for treatment 3 (chalk) were significantly higher (P < 0·5) than those

for treatments 4 and 5 in both extractants. In $CaCl_2$, treatments 1 and 2 gave values that were similar but were significantly greater than those for treatment 3 (Table 2), while in NH_4 acetate, solubilities in treatments 1, 2, and 3 were generally not significantly different, though the highest values were produced by treatment 3 (Fig. 2a, b). The close similarity between iodide and elemental iodine in their solubility in the various treatments, suggests that the two forms were retained in the same manner, one form possibly being converted to the other before being rendered insoluble.

TABLE 2

Percentage solubility in $CaCl_2$ of added iodine after incubation for 48, 103, and 160 days

		Soil treatment					
Form of iodine	Incubation time (days)	*1* Soil alone	*2* Soil with compost	*3* Soil with chalk	*4* Soil with Fe_2O_3	*5* Soil with Al_2O_3	Mean S.E.
Iodide	48	3·05a*	3·15a	2·50b	0·10d	0·50c	
	103	2·63a	2·85a	1·75b	0·20c	0·20c	0·081
	160	2·60a	2·15b	1·10c	0·05d	0·20d	(15 d.f.)
Elemental iodine	48	3·30a	3·45a	2·60b	0·30c	0·50c	
	103	3·15a	3·05a	2·00b	0·15c	0·15c	0·124
	160	2·80a	2·45a	1·20b	0·15c	0·25c	(15 d.f.)
Iodate	48	6·50c	2·35a	11·90e	3·80b	9·55d	
	103	4·10cd	2·05a	3·40bc	2·65ab	4·55d	0·296
	160	2·95ab	1·80a	1·90a	2·20ab	3·15b	(13 d.f.)

* Values not followed by identical letters are significantly different (P < 0·05) in horizontal comparisons between soil treatments.

With iodate, the effects of the treatments were different from those with iodide and elemental iodine and, in some treatments, including soil alone, iodate took longer than the other forms to reach an apparent equilibrium level of solubility. Treatment 2 (compost) produced solubility values at 48–160 days that were significantly lower than all other treatments in NH_4 acetate, and were generally lowest in $CaCl_2$ (see Table 2). The values were, surprisingly, slightly lower than the corresponding values for iodide and elemental iodine. In treatment 2, but not in the other treatments, the changes in iodate solubility with increasing incubation time were similar to the changes shown by iodide and elemental iodine. In soil alone, the solubility of iodate in both reagents declined less rapidly than iodide and elemental iodine, and a similar pattern of decline was shown by treatment 3 (chalk). In treatments 4 and 5 (ferric and aluminium oxides) the solubility of iodate in $CaCl_2$ was particularly low at the first extraction and showed only a slight decrease after 3 days' incubation (Fig. 1c), a result indicating that substantial sorption occurred during the 16 h extraction period. This was confirmed by the observations that ferric oxide (0·2 g D.M.), shaken alone for 16 h with each of the three forms of iodine in $CaCl_2$, sorbed more than 95 per cent of the

iodate but less than 10 per cent of the iodide and elemental iodine, and that, under the same conditions, aluminium oxide sorbed approximately 50 per cent of the iodate and less than 15 per cent of the iodide and elemental iodine.

In interpreting the effects produced by the various treatments during incubation, account must be taken both of direct retention by the materials added and of their possible modification of soil properties such as pH and redox potential. The generally low values for solubility obtained with both extractants suggest that chemical reactions were involved, since iodine retained only by physical adsorption is likely to have been displaced, particularly by the 1·0 M NH_4 acetate. Chemical reactions are possible with both organic components and sesquioxides in the soil. Thus elemental iodine will react readily with tyrosine (Roche and Michel, 1951), with thiol groups (Jirousek and Pritchard, 1971) and with polyphenols (Fawcett and Kirkwood, 1953). With ferric oxide, the substitution of hydroxyl groups by iodide is possible (Goldschmidt, 1958).

When the soil was partially replaced by composted roots (treatment 2) there was very little effect on the solubility of iodide and elemental iodine in comparison with soil alone, and also very little effect on pH in either extractant. However, this result does not exclude the possibility that organic matter is important in the retention of iodide by soils, since its sorption capacity appears to increase as its degree of decomposition increases (Whitehead, 1974). With iodate, the marked reduction in solubility in both extractants induced by the compost treatment was probably due largely to a change in redox potential. The likelihood of such an effect is indicated by the results obtained by Jeffery (1960) who reported that, when dried and ground grass roots were added to a silty clay loam soil at a rate of 16·5 per cent and incubated under waterlogged conditions in the absence of air, intensely reducing conditions developed for about 3 days before changing back to a condition of positive oxidation. A similar effect may well have occurred in this investigation, since, although air was not excluded from the samples, their water content was about 35 per cent. If, as a consequence, iodate underwent rapid reduction, this would explain why in treatment 2, but not in the other treatments, iodate was similar in solubility to iodide and elemental iodine.

The effects of the chalk treatment are likely to have been due mainly to its raising the pH of the incubated samples to 7·7 when measured in $CaCl_2$. No sorption of any of the three forms of iodine was detected when they were shaken with chalk alone for 16 h in 0·01 M $CaCl_2$, while, in earlier work, the sorption of iodide from solution by soil and soil components was found to be greatly influenced by pH (Whitehead, 1973c, 1974). Compared with soil alone, the effects of the chalk treatment on the solubility of each form of iodine in $CaCl_2$ changed with time, from increased solubility at the first 3–5 sampling dates to reduced solubility on more prolonged incubation.

The effect of ferric oxide (treatment 4) in reducing the solubility of iodide and elemental iodine in both extractants was apparently not due to pH since no change was induced by this treatment. The values of

> 90 per cent solubility which were obtained when ferric oxide alone was shaken with iodide and elemental iodine in 0·01 M $CaCl_2$ also suggest that direct sorption would not account for the reduction in solubility in treatment 4 compared with unamended soil. However, Jenne (1968) has pointed out that, in soils, ferric oxide may undergo reduction/oxidation reactions with organic matter which result in the ferric oxide being continually reprecipitated and consequently maintaining a high surface area. Such reactions could result in an increased sorption capacity of the ferric oxide, Sugawara et al. (1958) having demonstrated that iodide is retained when hydrated ferric oxide is precipitated from solution. If this interpretation that ferric oxide has a greater capacity for sorption when in the presence of moist soil is correct, and if the effect is appreciable at pH 6–7, it could explain the correlation, obtained in earlier work with a range of soils, between contents of total iodine and 'free' ferric oxide (Whitehead, 1973a). With iodate there appeared to be substantial direct sorption by ferric oxide during the extraction period and, as indicated above, this makes it difficult to assess the extent of retention during incubation.

Treatment 5 (aluminium oxide) produced a reduction in solubility similar to, although slightly less than, that produced by ferric oxide. With this treatment, the pH assessed in $CaCl_2$ was only 5·7 and this change, compared with soil alone (pH 6·5), may have augmented the effect on solubility. However, although aluminium oxide seems less likely than ferric oxide to undergo continual reprecipitation, this process could occur under conditions of fluctuating pH, with the removal of iodide from solution during precipitation (Sugawara et al., 1958).

Conclusions

The rapid decline in the solubility of iodide and elemental iodine when incubated with a sandy loam soil, and the acceleration of this process by sesquioxides, suggest that, for the majority of British soils, accessions of iodine from the atmosphere, and from the decomposition of organic materials, will be retained rather than leached. The results also suggest that the availability to plants, of iodine added as iodide or elemental iodine, would normally be low. The greater solubility of iodate indicates that this would generally be a more effective source of iodine for plants growing in soil, although the results obtained when the soil was treated with composted grass roots suggest that, in the presence of readily decomposable organic matter, iodate may be quickly reduced to elemental iodine or iodide.

Acknowledgements

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