Hassan Shetaya, Waleed Hares Abdou (2011) Iodine dynamics in soil. PhD thesis, University of Nottingham.

IODINE DYNAMICS IN SOIL

By

Waleed Hares Abdou Hassan Shetaya

(BSc Chemistry, 1998; MSc Chemistry 2007)

Thesis submitted to the University of Nottingham
for the degree of Doctor of Philosophy

2011

ABSTRACT

The principal aim of this investigation was to understand the transformation and reaction kinetics of iodide and iodate added to soil in relation to soil properties. In addition, to integrate the data into a predictive model of iodide and iodate sorption kinetics parameterised by soil properties. Solid phase fractionation coupled with solution phase speciation (HPLC-ICPMS) was used to follow the assimilation of $^{129}I^-$ and $^{129}IO_3^-$ spikes into 'steady state' soil microcosms.

The extraction efficiency of tetra-methyl ammonium hydroxide (TMAH) for soil iodine, and the effects of experimental procedures and conditions on the speciation of extracted iodine were tested. Moreover, the possibility of extracting 'reactive' inorganic iodine forms sorbed on soil metal oxides by competition with PO_4^{3-} ions was investigated. Results showed that changing TMAH concentration, extraction time, extraction temperature or soil particle size did not generally affect the concentrations of total iodine extracted. The ratio of iodide to total iodine in the TMAH extracts varied with the extraction conditions which led to the conclusion that part, or all, of the measured iodide is possibly produced by hydrolysis of organic iodine forms. This conclusion was also confirmed by the detection of high concentrations of iodide in TMAH extracts of a humic acid. Only iodide was measured in the phosphate extracts of soil and it constituted up to 33% of the total iodine in the KH_2PO_4 extracts which indicates that most of the iodine mobilised by KH_2PO_4 is organically bound. When soil / KH_2PO_4 suspensions were spiked with $^{129}I^-$ and $^{129}IO_3^-$, at least 50% of $^{129}I^-$ and 15% of $^{129}IO_3^-$ were recoverable after 72 hours of reaction. The lowest recoveries were observed with the highest concentration of KH_2PO_4, which also mobilised the greatest concentrations of DOC, indicating that although KH_2PO_4 is capable of releasing sorbed iodide and iodate in soil, it may also promote iodide and iodate reaction with soil organic matter. Iodine content of soil biomass was determined following chloroform fumigation of soil. The concentrations of total iodine in fumigated soil samples were only marginally higher than iodine concentration in the control samples indicating that microbial biomass iodine constitutes only a small fraction of total soil iodine (0.01 – 0.25 %).

The change in iodine (^{129}I) solubility and speciation in nine soils with contrasting properties (pH, Fe/Mn oxides, organic carbon and iodine contents), incubated for nine months at 10^oC and 20^oC, was also investigated. The rate of ^{129}I sorption was greater in soils with large organic carbon contents, low pH and at higher temperatures. Loss of iodide ($^{129}I^-$) from solution was extremely rapid, apparently reaching completion over minutes-hours; iodate (IO_3^-) loss from solution was slower, typically occurring over hours-days. In all soils an apparently instantaneous sorption reaction was followed by a slower sorption process for IO_3^-. For iodide a faster overall reaction meant that discrimination between the two processes was less clear. Instantaneous sorption of IO_3^- was greater in soils with high Fe/Mn oxide content, low pH and low organic content, whereas the rate of time dependent sorption was greatest in soils with higher organic contents. Phosphate extraction (0.15 M KH_2PO_4) of soils, ~100 h after ^{129}I spike addition, indicated that concentrations of sorbed inorganic iodine (^{129}I) were very low in all soils suggesting that inorganic iodine adsorption onto oxide phases has little impact on the rate of iodine assimilation into humus. Transformation kinetics of dissolved inorganic $^{129}IO_3^-$ and $^{129}I^-$ to sorbed organic forms was modelled using a range of reaction and diffusion based approaches. Irreversible and reversible first order kinetic models, and a spherical diffusion model, adequately described the kinetics of both IO_3^- and I^- loss from the soil solution but required inclusion of a distribution coefficient (K_d) to allow for instantaneous adsorption. A spherical diffusion model was also collectively parameterised for all the soils studied by using pH, soil organic carbon concentration and combined Fe + Mn oxide content as determinants of the model parameters (K_d and D/r^2). From the temperature-dependence of the sorption data the activation energy (Ea) for $^{129}IO_3^-$ transformation to organic forms was estimated to be ~43 kJ mol^{-1} suggesting a reaction mechanism slower than pore diffusion or physical adsorption, but faster than most surface reactions.

DEDICATION

I Dedicate This to My Parents

ACKNOWLEDGMENTS

I would like to gratefully acknowledge the sincere help, support and guidance I have received over the course of my PhD from my supervisors: Dr Scott Young and Dr Liz Bailey.

PhD scholarship and financial support from the Egyptian Government is gratefully acknowledged, as well as the administrative support from the Egyptian Cultural Centre and Educational Bureau staff.

Research grant from the Natural and Environmental Research Council (NERC) is also acknowledged.

I am also thankful for the technical and administrative help I have received from Mr Darren Hepworth, Mr John Corrie, Dr Sue Grainger and Mrs Emma Hooley.

I would like to thank all my colleagues in the Environmental Sciences Department for moral support over the last four years.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

1.1 BACKGROUND

Iodine is an important nutrient for humans and animals; it is used by the thyroid gland to form thyroid hormones that control various physiological processes. Thus, iodine deficiency may lead to a range of clinical abnormalities including mental retardation, deafness, stunted growth, neurological problems and goiter. These health issues are known collectively as iodine deficiency disorders (IDD) (Trotter, 1960; Underwood, 1977; Hetzel, 1986; Fuge, 2007). IDD are reported by the World Health Organization to affect around 35% of the world's population (WHO, 2004). To avoid iodine deficiency and associated disorders, a daily intake of 150-250 μg I is recommended (WHO et al., 2007).

As iodine supplied to humans and animals through diet is typically less than optimum, a range of approaches have been proposed to control endemic goiter and IDD in general. These include encouraging the consumption of iodised salt, iodised oil, dairy products and food of marine-origin which has higher iodine content than any other class of food (Underwood, 1977; Fuge, 2007). Other proposed measures include the use of iodine rich fertilizers in agriculture and adding iodine to water supplies (Coble et al., 1968; Ren et al., 2008). Nevertheless, in many areas around the world, iodine supply remains insufficient. Iodine availability in the absence of dietary seafood sources depends largely on its transfer from soil to food and fodder crops (Underwood, 1977; Johnson et al., 2002). Transfer of iodine from soil to plants is generally low and locally grown plants often cannot supply a population with the recommended daily intake of iodine (Johnson, 2003). There is therefore a need to increase understanding of iodine behaviour in soils if the resulting implications for transfer to crops and livestock are to be understood. In particular, there is a need to resolve (i) how iodine added to soil, via (e.g). rainfall or iodine-rich fertilizers, reacts with the soil and (ii) the mechanisms by which it is made available to plants.

Understanding the environmental behaviour of iodine, particularly the long lived iodine isotope ^{129}I ($t^{½}$ = 1.6 x 10^7 y) is also essential to the safety case for underground nuclear waste disposal. ^{129}I has been shown to be one of the more mobile radionuclides in soils, readily migrating into ground water (USDOE, 2005). Ingestion of radioiodine released from weapons testing, nuclear power stations and medical or research facilities may induce development of thyroid tumours or suppress thyroid function (Kazakov et al., 1992; Likhtarev et al., 1995; Zablotska et al., 2011).

1.2 IODINE IN THE ENVIRONMENT

1.2.1 Iodine Isotopes

Iodine has many isotopes; the half lives of most are only a few seconds. ^{131}I is produced during fission of ^{235}U which typically yields one ^{129}I atom and three ^{131}I atoms (USDOE, 2005). Nevertheless, because of its short half-life (8 days), ^{131}I is not generally an isotope of long-term environmental concern.

^{129}I is the only long-lived naturally occurring iodine isotope. It is naturally produced in small amounts by fission of Xe induced by cosmic rays in the atmosphere and by spontaneous fission of ^{235}U in the earth's crust (Yiou et al., 1994). In the pre-nuclear era the ^{129}I/^{127}I ratio has been estimated as 10^{-15}-10^{-12} (Szidat et al., 2000). The $^{129}I/^{127}I$ ratio has increased over recent decades due to human activities and the present amount of ^{129}I in the biosphere is dominated by anthropogenic ^{129}I (Frechou and Calmet, 2003; Aldahan et al., 2007; Atarashi-Andoh et al., 2007; Schnabel et al., 2007; Endo et al., 2008).

1.2.2 Iodine Species

Iodine has several valence states and exists naturally in inorganic and organic forms including iodide (I^-), iodate (IO_3^-), elemental iodine (I_2), methylated forms and iodine-substituted humic substances (Smith and Butler, 1979; Radlinger and Heumann, 1997; Abdel-Moati, 1999; Schwehr and Santschi, 2003; Muramatsu et al., 2004; Gilfedder et al., 2007 b,c; Liu et al., 2007; Yang et al., 2007; Yoshida et al., 2007). The chemical form of iodine depends on pH and the redox status of the surrounding environment. Iodide and organic iodine forms were reported as the most prevalent species of iodine in river water while iodate is believed to be the most common iodine form in oceans possibly produced by the relatively slow enzymatic or photo-oxidation of iodide (Smith and Butler, 1979; Abdel-Moati, 1999). In soil, iodide was reported to be the dominant inorganic iodine species in humid acidic soils whereas iodate prevails in the arid oxidising conditions (Fuge, 2005).

1.2.3 Iodine in Soil

The average iodine concentration in the earth's crust is approximately 0.25 mg kg^{-1} while higher (Fuge et al., 1978; Fuge and Johnson, 1986). Higher mean value of iodine concentrations in sedimentary rocks was reported (Fuge, 1996). The main iodine reservoir is the oceans. Iodine may transfer from seawater to the atmosphere via volatilisation of molecular iodine (I_2) or organic iodine forms such as CH_3I, CH_2I_2, or C_2H_5I which are produced by marine organisms (Amachi et al., 2005). Iodide and iodate possibly enter the atmosphere within marine aerosols. However, because the ratio of iodine to chlorine in the atmosphere is substantially greater than the ratio in seawater, it has been concluded that sea spray is not an important source of atmospheric iodine (Whitehead, 1984; Fuge, 2005). Moreover, Hou et al. (2009a) reported that atmospheric iodine is mostly gaseous (I_2, HI, HIO, CH_3I, CH_2I_2 and $CH_3CH_2CH_2I$).

From the atmosphere iodine is transferred to soils by both wet and dry deposition. However, the amount reaching soils through dry deposition is negligible compared to the amount washed out of the atmosphere by rain (Truesdale and Jones, 1996). Concentrations in rainfall are reported by several studies to be in the range of 0.5-5 $\mu g\ I\ L^{-1}$ (Truesdale and Jones, 1996; Neal et al., 2007; Hou et al., 2009b). A mixture of species including iodate, iodide and organic iodine species have all been reported; the proportion of each species depends on sampling location (Gilfedder et al., 2007c; Yoshida et al., 2007). Iodine concentrations in soils are generally greater than its concentrations in the bedrock. Average iodine concentration in surface soils is reported to be 5 mg kg^{-1} (Fleming, 1980). In UK soils concentrations range from 0.5 to 98.2 mg kg^{-1} (Whitehead, 1979). Iodine concentrations are usually greater in coastal soils in comparison to inland soils (Fuge, 2007). However, Iodine enrichment in the coastal areas is only limited to the soils in the immediate vicinity of the coastline and no clear correlation was found between iodine concentrations in a soil and its distance from the sea (Whitehead, 1984; Fuge, 1996).

Iodine sorption on soil metal oxides

In soil, inorganic iodine may be retained below pH 6 on positively charged hydrous iron and aluminium oxides and clay mineral edges (Whitehead, 1973a, 1974b, 1978; Ullman and Aller, 1985; Fukui et al., 1996; Dai et al., 2004; Um et al., 2004). The decrease in sorption of inorganic iodine as soil pH increases is similar to the behavior of non-specifically sorbed anions such as Cl^-, NO_3^-, and SO_4^{2-}. Iodide (pKa = -10) and iodate (pKa = 0.75) are both fully dissociated within the normal soil pH range and expected to be electrostatically attracted to variable charge Fe oxide surfaces. Therefore, sorption would normally be stronger under acidic conditions. However, other workers have observed inorganic iodine sorption up to pH 8 (Yoshida et al., 1992). Kaplan et al. (2000) also described significant iodide adsorption on illite (K_d = 22 L kg $^{-1}$) at pH values as high as 9.4. It was also reported that iodate is adsorbed more strongly than iodide, especially in acidic soils with low organic matter contents (Fukui et al., 1996; Yoshida et al., 1992; Shimamoto et al., 2010). This was attributed to the ability of iodate to bond chemically to Fe oxide surfaces through replacement of hydroxyl groups (Whitehead, 1973a, 1974b, 1978; Ullman and Aller, 1985; Fukui et al., 1996; Um et al., 2004)

Iodine in soil organic matter

Accumulation of iodine in soil organic matter has been widely reported and humus may constitute the primary reservoir of iodine in most soils

(Whitehead, 1973a; Francois, 1987 a,b; Fukui et al., 1996; Sheppard et al., 1996; Yu et al., 1996; Steinberg et al., 2008 a,c; Dai et al., 2009; Schwehr et al., 2009; Englund et al., 2010; Shimamoto et al., 2011; Smyth and Johnson, 2011). The fate of inorganic iodine and the mechanisms governing its incorporation into organic matter have been the focus of several investigations. Time-dependent iodide sorption in organic soils was explained by Sheppard and Thibault (1992) in terms of iodide diffusion into micropores and cavities in the fabric of soil organic matter. Francois (1987a) observed that the iodine content of humic substances increased following incubation with iodate for 5 days. The reduction of iodate, by humus, to I_2 and/or HOI and subsequent sorption by organic matter was suggested as a possible mechanism. This assumption was supported by the addition of resorcinol to the reaction medium; iodinated resorcinol compounds detected after incubation confirmed the formation of electrophilic iodine species such as HOI or polarised I_2. The same electrophilic substitution mechanism was suggested by Reiller et al. (2006) in their study of iodination of humic acids. Reduction of iodate by soil organic matter prior to conversion to organic forms was also reported by Whitehead (1974a) and Fukui et al. (1996). Steinberg et al. (2008b) confirmed that iodate heated with peat and lignin over a pH range of 3.5 - 9 was converted to organic forms and iodide. They also assumed that iodate was first reduced to a more reactive intermediate, I_2 or HOI, which then rapidly reacted with organic matter. The formation of HOI and I_2 was suggested following observation of the oxidation of leucocrystal violet (LCV) (added to the reaction medium) to crystal violet (CV). Bichsel and von Gunten (1999,

2000) also demonstrated that iodide can be oxidised to HOI and thereby react with organic compounds (e.g. substituted phenol and methyl carbonyl compounds) similar to those present in natural humic matter. Warner et al. (2000) found that iodination of soil organic matter followed the same mechanism as iodination of phenols, through reaction with molecular iodine, I_2. A comparison of iodine L_{III}-Edge XANES and EXAFS spectra of iodinated organic compounds with naturally iodated humic substances extracted from a range of soil types, indicated that organic iodine was primarily bonded to aromatic rings (Schlegel et al., 2006) indicating incorporation of iodine into soil organic matter via electrophilic substitution. Yamaguchi et al. (2010) observed that iodine K-edge XANES spectra of soils spiked with iodide and iodate and incubated for 60 days were similar to organic iodine standard spectra. Organic iodine standards were prepared by mixing iodide or iodate, for 60 days, with humic acids extracted from organic-rich soils. Iodide was fully transformed into organic forms after 1 day of incubation in highly organic soils, and was fully transformed in all soils after 60 days. By contrast, no measureable iodate transformation was observed after 1 day of incubation and up to 50% of the added iodate remained in the soils with relatively low organic matter contents at 60 days. They suggested that humic substances, which can act as electron donors and acceptors (Alberts et al., 1974; Wilson and Weber, 1979; Miles and Brezonik, 1981; Chen et al., 2003; Blodau et al., 2009; Keller et al., 2009), oxidised iodide and reduced iodate to I_2 or HOI which subsequently reacted with organic matter.

Oxidation of I^- to I_2 and then to IO_3^- may also be catalysed by δ-MnO_2 with subsequent IO_3^- adsorption on the δ-MnO_2 surface (Gallard et al., 2009). In the presence of humic substances oxidation to IO_3^- is limited as the I_2 formed can react to form organic iodine species, especially at lower pH (Gallard et al., 2009). Allard et al. (2009) and Fox et al. (2009) observed that oxidation of iodide to iodate on birnessite (δ-MnO_2) surface is thermodynamically possible up to pH 7.5. They also reported that the oxidation rate was directly proportional to the concentration of birnessite and inversely proportional to pH. Molecular iodine (I_2) was detected (spectrophotometrically) as an intermediate in the reaction.

Iodine retention in soil under reducing and oxidising conditions

Soil redox status is an important factor in iodine retention. Yuita and Kihou (2005) studied the distribution of iodine in three Japanese soil profiles. They observed that the iodine concentration decreased with increasing depth where surface layers were at a higher redox potential. By comparison, in paddy field soils the iodine content was low in the surface layer, where conditions were strongly reducing, but increased in the more oxidising conditions below the flooded topsoil. Reductive release of iodine from soil to soil solution under anoxic conditions has been repeatedly reported (Ullman and Aller, 1985; Yuita et al., 1991; Yuita, 1992; Muramatsu et al., 1996; Bird and Schwartz, 1997; Ashworth et al., 2003; Ashworth and Shaw, 2006; Yamaguchi et al., 2006; Shimamoto et al., 2011). Strong correlation between soil iodine concentration and soil sesquioxide content has been mainly attributed to the scavenging of inorganic iodine by soil metal oxyhydroxides. Such sorption is more favourable under oxidising conditions. Under reducing conditions, dissolution of metal oxides releases sorbed iodide and iodate into soil solution. Organic-I enrichment in aerobic surface soil horizons and the decrease in concentration with depth has been attributed to reduction of weakly-bound organic iodine to iodide at low redox potentials and the subsequent release of iodide into the soil solution (Francois, 1987a).

Soil microorganisms and iodine retention

Few studies have investigated the role of soil microorganisms in iodine transformations and retention. Koch et al. (1989) studied the effects of glucose, thymol and gamma-radiation on iodide removal from soil solution in twelve organic soils. Glucose generally increased iodide removal from soil solutions while addition of thymol or irradiation of soils resulted in lower rates of sorption which may suggest that soil microbes are in part responsible for iodine retention. Bors and Martens (1992) also found that the distribution coefficient (K_d) of $^{125}I^-$ on two different arable soils was reduced by 55–89% when soils were fumigated, killing ~90% of soil microorganisms. Increasing soil biomass, by addition of different concentrations of C, N and P (as glucose, KNO_3, and KH_2PO_4), the K_d of $^{125}I^-$ was increased up to 45% compared to its value in the untreated (control) soils. Similar results and conclusions were reported by Assemi and Erten (1994), Bird and Schwartz (1997), Yoshida et al. (1998), Muramatsu et al. (2004) and Ishikawa et al. (2011). By contrast, Sheppard and Hawkins (1995) and Yamaguchi et al. (2010) concluded that microorganisms do not have any central role or direct effect on iodine retention in soil. However, some of the above studies have only focused on measuring the effect of suppressing or stimulating microbial activities in relatively short term iodine sorption experiments which may fail to show the longer term microbial influence on the retention of iodine in soil. Moreover, stimulating or suppressing soil microbial activity by addition of chemical substrates, irradiating or heating soil may compromise conclusions on the relative importance of microbial retention of iodine by enhancing or hindering abiotic sorption/desorption processes.

1.2.4 Iodine in Plants

Iodine is not an essential nutrient for plants and can be toxic if supplied in high concentrations (c. 10 ppm) (Umaly and Poel, 1970) although it has also been reported that low quantities of iodine (c. 0.5 - 1 ppm) can stimulate growth of some plants (Weng et al., 2008; Landini et al., 2011). Iodine enters a plant either by root uptake from soil solution or through leaves from rain drops, atmospheric particulates and gaseous forms of iodine (Whitehead, 1984; Fuge, 2005). Studies of root uptake have suggested that most of the iodine remains in the roots and is not translocated to the rest of the plant (Whitehead, 1973c; Tsukada et al., 2008; Voogt et al., 2010). This would imply that atmospheric iodine may be the most important source of the total iodine inventory in the aerial parts of plants. In a recent study, however, Landini et al. (2011) found that $^{125}I^-$ supplied to tomatoes grown in a hydroponic system was widely distributed throughout the whole plant. Moreover, direct treatment of leaves with $^{125}I^-$ had little effect on the total $^{125}I^-$ accumulated by the plant. Re-distribution of iodide or iodate from nutrient or soil solutions via plants root to the edible parts of the plant has also been reported by Muramatsu et al. (1993), Zhu et al. (2004) and Weng et al. (2008).

The relative importance of iodide and iodate for plant uptake has also been investigated. Whitehead (1973c), Zhu et al. (2003) and Voogt et al. (2010) found that ryegrass, rice and lettuce, grown in hydroponic systems absorbed up to 20 times more iodide than iodate. When ryegrass was grown in soil, greater uptake of iodate than iodide was observed which was attributed to the longer residence time of iodate in soils compared to iodide which can be readily fixed into humus and rendered unavailable (Whitehead, 1975). In the same study, addition of organic matter (decomposed farmyard manure) to the soil decreased uptake of both iodide and iodate, whilst liming by addition of chalk enhanced iodate uptake. The addition of actively decomposing organic matter may have increased the rate of iodide and iodate incorporation in organic matter and substantially decreased the available (soluble) iodide and iodate pool. On the other hand, the alkaline conditions resulting from the addition of chalk may have hindered iodate fixation and enhanced its solubility. Iodate sorption on soil metal oxides and incorporation into soil organic matter (via reduction to I_2 or HOI) both happen to a greater extent under acidic conditions (Orlemann and Kolthoff, 1942; Whitehead, 1973a, 1974b, 1978; Brummer and Field, 1979; Ullman and Aller, 1985; Wels et al., 1991; Fukui et al., 1996; Anik, 2004; Dai et al., 2004; Um et al., 2004).

1.3 DETERMINATION OF IODINE IN ENVIRONMENTAL SAMPLES

1.3.1 Total Iodine

Iodine can be a difficult element to assay because of its volatility, especially in acidic conditions (Gilfedder et al., 2007a). It is usually found in nature at low concentrations, which necessitates a sensitive analytical tool. Neutron Activation Analysis (NAA) is one of the most accurate methods for determination of iodine in environmental samples and is characterised by both high sensitivity and selectivity. In addition, solid samples can be analysed directly without the matrix complications and potential losses which may result from extraction (Kucera et al., 2004). NAA has been widely used for iodine determination in a range of environmental samples, including foodstuffs, rock and soil samples, algae, seaweed, plant samples, and rain and river waters (Yuita et al., 1982; Muramatsu and Ohmomo, 1986; Ebihara et al., 1997; Kucera et al., 2004; Michel et al., 2005; Tsukada et al., 2005; Bejey et al., 2006; Osterc et al., 2007; Suzuki et al., 2007). The main limitation of NAA is that it requires access to a nuclear reactor and is generally expensive.

Generally, to determine elemental soil concentrations, acid digestion or alkali fusion is required. As iodine can readily volatilise from heated acidic media, total soil iodine is usually extracted using high pH reagents (Yamada et al., 1996b). Whitehead (1973b), for example, boiled air-dried soils with 2M NaOH for 45 minutes under reflux and validated the results by comparing them with the results obtained using an earlier method described by the Association of Official Agricultural Chemists (AOAC) which included heating soils with solid KOH. Satisfactory recovery of different iodine compounds added to the soils was also taken as evidence of the effectiveness of the extraction procedure. Crouch (1962), Yonehara et al. (1970), and Marchetti et al. (1994) also used fusion with KOH or NaOH to release iodine from silicate rocks and soils.

'Prohydrolysis' is a one of the methods applied to release halogens from soils and geological materials. The method utilises the volatility of halogens to effect separation from the solid phase with subsequent trapping in a suitable solution (Schnetger and Muramatsu, 1996). Rae and Malik (1996) described a pyrohydrolysis method in which soil, dried at 110°C, was mixed with a V_2O_5 flux and heated at 1060°C. Evolved iodine was absorbed in 0.05 M NaOH and then detected by automated colorimetery with a detection limit of 0.05 μg g^{-1}. The efficiency of the method was tested using eight international reference samples and gave good agreement with certified values. Muramatsu et al. (2008) used the same prohydrolysis method to determine ^{129}I concentration in Japanese soil but replaced the trap solution with 1% TMAH (tetramethyl ammonium hydroxide) + 0.1% Na_2SO_3 solution. The ^{129}I was successfully separated and determined using ICP-MS with a (solution) detection limit of 0.1 μg L^{-1}. The same method, with slight modification, has also been used to estimate total iodine content in soils, sediments, rocks and reference materials (Schnetger and Muramatsu, 1996; Gerzabek et al., 1999; Sahoo et al., 2009).

Bing et al. (2004) examined the efficiency of extracting total iodine from soil and biological samples with dilute ammonia under pressure. Samples were extracted in screw-top PTFE-lined stainless steel bombs using 10% v/v ammonia solution at 185°C for 18 hours; iodine in the extract was measured using ICP-MS. The method was applied to geological certified reference materials and gave good agreement with certified values (1.8 – 4.32 % RSD; n = 10).

Iodine extraction with tetra methyl ammonium hydroxide (TMAH) has recently become the favoured approach for extracting iodine from solid environmental samples including soils, sediments, plants, and food. One advantage of TMAH over inorganic extractants such as NaOH or KOH is that high pH values can be achieved without increasing the salt concentration of the extraction solution and hence reducing the possibility of precipitation in the ICP torch and nebuliser during analysis. According to Yamada et al. (1996a), strongly sorbed inorganic iodine and organically-bound iodine are solubilised by alkaline solutions such as TMAH. It is likely that iodate would also be released from sorption sites on Fe/Al hydrous oxides by increasing the negative charge on the oxide surface at high pH and ligand replacement with hydroxide ions. Humus-bound iodine would be solubilised by a combination of organic-iodine hydrolysis and mobilisation of humic and fulvic acids at high pH. Yamada et al. (1996a) used extraction with 5% TMAH at 70°C for 3 hours prior to analysis by ICP-MS, using ^{118}In as an internal standard. High reproducibility was observed between replicates (RSD <2%) and the iodine concentrations measured on four soil reference materials were in good agreement with certified values. Watts and Mitchell (2009) used a slightly different approach in which soils were extracted in 5% TMAH at 70°C for 3 h in tetrafluoroethene sample bottles prior to analysis by ICP-MS. Results showed good agreement with the reference concentration and good precision (±10%) between replicates. In other studies, more vigorous conditions have been applied. Mani et al. (2007) and Tagami et al. (2006) used 10% and 25% TMAH to extract iodine from soils in closed, pressurised vessels, at $60^{O}C$ and $80^{O}C$, and for 12 h or 6 h, respectively; measured values were in good agreement with certified values (%RSD <1%). In other studies, slightly varied approaches have been applied to extract iodine from food samples (Fecher et al., 1998; Radlinger and Heumann, 1998; Chen et al., 2007; Wang and Jiang, 2008; Mesko et al., 2010), marine sediments (Fitoussi and Raisbeck, 2007), coal and coke (Gao et al., 2007), plants samples (Tagami et al., 2006) and seaweed (Romaris-Hortas et al., 2009).

1.3.2 Iodine Speciation and Fractionation

Coupling of High Performance Liquid Chromatography (HPLC) (for separation) and ICP-MS (as detector) is now a commonly applied analytical approach for iodine speciation analysis. The flexibility of HPLC arises from the ability to change both mobile and stationary phases and to employ several mobile phases in a single analytical run using gradient-HPLC. ICP-MS is a highly selective and sensitive analytical tool which is ideal for determination of separated trace-elemental species at concentrations in the ppb range (Michalke, 2002; Agilent-Technologies, 2007). Furthermore, because ICP-MS is isotope-specific, it is possible to study the 'speciation kinetics' of a stable isotope tracer introduced into a dynamic geochemical or biological system. Uniquely, this approach can be employed to study steady state systems and quantify 'gross' rate constants.

HPLC-ICP-MS has been employed in numerous studies to investigate iodine speciation in biological and environmental matrices including milk (Fernandez Sanchez and Szpunar, 1999; Leiterer et al., 2001), thyroglobulin amino-acids (Takatera and Watanabe, 1993), rainwater, snow, freshwater, groundwater and seawater (Schwehr and Santschi, 2003; Gilfedder et al., 2007 b,c; Liu et al., 2007; Yang et al., 2007), soil solutions (Yoshida et al., 2007; Shimamoto et al. 2010, 2011), and (dissolved) humic substances (Radlinger and Heumann, 1997).

In solid samples different approaches have been proposed for iodine speciation and fractionation. Whitehead (1973b) investigated solubility of iodine in soils and agriculture materials using extracting reagents that have proved useful in characterising nutrients in soils. Whitehead (1973b) found that the amount of iodine extracted increased in the order 0.01 M $CaCl_2$ < 0.42 M acetic acid < 0.016 M KH_2PO_4 < 0.1M HCl < 0.05 M EDTA < boiling water < Tamm's reagent < 0.5 M oxalic acid < 0.1M NaOH and concluded that iodine was in part retained in soils via both organic matter and sesquioxide materials (iron, aluminium, and manganese oxides) depending on the nature of the soil. Organic and inorganic iodine forms in the extracts were transformed to iodate by oxidative acid digestion and then iodate was reduced to iodide by arsenious acid. Total iodine was determined colorimetrically as iodide.

Sequential extraction techniques, based on the sequential extraction protocol originally established by Tessier et al. (1979) to partition the particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn), have also been used to fractionate soil iodine. Five operationally defined fractions:

exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and 'residual' are typically used. Thus, Hou et al. (2003) separated ^{129}I from a soil contaminated by the Chernobyl explosion into four different fractions including (i) a water soluble fraction dissolved in deionised water at room temperature, (ii) an exchangeable fraction extracted in 1.0 M NH_4OAc (at pH 8.0) at room temperature, (iii) a carbonate-bound fraction dissolved in 1.0 M NH_4OAc (at pH 5.0), and (iv) hydrous oxides extracted with 0.04 M $NH_2OH.HCl$ in 25%(v/v) HOAc (pH 2.0) at 95°C. They found that ^{129}I was mainly bound to oxides and organic matter with only a small fraction designated 'readily available'. Similar approaches were applied by Sheppard and Thibault (1992) and Englund et al. (2010) to study iodine fractionation in organic and mineral soils and in lake sediments, respectively. It was concluded that most iodine in lake sediments and soils is organically bound.

Yamada et al. (1999) investigated iodine as four fractions: organic iodine in humic acids, organic iodine in fulvic acids, iodide, and iodate, following extraction with TMAH at ambient temperature to avoid thermal decomposition of organic iodine. The humic acids that were mobilised by the high pH of the TMAH extract were precipitated by acidification to pH 1.5, leaving the fulvic acid and inorganic iodine fractions in solution. To avoid precipitation of iodate with the humic acids, ascorbic acid was added to reduce iodate to iodide. Subsequently, addition of ammonium oxalate and calcium acetate resulted in precipitation of calcium oxalate which was believed to have flocculated fulvic acid iodine, leaving only inorganic iodine in solution. Considering all the original iodide would be soluble in potassium chloride solution, iodate was determined by subtracting soluble iodine from inorganic iodine determined in the TMAH extract; iodine was determined by ICP-MS. A similar approach was applied by the same author to soil solutions rather than soil extracts (Yamada et al., 1996b). Similar approaches to iodine speciation have been applied to seaweed (Hou et al., 1997) by addition of bismuth nitrate to a water leachate of dried and ground marine algae. Iodide was precipitated as BiI_3, iodate was then reduced to iodide and precipitated in the same way. Soluble organic iodine was determined by subtracting the inorganic soluble forms concentration from the total soluble iodine measured by NAA in different fractions. Steinberg et al. (2008a) estimated organic iodine in salt-impacted soils as CH_3I using pyrolysis GC-MS with volatilisation at 500°C for 20 s in a helium atmosphere. Soluble iodide was converted to CH_3I by reaction with methyl sulphate and iodate converted to iodide by adding sodium dithionite before both were estimated as CH_3I. The same approach was used by Dorman and Steinberg (2010) to determine iodide and iodate in lake and tap water.

X-ray absorption near edge structure (XANES) is also a promising tool to establish iodine speciation in environmental and soil samples. The superiority of XANES is its ability to determine iodine speciation in solid phases directly. This method has been applied to study iodine species in soils (Kodama et al., 2006; Yamaguchi et al., 2006; Shimamoto and Takahashi, 2008; Shimamoto et al., 2010, 2011), humic substances (Schlegel et al., 2006), mineral surfaces (Fuhrmann et al., 1998; Kodama et al., 2006; Nagata et al., 2009), cement (Bonhoure et al., 2002) and in waste solvent from nuclear fuel reprocessing (Reed et al., 2002).

1.4 STUDY AIMS

Understanding the temporal change in solubility and bioavailability of iodide or iodate added to soil in connection with soil properties is necessary for soil bio-fortification programmes or to predict the behaviour of naturally supplied iodine. However, it appears from the available literature that, although the reaction mechanisms by which iodine is retained in soil are largely understood, there is a knowledge gap regarding the kinetics of these reactions and how long iodide or iodate added to soil remains soluble, or bioavailable, in relation to soil properties.

The main aim of this work was to investigate the transformation and reaction kinetics of iodide and iodate added to soil, (e.g. via rainfall or by application of iodine-rich fertilisers) and to relate this to soil properties, principally pH, organic-C content and metal oxides content. Thus, the objectives of the project are listed below.

1- Develop chromatography methods, using both 'anion exchange' and 'size exclusion' columns, coupled to ICP-MS, for quantifying both inorganic and organic (humic/fulvic) iodine species in solution (Chapter 3).

2- Investigate the use of soil extraction to fractionate soil iodine (natural and spiked) using different reagents, including TMAH, KH_2PO_4 and KNO_3 and to identify the effect of the extraction procedure on the speciation of the extracted iodine (Chapter 4).

3- Study the adsorption and transformation of iodide and iodate, using isotopically labeled species $^{129}I^-$ and $^{129}IO_3^-$, in soils with a range of properties, to determine the kinetics of reaction and transformation of inorganic iodine (Chapters 5 and 6).

4- Develop kinetic and/or diffusive models that simulate the transformation of inorganic iodine in soil as a function of basic characteristics, such as humus content, pH and sesquioxide content (Chapter 6).

2. STANDARD METHODS

2.1 SOIL SAMPLING AND PRE-TREATMENTS

Soil samples were collected using a clean stainless steel spade, auger or trowel and sealed in plastic bags for transport. Soils were air dried in aluminium trays, gently disaggregated using a pestle and mortar (where necessary) and sieved to obtain a <2 mm fraction, and to remove stones and plants debris. Samples were homogenized using the 'cone method'; sieved soil was poured into a cone-shaped pile and strips from the cone base to the top used to build a new cone and the entire process repeated four times (Schumacher et al., 1990). Processed soil samples were stored in clean polyethylene bags. A sub-sample of each soil was ground to a fine powder (clay size) in an agate ball mill (Retsch, Model PM400), and stored in the same way.

2.2 SOIL PH

To determine pH, 5 g of soil (< 2mm) was suspended in 12.5 mL of MilliQ water (18.3 MΩ) and shaken on a reciprocal shaker for 30 minutes. The pH of the soil suspension was measured using a Hanna pH-209 pH meter and a combined glass electrode (Ag/AgCl; PHE 1004), calibrated with pH 7 and pH 4.01 buffers, allowing 5 minutes for the reading to stabilise.

2.3 SOIL CARBONATE CONTENT

Soil carbonate content was estimated by manometric assay using a Collins calcimeter. Soil samples, together with a vial containing 10 ml of 4 M hydrochloric acid were placed in a conical flask attached to a gas manometer held at constant temperature. After adjusting the water level in the manometer, the conical flask was shaken to mix the hydrochloric acid with the soil. The mass of carbonate present was estimated by measuring the displacement of water in the manometer which corresponds to the volume of carbon dioxide released. The efficiency of the method was determined using pure calcium carbonate samples. Full details of the procedure are published elsewhere (Piper, 1954).

2.4 LOSS ON IGNITION (LOI)

Triplicate samples of approximately 5 g oven-dried soil samples in silica crucibles were ignited in a muffle furnace for 16 h at 550°C. Crucibles were re-weighed after cooling and the % LOI was calculated.

2.5 SOIL CARBON, NITROGEN, AND SULPHUR CONTENT

Approximately 15-20 mg of dry, finely ground soil, including certified soil reference standards, were weighed into tin capsules and approximately 5 mg of vanadium pentoxide added. Capsules were carefully crimped, using tweezers, to avoid spillage. A capsule containing only vanadium pentoxide was used as a blank and certified soil standards were used as a calibration standard. Sandy and peat certified soil standards were provided by Elemental Microanalysis; product codes B2180 and B2176, respectively. Analysis was undertaken using a CNS analyser (Flash EA1112; CE Instruments); samples were introduced from a MAS200 auto-sampler. Sample capsules were dropped into a combustion tube packed with approximately 25 g copper oxide and 70 g electrolytic copper, and heated to 900°C. The resulting gas was passed through an absorption filter containing magnesium perchlorate to remove water before passing through a PTFE separation column and to a thermal conductivity detector. Helium was used as the carrier gas.

2.6 DISSOLVED ORGANIC CARBON (DOC) AND TOTAL NITROGEN (TN) IN SOIL SOLUTION

Concentration of DOC in soil solution was measured using a Shimadzu total organic carbon analyser (TOC-V_{CPH}) with a non-dispersive infrared detector. Total nitrogen concentration was determined using an attached Shimadzu TNM-1 total nitrogen measuring unit with a chemiluminescence detector. Organic carbon and nitrogen stock standards (1000 μg mL^{-1} C or N) were prepared from oven-dried potassium hydrogen phthalate and potassium nitrate in MilliQ water, respectively. Working standards were prepared freshly by dilution of the stock using a Compudil-D auto diluter (Hook and Tucker instruments). Concentration of DOC was measured as 'non-purgeable organic carbon' (NPOC) in which a small volume of hydrochloric acid was added to acidify the samples and thereby remove carbonates from the sample.

2.7 SPECTROPHOTOMETRIC DETERMINATION OF FULVIC ACID IN SOIL SOLUTIONS

Concentration of fulvic acid in soil solutions and extracts was determined spectrophotometrically, using a Cecil CE1011 spectophotometer, set to an absorbance wavelength of 350 nm, according to the method developed by Gan et al. (2007). Samples were diluted where necessary to obtain absorbance values in the range 0.0-1.2. Fulvic acid concentrations were calculated according to equation 2.1.

$$FA = \frac{A - 0.0035}{0.0101} \qquad 2.1.$$

Where, FA = fulvic acid concentration (mg L^{-1}) and A = measured absorbance.

2.8 SOIL MICROBIAL BIOMASS CARBON AND NITROGEN

A method was adapted from that described by Vance et al. (1987). Fresh (moist) soil samples were homogenized to ensure representative sub-sampling by sieving to <4 mm. Sub-samples (10 g) in small beakers were fumigated in a desiccator with a beaker containing chloroform and anti-bumping granules, moist tissue paper and a vial of soda lime. The desiccator was sealed using rubber gasket and silicon grease, placed in an operational fume cupboard and evacuated with a vacuum pump. When the chloroform started to boil, the valve was regulated to achieve constant boiling for a period of 5 minutes, before being closed and light excluded by wrapping the desiccator in aluminum foil. After 24 hours of fumigation the beaker containing chloroform was removed. The desiccator was then re-evacuated and the vacuum immediately released. This process was repeated 10 times to remove residual chloroform vapour. Control (non-fumigated) and fumigated samples were extracted in 50 ml 0.5 M K_2SO_4 by shaking for 30 min before centrifugation and filtration through syringe filters (0.22 μm). Filtered supernatants were analysed for DOC and TN as described in section 2.6. Microbial biomass carbon was calculated using equation 2.2.

$$C_M = \left\{\left(\frac{TOC_F}{W_{soil\ F}}\right) - \left(\frac{TOC_B}{W_{soil\ B}}\right)\right\} \text{ x } \left\{\frac{V_{ext}}{k_{EC}}\right\} \qquad 2.2$$

Where, C_M = microbial biomass carbon (mg C kg^{-1} soil), TOC_F = TOC in fumigated soil extract (μg mL^{-1}), TOC_B = TOC in blank soil extract (μg mL^{-1}), V_{ext} = extractant volume (mL), $W_{soil\ F}$ = dry weight of fumigated soil (g), $W_{soil\ B}$ = dry weight of blank soil (g), and k_{EC} = 0.45 (a coefficient to convert ‘chloroform-labile’ carbon to ‘microbial biomass carbon’; (Jenkinson et al., 2004).

Microbial biomass nitrogen (N_M) was calculated using the same approach.

2.9 SOIL IRON, ALUMINIUM AND MANGANESE OXIDES

2.9.1 Extraction of Fe, Al, and Mn Oxides

Total Fe, Al and Mn oxides were extracted by adapting methods described by Kostka and Luther (1994) and Anschutz et al. (1998). Triplicate samples of (c. 0.3 g) of finely ground soil were suspended in 25 mL aliquots of a solution containing 0.22 M tri-sodium citrate, 0.11 M sodium hydrogen carbonate and 0.1 M sodium dithionite in polycarbonate centrifuge tubes and shaken (with loosely closed lids) for 16 hours in a water bath at 40^{o}C. Samples were centrifuged (20 min at 3000 g) and filtered (<0.22 μm) before dilution (1:10) with MQ water, prior to analysis. Total Fe, Al, and Mn concentrations were assayed by ICPMS according to the method described in section 2.9.2. and concentrations (mg kg^{-1}) of Fe_2O_3, MnO_2, and $Al(OH)_3$ were then calculated.

2.9.2 Measurement of Fe, Al, and Mn by ICPMS

Iron, Aluminium, and Manganese analysis was undertaken using a Thermo-Fisher Scientific X-Series^{II} ICP-MS with a ‘hexapole collision cell’ (7% hydrogen in helium) prior to the analytical quadrupole. Samples were introduced from an autosampler (Cetac ASX-520 with 4 x 60-place sample racks) through a concentric glass venturi nebuliser (Thermo-Fisher Scientific; 1 mL min^{-1}) and Peltier-cooled spray chamber (3^{o}C). Internal standards were introduced to the sample stream via a T-piece and included Sc (100 μg L^{-1}), Rh (20 μg L^{-1}) and Ir (10 μg L^{-1}) in 2% 'trace analysis grade' (TAG; Fisher) HNO_3. External multi-element calibration standards (Claritas-PPT grade CLMS-2, Certiprep/Fisher), including Fe, Al and Mn, were all prepared in 2% TAG HNO_3 in the range 0-100 μg L^{-1}. Sample processing was undertaken using Plasmalab software (version 2.5.4; Thermo-Fisher Scientific) using internal cross-calibration where required.

2.10 TOTAL IODINE CONCENTRATION AND IODINE SPECIES IN SOIL

2.10.1 Extraction of Total Soil Iodine

The total iodine content of soil was extracted using the method described by Watts and Mitchell (2009). Triplicate samples of finely ground soil (c. 0.25 g) were suspended in 5 mL of 5% tetra-methyl ammonium hydroxide (TMAH) solution in polycarbonate centrifuge tubes. Tubes were heated at 70^0C (with lids loosened) for 3 hours (shaken at 1.5 hours). Tubes were weighed before and after extraction to correct for any evaporative losses. A 5 mL aliquot of MQ water was added to each tube before centrifugation (20 min at 3000 g) and filtration (<0.22 µm) prior to analysis for iodine by ICP-MS (section 2.10.2)

2.10.2 Analysis of Total ^{127}I Concentration by ICP-MS

Iodine concentration in the TMAH extracts was measured on a Thermo-Fisher Scientific X-Series^{II} ICP-MS in standard mode. Internal standards included 20 μg L^{-1} In, 20 μg L^{-1} Re, and 20 μg L^{-1} Rh, prepared in a matrix of 2% TMAH and 4% methanol, introduced to the sample stream via a T-piece. TMAH was used to adjust the pH as the high pH of the medium is important to preserve iodide ions through the aspiration process in the ICP-MS nebulizer (Liu et al., 2007; Yang et al., 2007). Methanol was added as it has been reported that the presence of carbon ions (C^+) in the argon plasma of the ICP enhances ionization efficiency and, consequently, sensitivity and stability (AbouShakra et al., 1997; Morita et al., 2007; Thermo-Electron, 2008). The presence of methanol should also eliminate any matrix differences between samples and standards arising from DOC in the former. Indium was the internal standard of first choice and normally compensated satisfactorily for instrumental drift during the course of analysis runs for both ^{127}I and ^{129}I. However, the inclusion of Re and Rh allowed the option of selecting different standards or using an extrapolation facility across all three internal standards. The sample line washing solution was 1% TMAH. A stock standard (1000 mg L^{-1}) was prepared from oven-dried analytical grade potassium iodide in a matrix of 5% TMAH and refrigerated at 4°C for storage.

2.10.3 Handling and Analysis of Total ^{129}I by ICPMS

An ^{129}I stock standard was obtained from the American National Institute of Standards (NIST), Gaithersburg, Maryland, USA; the primary stock (5 mL) was made up to 100 mL with 0.01 M NaOH and stored in a borosilicate glass bottle in the lead safe of a 'Controlled Laboratory'. Working standards were prepared by dilution of the stock standard. Analysis of ^{129}I was carried out following the same procedure used to assay ^{127}I (section 2.10.2); however, a correction for ^{129}Xe on the ^{129}I signal was applied directly in the Plasmalab software (equation 2.3.).

$$^{129}I_{CPS} = {}^{129}M_{CPS} - (1.24835 \times {}^{131}Xe_{CPS}) \qquad 2.3.$$

Where, $^{129}I_{CPS}$ = ^{129}I counts per second, $^{129}M_{CPS}$ = total measured counts per second at mass 129 (i.e. $^{129}I+^{129}Xe$), 1.24835 = $^{129}Xe:^{131}Xe$ natural isotopic ratio, and $^{131}Xe_{CPS}$ = ^{131}Xe counts per second.

2.10.4 Measurement of Iodine Species Using HPLC-ICP-MS

Chromatographic separation of $^{127}I^-$, $^{127}IO_3^-$, $^{129}I^-$ and $^{129}IO_3^-$ was undertaken using a Dionex ICS-3000 ion chromatography system operated in isocratic mode. Samples were introduced using an autosampler triggered by Chromeleon® software. Hamilton PRP-X100 anion exchange columns (250 x 4.6 mm and 50 x 4.6 mm both with 5 µm particle size) were used for separation. The mobile-phase solution contained 60 mmol L^{-1} NH_4NO_3, 1×10^{-5} mM L^{-1} Na_2-EDTA, 2% methanol, with pH adjusted to 9.5 with TMAH, and was pumped at a flow rate of 1.3 mL min^{-1}. The column outflow was connected directly to the nebuliser of the ICP-MS. Sample processing was undertaken using Plasmalab software; peaks of individual species were manually demarcated. Standard stock solutions of $^{127}I^-$ and $^{127}IO_3^-$ (1000 mg L^{-1}) were prepared from oven-dried analytical grade potassium iodide and potassium iodate, respectively, in a matrix of 5% TMAH, and stored at 4°C. Mixed $^{127}I^-$ and $^{127}IO_3^-$ working standards were prepared from stocks, immediately before analysis, using the mobile-phase as diluent. The sensitivity (counts per second per 1 µg L^{-1}; CPS µg L^{-1}) of a standard solution was repeatedly measured at intervals of six samples to correct for instrumental drift. The sensitivity (CPS µg L^{-1}) of individual samples was calculated from equation 2.4.

$$S_{(i)} = S_{(i-1)} + \frac{Std_j - Std_{(j-1)}}{n+1} \qquad 2.4.$$

Where, $S_{(i)}$ is the calculated sensitivity of $^{127}I^-$ or $^{127}IO_3^-$ for a given sample, $S_{(i-1)}$ is the calculated sensitivity of $^{127}I^-$ or $^{127}IO_3^-$ for the previous sample, $Std_{(j)}$ and $Std_{(j-1)}$ are the measured sensitivities for $^{127}I^-$ or $^{127}IO_3^-$ in the bracketing standards and n is the number of samples between the bracketing standards (j) and (j-1).

The concentrations of $^{127}I^-$ and $^{127}IO_3^-$ in samples were then calculated by dividing the corresponding values of CPS by the calculated sensitivity $S_{(i)}$ for each sample. Concentrations of $^{129}I^-$ and $^{129}IO_3^-$ were calculated by applying a mass discrimination factor (a 'K-factor') to correct for the different sensitivities of the ^{127}I and ^{129}I isotopes (equation 2.5.).

$$^{129}I_{conc} = \frac{^{129}I_{CPS}}{S_{127}} \times 1.085 \qquad 2.5.$$

Where, $^{129}I_{conc}$ = $^{129}I^-$ or $^{129}IO_3^-$ concentration (μg L^{-1}), $^{129}I_{CPS}$ = total counts per second of $^{129}I^-$ or $^{129}IO_3^-$, 1.085 = measured mass correction factor (see measurements in Chapter 3), S_{127} = $^{127}I^-$ or $^{127}IO_3^-$ sensitivity.

2.11 OXIDATION OF IODIDE TO IODATE

The iodine isotope ^{129}I was supplied as iodide ($^{129}I^-$) from which iodate ($^{129}IO_3^-$) was prepared. The primary stock was made up to 100 mL with 0.01 M NaOH, as recommended by the suppliers, and stored in a borosilicate glass bottle. Oxidation to form $^{129}IO_3^-$ was adapted from the method of (Yntema and Fleming, 1939). To 100 mL of $^{129}I^-$, 10 mL of 0.1 M HCl was added in an initial neutralization step, followed immediately by

10 mL of 0.2 M sodium chlorite for oxidation (see also method development in Chapter 3).

2.12 HUMIC ACID PREPARATION

Humic acid used in the current study was prepared by Marshall et al. (1995) from topsoil samples representing a wide range of soil types. Field moist soils were extracted with 0.1 M NaOH in glass bottles, filled to the top to exclude air, by shaking for 12 hours. Extracts were centrifuged at 10000 g for 15 minutes and the supernatant solutions were acidified to pH 2 with hydrochloric acid to precipitate humic acids. Separation of the soluble fulvic fraction from the non-soluble humic fraction was achieved by centrifugation. Metal and silica contaminants were removed by dialysing against a mixture of 1% (v/v) HCl and HF, with the external solution being changed twice each week. This was followed by repeated dialysis at intervals of two days, against de-ionised water. The purified humic acid was then freeze-dried, ground, and stored in dark glass bottles in a desiccator.

3. METHOD DEVELOPMENT

3.1 INTRODUCTION

3.1.1 Mobile-Phase for Iodine Speciation

Several studies have investigated developing a suitable mobile-phase for chromatographic separation of iodine species in environmental samples and solutions (Table 3.1). All of the approaches listed have successfully separated iodide and iodate peaks. However, regarding retention times, the trials of Yoshida et al. (2007) and Wang and Jiang (2008) were the most successful with column transit times of ~2 min and ~7 min for iodate and iodide, respectively.

Table 3.1
Mobile-phases used for chromatographic separation of iodine species in several published studies

Mobile-phase	Reference
35 mM L^{-1} NaOH	Gilfedder et al. (2007a,b)
3.5 mM L^{-1} Na_2CO_3 with 1.0 mM L^{-1} $NaHCO_3$	Leiterer et al. (2001)
50 mM L^{-1} $(NH_4)_2CO_3$ (at pH 9.4)	Liu et al. (2007)
30 mM L^{-1} $(NH_4)_2CO_3$	Yoshida et al. (2007)
Gradient method with 15 and 100 mM L^{-1} NH_4NO_3 (pH 10)	Wang and Jiang (2008)

The aim of this section was to investigate and test a suitable mobile-phase for iodine speciation by HPLC-ICP-MS. The possibility of using the same mobile-phase for speciation of other elements was also tested. The elements selected were, selenium (Se^{IV} and Se^{VI}), chromium (Cr^{III} and Cr^{VI}), arsenic (As^{III} and As^{V}), and antimony (Sb^{III} and Sb^{V}).

Selenium is vital in mammals for the production of several important enzymes; selenium deficiency can lead to several health complications such as heart diseases and hypothyroidism which can, along with iodine deficiency, cause goiter and mental slowing (Rotruck et al., 1973; Ganther and Lawrence, 1997; Sasakura and Suzuki, 1998; Rayman, 2000) but the difference between essential and toxic selenium doses for human beings is quite small (Rayman, 2000; ASTDR, 2003). Selenium is usually found in nature as two inorganic species, selenite and selenate (Se^{VI}), and several organic compounds (Bueno et al., 2007). Selenite (Se^{IV}) is reported to be more toxic than selenate (Se^{VI}) whereas both inorganic species are more toxic than organic selenium species (ASTDR, 2003; IAEA, 2007). Chromium is released to the environment in several chemical forms, mainly as Cr^{III} and Cr^{VI} (IAEA, 2007; Hagendorfer and Goessler, 2008). Chromite, Cr^{III}, is an essential nutrient, while Cr^{VI} is highly toxic and carcinogenic (Leist et al., 2006; IAEA, 2007). Arsenic is released to the environment through the use of agriculture chemicals and pesticides, and from several industries (Cocker et al., 2006; IAEA, 2007). In nature, arsenic is usually found as several inorganic and organic forms; mainly, As^{III}, As^{V}, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Cullen and Reimer, 1989; Lindemann et al., 1999). Arsenite, As^{III}, is known to be more toxic and more mobile than As^{V} and both of them are highly toxic compared to the methylated organic arsenic species (Cullen and Reimer, 1989; Florence, 1989, IAEA, 2007). Antimony can be found in the Earth’s crust in concentrations as low as 0.2–0.3 mg kg^{-1} (Wedepohl, 1995). Antimony exists in two inorganic oxidation states, Sb^{III} and Sb^{V}, in addition to several organic forms (Smith et al., 2002). Generally, antimony is considered as a toxic element and major pollutant; however, it has been reported that Sb^{III} is more toxic than Sb^{V} and both of them are highly toxic compared with organic forms of antimony (Leffler et al., 1984).

3.1.2 ICPMS Internal Standards for Iodine Speciation Analysis

Internal standards are normally used in ICPMS elemental analysis to compensate for (i) drift in sensitivity during an analytical run and (ii) differences in solution matrix between samples and calibration standards. A constant amount of the internal standard may be added to a fixed volume of all samples, blanks and standards. Alternatively, a separate line for the internal standard can be used with a T-piece connection to the sample line immediately before the nebuliser. Both approaches produce a constant aspiration of internal standard during the analysis. Ideally the internal standard should be completely absent from all samples and standards (prior to aspiration) and should be of a comparable atomic mass and ionization potential to the analyte. Several elements have been successfully used as internal standards for iodine determination by ICPMS, including tellurium (Bing et al., 2004), indium (Yamada et al., 1996a), and caesium (Gerzabek et al., 1999; Tagami et al., 2006).

The possibility of adding the internal standard to the mobile-phase during iodine speciation analysis by HPLC-ICP-MS was investigated. The selected internal standard had to be tested for (i) chemical neutrality towards iodine species and (ii) a low affinity for the anion exchange column. Ideally an internal standard should achieve equilibrium with the column immobile phase by occupying the minimum number of adsorption sites. It was decided to test both In and Cs as potential internal standards.

3.1.3 Mass Discrimination Factor (K-factor) for ^{127}I and ^{129}I Isotopes

In total iodine analysis, ^{129}I and ^{127}I working standards were prepared separately using $^{129}I^-$ and $^{127}I^-$ stock standards to avoid cross-contamination with $^{127}I^-$ present in the $^{129}I^-$ stock standard; thus two isotope-specific standards curves were produced. For speciation analysis, $^{127}I^-$ and $^{127}IO_3^-$ were prepared together in mixed working standards. Initially, $^{129}I^-$ and $^{129}IO_3^-$ were prepared separately, again because of the presence of $^{127}I^-$ and $^{127}IO_3^-$ in the $^{129}I^-$ or $^{129}IO_3^-$ stock standards and the risk of residual oxidising agent present the in the $^{129}IO_3^-$ stock standard. However, to avoid repeatedly running blocks of four isotope-specific species calibration standards (c. 48 minutes), $^{129}I^-$ and $^{129}IO_3^-$ standard curves were not used. The concentrations of $^{129}I^-$ and $^{129}IO_3^-$ in the samples were determined using the instrument sensitivity (calibration slopes) determined for $^{127}I^-$ and $^{127}IO_3^-$ standards. This was achieved by dividing values of `integrated counts per second' for $^{129}I^-$ or $^{129}IO_3^-$ by the corresponding $^{127}I^-$ or $^{127}IO_3^-$ calibration sensitivity, after drift correction was applied as described in Chapter 2 (section 2.10.4). However, the sensitivity (cps ppb^{-1}) is expected to differ between the two isotopes due mass discrimination effects, and so the sensitivity measured for ^{127}I was also adjusted by a mass discrimination factor (a 'K-factor') for the calculation of ^{129}I species concentrations.

3.1.4 Oxidation of Iodide to Iodate

$^{129}IO_3^-$ was prepared by oxidising $^{129}I^-$ standard (25 μg mL^{-1} $^{129}I^-$ in 0.01 M NaOH matrix) obtained from the American National Institute of Standards (NIST), Gaithersburg, Maryland, USA. The oxidation process was based on the method described by Yntema and Fleming (1939). The possibility of performing the oxidation in a highly alkaline medium (0.01 M NaOH) and the importance of the buffering solution used in the study of Yntema and Fleming (1939) were also tested.

3.2 EXPERIMENTAL

3.2.1 Mobile-Phase for Iodine Speciation

The mobile-phase used in the present study was adapted from the work published by Wang and Jiang (2008). The IC mobile-phase was 60 mM L^{-1} NH_4NO_3 with 10^{-5} mM L^{-1} Na_2-EDTA and 2% methanol; pH was adjusted to 9.4 with TMAH. TMAH was used to adjust the pH instead of NaOH or KOH to decrease the dissolved salt concentration and, consequently, the possibility of precipitation in the ICP-MS nebuliser and torch; the high pH of the mobile phase is important to preserve iodide ions through the column and through the aspiration process in the ICP-MS nebulizer (Liu et al., 2007; Yang et al., 2007). Di-sodium EDTA was added to facilitate working with soil solutions which have elevated Fe^{2+} and Mn^{2+} ion concentrations and therefore present a risk of precipitation in the guard column, due to the highly alkaline mobile-phase. Methanol was added because the presence of carbon ions (C^+) in the argon plasma of the ICP enhances ionization efficiency, sensitivity and stability (AbouShakra et al., 1997; Morita et al., 2007; Thermo-Electron, 2008).

The chromatographic separation and elemental analysis was undertaken using HPLC-ICP-MS as described in Chapter 2 (section 2.10.4) using a Hamilton anion exchange column (model PRP-X100, 250 x 4.6 mm). Separation was tested using a mixed standard solution containing 30 μg L^{-1} of $^{127}I^-$, $^{127}IO_3^-$, Fe and Mn, and a further two standards containing $^{129}I^-$ and $^{129}IO_3^-$ prepared separately. The mobile-phase was used for dilution of standards. To test the simultaneous assay of other species of environmental interest, a mixed standard solution containing 50 μg L^{-1} of I^-, IO_3^-, Cr^{III}, Cr^{VI}, As^{III}, As^{V}, Se^{IV}, Se^{VI}, Sb^{III}, and Sb^{V} was used. The Cr^{III} standard was prepared in 10^{-2} M Na_2-EDTA solution and left for approximately 16 hours before analysis.

3.2.2 ICP-MS Internal Standards for Iodine Speciation Analysis

A mixed standard of 20 μg L^{-1} of iodide, iodate, indium, and caesium was prepared and analysed for I^-, IO_3^-, In, and Cs by HPLC-ICPMS, as described in Chapter 2 (section 2.10.4) using the anion exchange column (Hamilton, model PRP-X100, 250 x 4.6 mm).

3.2.3 Mass Discrimination Factor (K-factor) for ^{127}I and ^{129}I Isotopes

The mass discrimination factor was measured by analysing standards of 10, 20, 30, and 40 μg L^{-1} $^{127}I^-$, $^{127}IO_3^-$, $^{129}I^-$ and $^{129}IO_3^-$ and determining sensitivity values for total ^{127}I and ^{129}I as described in Chapter 2 (sections 2.10.2 and 2.10.3).

3.2.4 Oxidation of Iodide to Iodate

Solutions of $^{127}I^-$ (25 μg mL^{-1}) were prepared in two different matrices: 0.01M NaOH and mQ water. Different combinations of $^{127}I^-$ solutions (in

0.01 M NaOH or mQ water), buffering reagent (0.2M acetic Acid + 2M sodium acetate) and oxidising agent (0.2 M sodium chlorite) were prepared as detailed in Table 3.3. Samples were left for 48 hours and then analysed for total ^{127}I concentration by ICP-MS (Chapter 2; section 2.10.2) and for $^{127}I^-$ and $^{127}IO_3^-$ on HPLC-ICP-MS (Chapter 2; section 2.10.4).

3.3 RESULTS AND DISCUSSION

3.3.1 Mobile-Phase for Iodine Speciation

Peaks for $^{127,129}IO_3^-$ and $^{127,129}I^-$ were detected at ~2.5 min and ~8.5 min respectively, after injection (Figure 3.1). Peaks for Mn and Fe were detected at ~7.5 and ~9 min, respectively, indicating that the addition of Na_2-EDTA to the mobile-phase successfully prevented the precipitation of Mn and Fe hydroxides in the guard column (Figure 3.2) and both metals were successfully eluted as a single EDTA complex. Using the shorter (50 x 4.1 mm) anion exchange column, iodate and iodide peaks were detected at ~0.5 and ~2.25 min, respectively (Figure 3.3). Peaks for Cr^{III}, Cr^{VI}, As^{III}, As^{V}, Se^{IV}, and Se^{VI} were detected with no apparent overlap between species of an individual element. For antinomy, only a single (Sb^{V}) peak was detected, followed by an elevated baseline, indicating possible oxidation of Sb^{III} within the column (Figure 3.4). Although fully resolved from Cr^{VI}, chromite (Cr^{III}) peaks showed poor repeatability and inconsistency between runs. It has been reported that, for Cr^{III} ions to be recovered using an anion-exchange column, chelation with a chelating agent like EDTA is necessary as Cr^{III} ions may precipitate at the high pH of the eluent solution (Byrdy et al., 1995; Gurleyuk and

Wallschlager, 2001; Inoue et al., 1995). Inoue et al. (1995) also demonstrated that the formation of the EDTA complex is a slow process. Accordingly, a Cr^{III} standard was prepared in 10^{-2} M Na_2-EDTA solution and left for approximately 16 hours to allow for the formation of the Cr^{III}-EDTA complex.

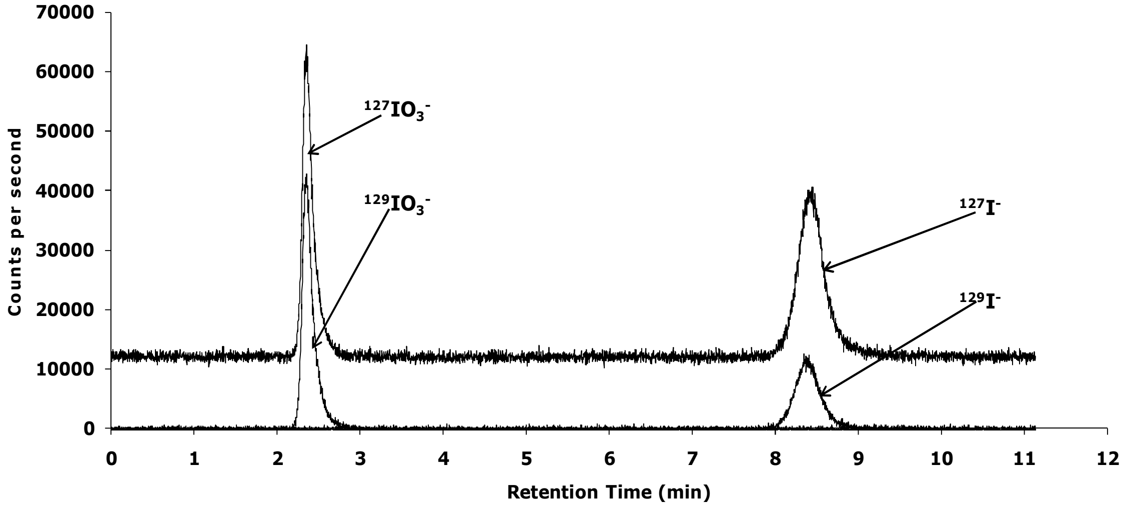


Figure 3.1 HPLC-ICP-MS chromatographs of standard solutions containing 30 μg L^{-1} of $^{127,129}IO_3^-$ and $^{127,129}I^-$. The mobile phase used was 60 mM L^{-1} NH_4NO_3 with $1x10^{-5}$ mM L^{-1} Na_2-EDTA and 2% methanol; the pH was adjusted to 9.5 with TMAH. The column used was a Hamilton PRP-X100 system (250 x 4.6 mm; 5 μm particle size)

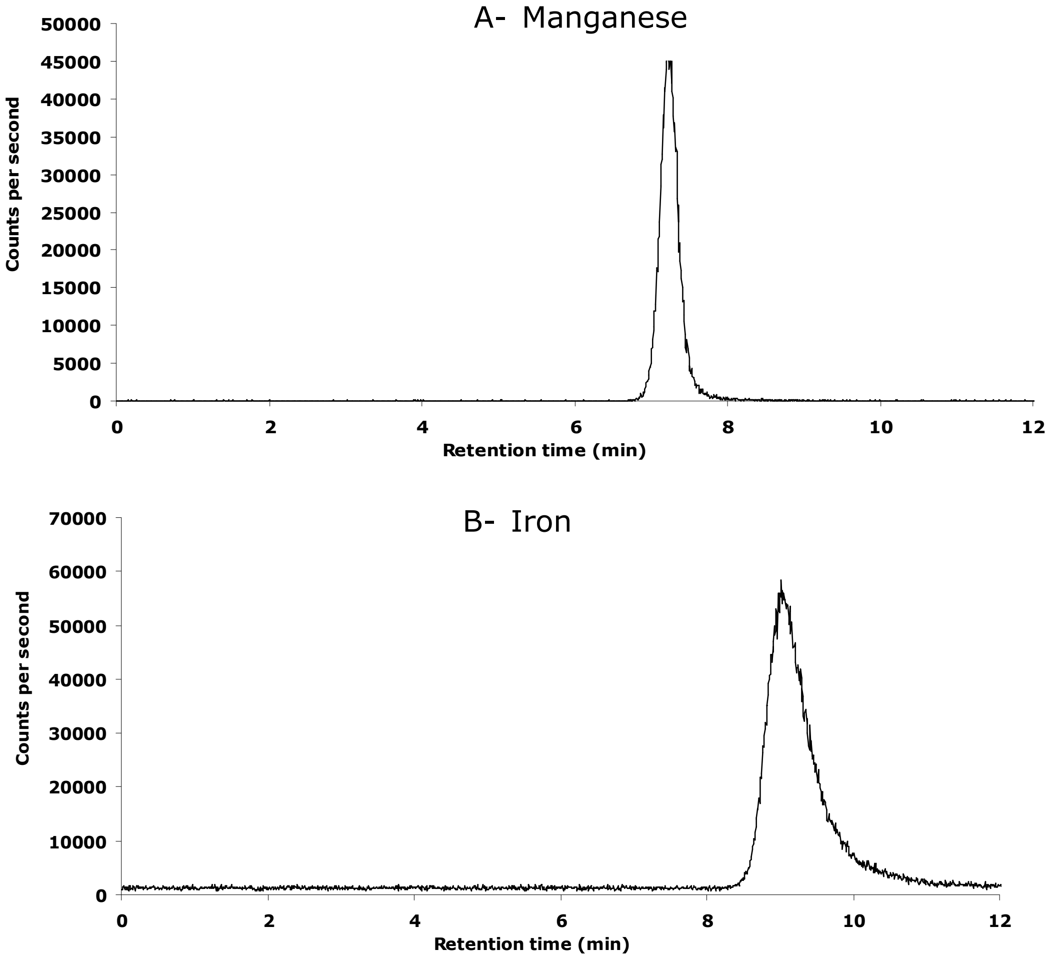


Figure 3.2 HPLC-ICP-MS chromatographs of standard solutions containing 30 μg L^{-1} of (A) Mn and (B) Fe. The mobile phase used was 60 mM L^{-1} NH_4NO_3 with $1x10^{-5}$ mM L^{-1} Na_2-EDTA and 2% methanol; the pH was adjusted to 9.5 with TMAH. The column used was a Hamilton PRP-X100 system (250 x 4.6 mm; 5 μm particle size)

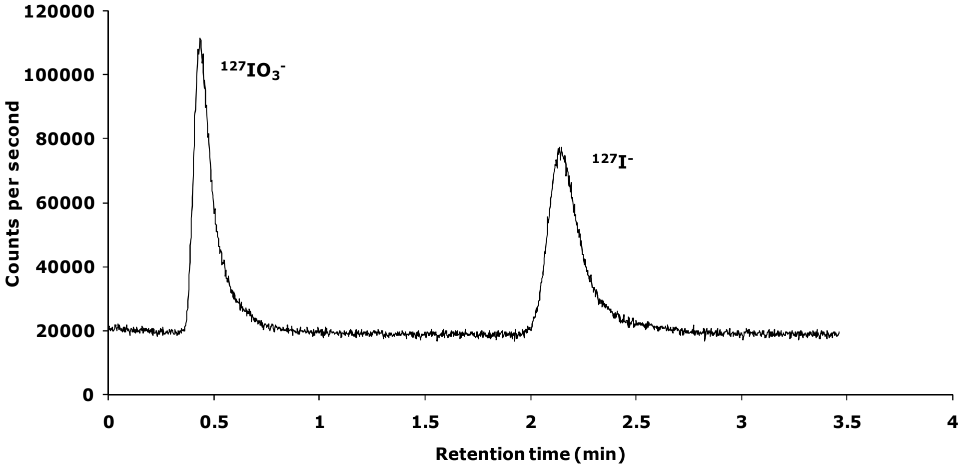


Figure 3.3 HPLC-ICP-MS chromatographs of a standard solution containing 30 μg L^{-1} of $^{127}IO_3^-$ and $^{127}I^-$. The mobile phase was 60 mM L^{-1} NH_4NO_3 with $1x10^{-5}$ mM L^{-1} Na_2-EDTA and 2% methanol; the pH was adjusted to 9.5 with TMAH. The column used was a Hamilton PRP-X100 system (50 x 4.1 mm; 5 μm particle size)

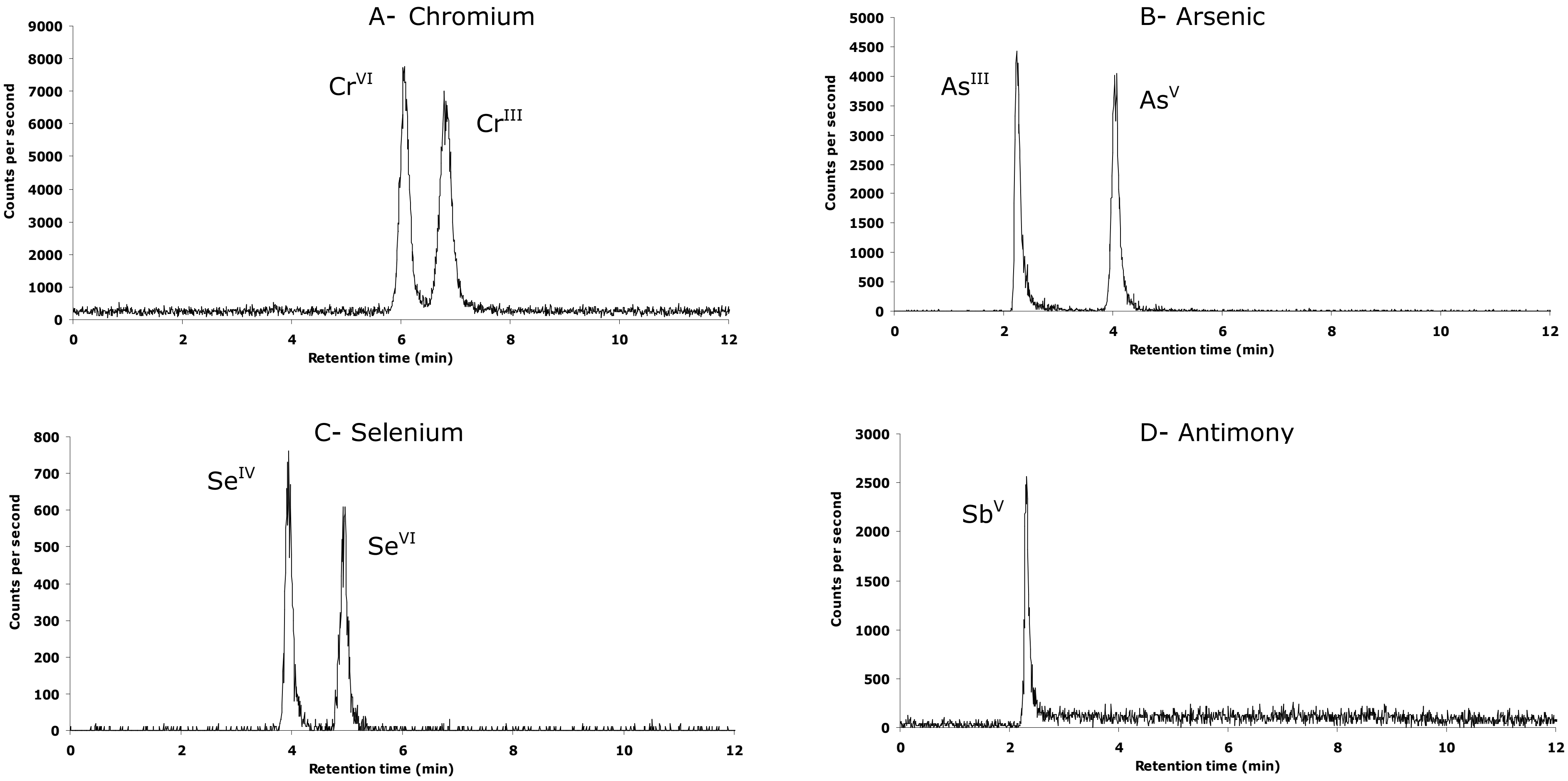


Figure 3.4 HPLC-ICP-MS chromatographs of a standard solution containing 50 μg mL^{-1} of (A) Cr^{III} and Cr^{VI}, (B) As^{III} and As^{V}, (C) Se^{IV} and Se^{VI}, and (D) Sb^{III} and Sb^{V}. The mobile phase used was 60 mM L^{-1} NH_4NO_3 with 1x10^{-5} mM L^{-1} Na_2-EDTA and 2% methanol; the pH was adjusted to 9.5 with TMAH. The column used was a Hamilton PRP-X100 system (250 x 4.1 mm; 5 μm particle size)

3.3.2 ICP-MS Internal Standards for Iodine Analysis

Both iodide and iodate peaks were detected at the expected retention times which indicates that neither Cs or In formed any complexes with iodine species. Moreover, the Cs signal was detected at a significantly shorter retention time than that of In signal indicating that Cs has less affinity for the column (Figure 3.5).

In practical application, however, when Cs was added to the mobile-phase, the Cs signal showed a high degree of instability which was reflected in the iodine chromatograms when correction with the Cs internal standard was implemented. Accordingly no internal standards were applied in the speciation analysis, and correction for instrumental drift was implemented manually using repeated runs of iodine species standards (see Chapter2; section 2.10.4). This approach only corrects for long term drift rather than matrix differences between samples. However, the latter are likely to be minimal in HPLC-ICP-MS due to the separation process.

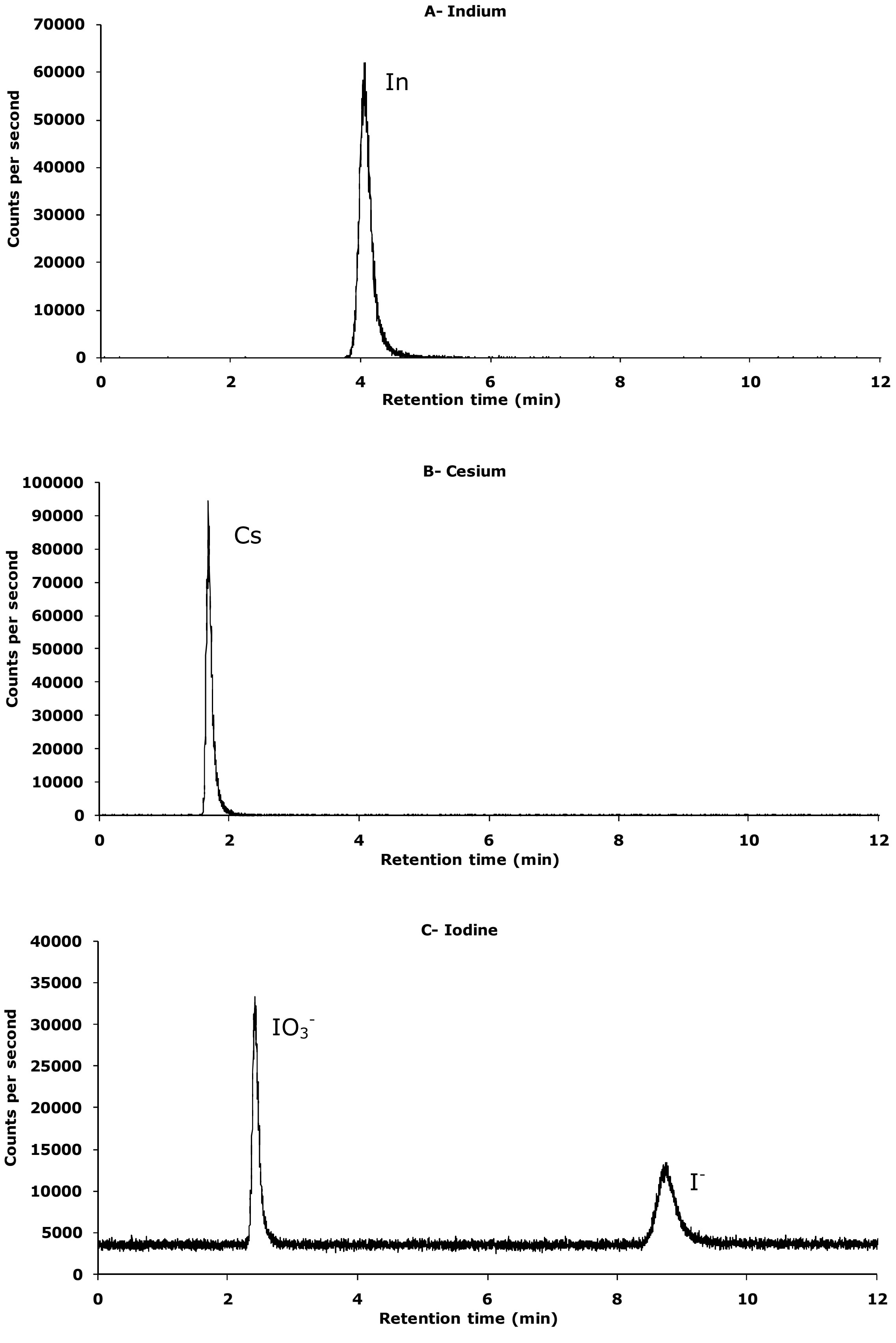


Figure 3.5 HPLC-ICP-MS chromatographs of a standard solution containing 20 μg mL^{-1} of (A) In, (B) Cs, and (C) I$^-$ and IO$_3^-$. The mobile phase used was 60 mM L^{-1} NH$_4$NO$_3$ with 1x10^{-5} mM L^{-1} Na$_2$-EDTA and 2% methanol; the pH was adjusted to 9.4 with TMAH.

3.3.3 Mass Discrimination Factor (K-factor) for ^{127}I and ^{129}I Isotopes

The sensitivities of each individual standard were calculated by dividing the total analyte counts per second by the standard concentration (μg L^{-1}). The average sensitivities were found to be (12872 ± 29) cps (μg L^{-1}) for ^{127}I and (11864 ± 65) cps ppb^{-1} for ^{129}I, giving a mass discrimination factor of 1.085 (^{127}I:^{129}I) (Table 3.2.).

Table 3.2
Estimation of ^{127}I:^{129}I mass discrimination factor (K-factor)

Isotope	Inorganic Form	Conc. (μg L^{-1})	Total CPS	Sensitivity (CPS)	Average Sensitivity (CPS)	^{127}I:^{129}I Mass Factor
^{127}I	^{127}I^{-}	10	127771	12777	12871 ± 29	1.085
		20	259293	12964		
		30	383000	12766		
		40	515148	12878		
	^{127}IO$_3^-$	10	128577	12857		
		20	257663	12883		
		30	385302	12843		
		40	520156	13003		
^{129}I	^{129}I^{-}	10	120474	12047	11863 ± 65	
		20	240029	12001		
		30	361135	12037		
		40	480286	12007		
	^{129}IO$_3^-$	10	116663	11666		
		20	231588	11579		
		30	355021	11834		
		40	469450	11736		

3.3.4 Oxidation of Iodide to Iodate

As shown in Table 3.3, iodide prepared in 0.01 M NaOH solution, was not completely oxidised to iodate; moreover, there was ~45-47% loss in total iodine. On the other hand, in the iodide solution prepared in mQ water, iodide was fully transformed to iodate with almost 95-99% recovery of total iodine. However, some iodide (~7%) was detected with the lowest concentration of oxidizing agent. Iodide can be oxidised to iodate using various oxidising agents; the oxidation process normally involves the production of several intermediate products covering the oxidation states range from +1 to +5, with molecular iodine (I_2) believed to be the most important intermediate (Yntema and Fleming, 1939; Melichercik et al., 1997; Schmitz, 2001). The rate of the oxidation reaction was found to be inversely proportional to pH and directly proportional to the concentration and strength of the oxidising agents (Allard et al., 2009; Fox et al., 2009; Gallard et al., 2009). The partial transformation of iodide to iodate and the loss of 45-47% of total iodine that occurred in the highly alkaline iodide solution suggests that the high pH of the medium suppressed oxidation and allowed the persistence of molecular iodine and hence loss by volatilisation as I_2.

Accordingly, it was concluded that the $^{129}I^-$ standard (in 0.01 M NaOH) had to be neutralized before being oxidized to $^{129}IO_3^-$. The buffer solution was therefore omitted and neutralization was achieved by addition of an equivalent amount of concentrated HCl; the oxidising agent was added in excess. This oxidation approach (Chapter 2; section 2.11) was applied successfully to the $^{129}I^-$ stock standard. Results showed that $^{129}I^-$ was fully transformed to $^{129}IO_3^-$ with 100% recovery of total ^{129}I.

Table 3.3

Oxidation efficiency of iodide solution (25 mg L^{-1}) in different reaction matrices (0.01 M NaOH or mQ water) and using different concentrations of oxidising agent (0.2 M sodium chlorite); the buffer solution was 0.2M acetic acid in 2 M sodium acetate.

Matrix	Iodide (25 mg L^{-1}) (mL)	Buffer solution (mL)	Oxidising agent (mL)	Recovery (total I) (%)	Recovery (as iodate) (%)	Recovery (as iodide) (%)
0.01M NaOH	5	5	1	53.8	53.2	0.00
	5	0	1	55.1	17.1	19.3
	5	0	0.1	54.8	0.00	51.3
mQ Water	5	5	1	98.8	94.8	0.00
	5	0	1	100	99.5	0.42
	5	0	0.1	100	95.2	7.29

4. IODINE FRACTIONATION IN SOIL

4.1 INTRODUCTION

4.1.1 Iodine in Soil and Soil Profiles

Iodine in soils has been studied extensively and a worldwide average concentration in surface soils reported to be ~5 mg kg^{-1} (Fleming, 1980; Ure and Berrow, 1982). Whitehead (1979) investigated the total iodine content in several UK soils and found it ranged from 0.5 to 98.2 mg kg^{-1}. Whitehead (1978) also investigated the vertical distribution of iodine in several UK soils down to 100 cm depth and found that iodine concentrations varied with soil type. The highest iodine concentrations were associated predominantly with iron and aluminium content rather than with soil organic matter. Yuita and Kihou (2005) studied iodine depth profiles in three Japanese soils and observed higher concentrations in topsoil compared to subsoil especially where the subsoil was more reducing. By contrast, in flooded paddy fields iodine concentration was low in the topsoil where the conditions were strongly reducing and increased with depth where conditions were mildly oxidative. Strong correlations were found between soil iodine and sesquioxide content which was attributed to the scavenging characteristics of soil metal oxyhydroxides for inorganic iodine forms (Whitehead, 1973a, 1974b, 1978; Ullman and Aller, 1985; Fukui et al., 1996; Dai et al., 2004; Um et al., 2004). Sorption of iodide and iodate on Fe and Al oxides is favourable under oxidative conditions. Under reducing conditions, dissolution of metal oxyhydroxides releases sorbed iodine (Ullman and Aller, 1985; Yuita et al., 1991; Yuita, 1992; Muramatsu et al., 1996; Bird and Schwartz, 1997; Ashworth et al., 2003; Ashworth and Shaw, 2006;

Yamaguchi et al., 2006). Close association of iodine with soil organic matter has also been widely reported leading to the conclusion that soil iodine is mainly organically-bound (Whitehead, 1973a; Francois, 1987a; Fukui et al., 1996; Sheppard et al., 1996; Yu et al., 1996; Steinberg et al., 2008 a,b). Francois (1987a) proposed that the observed decrease in iodine concentrations with depth in a typical soil could alternatively be a result of reduction of weakly organic-bound iodine to iodide at low redox potentials resulting in the release of iodine from soils into the soil solution.

4.1.2 Extraction and Fractionation of Soil Iodine

Extraction with tetra methyl ammonium hydroxide (TMAH) has recently become the favoured extractant for leaching iodine from solid environmental samples. Although iodate and organically-bound iodine are strongly fixed to soil (Yamada et al. 1996a), alkaline solutions such as TMAH are able to extract soil organic matter and, consequently, organically-bound iodine. Iodate is also released from sorption sites on Fe/Al hydrous oxides by replacement with hydroxide ions.

The inverse relationship between the sorption of iodide and/or iodate and soil pH (Whitehead, 1973a, 1974b, 1978; Fukui et al., 1996; Dai et al., 2004; Um et al., 2004) resembles that of other anions known to be non-specifically sorbed on soils such as Cl^-, NO_3^-, and SO_4^{2-} and those specifically adsorbed with low pKa values, such as F^- and PO_4^{3-}. Phosphate (PO_4^{3-}) is strongly adsorbed by aluminum and iron oxides and, therefore, can be used as an extractant for other ions of equal or lower adsorption affinity such as sulphate and iodine (Whitehead, 1973b;

Gerke, 1993; Geelhoed et al., 1997; Borggaard et al., 2005; Delfosse et al., 2005).

The role of soil microorganisms in soil iodine retention has been investigated by several workers (Koch et al., 1989; Bors and Martens, 1992; Assemi and Erten, 1994; Sheppard et al., 1996; Bird and Schwartz, 1997; Yamaguchi et al., 2006, 2010). However, the relative importance of soil microorganisms in the assimilation of soil iodine is a matter of disagreement.

4.1.3 Aims

To understand iodine fractionation in soils with different pH values, oxide concentration and organic matter contents, the total concentration of iodine in soils and soil profiles was measured by ICP-MS following extraction using TMAH. In profiles, the variation of total soil iodine concentration with depth relative to soil carbon was investigated. Moreover, the effects of the experimental conditions such as TMAH concentration, extraction temperature and extraction time on the extraction efficiency of total soil iodine and iodine speciation was also tested.

The use of PO_4^{3-} to extract adsorbed iodide and iodate and the effect of the extraction conditions (PO_4^{3-} concentration and extraction time) on iodine speciation was studied. In addition, a method of separately detecting biomass iodine (i.e. iodine present within soil microorganisms) by fumigation of soil with chloroform was also investigated to understand the potential size of the biomass iodine pool.

4.2 EXPERIMENTAL

4.2.1 Extraction of Iodine from Soil and Soil Profiles

Soils were sampled from an arable field of University of Nottingham farm, Leicestershire (52°49′48″N-1°14′88″W) and from the adjacent mature woodland and permanent grassland. Two samples were taken from the woodland and arable soils: topsoil (0-20cm depth) and subsoil (30-50 cm depth). Only a topsoil sample was taken from the grassland. Soil profiles were also sampled at two different locations in the arable field and the adjacent woodland by sampling consecutive 10 cm horizons down to 100 cm depth. Samples were air-dried, homogenised and finely ground (see section 2.1). Finely ground or sieved soils (<2 mm) were used to measure pH, (carbon and nitrogen content) and total iodine content as described in sections 2.2, 2.5. and 2.10, respectively.

4.2.2 Extraction and Speciation of Soil Iodine

4.2.2.1 Extraction with TMAH

The efficiency of TMAH extraction of soil iodine (see section 2.10.1.) was tested by extracting iodine from finely ground reference materials and measuring total iodine concentration using ICPMS. To test whether the efficiency of iodine extraction was related to particle size simultaneous extractions of sieved and ground soils were undertaken. The standard method as described in section 2.10.1 was used except that 2 g of sieved soil (<2mm) was extracted with 20 mL of 10% TMAH solution in polycarbonate centrifuge tubes.

There is evidence that TMAH extraction methods that include heating may result in thermal decomposition of organically-bound iodine and consequently alter the original speciation (Yamada et al., 1999). This was tested by HPLC-ICP-MS analysis of TMAH extracts. The efficiency of TMAH extraction at room temperature was also examined over a range of TMAH concentrations. Soil samples (2 g) were suspended in 20 mL of 5%, 10%, 15% and 20% TMAH solutions in polycarbonate centrifuge tubes and shaken reciprocally for 16 h at 200 rpm. The effect of TMAH concentration on ambient extraction of iodine was also tested on the woodland topsoil over a wide range of TMAH concentrations (0, 0.001, 0.01, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 3, 4, 5, and 10%).

The effect of heated and ambient TMAH extraction on iodide/iodate solutions and humic acid together with a test of the recovery of iodide and iodate spikes added to humic acid and soils was also investigated. Two sets of centrifuge tubes containing various combinations of iodide, iodate, humic acid, soil and TMAH solution (for extraction) were prepared as detailed in Table 4.1. The first group of suspensions was placed in an oven at 70°C for 3 hours and tubes were shaken at 1.5 h. The second set of tubes was shaken at room temperature on a reciprocal shaker for 16 hours.

After extraction, all tubes were centrifuged (20 min at 3000 g) and the supernatant was filtered (<0.22 µm). Solutions were then analysed for total ^{127}I and speciated for ($^{127}I^-$ and $^{127}IO_3^-$) using ICP-MS and HPLC-ICP-MS as described in section 2.10.

Table 4.1
Sample constituents

Sample	Iodide (μg)	Iodate (μg)	Humic Acid (g)	Woodland Subsoil (g)	Arable Topsoil (g)	TMAH (10%) (mL)
Sample 1	1	0	0	0	0	10
Sample 2	0	1	0	0	0	10
Sample 3	1	1	0	0	0	10
Sample 4	0	0	0.25	0	0	10
Sample 5	1	0	0.25	0	0	10
Sample 6	0	1	0.25	0	0	10
Sample 7	1	1	0.25	0	0	10
Sample 8	0	0	0	2	0	20
Sample 9	2	0	0	2	0	20
Sample 10	0	2	0	2	0	20
Sample 11	0	0	0	0	2	20
Sample 12	2	0	0	0	2	20
Sample 13	0	2	0	0	2	20

In some experiments the pH of the supernatant was measured (see section 2.2.) and in others the fulvic acid concentration was determined spectrophotometrically as detailed in section 2.7. All samples, standards and blanks were prepared in triplicate.

4.2.2.2 Extraction with Potassium Di-hydrogen Phosphate

To investigate the success of PO_4^{3-} extraction of adsorbed iodide and/or iodate , soil samples (2 g; <2mm sieved) of woodland subsoil and arable topsoil were suspended in 20 mL of 0.005, 0.01, 0.05 and 0.1 M KH_2PO_4 solutions and shaken on a reciprocal shaker for 16 h at room temperature. Recovery of spiked $^{129}I^-$ and $^{129}IO_3^-$ was also tested using a range of KH_2PO_4 concentrations. Sieved (<2mm) woodland subsoil and arable topsoil samples (2 g) were suspended in 20 mL of 0.01, 0.05 and

0.1 M KH_2PO_4 solutions in polycarbonate centrifuge tubes and then shaken on a reciprocal shaker for 16 h. Suspensions were spiked with $^{129}I^-$ or $^{129}IO_3^-$ (0.2 mg kg^{-1} soil) and shaken again for 24 hours. Two further identical sets of tubes were shaken for 48 and 72 hours to test the effect of time on extraction. All samples were prepared in triplicate and after extraction centrifuged (25 min at 3500 g) filtered (0.22 µm) and analysed for total ^{127}I and ^{129}I concentration and speciated (HPLC-ICP-MS) to determine $^{127}I^-$, $^{127}IO_3^-$, $^{129}I^-$ and $^{129}IO_3^-$ (see section 2.10.).

4.2.2.3 Extraction of soil biomass iodine

Arable and woodland top and sub soils were prepared, fumigated, extracted and assayed for biomass carbon and nitrogen as described in section 2.8. A second set of samples was extracted with 0.2 M KH_2PO_4. Total ^{127}I concentration was determined in the filtered extracts of the fumigated and the non-fumigated soils by ICP-MS (section 2.10).

4.3 RESULTS AND DISCUSSION

4.3.1 Iodine in Soils and Soil Profiles

Soil properties are given in Table 4.2. Woodland and grassland topsoils have the highest organic matter content (4.6-5 % C). Lowest carbon contents were recorded in the subsoils. Soil pH was low (~ pH 4.5) in the woodland and grassland soils and ~ pH 6 in the arable soils. Total soil iodine concentrations were mainly in the range 2 - 3 mg kg^{-1}, lower than the worldwide average of 5 mg kg^{-1} (Fleming, 1980; Ure and Berrow, 1982) and the UK average of 9.2 mg kg^{-1} (Whitehead, 1979).

Table 4.2
Soil characteristics

Soil	pH	C (%)	N (%)	Iodine Content (mg/kg)
Woodland Topsoil	4.8	5.01	0.36	3.11 ± 0.07
Woodland Subsoil	4.3	1.17	0.08	2.05 ± 0.04
Arable Topsoil	6.5	1.98	0.16	2.99 ± 0.04
Arable Subsoil	6.9	0.43	0.04	2.85 ± 0.02
Grassland Topsoil	4.7	4.59	0.35	2.83 ± 0.15

Concentration of iodine typically decreased with depth (Figure 4.1). This agrees with other studies (e.g. Whitehead (1978)) which have also observed a decrease in iodine with depth, especially in soils with high organic content in the top layers, and indicates that the majority of iodine is retained in the topsoil. In addition, reductive release of soil iodine to soil solution in deep soil horizons is described by many studies (Yuita et al., 1991; Yuita, 1992; Muramatsu et al., 1996; Bird and Schwartz, 1997; Yuita and Kihou, 2005; Ashworth and Shaw, 2006; Yamaguchi et al., 2006) which may result in depletion from the subsoil. Although iodine concentration decreased with depth the iodine : carbon ratio increased with depth for both soils (Figure 4.2) demonstrating that whilst the majority of iodine reaching soils (e.g. via rainfall) is retained in the top soil the smaller amounts of humus present at depth have a crucial role in scavenging and retaining iodine within the soil profile. Coupled with the continuous input of fresh organic matter at the surface the overall pattern suggests a greater soil residence time for iodine than for organic carbon. Thus iodine moving beyond the topsoil during rainfall or drainage events appears to be effectively retained in the deeper soil horizons by the substantial adsorption capacity provided by relatively small amounts of humus.

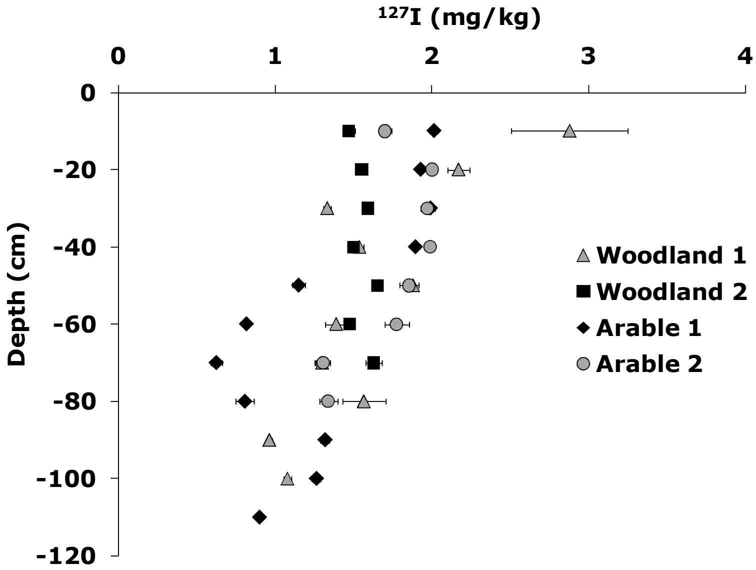


Figure 4.1. Total iodine concentration as a function of depth in woodland and arable soil profiles.

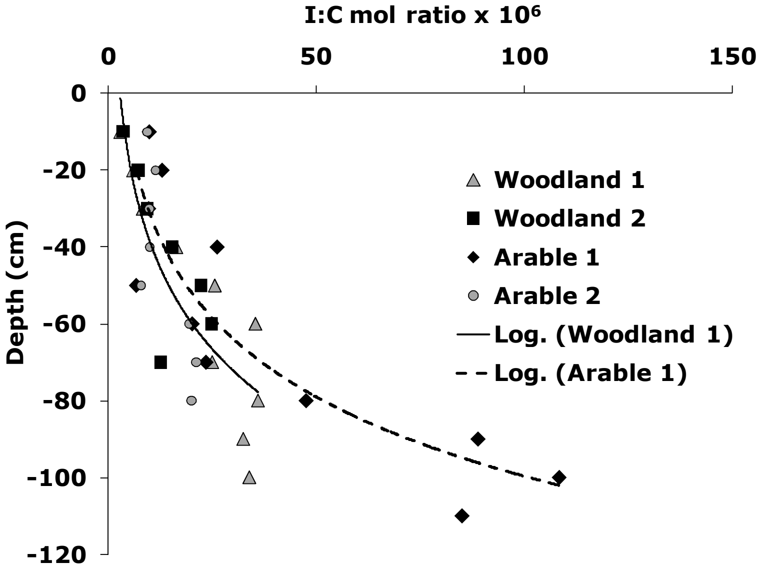


Figure 4.2. Mole ratio (x 10^6) of iodine to organic carbon as a function of depth in woodland and arable soil profiles.

4.3.2 Extraction and Speciation of Soil Iodine

4.3.2.1 Extraction with TMAH

Total iodine concentrations determined for the certified reference materials showed good agreement with the certified values (Table 4.3). In most of the soils the agreement was comparable to the results obtained by Watts and Mitchell (2009) where the extraction method was developed. However, in the current work and in Watts and Mitchell (2009) the results obtained for the reference material GSS 8 (loess) were, respectively, 20% and 32% less than the certified concentrations suggesting that for some soils/materials more rigorous extraction procedure may be required.

Table 4.3

Certified and measured iodine concentrations in standard reference materials after extraction with 5% TMAH at 70°C. Results are the average of three replicates.

Reference Material	^{127}I Measured (current work) (mg kg^{-1})	^{127}I Measured (Watts and Mitchell, 2008) (mg kg^{-1})	^{127}I Certified (mg kg^{-1})
GSS 2 (chestnut soil)	1.67 ± 0.01	1.6 ± 0.2	1.8 ± 0.2
GSS 3 (yellow-brown soil)	1.32 ± 0.01	1.3 ± 0.1	1.3 ± 0.4
GSS 5 (yellow-red soil)	3.61 ± 0.03	3.5 ± 0.4	3.8 ± 0.5
GSS 6 (yellow-red soil)	21.4 ± 0.26	20.6 ± 1.5	19.4 ± 1
GSS 7 (laterite)	18.9 ± 0.09	17.3 ± 0.6	19.3 ± 1.1
GSS 8 (loess)	1.27 ± 0.01	1.1 ± 0.1	1.6 ± 0.5

Comparing finely ground and <2mm sieved soil the latter produced approximately 94-98% recovery (Figure 4.3) suggesting that the degree of surface exposure had a minor but measurable effect. Speciation analysis (HPLC-ICP-MS) indicated that iodide was the only inorganic species present, ranging in ground soils from 0.69 to 1.55 mg kg^{-1}, and in <2mm sieved soils between 0.74 and 1.42 mg kg^{-1} (Table 4.4). The concentration ratio of iodide : total iodine varied between soils with the lowest ratios in ground and sieved soils found in the arable topsoil and the arable subsoil, respectively (Table 4.4). The highest ratios were observed in the highly organic woodland topsoil and grassland topsoil. The results suggest that soil particle size has little influence on the total concentration of iodine extracted by 5% TMAH extraction (at 70°C) or the observed speciation of iodine in the extract solution.

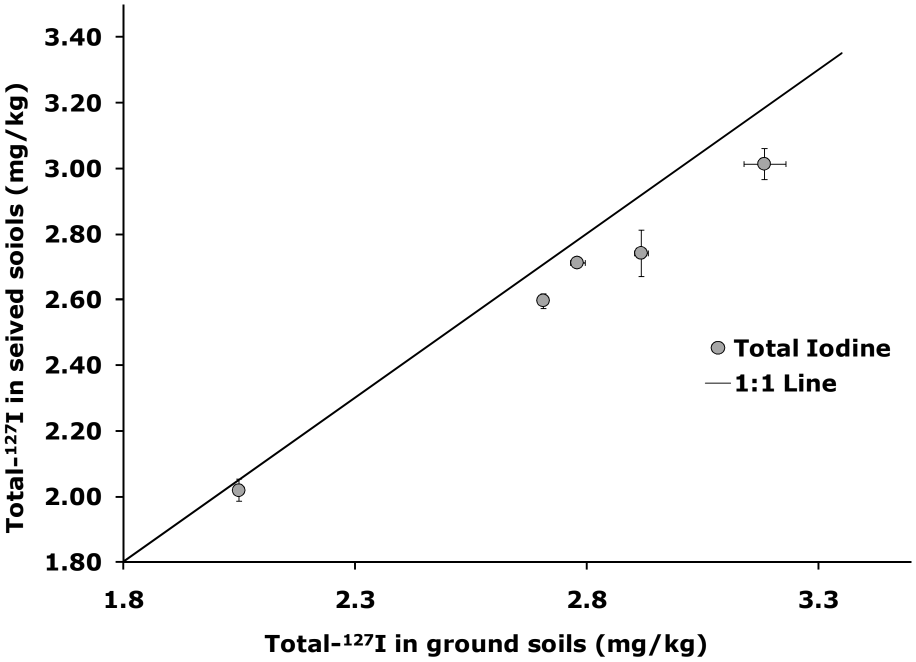


Figure 4.3. Total extracted iodine concentrations (mg kg^{-1}) from finely ground soils and <2 mm sieved soils; the extraction was carried out with 5% TMAH at 70°C.

Table 4.4

Iodide and total ^{127}I concentrations measured in TMAH extracts of both <2 mm sieved and finely ground soils; the extraction was carried out with 5% TMAH at 70^{o}C.

Soil	Ground soils		Sieved soils	
	$^{127}I^{-}$ (mg kg^{-1})	Total-^{127}I (mg kg^{-1})	$^{127}I^{-}$ (mg kg^{-1})	Total-^{127}I (mg kg^{-1})
Woodland topsoil	1.55 ± 0.03	3.18 ± 0.04	1.42 ± 0.04	3.01 ± 0.05
Woodland subsoil	0.69 ± 0.03	2.05 ± 0.00	0.74 ± 0.00	2.02 ± 0.03
Arable topsoil	0.88 ± 0.04	2.92 ± 0.01	1.06 ± 0.03	2.74 ± 0.07
Arable subsoil	0.96 ± 0.04	2.78 ± 0.02	0.83 ± 0.01	2.71 ± 0.01
Grassland topsoil	1.09 ± 0.05	2.71 ± 0.01	1.16 ± 0.07	2.60 ± 0.02

Temperature and TMAH concentrations greater than 5% (10, 15 and 20%) also had negligible impact on the total iodine extracted from different soils (Table 4.5 and Figure 4.4). Typically no change in total iodine content was observed when TMAH concentration was increased with the possible exception of the arable subsoil where an increase in the total ^{127}I extracted was discernable ($P << 0.05$). The maximum total iodine concentrations extracted at ambient temperatures ranged from 95 to 115% of the concentrations measured using 5% TMAH as the extractant at 70^{o}C (Tables 4.4 and 4.5). This suggests that soil iodine can be effectively extracted with 5% TMAH at room temperature. Speciation of the extracts showed that iodide was the only inorganic species present and this represented 20 to 30% of total iodine, lower percentages than obtained using 70^{o}C extraction (31%-48%). This difference suggests that iodide may be produced by thermally assisted hydrolysis of organically bound iodine during heating.

Table 4.5

Iodide and total iodine concentrations in soil extracts; extraction was carried out using different concentrations of TMAH by shaking for 16 h at room temperature.

Soil	TMAH (%)	Iodide (mg kg^{-1})	Total Iodine (mg kg^{-1})
Woodland Topsoil	5	0.84 ± 0.04	2.94 ± 0.09
	10	0.92 ± 0.01	3.13 ± 0.04
	15	0.84 ± 0.02	2.95 ± 0.06
	20	0.98 ± 0.06	3.12 ± 0.02
Woodland Subsoil	5	0.49 ± 0.01	2.14 ± 0.04
	10	0.48 ± 0.03	2.19 ± 0.04
	15	0.54 ± 0.01	2.18 ± 0.03
	20	0.59 ± 0.07	2.13 ± 0.07
Arable Topsoil	5	0.60 ± 0.03	2.50 ± 0.02
	10	0.59 ± 0.01	2.49 ± 0.02
	15	0.65 ± 0.03	2.58 ± 0.02
	20	0.61 ± 0.06	2.63 ± 0.04
Arable Subsoil	5	0.47 ± 0.00	2.35 ± 0.02
	10	0.52 ± 0.01	2.47 ± 0.01
	15	0.56 ± 0.01	2.61 ± 0.04
	20	0.60 ± 0.03	2.62 ± 0.02
Grassland Topsoil	5	0.72 ± 0.01	2.65 ± 0.03
	10	0.88 ± 0.05	2.80 ± 0.05
	15	0.99 ± 0.04	3.01 ± 0.10
	20	0.83 ± 0.04	2.86 ± 0.06

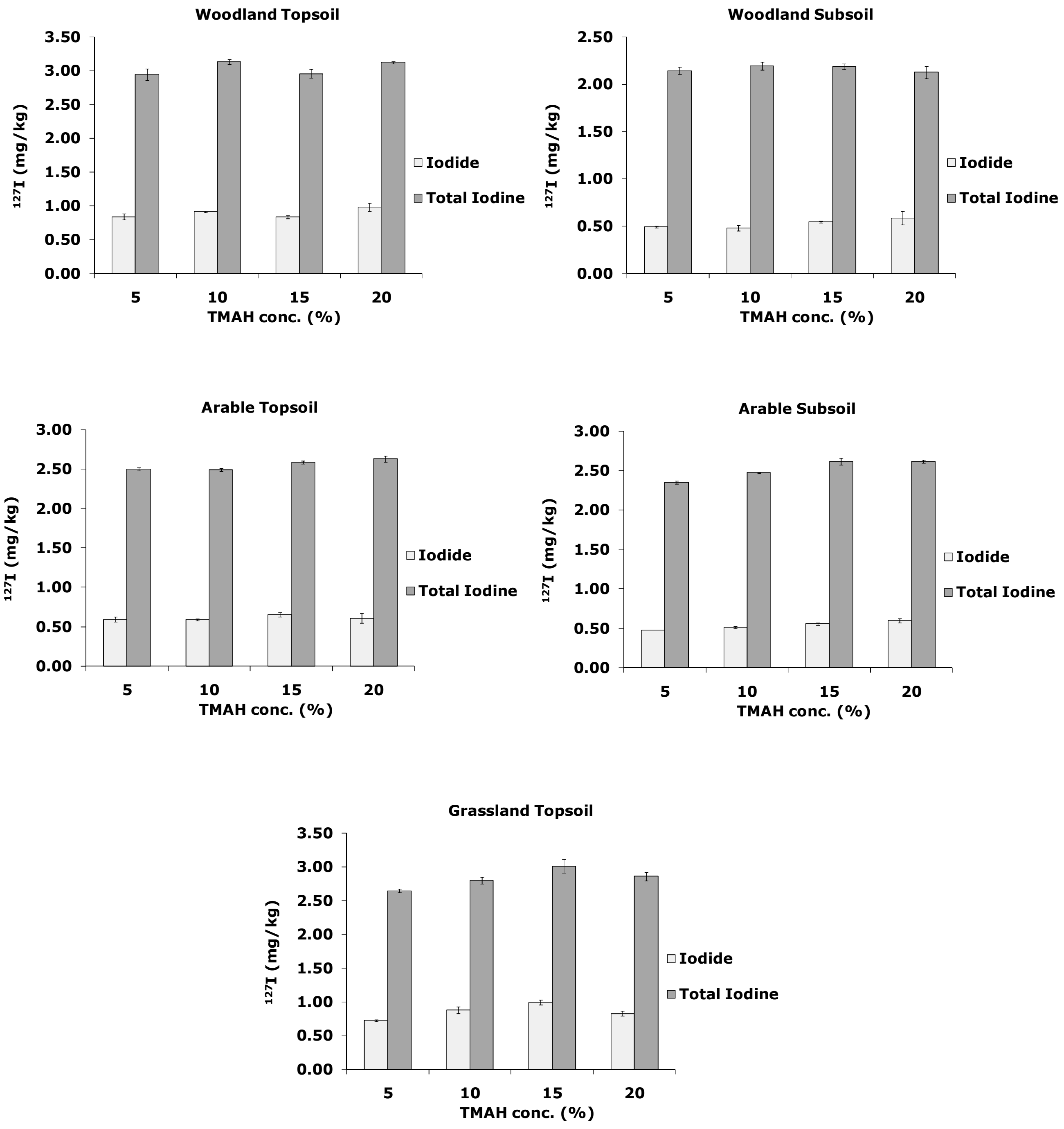


Figure 4.4. Iodide and total iodine concentrations in soil extracts of woodland topsoil, woodland subsoil, arable topsoil, arable subsoil and grassland topsoil; extraction was carried out using a range of concentrations of TMAH by shaking for 16 h at room temperature.

It is not clear however if extraction at ambient temperature conserves the original speciation of solid phase iodine or, if it too releases organically bound iodine as iodide, but to a lesser extent than when heated.

A more detailed study of the effect of TMAH concentration on iodine extraction and iodine speciation in the organic woodland topsoil is shown in Table 4.6. Concentration of extracted iodine increased slightly from 0.14 to 0.2 mg kg^{-1} over the TMAH concentrations range of 0-0.01% (pH 4.85-5.35) before increasing substantially to 1.7 mg kg^{-1} at a TMAH concentration of 0.1% (pH 8.23), the first extraction where pH was alkaline (Figure 4.5 and Table 4.6). As TMAH concentration was further increased (0.2-10%) a further slight increase in extracted iodine (2.4-2.75 mg kg^{-1}) was observed.

No iodate was detected in the extracts. Iodide concentrations ranged from 0.006-0.723 mg kg^{-1} (4 -26% of total iodine) and followed the trend for total iodine with concentrations increasing with pH value. The strength of iodide and iodate sorption on hydrous oxides of iron and aluminium is inversely proportional to pH due to the loss of positively charged sites and competition with hydroxyl ions in alkaline medium (Whitehead, 1973a; Muramatsu et al., 1990). Consequently, most of the sorbed iodide in soil is expected to be released by alkaline extraction solution.

Table 4.6

Concentrations of total iodine, organic iodine (calculated by subtracting iodide from total iodine), iodide, and fulvic acid extracted from woodland topsoil by different concentrations of TMAH. Samples were extracted by shaking for 16 h at room temperature.

TMAH	pH	$^{127}I^-$ (mg kg^{-1})	Total-^{127}I (mg kg^{-1})	Organic Iodine (mg kg^{-1})	FA (mg kg^{-1})
0	4.8	0.006 ± 0.001	0.14 ± 0.002	0.133 ± 0.003	1390 ± 26
0.001	4.8	0.015 ± 0.004	0.15 ± 0.002	0.132 ± 0.006	1370 ± 42
0.01	5.3	0.011 ± 0.001	0.19 ± 0.006	0.179 ± 0007	1750 ± 98
0.1	8.2	0.075 ± 0.002	1.74 ± 0.016	1.660 ± 0.017	24200 ± 404
0.2	10.9	0.288 ± 0.022	2.34 ± 0.023	2.050 ± 0.045	39800 ± 326
0.4	12.4	0.399 ± 0.022	2.46 ± 0.031	2.057 ± 0.018	45000 ± 367
0.6	12.7	0.410 ± 0.042	2.41 ± 0.046	1.999 ± 0.013	45500 ± 1080
0.8	13	0.486 ± 0.02	2.46 ± 0.006	1.971 ± 0.017	47100 ± 536
1	13	0.500 ± 0.012	2.41 ± 0.034	1.907 ± 0.037	46000 ± 877
2	13.3	0.537 ± 0.004	2.49 ± 0.048	1.953 ± 0.049	47600 ± 1100
3	13.6	0.591 ± 0.023	2.59 ± 0.050	1.996 ± 0.03	49100 ± 2260
4	13.7	0.635 ± 0.025	2.61 ± 0.035	1.971 ± 0.036	48800 ± 319
5	13.8	0.668 ± 0.016	2.69 ± 0.026	2.025 ± 0.012	48500 ± 1160
10	14	0.723 ± 0.006	2.76 ± 0.055	2.037 ± 0.058	51000 ± 1840

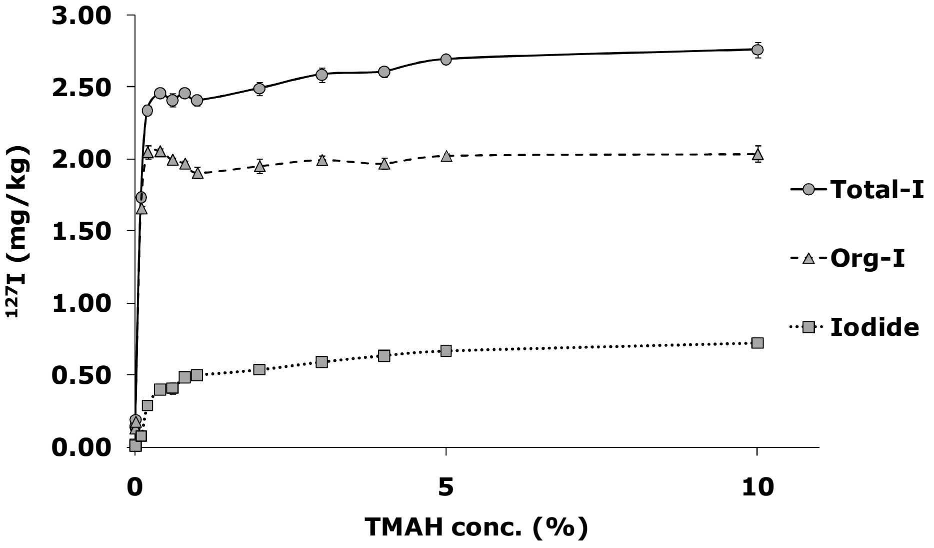


Figure 4.5. Total iodine, organic iodine (calculated by subtracting iodide from total iodine), and iodide concentrations extracted from woodland topsoil in different concentrations of TMAH; extraction was carried out at room temperature by shaking for 16 h.

The continued increase in the ratio of iodide to total iodine extracted, with increasing pH (up to pH 14) (Table 4.6 and Figure 4.5) suggests that the majority of iodide is produced by hydrolysis of organic iodine rather than desorption from soil metal oxides. The correlation between fulvic acid (FA) concentration (measured independently) and total iodine is slightly better than FA correlation with organic iodine (calculated by subtracting iodide from total iodine) (Figure 4.6). FA would be expected to give an equally good, or better, correlation with organic iodine than total iodine if the soil iodine is dominantly organically bound. Since organic iodine concentrations were not measured independently, any loss of organically-bound iodine by hydrolysis to iodide would make the correlation between FA and organic iodine worse not better. This therefore supports the theory that the majority of iodide measured was a result of hydrolysis of organic iodine as a result of the TMAH extraction.

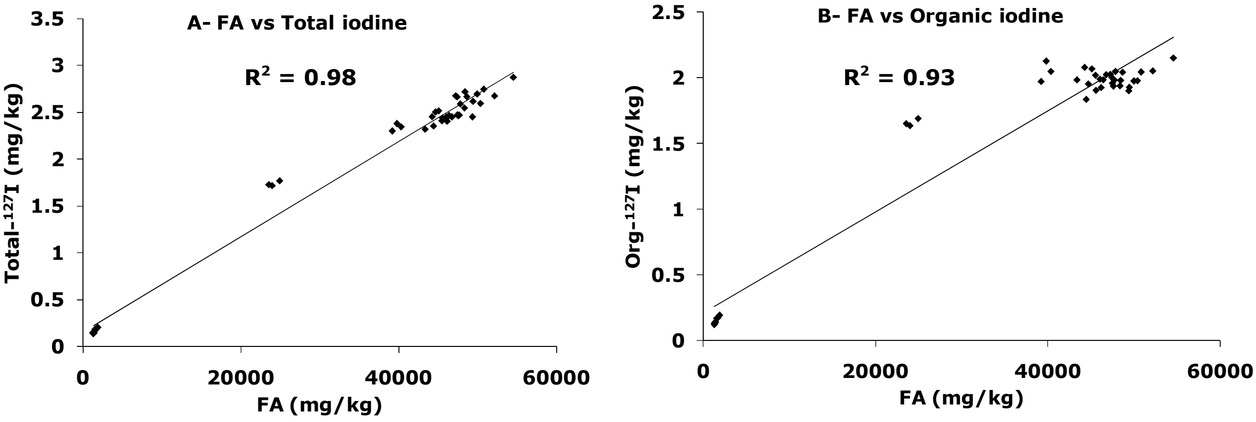


Figure 4.6. Concentration of fulvic acid extracted from woodland topsoil versus (A) total iodine, and (B) organic iodine concentrations. Soil was extracted with different concentrations (0 – 10 %) of TMAH by shaking for 16 h at room temperature

Recoveries of iodide when solutions of iodide or iodide/iodate were mixed with TMAH ranged from 92.8 % to 97.3 % for the hot extraction and were ~ 103 % for the room temperature extraction (Table 4.7). Recoveries of iodate were generally less (c. 90%) (Table 4.7). As the recovery of total iodine was close to 100% this suggests that ~ 10% of iodate was transformed to an unknown form.

Good recovery of total iodine was achieved from humic acid samples spiked with iodide or iodate. Recovery was between 97 to 103 % for samples extracted at 70°C, and from 98 to 101 % for samples extracted at room temperature (Figure 4.7 and Table 4.7). Recovery of total iodine from soil samples spiked with iodide or iodate was generally less successful (91-93 %) (Figure 4.8 and Table 4.7). Expected values were taken as the average of three replicate measurements of unspiked humic acid or soil, plus the added iodide or iodate.

In the samples that contain unspiked humic acid or soil, no iodate peaks were detected. In contrast, in extractions of pure humic acid relatively high concentrations of iodide were measured (38% and 24% of total iodine for extraction at 70°C and room temperature, respectively). As the iodine in humic acids is presumably 100% organically bound, the detection of appreciable concentrations of iodide is further evidence that both ambient and heated extraction with TMAH results in hydrolysis of organically-bound iodine forms, altering the original speciation of the solid phase iodine. In spiked humic acid or soils samples, recovery of iodide was 90%-97%. In iodate spiked systems no iodate was detected; most of the iodate spiked in humic acid, woodland subsoil and arable topsoil was converted to iodide (Table 4.7). This agrees with the findings of Yamada et al. (1999) where 82% of iodate spiked in a soil solution was reduced to iodide as a result of TMAH extraction (Extraction was undertaken using 10mL of 5% TMAH by shaking for 4 h at room temperature).

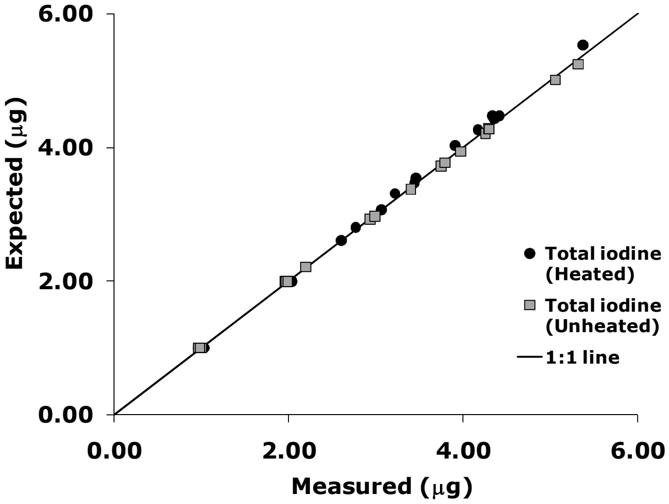


Figure 4.7. Recovery of total iodine from humic acid samples spiked with iodide or iodate (4 mg kg^{-1} HA). Extraction was carried out with 10% TMAH at either 70°C for 3 h or at room temperature by shaking for 16 h. Expected values were taken as the average of three replicate measurements of unspiked humic acid, plus the added iodide or iodate.

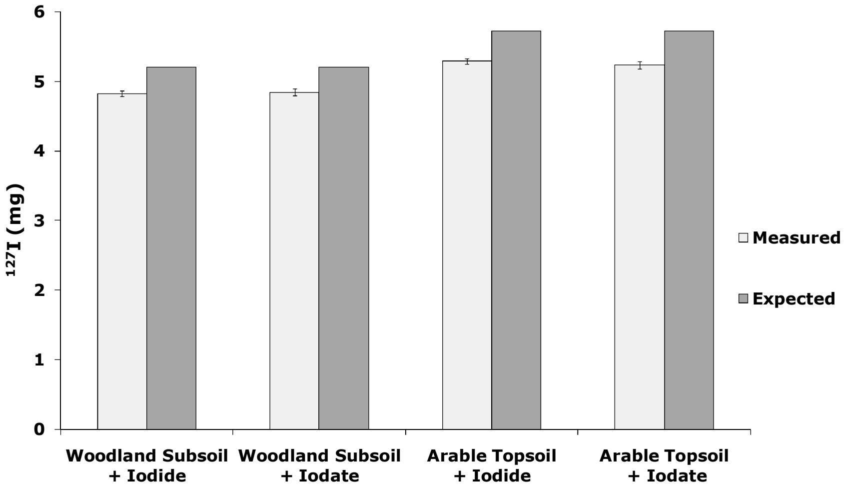


Figure 4.8 Recovery of total iodine from soil samples spiked with iodide or iodate (1 mg kg^{-1} soil). Extraction was carried out with 10% TMAH at room temperature by shaking for 16 h. Expected values were taken as the average of three replicate measurements of soil, plus the added iodide or iodate.

Table 4.7

Recovery of iodide, iodate and total iodine following extraction with 10% TMAH of iodide, iodate, and iodide/iodate solutions, and iodide and iodate spikes addedto humic acid and a range of soils. Hot extraction was carried out at 70°C for 3 h and unheated extraction was done by shaking for 16 h at room temperature. NA= not applicable.

Extraction	Sample Description	Iodate			Iodide			Total Iodine		
		Measured (μg)	Expected (μg)	Recovery (%)	Measured (μg)	Expected (μg)	Recovery (%)	Measured (μg)	Expected (μg)	Recovery (%)
Hot Extraction	Iodide	0.00	0.00	NA	0.93	1.00	92.8	0.97	1.00	96.7
	Iodate	0.89	1.00	89.3	0.00	0.00	NA	1.03	1.00	103
	Iodide+Iodate	0.92	1.00	92.3	0.97	1.00	97.3	2.03	2.00	102
	Humic Acid	0.00	0.00	NA	1.07	1.07	100	2.81	2.82	99.5
	HA+Iodide	0.00	0.00	NA	1.99	2.14	92.7	3.93	4.01	97.9
	HA+Iodate	0.00	1.00	0.00	1.75	1.02	172	3.61	3.68	98
	HA+Iodide+Iodate	0.00	1.00	0.00	2.82	2.07	136	4.69	4.81	97.4
Unheated Extraction	Iodide	0.00	0.00	NA	1.03	1.00	103	0.99	1.00	99.5
	Iodate	0.90	1.00	90.2	0.00	0.00	NA	0.98	1.00	97.6
	Iodide+Iodate	0.90	1.00	90.3	1.03	1.00	103	1.97	2.00	98.6
	Humic Acid	0.00	0.00	NA	0.65	0.65	100	2.71	2.70	100
	HA+Iodide	0.00	0.00	NA	1.67	1.76	94.7	3.65	3.62	101
	HA+Iodate	0.00	1.00	0.00	1.44	0.63	227	3.65	3.62	101
	HA+Iodide+Iodate	0.00	1.00	0.00	2.46	1.69	146	4.89	4.84	101
	Woodland Subsoil	0.00	0.00	NA	0.64	0.64	100	3.10	3.10	100
	Woodland Subsoil + Iodide	0.00	0.00	NA	2.59	2.67	97.3	4.82	5.20	92.7
	Woodland Subsoil + Iodate	0.00	2.00	0.00	2.42	0.67	363	4.84	5.20	93
	Arable Topsoil	0.00	0.00	NA	0.74	0.74	100	3.61	3.61	100
	Arable Topsoil + Iodide	0.00	0.00	NA	2.50	2.77	90.4	5.29	5.73	92.3
	Arable Topsoil + Iodate	0.00	2.00	0.00	2.39	0.77	313	5.23	5.73	91.3

4.3.2.2 Extraction with Potassium Di-hydrogen Phosphate

The amount of total iodine extracted increased with increasing concentration of KH_2PO_4 (Table 4.8) but did not achieve a plateau indicating that further iodine could be extracted with higher concentrations (Figure 4.9 A). The low solubility of KH_2PO_4 and problems associated with analysis of solutions with high dissolved solid concentrations by ICPMS made it impractical to use higher concentrations. The total amount of iodine extracted with the highest concentration of KH_2PO_4 (0.1 M) was 18% and 6% of total soil iodine content (as extracted by TMAH; see Table 4.2) for woodland subsoil and arable topsoil, respectively.

No iodate was detected after phosphate extraction. Iodide concentrations were between 0.025 to 0.05 mg kg^{-1} in the woodland subsoil and 0.021 to 0.064 mg kg^{-1} in the arable topsoil (Table 4.8). Concentrations of extracted iodide also increased with increasing concentration of KH_2PO_4 (Figure 4.9) but only constituted ~13 % of total iodine measured in woodland subsoil extracts and ~35% in the arable topsoil extracts. This suggests that the majority of iodine mobilised by KH_2PO_4 is organically bound, apparently displaced by HPO_4^{2-} ions through competition with negatively charged soil organic matter for adsorption sites at the surface of hydrated iron and aluminium oxides (Gerke, 1993; Borggaard et al., 2005).

Table 4.8

Concentrations of iodide and total iodine extracted by different KH_2PO_4 concentrations. Extraction was carried out by shaking soil suspensions for 16 h at room temperature.

Soil	KH_2PO_4 (M)	$^{127}I^-$ (mg kg^{-1})	Total-^{127}I (mg kg^{-1})	$^{127}I^-$ / Total-^{127}I (%)
Woodland Subsoil	0.1	0.050 ± 0.003	0.376 ± 0.003	13.4
	0.05	0.042 ± 0.005	0.323 ± 0.004	13.1
	0.01	0.035 ± 0.005	0.274 ± 0.007	12.7
	0.005	0.025 ± 0.001	0.271 ± 0.002	9.2
Arable Topsoil	0.1	0.064 ± 0.003	0.179 ± 0.002	36
	0.05	0.053 ± 0.004	0.160 ± 0.002	33.3
	0.01	0.043 ± 0.002	0.122 ± 0.004	35.3
	0.005	0.021 ± 0.001	0.113 ± 0.003	19

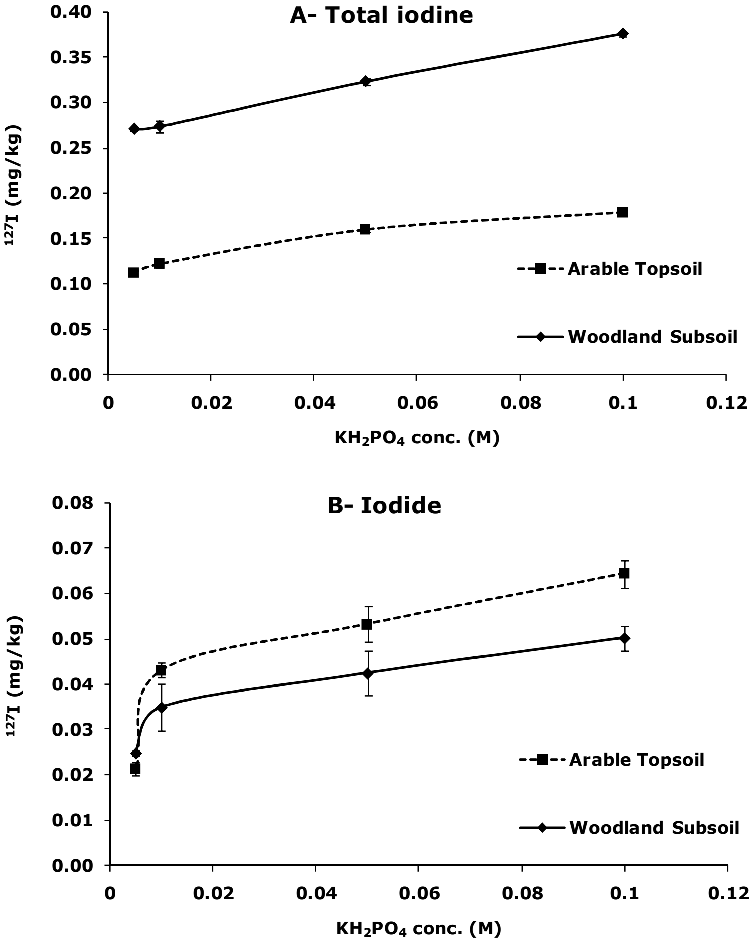
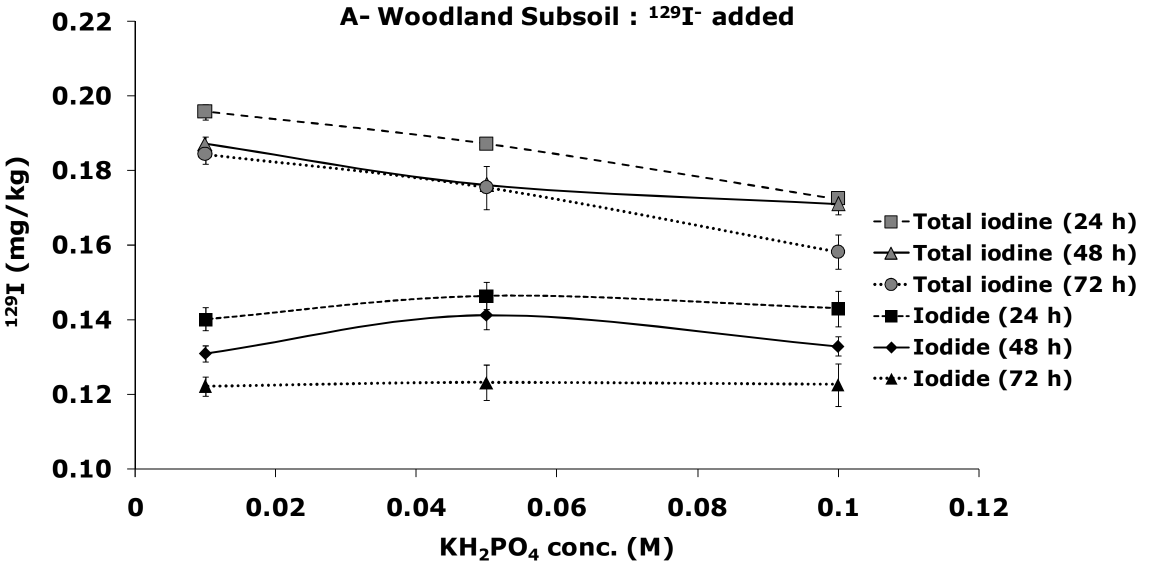


Figure 4.9. Phosphate extractable iodine (A) and iodide (B) from woodland subsoil and arable topsoil using different concentrations of KH_2PO_4. Extraction was undertaken by shaking soil suspensions for 16 h at room temperature.

In the samples spiked with $^{129}I^-$, concentrations of $^{129}I^-$ and total ^{129}I generally decreased with time (Figure 4.10 and Table 4.9). Total concentrations of ^{129}I recovered were inversely proportional to the concentrations of KH_2PO_4 and decreased with increasing time. However, similar $^{129}I^-$ concentrations were extracted regardless of KH_2PO_4 concentration at any given time. Highest total ^{129}I recoveries were achieved with the lowest KH_2PO_4 concentration and shortest shaking times whilst lowest recoveries were associated with longer shaking times and higher KH_2PO_4 concentrations. Similar behaviour was observed in $^{129}IO_3^-$ spiked samples, with the concentrations of both total ^{129}I and $^{129}IO_3^-$ decreasing with time (Figure 4.11 and Table 4.10). Recovery of $^{129}IO_3^-$ was more affected by KH_2PO_4 concentration than was $^{129}I^-$, with the highest recoveries of $^{129}IO_3^-$ at the lowest KH_2PO_4 concentrations. Total ^{129}I and $^{129}IO_3^-$ recoveries were lower overall than in $^{129}I^-$ spiked samples. As $^{129}IO_3^-$, percentage recoveries were 41%-71% for woodland subsoil and 15%-70% for arable topsoil. Appreciable concentrations of $^{129}I^-$ were also detected in $^{129}IO_3^-$ spiked samples indicating reduction of $^{129}IO_3^-$ to $^{129}I^-$ was occurring (Table 4.10). Reduction in ^{129}I concentrations (as total ^{129}I, $^{129}IO_3^-$ or $^{129}I^-$) is unlikely to be due to sorption on sesquioxides because of the large concentrations of PO_4^{3-} ions in the extraction solutions. Phosphate is strongly sorbed onto soil hydrous oxides in preference to other anions (Gerke, 1993; Borggaard et al., 2005). That recovery of ^{129}I was lower at higher KH_2PO_4 concentrations where competition of PO_4^{3-} ions with $^{129}IO_3^-$ or $^{129}I^-$ on adsorption sites would be greater also supports this hypothesis. Moreover, higher concentrations of TOC were observed with increasing KH_2PO_4 concentrations (Table 4.9).

Since, recovery as $^{129}I^-$ or $^{129}IO_3^-$ was always less than total ^{129}I there was clear transformation of $^{129}I^-$ into soluble organic ^{129}I forms (Table 4.9 and Table 4.10). The overall reduction in total ^{129}I concentrations also suggests that soluble organic ^{129}I forms were gradually fixed as insoluble forms through the cycling of soil organic matter between soluble and insoluble pools. Incorporation of iodide and iodate into organic matter is widely understood to occur through oxidation (of iodide) or reduction (of iodate) to electrophilic species such as I_2 or HOI which can then react with the moieties on the humic structure via electrophilic substitution (see e.g. Whitehead, 1974a; Francois, 1987a; Fukui et al., 1996; Bichsel and von Gunten, 1999, 2000; Radlinger and Heumann, 2000; Warner et al., 2000; Schlegel et al., 2006). Soil organic matter can act as both a reducing and oxidizing agent (Alberts et al., 1974; Wilson and Weber, 1979; Miles and Brezonik, 1981; Chen et al., 2003; Blodau et al., 2009; Keller et al., 2009). This may explain the lower percentage recoveries of $^{129}I^-$, $^{129}IO_3^-$ and total ^{129}I in the arable topsoil which has 60% more C and 100% more N compared to the woodland susbsoil (Table 4.2). Concentrations of $^{129}I^-$, which can be produced by reduction of $^{129}IO_3^-$ (Fukui et al., 1996), measured in $^{129}IO_3^-$ spiked samples, were higher in the arable topsoil samples than in woodland subsoil samples indicating that the higher organic matter content may result in more $^{129}IO_3^-$ reduction.



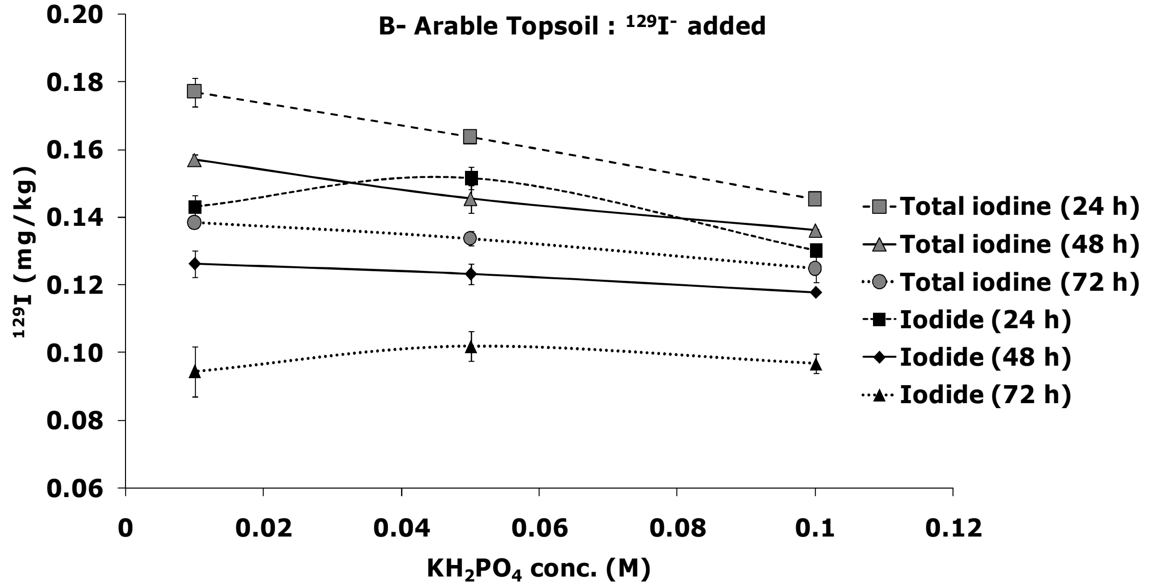
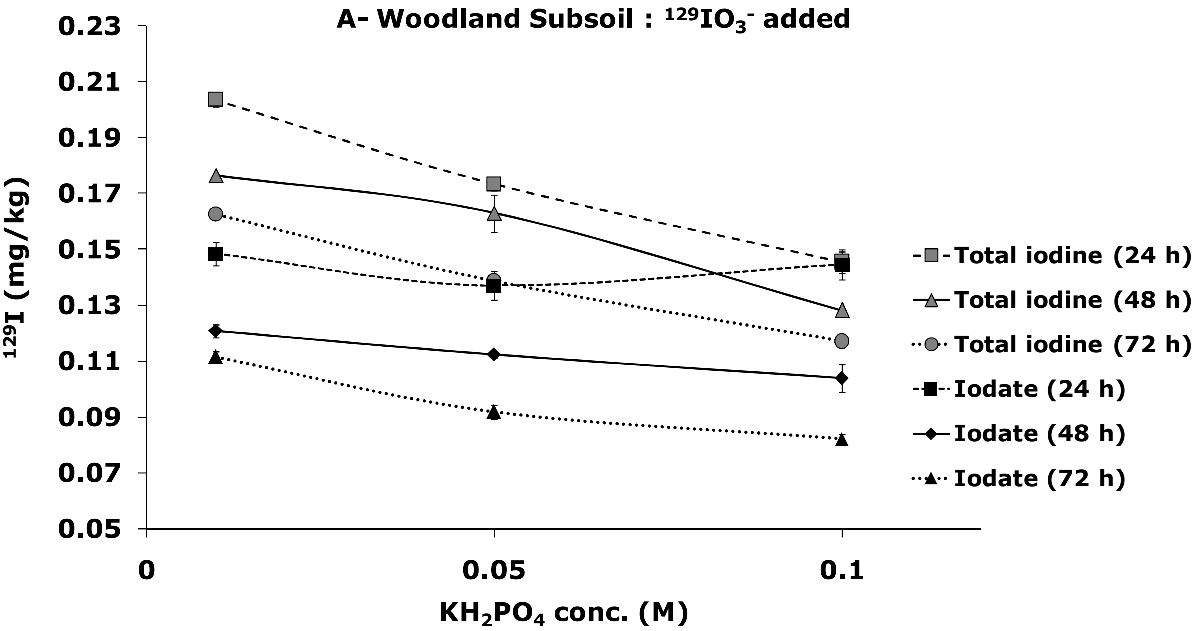


Figure 4.10. Changes in total-^{129}I and $^{129}I^-$ concentrations in woodland subsoil (A) and arable topsoil (B) at different equilibration times and KH_2PO_4 concentrations after spiking suspensions with 0.2 mg kg^{-1} $^{129}I^-$.

Table 4.9

Concentrations of $^{129}\text{I}^-$ and total ^{129}I recovered from soil suspended in KH_2PO_4 solution spiked with $^{129}\text{I}^-$ (0.2 mg kg^{-1} soil). Spiked suspensions were shaken for 24, 48 and 72 hours. TOC and pH were measured in all suspensions.

Soil	Shaking time (h)	KH_2PO_4 (M)	$^{129}\text{I}^-$ (mg kg^{-1})	Total ^{129}I (mg kg^{-1})	Recovery as $^{129}\text{I}^-$ (%)	Recovery as Total ^{129}I (%)	TOC (mg kg^{-1})	pH
Woodland Subsoil	24	0.1	0.143 ± 0.005	0.172 ± 0.001	71.5	86.2	859	4.1
		0.05	0.146 ± 0.004	0.187 ± 0.001	73.2	93.5	702	4.0
		0.01	0.140 ± 0.003	0.196 ± 0.002	70.1	97.9	593	4.0
	48	0.1	0.133 ± 0.003	0.171 ± 0.003	66.5	85.5	847	4.1
		0.05	0.141 ± 0.004	0.176 ± 0.001	70.6	88.1	706	4.1
		0.01	0.131 ± 0.002	0.187 ± 0.002	65.5	93.6	598	4.2
	72	0.1	0.123 ± 0.006	0.158 ± 0.005	61.3	79.1	866	4.2
		0.05	0.123 ± 0.005	0.175 ± 0.006	61.6	87.7	769	4.1
		0.01	0.122 ± 0.003	0.184 ± 0.003	61.1	92.2	575	4.3
Arable Topsoil	24	0.1	0.130 ± 0.001	0.145 ± 0.001	65.1	72.7	448	5.1
		0.05	0.152 ± 0.003	0.164 ± 0.001	75.8	81.8	368	5.3
		0.01	0.143 ± 0.004	0.177 ± 0.004	71.6	88.5	307	5.9
	48	0.1	0.118 ± 0.001	0.136 ± 0.001	59.0	68.1	459	5.1
		0.05	0.123 ± 0.003	0.145 ± 0.004	61.7	72.7	424	5.3
		0.01	0.126 ± 0.004	0.157 ± 0.002	63.1	78.5	354	5.8
	72	0.1	0.097 ± 0.003	0.125 ± 0.004	48.4	62.4	455	5.2
		0.05	0.102± 0.004	0.134 ± 0.002	51.0	66.9	380	5.4
		0.01	0.095 ± 0.007	0.138 ± 0.001	47.3	69.2	300	5.8



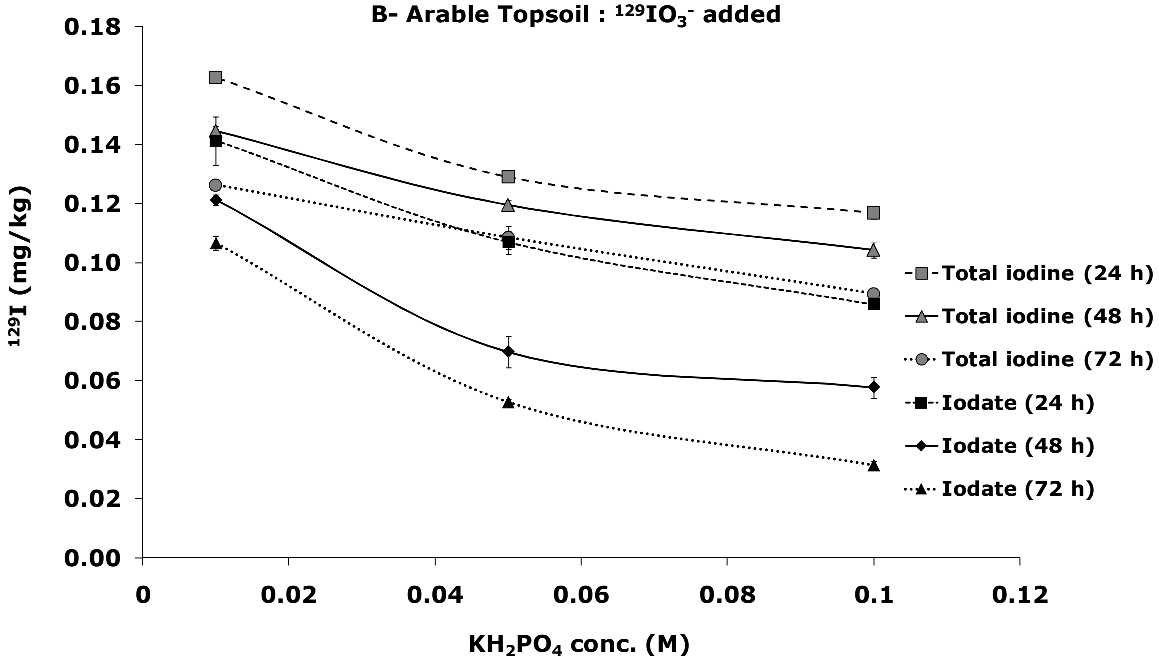


Figure 4.11. Changes in total-^{129}I and $^{129}IO_3^-$ concentrations in woodland subsoil (A) and arable topsoil (B) at different equilibration times and KH_2PO_4 concentrations after spiking suspensions with 0.2 mg kg^{-1} $^{129}IO_3^-$

Table 4.10

Concentrations of $^{129}IO_3^-$, $^{129}I^-$ and total ^{129}I recovered from soil suspended in KH_2PO_4 solutions spiked with $^{129}IO_3^-$ (0.2 mg kg^{-1} soil). Spiked suspensions were shaken for 24, 48 and 72 hours.

Soil	Shaking time (h)	KH_2PO_4 (M)	$^{129}IO_3^-$ (mg kg^{-1})	$^{129}I^-$ (mg kg^{-1})	Total ^{129}I (mg kg^{-1})	Recovery as $^{129}IO_3^-$ (%)	Recovery as $^{129}I^-$ (%)	Recovery as Total ^{129}I (%)
Woodland Subsoil	24	0.1	0.145 ± 0.005	0.007 ± 0.000	0.145 ± 0.004	72.3	3.6	72.7
		0.05	0.137 ± 0.005	0.005 ± 0.003	0.173 ± 0.002	68.5	2.6	86.6
		0.01	0.148 ± 0.004	0.005 ± 0.001	0.203 ± 0.002	74.2	2.4	101.7
	48	0.1	0.104 ± 0.005	0.011 ± 0.000	0.128 ± 0.000	51.9	5.6	64.1
		0.05	0.112 ± 0.001	0.009 ± 0.004	0.163 ± 0.007	56.2	4.7	81.5
		0.01	0.121 ± 0.002	0.008 ± 0.001	0.176 ± 0.001	60.4	4.2	88.1
	72	0.1	0.082 ± 0.002	0.016 ± 0.001	0.117 ± 0.001	41.1	8.2	58.5
		0.05	0.092 ± 0.002	0.016 ± 0.001	0.139 ± 0.002	45.9	8.0	69.3
		0.01	0.111 ± 0.002	0.014 ± 0.003	0.162 ± 0.001	55.7	7.0	81.2
Arable Topsoil	24	0.1	0.086 ± 0.001	0.033 ± 0.003	0.117 ± 0.002	43.0	16.4	58.5
		0.05	0.107 ± 0.004	0.028 ± 0.003	0.129 ± 0.001	53.5	14.1	64.5
		0.01	0.141 ± 0.008	0.007 ± 0.000	0.163 ± 0.001	70.7	3.3	81.3
	48	0.1	0.058 ± 0.004	0.046 ± 0.004	0.104 ± 0.003	28.9	22.9	52.1
		0.05	0.070 ± 0.005	0.041 ± 0.002	0.120 ± 0.001	34.9	20.7	59.8
		0.01	0.121 ± 0.002	0.015 ± 0.002	0.145 ± 0.002	60.6	7.3	72.4
	72	0.1	0.031 ± 0.001	0.049 ± 0.002	0.089 ± 0.000	15.7	24.7	44.7
		0.05	0.053 ± 0.001	0.046 ± 0.004	0.108 ± 0.004	26.4	23.0	54.2
		0.01	0.107 ± 0.002	0.017 ± 0.001	0.126 ± 0.001	53.3	8.5	63.2

4.3.2.3 Extraction of soil biomass iodine

Concentrations of microbial biomass carbon and nitrogen were similar in samples extracted with KH_2PO_4 and those extracted with K_2SO_4 (Table 4.11). Microbial biomass iodine concentrations (the difference between iodine concentration in the fumigated and non-fumigated soils) in the KH_2PO_4 extracts of arable topsoil and arable subsoil were also in the same range as those in the K_2SO_4 extracts of the same soils. However concentrations of biomass iodine were higher in KH_2PO_4 extraction solutions of woodland topsoil and subsoil than in K_2SO_4 extracts (Table 4.11). In general, concentrations of biomass iodine estimated by this method constituted a very small proportion of the total soil iodine content (0.01 – 0.25 %) regardless of extractant.

Table 4.11

Microbial biomass carbon, nitrogen and iodine concentrations in fumigated and non-fumigated soils; extraction was carried out with either of 0.5 K_2SO_4 or 0.2 M KH_2PO_4 solutions after soils were fumigated with chloroform for 24 hours in an evacuated desiccators (section 2.8)

Extraction	Soil	Microbial Biomass Carbon (CM) (mg kg^{-1})	Microbial Biomass Nitrogen (NM) (mg kg^{-1})	Microbial Biomass Iodine (mg kg^{-1})
K_2SO_4	Woodland Topsoil	482	69.7	0.0003
	Woodland Subsoil	128	17.1	0.0007
	Arable Topsoil	312	63.4	0.0032
	Arable Subsoil	154	24.7	0.0055
KH_2PO_4	Woodland Topsoil	401	53.8	0.029
	Woodland Subsoil	95.2	25.6	0.017
	Arable Topsoil	322	54.1	0.007
	Arable Subsoil	167	21.4	0.005

4.4 CONCLUSIONS

Results showed that iodine concentrations in the soils studied in this chapter were lower than both the worldwide average (5 mg kg^{-1}) and the UK average (9.2 mg kg^{-1}). Iodine concentrations generally decreased with depth up to 100 cm, while the I:C ratio increased indicating that, although the majority of iodine deposited on soils is mostly retained in the topsoil, smaller amounts of soil organic matter in deeper soil horizons contain higher concentrations of iodine and effectively scavenge iodine against leaching.

The efficiency of extraction of total soil iodine with TMAH at 70^{o}C was tested on some certified soils and the measured iodine concentrations were mostly in good agreement with the certified values. Further investigation of the effects of extraction conditions on the extraction efficiency showed that changing TMAH concentration (5% - 20 %), the extraction time (3 - 16h), the extraction temperature (room temperature or 70^{o}C) or soil particle size (finely ground or <2mm sieved) had little influence on the concentrations of total iodine extracted, with the possible exception of an arable subsoil (low organic and slightly acidic) as it showed more sensitivity toward changing the concentration of the TMAH ($P<<0.05$).

Considerable amounts of iodide were measured in the TMAH extracts of soil; however the proportion of iodide to total iodine varied depending on the extraction conditions, mainly the TMAH concentration and extraction temperature. This has led to the conclusion that part, or all, of the measured iodide may have been originally organically-bound and was hydrolysed as iodide as a result of the extraction. There was other evidence that extraction with TMAH alters the original speciation of soil iodine. For example, the detection of appreciable concentrations of iodide in the TMAH extracts of humic acid where 100% organic iodine would be expected; in addition, iodate spiked into humic acid and soil/TMAH suspensions was totally transformed to other iodine forms.

Since the extraction of soil iodine with TMAH was proven unsuitable for speciation purposes, the possibility of extracting specifically-sorbed inorganic iodine utilising competition with phosphate ions was investigated. The total iodine extracted with 0.1 M KH_2PO_4 was 6 - 18% of total soil iodine (as extracted by TMAH at 70°C). No iodate was measured and iodide constituted only 13% and 33% of total iodine (in KH_2PO_4 extracts) in the woodland subsoil and arable topsoil, respectively, which indicates that most of the iodine mobilized by KH_2PO_4 is organic in nature. When soil suspended in KH_2PO_4 solution was spiked with $^{129}I^-$ and $^{129}IO_3^-$, at least 50% of $^{129}I^-$ and 15% of $^{129}IO_3^-$ were recoverable after 72 hours of reaction. However, the lowest recoveries were observed at the highest KH_2PO_4 concentrations (with highest TOC concentrations in extracts) suggesting that, although KH_2PO_4 could be useful in releasing any inorganic iodine forms in soils, it also facilitates inorganic iodine incorporation in organic matter by mobilising soluble forms of soil organic matter. Nevertheless, although the information obtained from KH_2PO_4 extraction is not conclusive about iodine speciation in soil because of the possible inter-conversion between soil iodine forms, it may be useful as a second extraction step after soils were extracted for soluble iodine forms e.g. using non-specifically sorbed ions such as NO_3^-.

An attempt was also made to fractionate and measure the microbial biomass iodine pool by fumigated soil with chloroform and extracting released iodine. However, results showed that the concentrations of total iodine extracted constituted a very small proportion of the soil organic iodine pool.

5. ADSORPTION OF IODINE ON SOIL

5.1 INTRODUCTION

5.1.1 Adsorption of Iodine by Soil

The adsorption behaviour of iodine has been extensively investigated. One of the earliest substantial investigations was a study by Whitehead (1973a) which examined the adsorption of iodide by several soils covering a range of properties. It was found that sorption generally decreased with increasing pH but with two adsorption maxima. The first adsorption peak was around pH 2-4 and was attributed to sorption on iron and aluminium oxides as it resembled the adsorption pattern of phosphate and sulfate anions. The second peak around pH 8 was only found in the highly organic soils and was therefore interpreted as retention by humus. The removal of organic matter and hydrous metal oxides, using hydrogen peroxide and Tamm's reagent, respectively, produced a considerable reduction in sorption in both cases (35 - 76%). In a later study, Whitehead (1974b) measured iodide sorption on grass compost, as a surrogate for soil organic matter, and hydrated iron and aluminium oxides, over a range of pH values. Iodide was found to be strongly sorbed by organic matter up to pH 9; however, sorption on oxides was only apparent up to pH 5.5 and was greatly reduced when pH was further increased. Similar results were obtained in other studies of iodine adsorption (Yoshida et al., 1992; Fukui et al., 1996; Sheppard et al., 1996; Yoshida et al., 1998; Dai et al., 2004, 2009); but while all of them agreed on the general trend with soil pH, there was disagreement on the relative importance of sesquioxides and soil organic matter. For example, Sheppard et al. (1996) and Yoshida et al. (1998) reported that organic matter content was the most important factor affecting iodine retention in soils. On the other hand, Dai et al. (2004 and 2009) found that iodine sorption was higher in soils rich in iron and aluminum oxides. The difference in the affinity of iodide and iodate for soil was also investigated and it was reported that iodate is adsorbed more strongly than iodide, especially in acidic soils with low organic matter contents (Fukui et al., 1996; Yoshida et al., 1992; Shimamoto et al., 2010).

The adsorption behaviour of a chemical species in soil is often described by deriving an 'adsorption isotherm' which shows the relationship between the equilibrium concentrations in the soil solution and in the soil solid phase. Perhaps the most extensively used adsorption models are the Freundlich and Langmuir equations (Sparks, 2003). Adsorption of iodine in soils appears to fit the Freundlich model best (Assemi and Erten, 1994; Sheppard et al., 1996; Dai et al., 2004, 2009).

5.1.2 Isotopically Exchangeable Soil Iodine (E-value)

Inductively coupled plasma isotope dilution mass spectrometry (ICP-ID-MS) is one of the best techniques to achieve high analytical accuracy and precision in elemental assays. ID-MS involves spiking solution samples with a known amount of one of the stable isotopes of the analyte. The isotopic abundance of the analyte isotopes is then used to determine the analyte concentration in spiked samples. In contrast to concentrations estimated with the use of external calibrations, the isotopic abundance is not affected by the sample matrix (Heumann, 1992; USEPA, 2007). ICP-IDMS has been used in several studies to accurately determine iodine concentration in environmental and biological samples, including food samples (Radlinger and Heumann, 1998) and urine (Haldimann et al., 1998).

Isotopic dilution techniques can be also utilised to quantify the 'isotopically exchangeable pool' or 'E-value' of analytes in soil. This is the amount of an analyte that can freely exchange between soil and the soil solution and which is therefore potentially accessible to plants. In this case, the spike isotope is typically added to a soil suspension and must achieve equilibrium between the soil particles and the suspending solution. The technique has been widely used to determine E-values for several elements, including cadmium (Young et al., 2000; Sivry et al., 2006), copper (Nolan et al., 2004), lead (Tongtavee et al., 2005), zinc (Young et al., 2000), and for multiple elements (Gabler et al., 2007). However, the method has not been used to try and quantify a 'labile' pool of iodide or iodate in soils.

5.1.3 Aims

The main goal of this chapter was to study the adsorption behaviour of ^{129}I and ^{127}I, as iodide and iodate, on a range of soils. The results were required to determine the concentration range in which further studies with the tracers $^{129}I^-$ and $^{129}IO_3^-$ would be undertaken (Chapter 6). Moreover, data from the study of $^{129}I^-$ adsorption on soil was used to examine the possibility of estimating an isotopically exchangeable (labile) soil iodine pool (an iodide E-value).

5.2 EXPERIMENTAL

5.2.1 Adsorption of Iodine on Soil

Air-dried, sieved (<2 mm) soil samples (see chapter 4, section 4.2.1 for soil sampling and preparation) were suspended in 20 mL of 0.01 M $Ca(NO_3)_2$ solutions containing 0.2, 0.5, 1.3, 3.2, and 8 μg $^{127}I^-$ or $^{127}IO_3^-$. Suspensions were shaken in polycarbonate centrifuge tubes on a reciprocal shaker for 48 h and centrifuged (3000 g for 25 min). The supernatant solutions were filtered through 0.22 μm syringe filters before total ^{127}I was assayed using ICP-MS (section 2.10). Samples, standards and blanks were all prepared in triplicate.

Adsorption isotherms for both $^{127}I^-$ and $^{127}IO_3^-$ (determined as total iodine) were modelled for each type of soil using equation 5.1. which is adapted from the Freundlich isotherm equation (Sparks, 2003).

$$I_{ads} = K_d \left(I_{soln}\right)^n \qquad 5.1.$$

Where, I_{ads} is the total concentration of $^{127}I^-$ or $^{127}IO_3^-$ adsorbed (mg kg^{-1} soil), I_{soln} is the concentration of total ^{127}I in equilibrium solution (mg L^{-1}), K_d is the Freundlich distribution coefficient (L kg^{-1}) and n is Freundlich equation power term.

Using the 'solver' function within Microsoft Excel 2007, the Freundlich parameters (K_d and n) were optimised by fitting the data to a mass balance which included the pre-existing *reactive* soil $^{127}I^-$ or $^{127}IO_3^-$ content (I_{soil}) as a fitting parameter (equation 5.2).

$$I_{add} = K_d \left(I_{soln}\right)^n + I_{soln}\frac{V}{W} - I_{soil} \qquad 5.2.$$

The variable I_{add} is the amount of of $^{127}I^-$ or $^{127}IO_3^-$ added (mg kg^{-1} soil), v is the equilibrium solution volume (mL) and w is the soil weight (g).

5.2.2 Isotopically Exchangeable Soil Iodine (E-value)

Triplicate samples (c. 2.0 g) of air-dried and sieved (< 2 mm) soil (see chapter 4, section 4.2.1 for soil sampling and preparation) were suspended in 20 mL of 0.01M KNO_3 solution containing final $^{129}I^-$ concentrations of 0, 0.1, 0.25, 0.375, and 0.5 mg kg^{-1} soil. Suspensions were shaken in polycarbonate centrifuge tubes on a reciprocal shaker for 48 hours before pH was measured as described in chapter 2 (section 2.2). Samples were then centrifuged for 30 min (3000 g) and the supernatant solutions were filtered through 0.22 μm syringe filters. Filtered supernatants were analysed for total ^{127}I and ^{129}I concentration and for the species $^{127}I^-$, $^{127}IO_3^-$, $^{129}I^-$ and $^{129}IO_3^-$ by HPLC-ICP-MS (see section 2.10).

The concentration of labile iodine (E-value) in the soil was calculated from equation 5.3 (Young et al., 2000).

$$I_L = I_s \left(K_d + \frac{v}{w}\right) \quad 5.3$$

Where, I_L is the concentration of labile iodine (mg kg^{-1} soil), I_s is the concentration of $^{127}I^-$ in solution (mg L^{-1}), k_d is the distribution coefficient of the spiked isotope $^{129}I^-$, v is the solution volume (mL) and w is the soil mass (g).

5.3 RESULTS AND DISCUSSION

5.3.1 Adsorption of Iodine on Soil

In all soils (see chapter 4; section 4.3.1 and Table 4.1. for soil properties), the Freundlich adsorption isotherm provided a good fit to both iodide and iodate adsorption data (Figure 5.1). The Freundlich K_d values (Equation 5.1) ranged from 1.1 to 5.3 L kg^{-1} for iodide and from 0.5 – 21.5 L kg^{-1} for iodate (Table 5.1). Sorption of iodate was greater than iodide in the acidic woodland soils whereas iodide was more strongly adsorbed in the arable neutral soils (Figure 5.1 and Table 5.1). The greater sorption of iodate than iodide, particularly in acidic soils with low organic matter contents, has been reported previously (Fukui et al., 1996; Yoshida et al., 1992; Shimamoto et al., 2010) and was attributed to the greater intrinsic strength of iodate sorption on iron and aluminium hydrous oxides. Both iodide (pKa = -10) and iodate (pKa = 0.75) are fully dissociated within the normal soil pH range and so might be expected to behave as conserved solutes subject only to electrostatic attraction to variable charge Fe oxide surfaces. Therefore, sorption would normally be stronger under acidic conditions. However, it is thought that iodate is also able to bond chemically to Fe oxide surfaces through replacement of hydroxyl groups and so is likely to be adsorbed more strongly than iodide (Whitehead, 1973a, 1974b, 1978; Ullman and Aller, 1985; Fukui et al., 1996; Um et al., 2004). In the current experiment iodide and iodate were measured only as total iodine (in solution) so possible chemical transformations, in the solid or solution phases, could not be followed. However, the greater *apparent* sorption of iodate on the highly organic woodland topsoil (K_d = 21.5 L kg^{-1}) than in the more acidic (but less organic) woodland subsoil (K_d = 7.2 L kg^{-1}) strongly suggests iodine incorporation into soil organic matter.

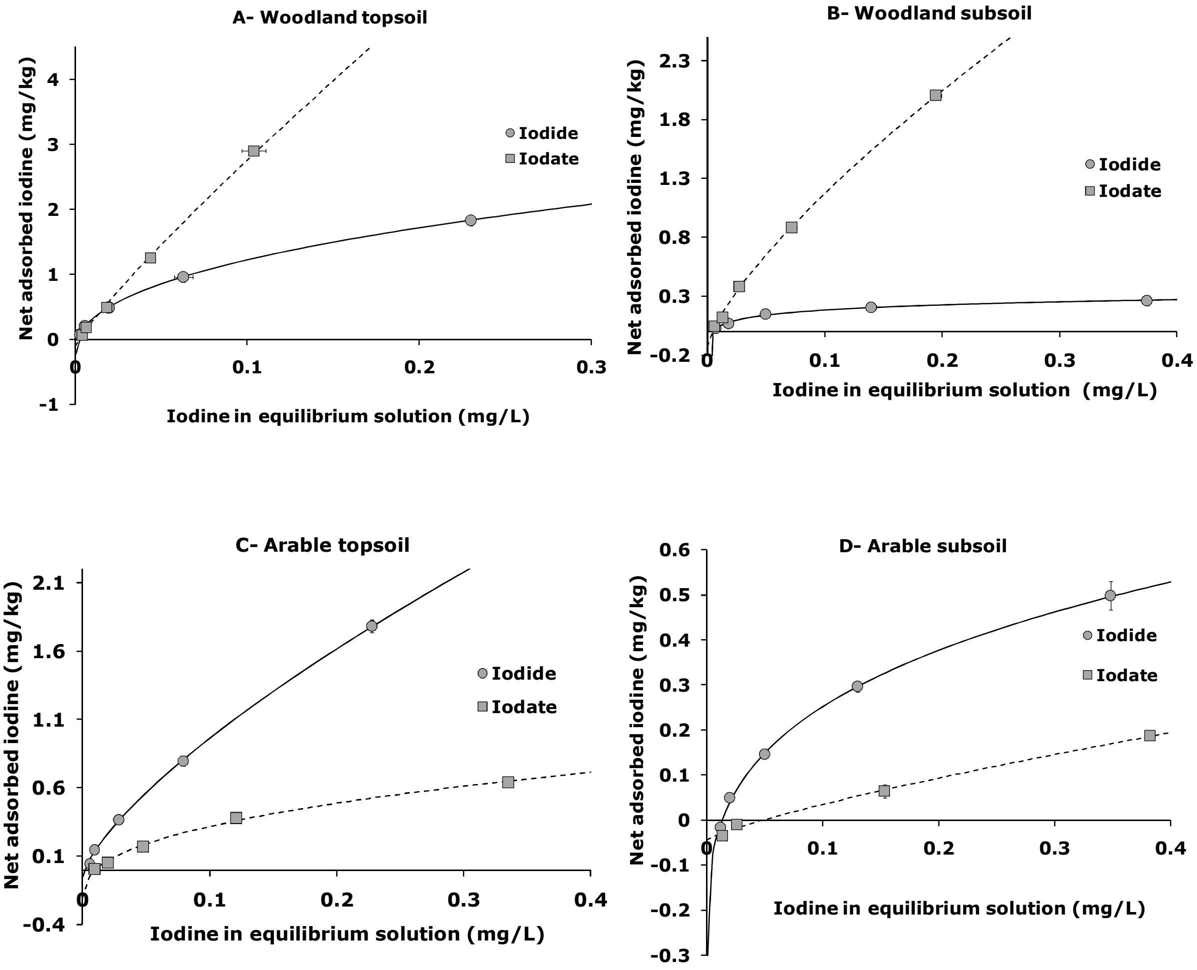


Figure 5.1 Adsorption of iodide and iodate in Woodland topsoil (A), Woodland subsoil (B), Arable topsoil (C) and Arable subsoil (D) following equilibration for 48 hours. The solid and broken lines represent optimised fits of the Freundlich adsorption isotherm equation to iodide and iodate adsorption respectively. All soils were suspended in 0.01 M $Ca(NO_3)_2$ at a solid:solution ratio of 1:10 (w/v).

Table 5.1

Modelled Freundlich parameters (K_d & n) and pre-existing reactive iodine content (I_{soil}) (Equations 5.1 and 5.2) for iodide and iodate on woodland and arable topsoils and subsoils. Soil pH and carbon content are also displayed.

Soil	pH	C	Iodide			Iodate		
		(%)	K_d (L kg^{-1})	n	I_{soil} (mg kg^{-1})	K_d (L kg^{-1})	n	I_{soil} (mg kg^{-1})
Woodland topsoil	4.8	5.01	3.8	0.42	0.25	21.5	0.88	0.1
Woodland subsoil	4.3	1.17	2.2	0.03	1.85	7.2	0.74	0.13
Arable topsoil	6.5	1.98	5.3	0.72	0.06	1.3	0.4	0.21
Arable subsoil	6.9	0.43	1.1	0.28	0.33	0.5	0.79	0.04

It is generally agreed that iodine incorporation in soil organic matter happens via iodate reduction or iodide oxidation to the more reactive intermediate species I_2 and HOI which are capable of undergoing electrophilic substitution on the aromatic rings and reactive functional groups found within humus molecules (Francois, 1987 a & b; Bichsel and von Gunten, 1999 & 2000; Radlinger and Heumann, 2000; Warner et al., 2000; Reiller et al., 2006; Schlegel et al., 2006; Steinberg et al., 2008 a & b; Yamaguchi et al., 2010). The reduction of iodate reaction rate is known to decrease with increasing pH of the reaction medium (Equation 5.4) (Orlemann and Kolthoff, 1942; Brummer and Field, 1979; Wels et al., 1991; Anik, 2004).

$$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2} I_2 + 3H_2O \qquad 5.4.$$

Therefore, the current results seem to confirm that soil pH is the most influential factor on iodate sorption, whether retention occurs by adsorption on soil oxyhydroxides or by chemical bonding to soil organic matter; however, in soils with similar pH values, sorption is greater in soils with higher organic matter contents. Iodide oxidation rate is also known to be inversely proportional to pH (Yntema and Fleming, 1939; Roman and Dunford, 1972; Schmitz, 2001) (Equation 5.5).

$$2I^- + 2H^+ + H_2O_2 \rightarrow I_2 + 2H_2O \qquad 5.5.$$

In soil, an oxidising agent could be either metal oxides e.g. MnO_2 (Allard et al., 2009; Fox et al., 2009; Gallard et al., 2009) or soil organic matter (Blodau et al., 2009, Keller et al., 2009). Nevertheless, iodide sorption was greater in the high organic topsoils than in the low organic subsoils (Figure 5.1 and Table 5.1) regardless of the soil pH suggesting that iodide sorption was much more influenced by organic matter content than pH and that iodide is mostly retained in soils by chemical incorporation in soil organic matter.

With the exception of iodate in the arable subsoil it appears that the equilibrium concentration of iodine in solution (intercept on X-axis in Fig. 5.1) lies around 10 μg L^{-1} in soil pore water for both iodide and iodate (Figure 5.1). This is the experimental range in which the primary incubation study with the tracer isotope ^{129}I (Chapter 6) will concentrate.

5.3.2 Isotopically Exchangeable Soil Iodine (E-value)

The pH value of all spiked suspensions were measured (section 5.2.2), partly to determine whether the addition of an aliquot of the alkaline ^{129}I stock solution had changed the soil pH. Results showed that, in all cases, the final suspension pH values had not been affected by addition of the $^{129}I^-$ spike (Table 5.2).

Table 5.2

Final pH (after 48 h equilibration) of soil suspensions spiked with a range of concentrations of $^{129}I^-$

Spiked $^{129}I^-$ (mg kg^{-1} soil)	pH				
	Woodland Topsoil	Woodland Subsoil	Arable Topsoil	Arable Subsoil	Grassland Topsoil
0	4.81	4.51	6.21	6.85	4.84
0.1	4.86	4.43	6.30	6.81	4.79
0.25	4.81	4.47	6.33	6.30	4.78
0.375	4.83	4.47	6.32	6.75	4.80
0.5	4.83	4.47	6.29	6.78	4.81

The concentrations of isotopically exchangeable soil iodine (E-value) in the five soils were plotted against the concentrations of adsorbed ^{129}I (Figure 5.3). The E-value calculation for iodide in equation 5.3 assumes that both $^{129}I^-$ in the soil solution and the adsorbed $^{129}I^-$ has not been transformed to other iodine forms and that both are in dynamic equilibrium with each other. Any chemical transformation of either the spiked or the adsorbed $^{129}I^-$ produces an error in measuring E-value because the E-value will no longer truly represent the 'istopically exchangeable iodide'. Hamon et al. (2004) and Collins et al. (2006) discuss this issue for elements (As and Se) with several co-existing oxidation states.

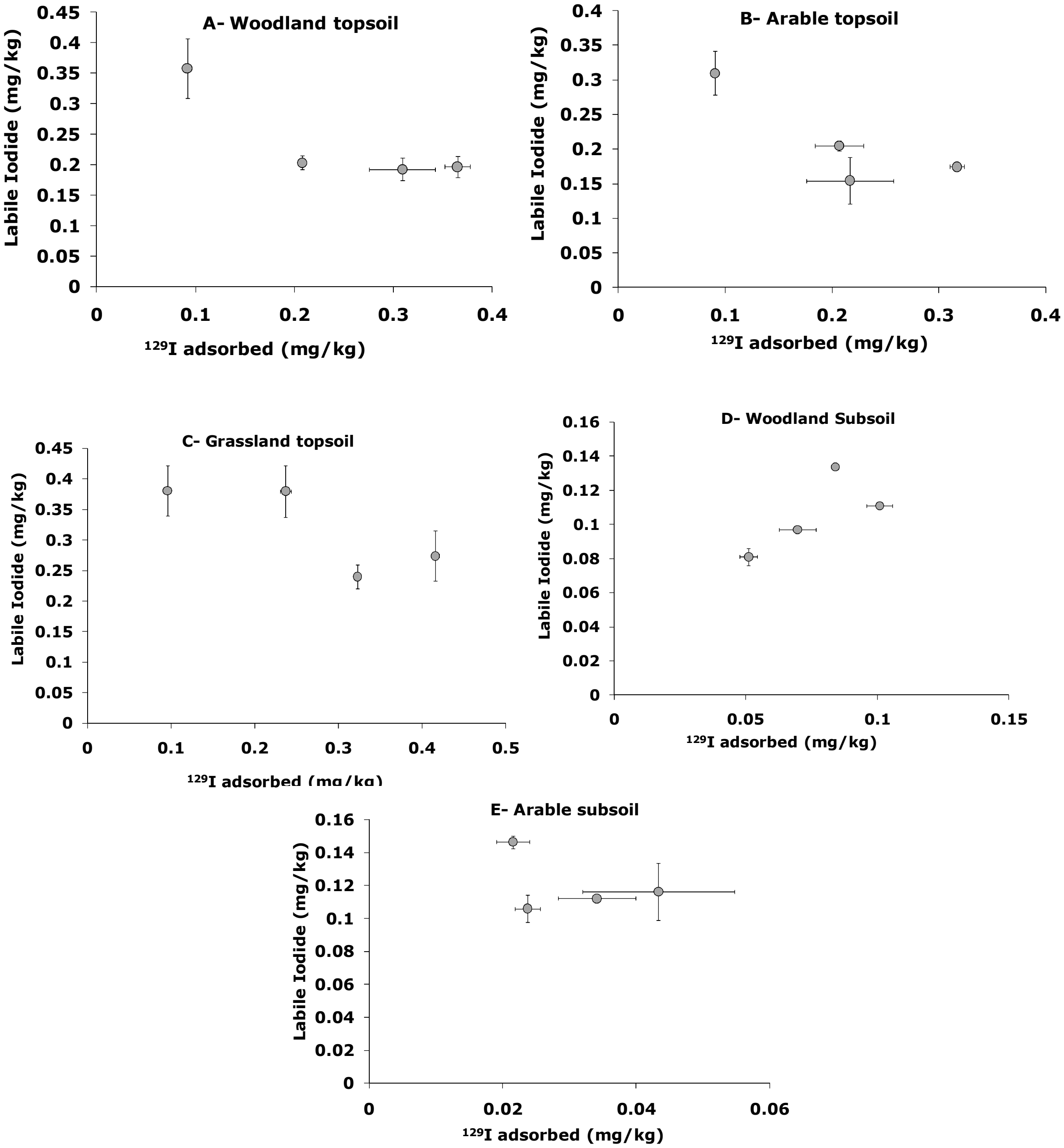


Figure 5.2 Concentrations of total-^{129}I adsorbed vs calculated soil iodine labile pool or E-value in Woodland topsoil (A), Arable topsoil (B), Grassland topsoil (C), Woodland subsoil (D) and Arable subsoil (E). Soil suspensions in 20 mL 0.01 M KNO_3, were spiked with different $^{129}I^-$ concentrations and equilibrated by shaking for 48h. E-value of soil iodine was then calculated at each spike concentration by calculating the K_d of the spiked ^{129}I between soil and soil solution

Substantial errors in E-value can occur if every species is not identified and precisely quantified unless, by coincidence, the K_d value is identical for all labile species present. The woodland topsoil (highly organic and acidic) is closest to giving a constant value for labile iodine (nominally iodide) (Table 5.3 and Figure 5.2 A). This is surprising as it might be expected that the chemical reaction of the spiked $^{129}I^-$ with soil organic matter would preclude this. All the other soils (Table 5.3 and Figure 5.2 B, C, D, E) seem to demonstrate inconsistent apparent E-values with different ^{129}I adsorption which suggests irreversible adsorption of the isotope $^{129}I^-$ such as would be expected by covalent bonding to humus-carbon. Ideally, E-values for iodide represent the same reactive iodide pool (I_{soil} in equation 5.2); however, this is only true if no chemical transformation of iodide occurs and the dominant process is the reversible adsorption of iodide. Nevertheless, it can be observed from Tables 5.1 and 5.3 that again woodland topsoil was closest to giving similar E-value and I_{soil} for iodide; in arable subsoil the two values were of the same order of magnitude. In general, the level of the isotopically exchangeable iodine was very low in all the soils (0.04-0.18 mg/kg) which qualitatively supports the idea that the majority of the native iodine is organically-bound and thus non-reactive.

Table 5.3

Iodide E-value calculated as a function of adsorbed $^{129}I^-$ (Equation 5.3). Soil suspensions in 20 mL 0.01 M KNO_3, were spiked with different $^{129}I^-$ concentrations and equilibrated by shaking for 48 h

Soil	Adsorbed $^{129}I^-$ (mg kg^{-1})	Labile Iodide (mg kg^{-1})
Woodland Topsoil	0.09 ± 0.001	0.36 ± 0.048
	0.21 ± 0.004	0.20 ± 0.011
	0.31 ± 0.033	0.19 ± 0.018
	0.36 ± 0.013	0.20 ± 0.017
Woodland Subsoil	0.05 ± 0.003	0.08 ± 0.005
	0.07 ± 0.007	0.10 ± 0.002
	0.10 ± 0.005	0.11 ± 0.002
	0.08 ± 0.001	0.13 ± 0.002
Arable Topsoil	0.09 ± 0.001	0.31 ± 0.031
	0.21 ± 0.023	0.21 ± 0.007
	0.22 ± 0.041	0.15 ± 0.034
	0.32 ± 0.007	0.17 ± 0.003
Arable Subsoil	0.02 ± 0.002	0.11 ± 0.008
	0.03 ± 0.006	0.11 ± 0.001
	0.04 ± 0.011	0.12 ± 0.017
	0.02 ± 0.002	0.15 ± 0.004
Grassland Topsoil	0.10 ± 0.000	0.38 ± 0.041
	0.24 ± 0.007	0.38 ± 0.042
	0.32 ± 0.001	0.24 ± 0.019
	0.42 ± 0.005	0.27 ± 0.041

6. IODINE KINETICS AND SPECIATION IN SOIL

6.1 INTRODUCTION

Iodine is found in nature in several valence states and in a range of inorganic and organic forms including iodide (I^-), iodate (IO_3^-), elemental iodine (I_2) and organic iodine (Radlinger and Heumann, 1997; Schwehr and Santschi, 2003; Muramatsu et al., 2004; Gilfedder et al., 2007a,b; Liu et al., 2007; Yang et al., 2007; Yoshida et al., 2007). Its form depends on pH and the redox status of the surrounding environment; thus iodide is reported as the most prevalent form of iodine in river waters while iodate is most common in the oceans (Smith and Butler, 1979; Abdel-Moati, 1999). In rainwater a mix of species including iodate, iodide and organic iodine species have been reported (Gilfedder et al., 2007 b,c). Inorganic iodine forms may be retained in acidic soils by sorption on positively charged hydrous iron and aluminium oxides (Whitehead, 1973a, 1974b, 1978; Ullman and Aller, 1985; Fukui et al., 1996; Sheppard et al., 1996; Yoshida et al., 1998; Dai et al., 2004, 2009; Um et al., 2004; Shimamoto et al., 2010). However, strong assimilation of iodine into soil organic matter has been widely reported (Whitehead, 1973a; Francois, 1987 a,b; Fukui et al., 1996; Sheppard et al., 1996; Yu et al., 1996; Steinberg et al., 2008 a,c; Dai et al., 2009; Schwehr et al., 2009; Englund et al., 2010; Shimamoto et al., 2011; Smyth and Johnson, 2011) and humus may constitute the primary reservoir of iodine in most soils. The fate of inorganic iodine and the mechanisms governing its incorporation into organic matter have been the focus of a number of investigations. Reduction of iodate by soil organic matter may precede conversion of inorganic iodine into organic forms (Whitehead, 1974b, Fukui et al., 1996). Steinberg et al. (2008b) confirmed that iodate heated with peat and lignin over a pH range of 3.5-9 was converted to organic iodine forms and iodide. Francois (1987a) observed that the iodine content of humic substances increased following incubation with iodate for 5 days. In both cases it was shown that iodate was first reduced to reactive intermediate products, I_2 or HOI, which then reacted rapidly with the organic matter. From a study of reaction kinetics, Warner et al., (2000) concluded that iodination of natural organic matter followed the same mechanism as iodination of phenols, through reaction with molecular iodine, I_2. The same electrophilic substitution mechanism was suggested by Reiller et al., (2006) in their study of iodination of humic acids. Bichsel and von Gunten (1999, 2000) also demonstrated that iodide can be oxidised to HOI and thereby react with organic compounds (e.g. substituted phenol and methyl carbonyl compounds) similar to natural humic matter. A comparison of iodine L_{III}-Edge XANES and EXAFS spectra of iodinated organic compounds with naturally iodated humic substances, extracted from a range of soil types, indicated that organic iodine is primarily bonded to aromatic rings (Schlegel et al., 2006). Yamaguchi et al. (2010) suggested that soil organic matter may cause iodide oxidation and iodate reduction because it can work as both electron donor and electron acceptor (Alberts et al., 1974; Wilson and Weber, 1979; Miles and Brezonik, 1981; Chen et al., 2003; Blodau et al., 2009; Keller et al., 2009). Metal oxides and hydroxides (eg $Fe(OH)_3$, $Al(OH)_3$, MnO_2) may play an important role in controlling iodine behavior in soils, both through adsorption of inorganic iodine and oxidation of iodide. Ferric and aluminium oxides adsorb iodate more strongly than iodide (e.g. Whitehead, 1974a; Kodama et al., 2006). Oxidation of I^- to I_2 and then to IO_3^- has been shown to be catalysed by δ-MnO2 with IO_3^- adsorbing on the δ-MnO2 surface (Allard et al., 2009; Gallard et al., 2009; Fox et al., 2009). In the presence of humic substances the oxidation to IO_3^- is limited as I_2 can react to form organic iodine (org-I) species, especially at lower pH (Gallard et al., 2009).

In view of the importance of iodine sorption by soils in regulating plant bio-availability and losses to drainage water, and also considering the current lack of information regarding which soil factors govern reaction mechanisms and rates, the aims of the work carried out in this chapter were to:

1- measure the dynamics of iodide and iodate (^{129}I) transformation in soils, both in the solution and solid phases, in order to increase our understanding of the reaction process and rate;

2- account for the effects of soil factors likely to influence the adsorption and transformation of iodine species, including temperature, pH value and concentrations of soil organic carbon, Fe/Mn oxides and native iodine;

3- integrate the data from ^{129}I incubation experiments into a predictive model of iodate and iodide sorption kinetics parameterised by soil properties.

6.2 MATERIALS AND METHODS

6.2.1 Soil Sampling and Preparation

Topsoil and subsoil were sampled from two areas in the East Midlands of England, chosen to represent contrasting land-uses, soil pH values and concentrations of Fe/Mn oxides, organic matter, carbonate and iodine. Wick series (sandy loam) soil samples were taken from an arable field, a permanent grassland strip and adjacent mature deciduous woodland (Grid Reference 52°49’48”N-1°14’88”W) on the University of Nottingham farm, Sutton Bonington, Leicestershire (UK). Topsoil (0-20 cm depth) and subsoil (30-50 cm depth) samples were taken from the arable and woodland sites; only topsoil was sampled from the grassland as its associated subsoil was thought to be similar to the arable subsoil. Iodine concentrations in these soils were known to be low (2 - 4 mg kg^{-1}) from previous analysis. Soils with higher iodine concentrations (c. 8 – 12 mg kg^{-1}) (Johnson et al., 2005) were sampled on the Stoke Rochford Estate, Lincolnshire from the Elmton soil series, described as shallow, well-drained brashy calcareous fine loamy soils developed over Jurassic limestone. Grassland and woodland topsoils (0-20 cm) were collected from a valley with permanent grassland (52°50’53”N-0°40’26”W) and adjacent mature woodland (52°50’56”N-0°40’22”W); these are Lithomorphic Rendzina soils over limestone and thus have no associated subsoil. Arable topsoil (0-20 cm) and subsoil (30-50 cm) samples were taken from a field nearby (52°51’25”N-0°38’55”W).

Samples were collected with clean stainless steel spades, augers and trowels and sealed in plastic bags for transport. Soils were air dried until they could be sieved to <4 mm but were not allowed to dry completely so as to maintain microbial activity; they were then kept unsealed in a cold room (at 10°C) prior to use, to ensure they remained aerobic and to preserve remaining moisture content.

6.2.2 Soil Chemical Properties

Approximately 250 g of each soil was air dried, sieved and homogenised as described in section 2.1. Soil pH, carbonate content, loss on ignition (LOI), organic carbon content, (iron, aluminium, and manganese hydrous oxides), and total soil iodine were measured as detailed in sections 2.2, 2.3, 2.4, 2.5, 2.9 and 2.10, respectively.

6.2.3 Soil Incubation

Samples of ^{129}I, as sodium iodide solution (SRM 4949C, 0.004 mol L^{-1} $Na^{129}I$, 3451 Bq mL^{-1}), were obtained from the American National Institute of Standards (NIST), Gaithersburg, Maryland, USA. Iodate ($^{129}IO_3^-$) was prepared from $^{129}I^-$ by oxidation using sodium chlorite as described in section 2.11. Soil samples for incubation were prepared by mixing moist sieved soil (< 4 mm) in a food mixer with Milli-Q water (controls) or an equivalent volume of $^{129}I^-$ or $^{129}IO_3^-$ solution to give a final ^{129}I concentration of 0.15 mg kg^{-1} of dry soil. The water content of the incubated soil is inevitably an arbitrary choice. Therefore, the total volume of solution added to each soil was simply judged from the friability of the aggregated soil rather than being based on a fixed proportion of water holding capacity or a specific soil moisture tension. The need to maintain moist but aerobic soils capable of free gas exchange and able to be sub-sampled for periodic analysis was considered. Spiked soils were distributed between triplicate 500 mL Duran bottles (~180 g dry weight of soil per replicate) with a hole drilled in the lid to allow gas exchange, and incubated in the dark at 10^oC or 20^oC (± 2^oC). Moisture loss was monitored regularly and restored when necessary by re-mixing the soil in a food mixer with the required volume of Milli-Q water before returning the soil to the microcosm bottle and incubator.

6.2.4 Iodine Extraction and Analysis

After incubation for 114, 306, 810 and 3975 hours, samples (~4.5 g) of moist soil were equilibrated with 20 mL of 0.01 M KNO_3, followed by extraction with 0.15 M KH_2PO_4 and then 10 % TMAH, in 40 mL polycarbonate centrifuge tubes. At each stage soil suspensions were shaken for 16 hours on a reciprocal shaker, centrifuged (25 min at 3500 rpm), and filtered through 0.22 μm PTFE syringe filters. Calculation of phosphate-extractable iodine accounted for carry over from the previous KNO_3 equilibration gravimetrically. To follow shorter term iodine dynamics (< 72 hours), samples equivalent to ~3.5 g dry soil were taken from control microcosms and equilibrated in centrifuge tubes with 20 mL 0.01 M KNO_3 spiked with $^{129}I^-$ or $^{129}IO_3^-$ (0.15 mg kg^{-1} of soil) and shaken for a known time before centrifugation and filtration. Nitrate and phosphate extract solutions were analysed for dissolved organic carbon (DOC) (section 2.6), iodine species ($^{127}I^-$, $^{127}IO_3^-$, $^{129}I^-$, and $^{129}IO_3^-$) and total ^{127}I and ^{129}I concentrations (section 2.10). TMAH extracts were analysed for total ^{127}I and ^{129}I only.

6.2.5 ^{129}I Recovery

Approximately 4000 h after spiking with $^{129}I^-$ or $^{129}IO_3^-$ weighed samples of ~3 g (wet weight) of soil were extracted with 20 mL 10% TMAH at 70°C for 3 hours, centrifuged at 3500 rpm for 25 min and filtered. To ensure complete recovery of iodine, the extraction was repeated three times, followed by a further two washing steps using 20 mL of MilliQ water with shaking for 3 hours. Filtered supernatant solutions from each extraction step, including the two washing steps, were accumulated in 100 mL volumetric flasks and made to the mark with milliQ water. Total ^{127}I and ^{129}I concentrations were then determined using ICP-MS as described in section 2.10.

6.2.6 Modelling $^{129}I^-$ and $^{129}IO_3^-$ Transformation Kinetics

For each soil, the reduction in solution concentration (in 0.01 M KNO_3) of $^{129}IO_3^-$ and $^{129}I^-$ as a function of time was modeled using a range of kinetic expressions described briefly in Table 6.1. The 'first-order' models assume that reaction kinetics proceed either to an equilibrium position with respect to dissolved IO_3^- or I^- (reversible; RFO model) or to zero concentration of inorganic iodine (irreversible; IFO model). In addition, to allow for initially instantaneous adsorption, the models were tested with initial concentrations of $^{129}I^-$ or $^{129}IO_3^-$ (I_0) equal to (i) the total amount of ^{129}I added (i.e. 0.15 mg kg^{-1} soil) or (ii) a concentration determined by the application of a partition coefficient (K_d). The addition of the coefficient K_d allows for instantaneous adsorption of inorganic iodine, possibly on metal oxide sites; the value of K_d was optimized alongside the kinetic parameters.

Table 6.1

Equations used to model the transformation kinetics of $^{129}I^-$ or $^{129}IO_3^-$

Model	Equation			Reference
Irreversible First Order (IFO)	$I_t = I_0\, e^{-kt}$ and $I_0 = \frac{I_{tot}}{1 + K_{d(0)}\frac{W}{V}}$	(6.1) (6.2)	I_t is the concentration of $^{129}I^-$ or $^{129}IO_3^-$ in solution at time t (mg kg^{-1} soil), k is the reaction rate constant (h^{-1}), t is time (h) and I_0 is the total concentration of $^{129}I^-$ or $^{129}IO_3^-$ at time t =0. I_{tot} is the total concentration of $^{129}I^-$ or $^{129}IO_3^-$ (amount added,mg kg^{-1} soil), W is the soil mass (g), V is the solution volume (mL) and $k_{d(0)}$ is apparent distribution coefficient of $^{129}I^-$ or $^{129}IO_3^-$ at time t = 0	see e.g. Sparks (1989)
Reversible First Order (RFO)	$I_t = I_{t-1}\,(1-k_F) + k_R\,(I_0 - I_{t-1})$	(6.3)	I_{t-1} is the concentration of $^{129}I^-$ or $^{129}IO_3^-$ (mg kg^{-1} soil) in solution at time t_{-1}, and k_F and k_R are the forward and reversible reaction rate constants (h^{-1}), respectively.	Empirical
Elovich	$I_t = I_0 - \left(\frac{1}{\beta}\ln \alpha\beta + \frac{1}{\beta}\ \ln t\right)$	(6.4)	α and β are constants	see e.g. Chien and Clayton (1980)
Infinite Series Exponential (ISE)	$I_t = I_0\,(t+ {I_0}^{1/\alpha})^{-\alpha}$	(6.5)	α is a constant	see e.g. Sinaj et al. (1999)
Parabolic Diffusion (Par-Diffn)	$I_t = I_0\,(1 - R_D\,\sqrt{t} + \alpha)$	(6.6)	R_D is the overall diffusion coefficient and α is a constant	see e.g. Sparks (2003)
Spherical Diffusion (Sph-Diffn)	$I_t = I_0\left(\frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{n^2}\ \exp - \left(\frac{n^2\pi^2 Dt}{r^2}\right)\right)$	(6.7)	n is an integer, D is the intra-aggregate diffusion coefficient ($m^2\ h^{-1}$) and r is the aggregate radius (m)	see e.g. Brown et al. (1971)

The empirical Elovich equation has been shown to describe the reaction kinetics of a wide range of inorganic compounds with soils and soil components (Atkinson et al., 1970; Chien and Clayton, 1980; Martin and Sparks, 1983). It is characterised by a greater ability to describe kinetics over a wide range of timescales, in contrast to other models, because it includes both a constant term which effectively describes instantaneous adsorption and an exponential term. Echevarria et al., (1998) and Sinaj et al., (1999) applied an equation based on an infinite series of exponential terms to describe the progressive mixing of metal isotopes with the native soil metal pool - described here as the 'ISE' model.

Where diffusion or transport-controlled processes are the rate-limiting steps a parabolic diffusion expression (Par-diffn model here) has been used previously (Chute and Quirk, 1967, Jardine and Sparks, 1984, Havlin et al., 1985). Application of the spherical diffusion equation (Sph-diffn model here; e.g. Brown et al., 1971) assumes that reactions are controlled by diffusion into uniform spherical aggregates of adsorption surfaces (e.g. humic acid or porous Fe oxides). It has been applied successfully to describe diffusion-controlled kinetics in minerals and soils (Cliff et al. 2002; Altfelder and Streck, 2006; Iznaga et al., 2007).

Altfelder and Streck (2006) demonstrated the greater consistency of the spherical diffusion approach over a first order kinetic equation when parameterised for short time periods and applied to longer reaction times (days-months) because the rate constants of the first order approach are strongly time dependent, unlike the diffusion approach. Thus predicting long-term behaviour on the basis of parameters derived at a shorter timescale using a first-order approach is particularly problematic (Altfeder & Streck, 2006).

All the models were optimised for individual soils by minimising the residual standard deviation (RSD) between modeled and experimental data, while systematically changing the values of model parameters, using the ‘Solver’ function in the software package Excel 2007. In addition, an attempt was made to fit a single spherical diffusion model to all soils simultaneously by relating model parameters to soil variables; this is described in section 6.3.6.

6.3 RESULTS AND DISCUSSION

6.3.1 Soil Characteristics

Measured soil characteristics are presented in Table 6.2. Soils from Sutton Bonington (SB) were typically lower in pH (4-7) and total iodine concentration (I_{tot} = 2-4 mg kg^{-1}) than those from Stoke Rochford (ST) (pH ~7, I_{tot} = 7.5-12 mg kg^{-1}). Woodland topsoils (SB-WT, ST-WT) and the Stoke Rochford grassland soil (ST-GT) had relatively large organic carbon contents (6-10%) and loss on ignition (LOI), compared to the arable soils from the same sites. Carbonate content was greatest in soils from Stoke Rochford where the underlying geology is limestone. A value of 2.5% carbonate in the SB arable topsoil (SB-AT) may reflect liming shortly before the soil was sampled. Iron and Mn oxide concentrations were typically higher in soils from the ST site.

Table 6.2

Soil properties

Soil	Code	Moisture Content* (%)	pH	^{127}I (mg/kg)	Org-C (%)	LOI (%)	Carbonate (%)	Al(OH)$_3$ (%)	MnO$_2$ (%)	Fe$_2$O$_3$ (%)
Stoke Rochford Woodland Topsoil	STWT	27	7.2	9.07 ± *0.04*	5.93	16.8 ± *0.12*	42.8 ± *0.99*	0.226 ± *0.002*	0.063 ± *0.0004*	1.76 ± *0.02*
Stoke Rochford Grassland Topsoil	STGT	29	6.85	11.8 ± *0.10*	8.39	20.1 ± *0.15*	1.47 ± *0.36*	0.505 ± *0.018*	0.094 ± *0.0005*	3.56 ± *0.21*
Stoke Rochford Arable Topsoil	STAT	16	7.34	7.48 ± *0.09*	2.88	9.04 ± *0.22*	5.37 ± *0.34*	0.361 ± *0.004*	0.061 ± *0.0005*	2.08 ± *0.01*
Stoke Rochford Arable Subsoil	STAS	14	7.05	9.72 ± *0.06*	2.41	9.37 ± *0.19*	6.65 ± *0.46*	0.481 ± *0.007*	0.084 ± *0.0004*	2.80 ± *0.08*
Sutton Bonington Woodland Topsoil	SBWT	36	4.38	4.41 ± *0.12*	10.14	23.4 ± *0.39*	0.00 ± *0.00*	0.286 ± *0.003*	0.011 ± *0.0002*	1.07 ± *0.004*
Sutton Bonington Woodland Subsoil	SBWS	12	3.86	1.98 ± *0.06*	1.66	4.4 ± *0.73*	0.00 ± *0.00*	0.243 ± *0.001*	0.007 ± *0.0001*	1.02 ± *0.01*
Sutton Bonington Arable Topsoil	SBAT	16	6.98	4.87 ± *0.10*	2.24	6.56 ± *0.18*	2.50 ± *0.12*	0.283 ± *0.001*	0.040 ± *0.0002*	1.49 ± *0.01*
Sutton Bonington Arable Subsoil	SBAS	11	6.50	2.35 ± *0.0*	0.79	3.54 ± *0.07*	0.00 ± *0.00*	0.241 ± *0.003*	0.026 ± *0.0004*	1.28 ± *0.02*
Sutton Bonington Grassland Topsoil	SBGT	15	6.63	2.57 ± *0.07*	2.44	5.89 ± *0.10*	0.00 ± *0.00*	0.195 ± *0.001*	0.022 ± *0.0002*	1.00 ± *0.01*

*Moisture content in incubated soils.

6.3.2 Equilibration in 0.01 M KNO_3 solution

The progressive changes in $^{129}IO_3^-$, $^{129}I^-$, and total ^{129}I concentrations in solution (expressed as mg kg^{-1} soil), following equilibration in 0.01 M KNO_3, are shown for all nine soils in Figures 6.1 and 6.2 for incubation at 10°C and Figures 6.3 and 6.4 for incubation at 20°C. The decline in total ^{129}I concentration varied with soil type, incubation temperature and the nature of the spiked species ($^{129}I^-$ or $^{129}IO_3^-$). Typically, sorption of ^{129}I from solution was fastest in soils at higher temperatures with lower pH and higher organic carbon contents. Sorption was faster for $^{129}I^-$ than for $^{129}IO_3^-$ spiked soils; $^{129}I^-$ was generally undetectable in the solution phase within ~ 100 h of spike addition whereas $^{129}IO_3^-$ was still detectable in solution for most soils at >300 h (at 10°C). Total ^{129}I concentrations in solution were always greater than those of the inorganic ^{129}I species, indicating rapid transformation of $^{129}I^-$ and $^{129}IO_3^-$ to unknown forms of soluble organic ^{129}I species. Concentrations of organic ^{129}I species in solution also decreased with time but persisted longer than the inorganic species resulting in an increasing proportion of organic ^{129}I species in the solution phase over time.

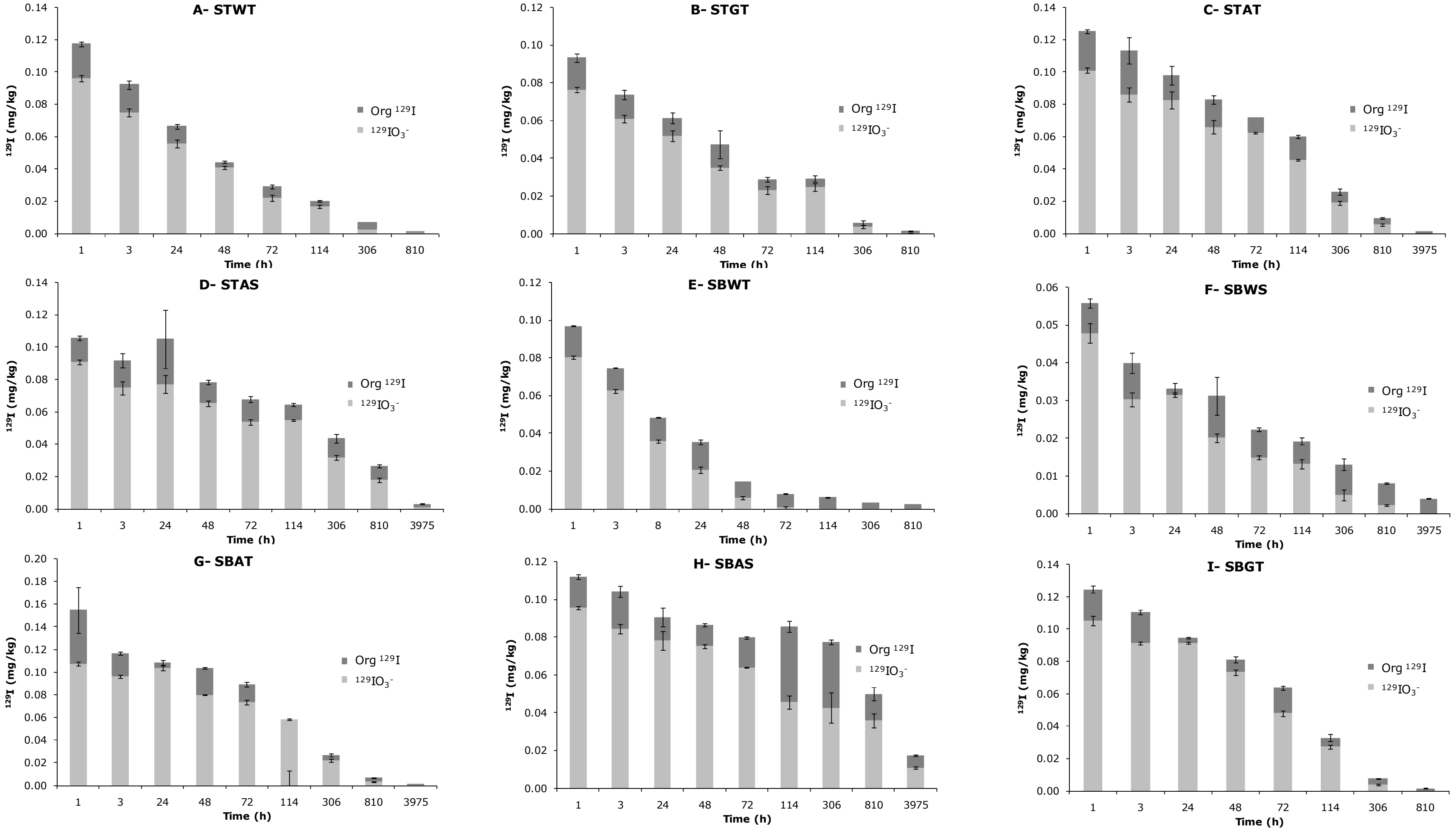


Figure 6.1. Iodate, 10^{o}C. Stacked plots where the total height of the bar represents total ^{129}I in solution in soil samples spiked with $^{129}IO_3^-$ (0.15 mg kg^{-1}), incubated at 10^{o}C and equilibrated with 0.01 M KNO_3. The light grey bar represents amount present as $^{129}IO_3^-$, with associated error. The difference between the total ^{129}I and $^{129}IO_3^-$, given by the dark grey bar represents the amount of organic ^{129}I in solution, again with associated error bars.

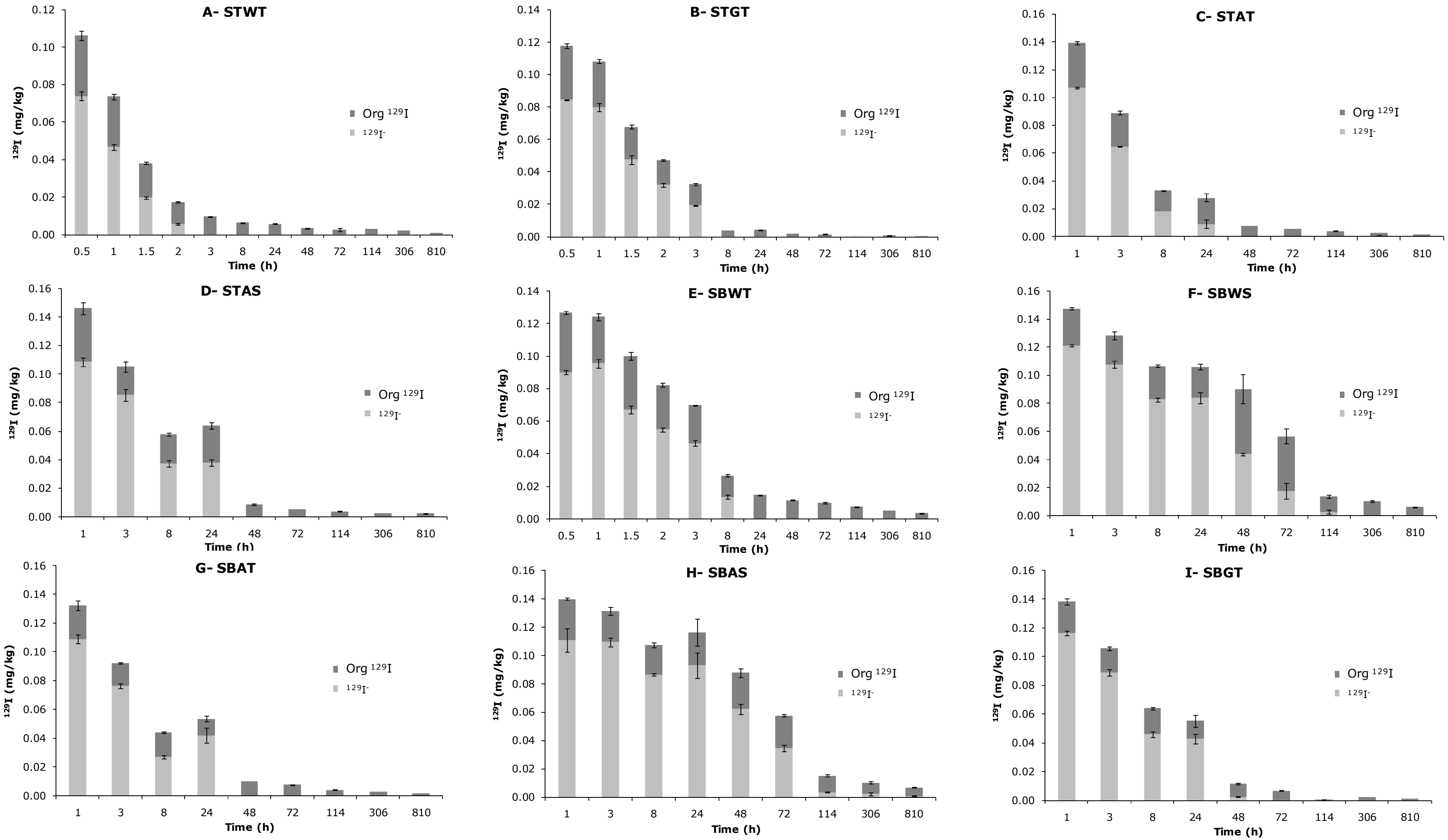


Figure 6.2. Iodide, 10^{o}C. Stacked plots where the total height of the bar represents total ^{129}I in solution in soil samples spiked with ^{129}I$^-$ (0.15 mg kg^{-1}), incubated at 10^{o}C and equilibrated with 0.01 M KNO_3. The light grey bar represents amount present as ^{129}I$^-$, with associated error. The difference between the total ^{129}I and ^{129}I$^-$, given by the dark grey bar represents the amount of organic ^{129}I in solution, again with associated error bars.

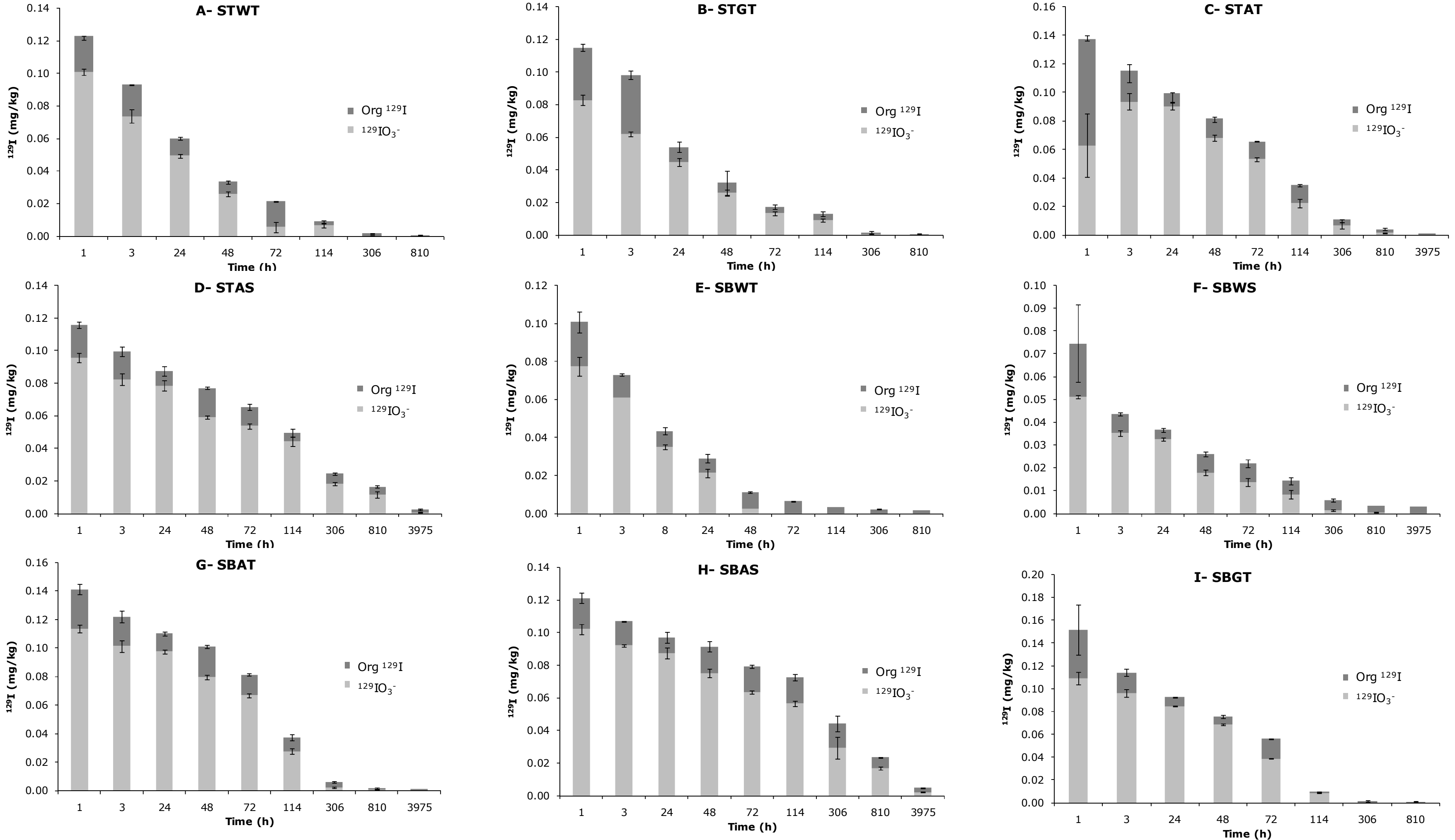


Figure 6.3. Iodate, 20^{o}C. Stacked plots where the total height of the bar represents total ^{129}I in solution in soil samples spiked with $^{129}IO_3^-$ (0.15 mg kg^{-1}), incubated at 20^{o}C and equilibrated with 0.01 M KNO_3.l The Light grey bar represents amount present as $^{129}IO_3^-$, with associated error. The difference between the total ^{129}I and $^{129}IO_3^-$, given by the dark grey bar represents the amount of organic ^{129}I in solution, again with associated error bars.

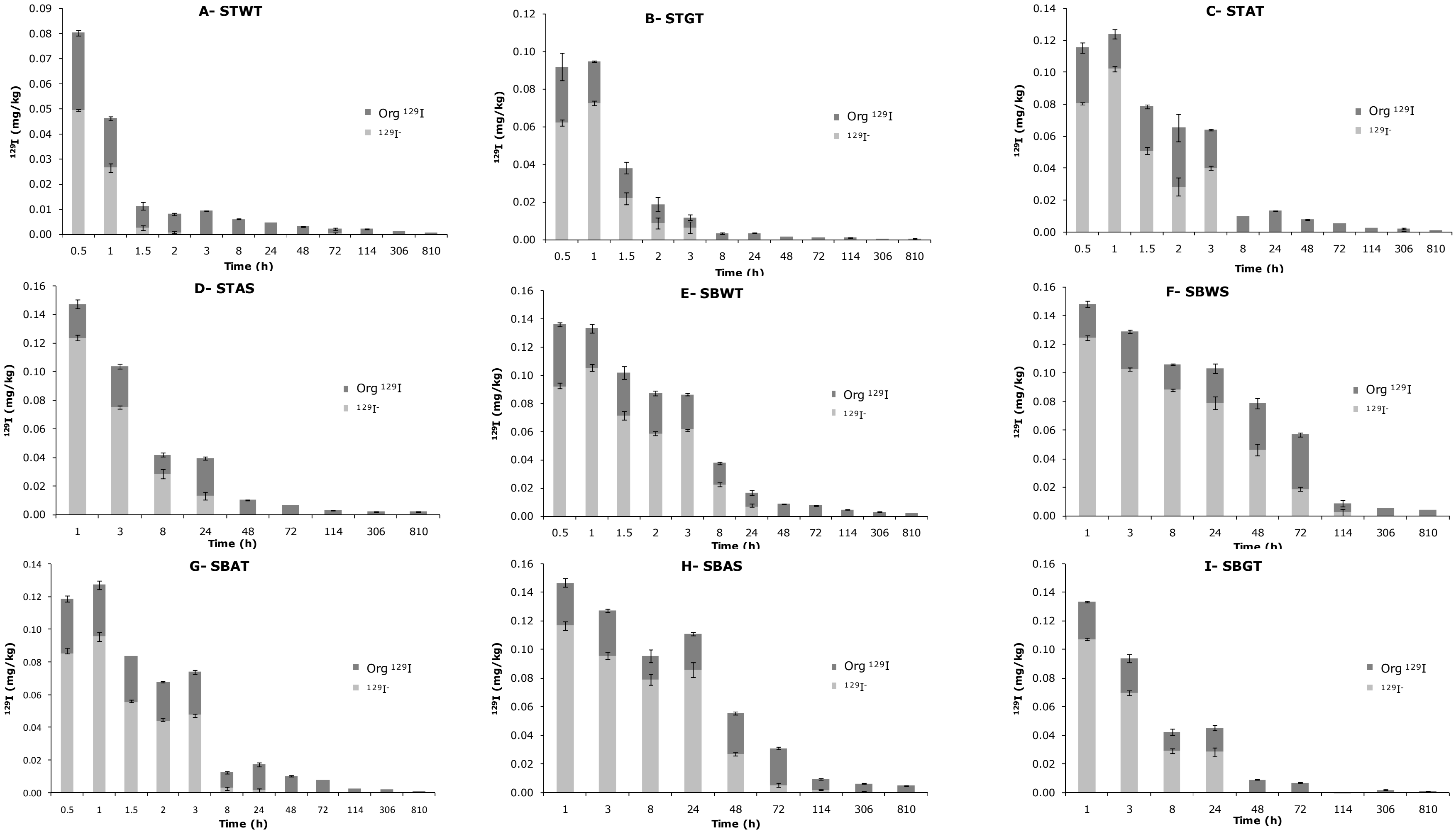


Figure 6.4. Iodide, 20^{o}C. Stacked plots where the total height of the bar represents total ^{129}I in solution in soil samples spiked with ^{129}I$^-$ (0.15 mg kg^{-1}), incubated at 20^{o}C and equilibrated with 0.01 M KNO$_3$. The light grey bar represents amount present as ^{129}I$^-$, with associated error. The difference between the total ^{129}I and ^{129}I$^-$, given by the dark grey bar represents the amount of organic ^{129}I in solution, again with associated error bars.

Time-dependent sorption of iodine

(i) $^{129}IO_3^-$

Figures 6.1 and 6.3 show that the greatest rate of $^{129}IO_3^-$ sorption was found in soil SBWT (highly organic and acidic), where $^{129}IO_3^-$ was not measureable in solution after ~100h (10°C) and ~70h (20°C). The sorption rates of $^{129}IO_3^-$ were also high where either pH was low or organic matter content high, seen by comparison of soils SBGT (moderately organic and slightly acidic), STWT (highly organic and slightly alkaline), and STGT (highly organic and slightly acidic) (Figures 6.1 and 6.3 (I), (A) & (B)). The slowest $^{129}IO_3^-$ sorption was observed in the arable subsoil (SBAS, Figures 6.1 and 6.3 (H)) which has a low organic content and relatively high pH, with ~ 7% of the $^{129}IO_3^-$ spike was still detectable in solution after 3975 h at 10°C.

This may suggest that the reduction in solution phase $^{129}IO_3^-$ concentration is controlled by a combined effect of soil organic matter content and pH. The long term (time dependent) sorption of $^{129}IO_3^-$ could be explained in terms of reaction with soil organic matter. Iodate is non reactive toward organic matter and has to be reduced to electrophilic species such HOI or I_2 before iodine can be incorporated into the organic structure of humus (Francois, 1987a; Warner et al., 2000; Reiller et al., 2006; Schlegel et al., 2006; Steinberg et al., 2008 b,c). The reduction reaction of iodate to iodide is faster under acidic conditions and HOI and I_2 have been suggested as possible intermediates (Orlemann and Kolthoff, 1942; Brummer and Field, 1979; Wels et al., 1991, Anik, 2004). In soils, humic substances can also reduce iodate due to their electron-donor characteristic (Chen et al., 2003; Wilson and Weber, 1979). This assumption is supported by comparing the rate of $^{129}IO_3^-$ disappearance from soil solution in soils with contrasting organic-C contents or pH values. The sorption rate for $^{129}IO_3^-$ was greater in acidic soils than in alkaline ones, at comparable organic matter contents (e.g. SBWT/STWT and SBWS/SBAS). Likewise, in soils with similar pH values the reaction rate of $^{129}IO_3^-$ was greater in soils with more humus such as SBWS compared to SBWT and SBAS to SBGT.

(ii) $^{129}I^-$

The highest rates of $^{129}I^-$ sorption were seen in STWT, STGT and SBWT soils where no detectable $^{129}I^-$ was found in solution after 2, 3 and 8 hours respectively, at 10°C or 20°C (Figures 6.2 and 6.4). In general, $^{129}I^-$ concentrations in the solution phase fell faster in the Stoke Rochford soils, with higher pH and greater carbonate and Fe-oxide contents, compared to soils with comparable land-use at Sutton Bonington. However, within soils sampled from the same site, reduction in $^{129}I^-$ solution concentration was fastest in soils with higher organic matter contents. Iodide must be oxidised to I_2 or HOI in order to form valence bonds with soil organic matter (Bichsel and von Gunten, 1999, 2000; Radlinger and Heumann, 2000; Warner et al., 2000; Reiller et al., 2006; Schlegel et al., 2006). The oxidation process, possibly through reaction with soil metal oxides, is directly proportional to the oxidising agent concentration, inversely proportional to pH and thermodynamically possible up to pH 7.5 (Allard et al., 2009; Gallard et al., 2009; Fox et al., 2009). Humic substances, which contain some electron acceptor sites (Blodau et al., 2009; Keller et al., 2009), can also work as oxidising agents for iodide. This may explain the faster loss of $^{129}I^-$ from solution in organic soils and soils with larger concentrations of Fe, Mn, and Al oxides. Soil pH value also affected the rate of iodide sorption. For example, the sorption rate of $^{129}I^-$ was considerably faster in the SBWS soil than in the SBAS soil. In the SBWS soil, $^{129}I^-$ was not found in soil solution in measurable amounts after 114 h contact with soil, whereas up to 12% of $^{129}I^-$ remained after 810 h in the SBAS soil (Figures 6.2 and 6.4). Both of these soils had approximately the same content of organic matter and metal oxides, but the pH of the SBWS soil was 3.86 whereas soil SBAS had a pH value of 6.5 (Table 6.2). Moreover, the transformation rate of $^{129}I^-$ in SBWT was greater than the rate in STAT and STAS soils despite having a much lower oxide content - possibly due to a combination of a very high organic matter content and the acidic pH of a woodland surface horizon.

(iii) Total-^{129}I

The total concentrations of ^{129}I in the solution phase, in both $^{129}I^-$ and $^{129}IO_3^-$ spiked soils, also declined with time. However, the concentrations of total-^{129}I were always higher than those of the added species ($^{129}I^-$ or $^{129}IO_3^-$) in the same sample indicating transformation of $^{129}I^-$ and $^{129}IO_3^-$ to unknown soluble ^{129}I forms. It is likely that these species arise from reaction of ^{129}I with dissolved organic matter, mainly fulvic acid. The concentrations of organic-I in the solution phase also decreased with time. This may suggest that some $^{129}I^-$ and $^{129}IO_3^-$ was first transformed to soluble organic-^{129}I as an intermediate step. This may have been followed by adsorption of the soluble organic-^{129}I on the solid phase as part of the dynamic equilibrium of humic acids between the soil solid and solution phases. Alternatively, the rapidly formed soluble organic-^{129}I complexes may have dissociated as the inorganic-I fell with time, resulting in further adsorption of inorganic I on to soil humus (in the solid phase).

Short term (instantaneous) sorption

Figures 6.1 to 6.4 illustrate a very rapid decline in solution phase ^{129}I concentrations immediately after addition of $^{129}I^-$ and $^{129}IO_3^-$ to soil. The gradual longer term sorption/transformation of $^{129}I^-$, $^{129}IO_3^-$, and total ^{129}I can be attributed to the oxidation and reduction of $^{129}I^-$ and $^{129}IO_3^-$, respectively, with eventual bonding to soil organic matter (previous section). However, the instantaneous decline in the solution phase concentrations of the inorganic species could be due to volatilisation, electrostatic attraction and 'chemi-sorption' on inorganic (oxide) soil phases or a very rapid reaction with solid and solution phase organic matter. Volatilisation of ^{129}I from solution is considered unlikely as such losses have been shown to be small in previous studies (Sheppard et al., 2006). Sheppard and Thibault (1992) also described immediate adsorption of iodide on organic soils which was interpreted in terms of rapid iodide diffusion into micropores and cavities in the fabric of soil organic matter. For iodide, Figures 6.2 and 6.4 show that soils which had fast initial $^{129}I^-$ sorption also showed rapid kinetics for (time-dependent) $^{129}I^-$ loss from solution. Soil STWT, for example, showed a sharp decline in iodide concentration; after only 0.5 h, iodide concentration was reduced by 50% at 10°C and 66% at 20°C. However, because the subsequent rate of $^{129}I^-$ loss from solution in some soils was also very high, (e.g. STWT, STGT, and SBWT), it was not possible to really distinguish separate processes. By contrast, the initial $^{129}IO_3^-$ adsorption was even greater than that of $^{129}I^-$ (Figures 6.1 to 6.4). and this was followed by markedly slower iodate sorption kinetics. Therefore, the initial sorption of iodate coult more easily be distinguished as a separate process from the longer term reaction. Figures 6.1 and 6.3 show that the greatest initial $^{129}IO_3^-$ adsorption (69% at 10°C and 82% at 20°C) was observed in soils with a low pH and a low organic carbon content, such as SBWS (Figures 6.1 and 6.3 (F)). High initial $^{129}IO_3^-$ adsorption was also observed in soil STGT (47% and 52% at 10°C and 20°C, respectively) (Figures 6.1 and 6.3 (B)) which had the highest measured iron-oxide content (Table 6.2). It is widely recognised that both iodide and iodate are adsorbed on soil Fe/Al oxides to greater extent under acidic conditions (Whitehead, 1973a, 1974b; Yoshida et al., 1992; Fukui et al., 1996; Sheppard et al., 1996; Yoshida et al., 1998; Dai et al., 2004, 2009). In addition, iodate is commonly reported to be more strongly adsorbed by soil metal oxides than iodide - especially in acidic soils with low organic matter contents (Ullman and Aller, 1985; Yoshida et al., 1992; Fukui et al., 1996; Um et al., 2004; Shimamoto et al., 2010). Adsorption may also be greater in soils with low humus contents because Fe oxide sites for anion adsorption will be less occupied by negatively charged humic acids which will increase their affinity for inorganic anions, such as IO_3^- (Gallard et al., 2009). The greater instantaneous sorption of $^{129}IO_3^-$ than $^{129}I^-$, especially in soils with low pH, low humus contents and large oxides contents all strongly suggests that the initial decline in $^{129}IO_3^-$, and possibly $^{129}I^-$, is due to sorption on soil Fe/Al oxides.

Cross-transformation between solution phase $^{129}IO_3^-$ and $^{129}I^-$

Where $^{129}IO_3^-$ was added no evidence for its reduction to $^{129}I^-$ was observed – i.e. there was no measureable $^{129}I^-$ in solution in soil microcosms to which $^{129}IO_3^-$ had been added. If the mechanism by which $^{129}IO_3^-$ is removed from solution into the soil phase involves its reduction to $^{129}I^-$ as an intermediate step then the kinetics of the $^{129}I^-$ assimilation into humus must therefore be faster than the kinetics of its production from IO_3^-. Similarly, in samples spiked with $^{129}I^-$, there was no evidence for its oxidation to $^{129}IO_3^-$.

6.3.3 Phosphate Extraction

Phosphate has been effectively used as an extractant for specifically adsorbed anions such as sulphate (Delfosse et al., 2005), selenite (Stroud et al., 2010) and iodine (Whitehead, 1973b).

In this study extraction with 0.16 M KH_2PO_4 was used to determine the amount of $^{129}IO_3^-$ and $^{129}I^-$ adsorbed on Fe/Mn oxides, implemented following KNO_3 equilibration at selected sampling times. Across all soils, iodine spikes and temperatures, the total amount of phosphate-extractable ^{129}I from spiked soils after ~100 h was very low, between 0.0015 mg kg^{-1} (1%) and 0.014 mg kg^{-1} (~9%). The largest extractable concentrations were found in subsoils with low organic matter contents

(SBAS, STAS, and SBWS), whereas the lowest levels of extractable ^{129}I were in the organic-rich topsoils (SBWT, STWT, and STGT). Of the total ^{129}I extracted, the majority was inorganic iodine ($^{129}IO_3^-$ and $^{129}I^-$) for most soils. In the higher pH arable subsoil (STAS) ~90% was inorganic with slightly less in the lower pH arable subsoil (SBAS). The woodland topsoil with a relatively high pH value (STWT) had the lowest proportion of inorganic iodine in the phosphate extract (20-40%), perhaps due to greater solubility of humic acid at high pH. Over time the proportion of inorganic iodine in the phosphate extraction decreased for all soils as the ^{129}I became progressively assimilated into the organic pool.

In iodate-129 spiked soils, $^{129}IO_3^-$, as a species, was only detected in phosphate extracts of arable subsoils (low organic content and neutral pH values), where it represented less than 3% of the initial spike concentration. This suggests that the initial 'instantaneous' sorption seen for iodate-spiked soils may not be inorganic adsorption of IO_3^- ions on Fe/Mn oxides and that the overall trend seen in Figures 6.1 and 6.3 may arise simply from rapid organic fixation, until exhaustion of initially available reduction capacity subsequently produces a slower assimilation rate. However, phosphate extraction was only carried out at extraction times >114 h. Therefore, in the soils that showed faster $^{129}IO_3^-$ kinetics than those observed in the SBAS and STAS soils, it is not possible to rule out immediate sorption of inorganic species on to Fe/Mn oxides. $^{129}IO_3^-$ may have been simply detectable in the phosphate extracts of the SBAS and STAS soils because of the slower fixation kinetics which enabled it to persist longer as sorbed (inorganic) $^{129}IO_3^-$. Moreover, the results obtained in chapter 4 of this study showed that phosphate extraction may actually catalyse the reaction of iodide and iodate with soil organic matter by mobilising solid phase soil organic matter into solution. Accordingly, in soils where $^{129}IO_3^-$ overall reaction rates were faster than those of the SBAS and STAS soils, the very small amounts of $^{129}IO_3^-$ remaining (sorbed on metal oxides) may have reacted with soil organic matter during the phosphate extraction process.

Whether ^{129}I was added as either $^{129}I^-$ or $^{129}IO_3^-$ measurable concentrations of phosphate-extractable iodide ($^{129}I^-$) were found (0.0025-0.01 mg kg^{-1}, 1.6 - 6.6 %) in all the soils. This suggests that iodide may be specifically adsorbed to some extent (i.e. adsorbed in the presence of 0.01 M NO_3^-) and is not a wholly conserved solute. It also indicates, for the $^{129}IO_3^-$ spiked soils, that iodide may be an intermediate in the overall process whereby iodate is assimilated into humus.

6.3.4 TMAH Extraction

Tetra methyl ammonium hydroxide (TMAH) has recently been shown to quantitatively extract the total iodine content from environmental samples e.g. soils, sediments, plants, and food (Watts & Mitchell, 2009). Alkaline extractants such as TMAH mobilise humic acids (and organic I) by negative charge generation and may also cause some degree of hydrolysis of organic I compounds. In addition, TMAH releases iodate from specific sorption sites on Fe/Al hydrous oxides by replacement with hydroxide ions and negative charge generation on the oxide surface (Yamada et al., 1996).

A single TMAH (10%) extraction was used as a final step for some samples, following phosphate extraction. On average, total ^{129}I extracted ranged from 0.109 – 0.129 mg kg^{-1} (representing 73-86% recovery of the 0.15 mg kg^{-1} spike). Recovery was generally slightly worse in organic rich soils (e.g. 75-80% in STWT) and better in those with lower organic matter contents (e.g. arable subsoils, SBAS and STAS, 85-90%). The amount of total ^{129}I extracted was unaffected by incubation temperature or the iodine species used for initial spiking. Consequently an exhaustive extraction procedure using three sequential extraction steps with 10% TMAH was undertaken on two soils (SBWT and SBAS) chosen to represent 'end members' in terms of soil properties (pH and % organic C). This more rigorous extraction produced c. 100% recovery of ^{129}I spikes (Table 6.3) and confirmed that loss of ^{129}I from solution was due to sorption on soil components rather than volatilization. It can also be observed from Table 6.3 that the concentrations of total ^{127}I were 22% higher for SBWT and 16% higher for SBAS than the total ^{127}I concentrations measured for the same soils using the standard method described in section 2.10 (see Table 6.2 for comparison). Tagami et al. (2010) also noticed that the concentrations of total soil iodine measured by Energy-Dispersive-X-Ray-Fluorescence (EDXRF) were 25 - 40 % higher than those measured by ICP-MS following a single-step TMAH extraction of some soil samples. They presumed that this difference is a 'plant-unavailable' iodine pool in contrast to the 'TMAH-extractable' iodine which is potentially plant-available. The results obtained here confirm only that all soil iodine is extractable by TMAH; however a multiple-step extraction is required.

Table 6.3

Total ^{127}I and ^{129}I extracted from $^{129}I^-$ and $^{129}IO_3^-$ spiked SBWT and SBWS soils. Extraction was carried out using an exhaustive TMAH extraction procedure in which soils were extracted with 10% TMAH solution at 70°C for three sequential extraction steps followed by a washing step using mQ water.

Soil	Spike	^{127}I (mg/kg)	^{129}I (mg/kg)
SBWT	$^{129}I^-$	5.38 ± 0.07	0.153 ± 0.001
	$^{129}IO_3^-$	5.38 ± 0.03	0.148 ± 0.001
SBAS	$^{129}I^-$	2.78 ± 0.04	0.150 ± 0.002
	$^{129}IO_3^-$	2.68 ± 0.03	0.144 ± 0.001

6.3.5 Modelling $^{129}I^-$ and $^{129}IO_3^-$ Kinetics

Model parameters and residual standard deviations (RSD) for individual model fits are given in Tables 6.4 and 6.5 for $^{129}I^-$ or $^{129}IO_3^-$, respectively. Figure 6.5 shows a box and whisker comparison of the average RSD as produced by individual models fit for $^{129}I^-$ or $^{129}IO_3^-$ across all soils.

For $^{129}IO_3^-$, models in which no instantaneous adsorption was allowed (i.e. irreversible first order (IFO), infinite exponential (ISE), reversible first order (RFO) and parabolic diffusion) gave a poorer fit, with a greater range of RSD values, than those that incorporated a K_d value (Figure 6.5 A). The reversible first order + K_d (RFO-K_d), irreversible first order + K_d (IFO- K_d) and spherical diffusion + K_d (Sph-Diffn- K_d) models generated the best fits and the smallest range of RSD values across the soils. The Sph-Diffn-K_d model gave marginally the lowest average RSD value overall (6.64 μg kg^{-1}) as compared to the IFO- K_d model RSD (6.68 μg kg^{-1}) and the RFO- K_d model RSD (7.15 μg kg^{-1}).

For $^{129}I^-$, with the exception of the ISE and Par-Diffn models, all models generated a similar average RSD value and the influence of instantaneous adsorption and requirement for inclusion of K_d in the model was less clear. The reasons for this may be weaker instantaneous adsorption of inorganic iodide on Fe/Mn oxides or a more sustained reaction with SOC in which either generation of intermediary iodine species is not limiting or diffusion into humic aggregates is faster.

Also important to note is that the errors in the fits of the $^{129}I^-$ models are likely to be greater than those for iodate as the faster kinetics resulted in fewer measured values being obtained and fitted. The three $^{129}I^-$ sorption models that generated the lowest RSD values are the same as those indentified as most successful in fitting iodate data - i.e. reversible first order + K_d (RFO-K_d, average RSD 13.5 μg kg^{-1}), irreversible first order + K_d (IFO-K_d, average RSD 13.6 μg kg^{-1}) and spherical diffusion + K_d (Sph-Diffn- K_d, average RSD 14.2 μg kg^{-1}) (Figure 6.5 B).

Table 6.4

Iodate sorption kinetics: summary of model outputs for each soil type at 10°C and 20°C. For a definition of each parameter please see Table 6.1. Residual standard deviations (RSD values) were calculated for individual models optimized over both temperatures simultaneously.

	ST-WT		ST-GT		ST-AT		ST-AS		SB-WT		SB-WS		SB-AT		SB-AS		SB-GT	
	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C
Parabolic Diffusion																		
RD - overall diffn coeff	0.021	0.021	0.017	0.018	0.010	0.010	0.009	0.009	0.016	0.016	0.004	0.004	0.012	0.012	0.008	0.010	0.027	0.028
Constant	0.529	0.577	0.603	0.624	0.488	0.527	0.530	0.536	0.694	0.705	0.821	0.815	0.396	0.448	0.466	0.446	0.361	0.383
RSD (μg/kg)	*23.37*		*17.14*		*25.08*		*17.40*		*24.49*		*13.22*		*29.11*		*15.30*		*21.98*	
Elovich																		
α	0.574	0.610	5.785	2.835	0.284	0.370	2.093	0.719	4.560	6.191	948404	48898	0.085	0.078	1.189	0.223	0.115	0.097
β	65.812	62.437	85.088	75.376	74.089	72.727	94.896	80.816	74.085	76.126	175.144	151.576	67.495	60.177	100.097	76.886	59.066	53.846
RSD (μg/kg)	*9.40*		*6.84*		*15.44*		*8.61*		*12.30*		*5.89*		*19.36*		*9.24*		*17.56*	
Irreversible 1st order + Kd																		
Kd (L kg^{-1})	3.514	3.163	5.776	4.863	3.008	2.735	5.015	3.635	4.094	4.368	13.759	11.615	2.122	1.579	4.259	2.910	2.180	1.857
Rate const (hr^{-1})	0.017	0.028	0.014	0.023	0.006	0.009	0.003	0.007	0.069	0.069	0.013	0.017	0.005	0.009	0.002	0.004	0.010	0.014
RSD (μg/kg)	*6.24*		*6.12*		*6.46*		*9.10*		*3.40*		*4.90*		*6.84*		*8.98*		*8.09*	
Irreversible 1st order																		
Rate const (hr^{-1})	0.041	0.275	0.413	0.381	0.015	0.018	0.018	0.020	0.282	0.302	0.959	0.851	0.010	0.014	0.013	0.013	0.017	0.021
RSD (μg/kg)	*26.68*		*25.39*		*28.64*		*35.35*		*16.78*		*16.96*		*23.00*		*33.23*		*24.36*	
Reversible 1st order + Kd																		
Kd (L kg^{-1})	3.487	3.161	5.682	4.843	2.965	2.735	4.811	3.466	4.035	4.350	7.194	11.580	2.122	1.579	3.526	2.748	2.180	1.857
Forward Rate constant (hr^{-1})	0.018	0.028	0.014	0.023	0.006	0.009	0.003	0.008	0.069	0.067	0.224	0.017	0.004	0.009	0.004	0.005	0.010	0.014
Reverse Rate constant (hr^{-1})	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.054	0.000	0.000	0.000	0.001	0.001	0.000	0.000
RSD (μg/kg)	*6.78*		*6.53*		*6.85*		*9.04*		*3.61*		*8.17*		*7.39*		*7.16*		*8.86*	
Reversible 1st order																		
Forward Rate constant (hr^{-1})	0.263	0.254	0.389	0.341	0.229	0.231	0.310	0.253	0.271	0.287	0.660	0.621	0.189	0.014	0.274	0.015	0.201	0.021
Reverse Rate constant (hr^{-1})	0.049	0.028	0.072	0.042	0.085	0.071	0.117	0.081	0.014	0.015	0.065	0.057	0.096	0.000	0.147	0.002	0.075	0.000
RSD (μg/kg)	*20.12*		*18.81*		*33.28*		*24.92*		*16.62*		*12.36*		*31.26*		*26.20*		*30.10*	
Inf-exp + Kd																		
Kd (L kg^{-1})	2.395	2.228	4.285	3.627	1.725	2.039	2.799	2.191	3.440	3.705	10.745	9.254	1.086	0.809	2.249	1.557	1.424	1.176
Constant (n)	0.312	0.399	0.277	0.358	0.204	0.219	0.174	0.212	0.486	0.490	0.282	0.317	0.181	0.234	0.141	0.178	0.228	0.271
RSD (μg/kg)	*12.30*		*10.32*		*21.56*		*13.97*		*9.90*		*6.16*		*26.26*		*15.05*		*24.50*	
Inf-exp																		
Constant (n)	0.441	0.565	0.511	1.335	0.271	0.297	0.279	0.300	1.102	1.251	2.609	2.466	0.222	0.267	0.223	0.237	0.289	0.325
RSD (μg/kg)	*22.47*		*28.09*		*26.84*		*25.05*		*21.37*		*17.30*		*26.75*		*24.72*		*26.59*	
Spherical Diffusion + Kd																		
Kd (L kg^{-1})	2.328	1.814	4.420	3.358	2.116	1.925	3.816	2.698	2.218	1.156	11.449	9.325	1.337	0.819	3.285	2.086	1.360	0.987
D/r^2	0.001	0.002	0.001	0.002	0.000	0.001	0.000	0.000	0.005	0.005	0.001	0.001	0.000	0.001	0.000	0.000	0.001	0.001
RSD (μg/kg)	*5.11*		*4.72*		*8.88*		*6.75*		*2.67*		*4.44*		*10.72*		*5.69*		*10.80*	

Table 6.5

Iodide sorption kinetics: summary of model outputs for each soil type at 10°C and 20°C. For a definition of each parameter please see Table 6.1. Residual standard deviations (RSD values) were calculated for individual models optimized over both temperatures simultaneously.

	ST-WT		ST-GT		ST-AT		ST-AS		SB-WT		SB-WS		SB-AT		SB-AS		SB-GT	
	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C	10°C	20°C
Parabolic Diffusion																		
RD - overall diffn coeff	0.6606	0.4923	0.4740	0.4592	0.1580	0.3944	0.1201	0.1773	0.2594	0.1462	0.0294	0.0832	0.1092	0.1410	0.0295	0.0273	0.1145	0.1261
Constant	0.0386	0.3329	0.0728	0.2121	0.2554	0.1176	0.2376	0.1355	0.2070	0.3137	0.3901	0.1315	0.2914	0.4062	0.3570	0.4446	0.2067	0.2796
RSD (μg/kg)	*4.84*		*14.01*		*23.80*		*24.17*		*13.68*		*24.13*		*23.50*		*30.12*		*20.27*	
Elovich																		
α	0.437	1.075	0.338	0.564	0.148	0.366	0.146	0.090	0.308	0.332	0.065	0.048	0.188	0.530	0.066	0.100	0.096	0.174
β	20.01	26.51	25.01	25.77	31.02	30.16	40.76	27.86	32.78	39.07	46.89	40.50	42.31	38.89	50.11	49.05	36.22	38.10
RSD (μg/kg)	*4.68*		*14.90*		*20.09*		*16.39*		*11.23*		*15.53*		*17.12*		*18.84*		*13.33*	
Irreversible 1st order + Kd																		
Kd (L kg^{-1})	0.214	0.958	1.133	1.693	0.460	1.532	1.892	0.000	1.801	1.995	1.416	1.357	1.193	1.867	1.631	1.690	1.685	1.113
Rate const (hr^{-1})	1.2721	1.8129	0.5999	0.8722	0.2509	0.4448	0.0804	0.2139	0.2940	0.2085	0.0219	0.0228	0.1455	0.3512	0.0156	0.0259	0.0660	0.1680
RSD (μg/kg)	*6.27*		*14.09*		*17.57*		*16.83*		*9.95*		*9.47*		*18.05*		*11.50*		*18.28*	
Irreversible 1st order																		
Rate const (hr^{-1})	1.3213	2.0751	0.7682	1.1638	0.2872	0.6474	0.1839	0.2139	0.5013	0.4168	0.0323	0.0331	0.2281	0.5764	0.0236	0.0408	0.1467	0.2458
RSD (μg/kg)	*5.39*		*14.24*		*16.95*		*17.10*		*15.94*		*19.65*		*18.89*		*22.15*		*19.51*	
Reversible 1st order + Kd																		
Kd (L kg^{-1})	0.214	0.958	1.217	1.780	0.346	1.473	0.516	0.000	1.698	1.892	1.417	1.357	0.196	1.977	1.631	1.690	0.723	0.274
Forward Rate constant (hr^{-1})	0.9412	1.1921	0.5055	0.6948	0.2497	0.4168	0.1813	0.2056	0.2878	0.2102	0.0217	0.0226	0.2516	0.3093	0.0154	0.0256	0.1234	0.2392
Reverse Rate constant (hr^{-1})	0.0000	0.0000	0.0000	0.0000	0.0153	0.0429	0.0603	0.0175	0.0197	0.0154	0.0000	0.0000	0.0772	0.0000	0.0000	0.0000	0.0211	0.0533
RSD (μg/kg)	*8.87*		*17.23*		*22.40*		*8.91*		*11.01*		*10.37*		*13.76*		*12.42*		*16.17*	
Reversible 1st order																		
Forward Rate constant (hr^{-1})	0.9670	1.2914	0.6891	0.9017	0.2770	0.6557	0.2197	0.2056	0.4872	0.4089	0.0332	0.0382	0.2690	0.5121	0.0240	0.0416	0.1697	0.2615
Reverse Rate constant (hr^{-1})	0.0000	0.0000	0.0810	0.0265	0.0185	0.1709	0.0679	0.0175	0.0745	0.0533	0.0008	0.0035	0.0795	0.0245	0.0005	0.0009	0.0300	0.0567
RSD (μg/kg)	*6.60*		*16.16*		*18.43*		*7.25*		*15.71*		*20.95*		*15.56*		*23.61*		*13.47*	
Inf-exp + Kd																		
Kd (L kg^{-1})	14.54	29.91	7.47	13.27	1.63	6.16	1.72	0.78	4.94	4.22	0.47	0.54	1.85	5.87	0.74	0.76	1.13	1.88
Constant (n)	1.2483	1.8208	0.6439	0.8730	0.6857	0.4699	0.3793	0.6279	0.4494	0.4202	0.3316	0.2991	0.4223	0.5469	0.2750	0.3551	0.4321	0.4905
RSD (μg/kg)	*9.87*		*18.60*		*20.26*		*11.56*		*15.60*		*22.19*		*17.34*		*24.57*		*13.78*	
Inf-exp																		
Constant (n)	4.2156	5.4323	3.3219	4.2523	1.0241	3.1066	0.5759	0.7549	2.7232	2.4484	0.3577	0.3329	0.6787	2.9768	0.3124	0.3994	0.5426	0.7989
RSD (μg/kg)	*15.84*		*34.34*		*38.61*		*19.20*		*48.64*		*21.40*		*36.63*		*24.38*		*20.53*	
Spherical Diffusion + Kd																		
Kd (L kg^{-1})	0.000	0.000	0.000	0.000	0.000	0.000	0.585	0.000	0.144	0.385	0.329	0.300	0.724	0.079	0.659	0.501	0.270	0.043
D/r^2	0.0847	0.1440	0.0436	0.0741	0.0146	0.0343	0.0054	0.0100	0.0232	0.0160	0.0017	0.0016	0.0062	0.0290	0.0011	0.0020	0.0051	0.0105
RSD (μg/kg)	*10.31*		*15.33*		*19.19*		*17.86*		*10.02*		*10.44*		*16.97*		*13.42*		*14.29*	

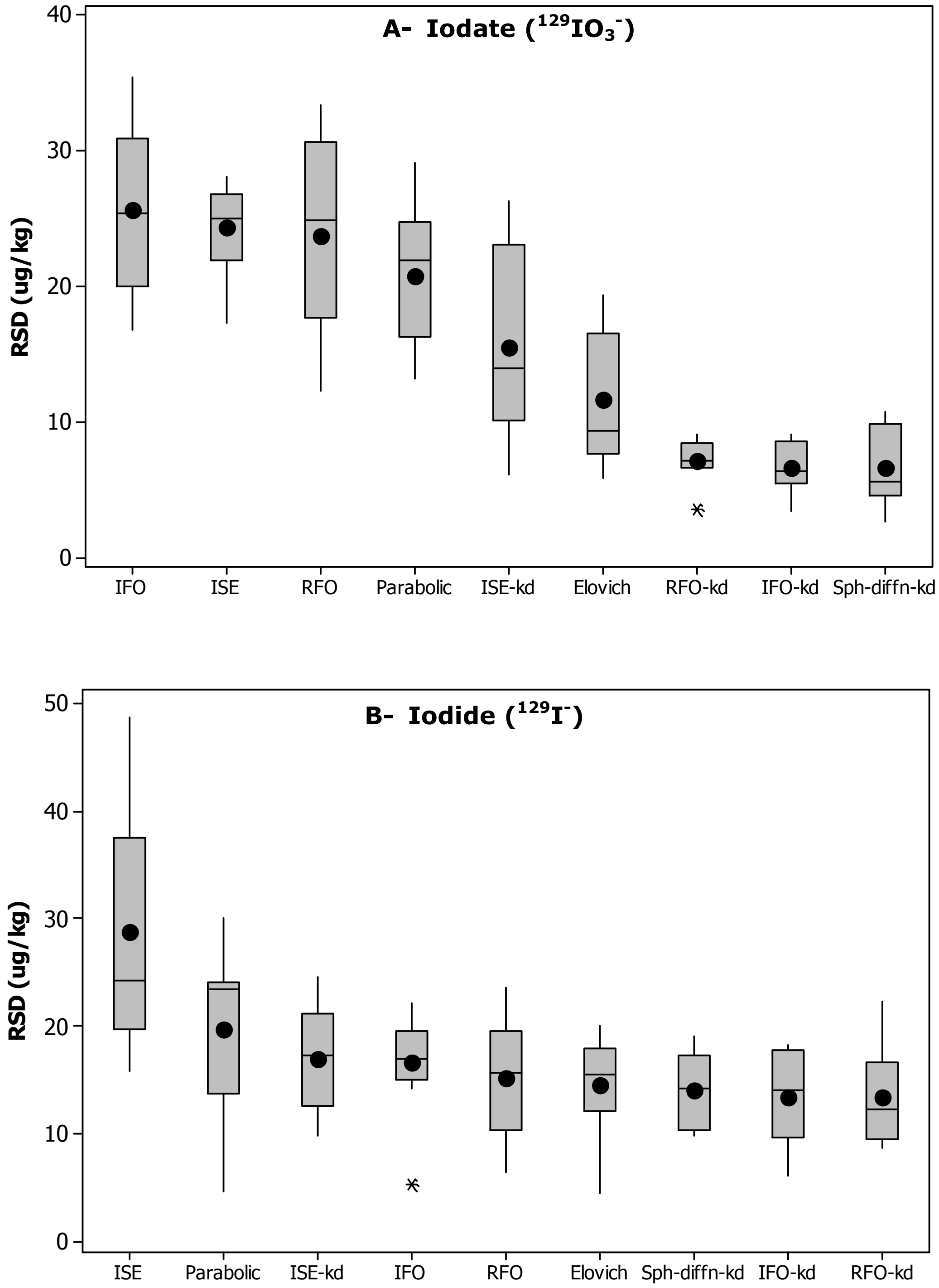


Figure 6.5 Modelling kinetics of (A) $^{129}IO_3^-$ and (B) $^{129}I^-$. Box and whisker plots showing the distribution of residual standard deviations (RSD; μg kg^{-1}) across nine contrasting soils for each of the nine models tested. The median value (horizontal line), the mean value (•) and outliers (*) are shown.

Reaction rate constants and distribution coefficients (K_d values) calculated for all models are given in Tables 6.4 and 6.5 for $^{129}IO_3^-$ and $^{129}I^-$, respectively. Comparison of the reaction rate constants generated by the irreversible first order model for soils incubated at 20°C with those incubated at 10°C showed that rates were on average 1.75 times higher at the higher temperature (Q_{10} = 1.75). The reaction rates for both $^{129}IO_3^-$ and $^{129}I^-$ were greatest in the acidic woodland topsoil and subsoil (SBWT and SBWS) and lowest in the organic-poor, higher pH arable sub soil (SBAS) from the same location, but there was no clear correlation with any individual soil property when reaction rates for individual soils were compared. Modelled (optimised) K_d values showed that instantaneous adsorption was usually greater for iodate than iodide (Tables 6.4 and 6.5). Reaction rates for $^{129}I^-$, were typically faster than those of $^{129}IO_3^-$ with the half life of $^{129}I^-$, ranging from a minimum of 0.38 h (STWT, 20°C) to a maximum of 45 h (SBAS, 10°C). Half lives for $^{129}IO_3^-$ were longer, between 9 h (SBWT, 20°C) and 412 h (SBAS, 10°C). Iodine concentration in rainfall is reported to be in the range of 0.5-5 μg L^{-1} (e.g. Truesdale and Jones, 1996; Neal et al., 2007; Hou et al., 2009) but there is little agreement on the mix of species present with I^-, IO_3^- and organic iodine all reported as 'major species', the relative proportions of each varying with location (e.g. Gilfedder et al., 2007; Yoshida et al., 2007). Low intensity rainfall will infiltrate the soil more easily than high intensity rainfall which 'seals' the surface of the soil increasing run-off. Coarse textured (e.g. sandy) soils will allow easier infiltration (> 50 mm h^{-1}) but will also drain completely within a few hours whereas a fine textured (e.g. clayey) soil allows less infiltration (<15 mm hr^{-1}) and will take 2-3 days to drain. For a shallow sandy soil with low organic matter content and a saturated hydraulic conductivity (K_{sat}) of ~10 cm h^{-1} it is possible that during a period of intense rainfall over several hours a substantial proportion of rainfall iodine may be lost from the topsoil. However, the range of rate constants calculated by the irreversible 1st order model suggest that under light / moderate rainfall conditions (2.5-7 mm/h) the rate of iodine reactions in the topsoil are sufficiently rapid for the majority of the iodine to be retained in this layer.

A comparison of modelled $^{129}I^-$ and $^{129}IO_3^-$ concentrations with experimentally measured concentrations for individual soils using various model approaches (Sph-Diffn-K_d, IFO-K_d, RFO-K_d, Elovich, Parabolic Diffusion and ISE-K_d) as a function of time are shown in Figures 6.6 to 6.17. Overall the best model fits to both $^{129}IO_3^-$ and $^{129}I^-$ were achieved using a spherical diffusion approach (Figures 6.5, 6.6 and 6.7). The success of the spherical diffusion model (Sph-Diffn-K_d) for $^{129}IO_3^-$appears to confirm its ability to describe processes over a relatively wide range of times (Altfelder and Streck 2006). That it also worked well for $^{129}I^-$ suggests that it is useful for describing faster reaction kinetics as well. IFO-K_d and RFO-K_d approaches also described $^{129}IO_3^-$ and $^{129}I^-$ reaction kinetics fairly well (Figures 6.5 and 6.8 to 6.11), with the most important factor in achieving a good fit for $^{129}IO_3^-$ being the inclusion of a K_d value to allow for instantaneous adsorption occurring at t=0. By contrast, for $^{129}I^-$, these models were only slightly better than those in which instantaneous adsorption was not included. However, the success of these two models was not universal across all soils. They tended in some soils to successfully describe the early phases of the reactions and then showed poorer fit at longer contact times (e.g. Figure 6.10 E, H, and Figure 6.11 B, C, D, I). This is perhaps an inevitable failing of models which apply a single diffusion or reaction rate to a heterogeneous system, such as soil.

An Elovich modeling approach, which is typically used to describe soil processes occurring across a range of timescales, generated a reasonably good fit for $^{129}I^-$ and $^{129}IO_3^-$ (Figures 6.5, 6.12 and 6.13). Nevertheless, it showed high sensitivity to the starting values of the parameters α and β (Eq. 6.4) which resulted in some instability and irreproducibility when the fitting was performed.

Parabolic diffusion and infinite exponential models gave the poorest overall fittings for both $^{129}I^-$ and $^{129}IO_3^-$ (Figures 6.5 and 6.14 to 6.17).

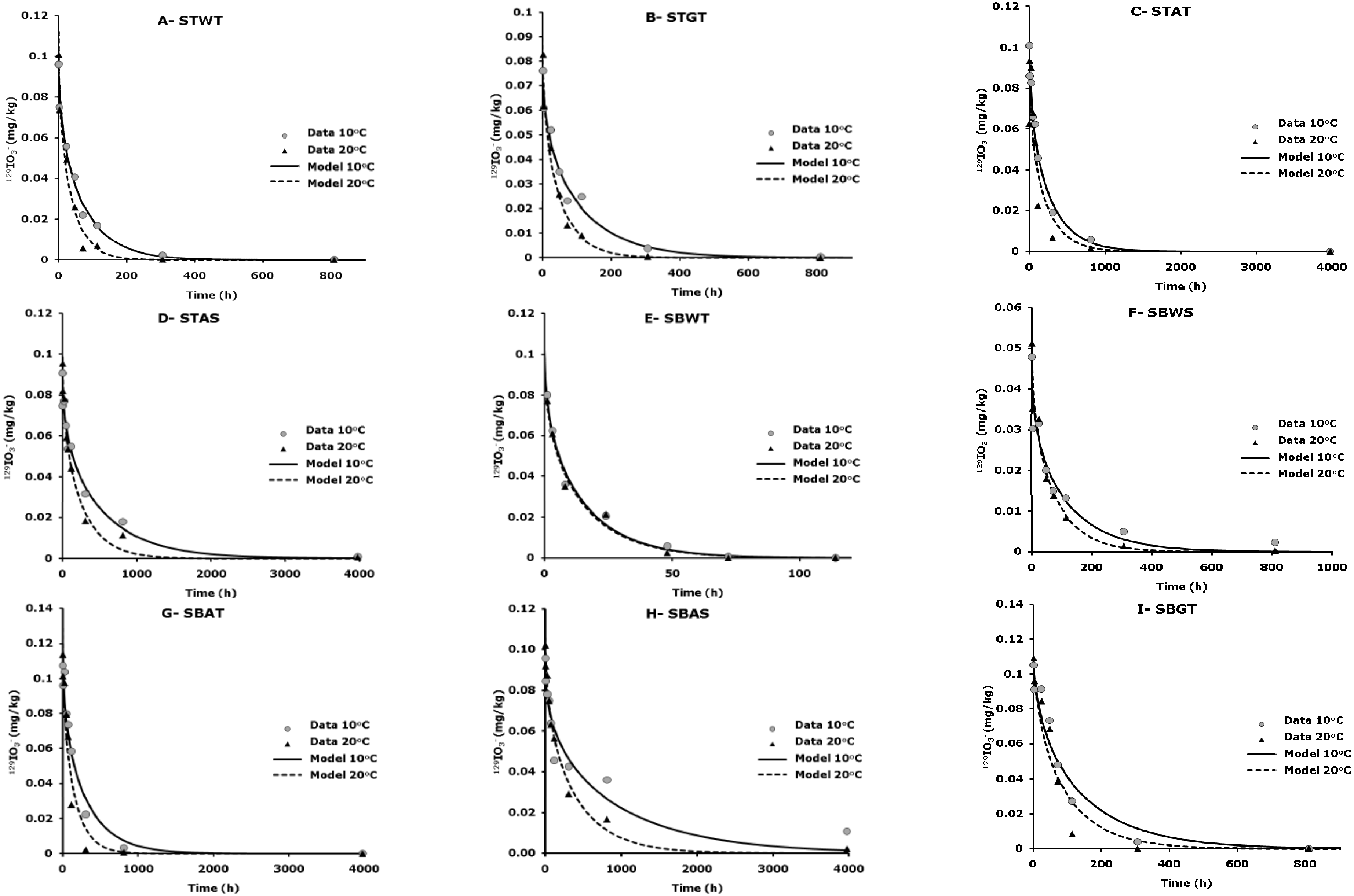


Figure 6.6 Iodate sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}IO_3^-$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using a spherical diffusion model with K_d (Sph-Diffn+K_d).

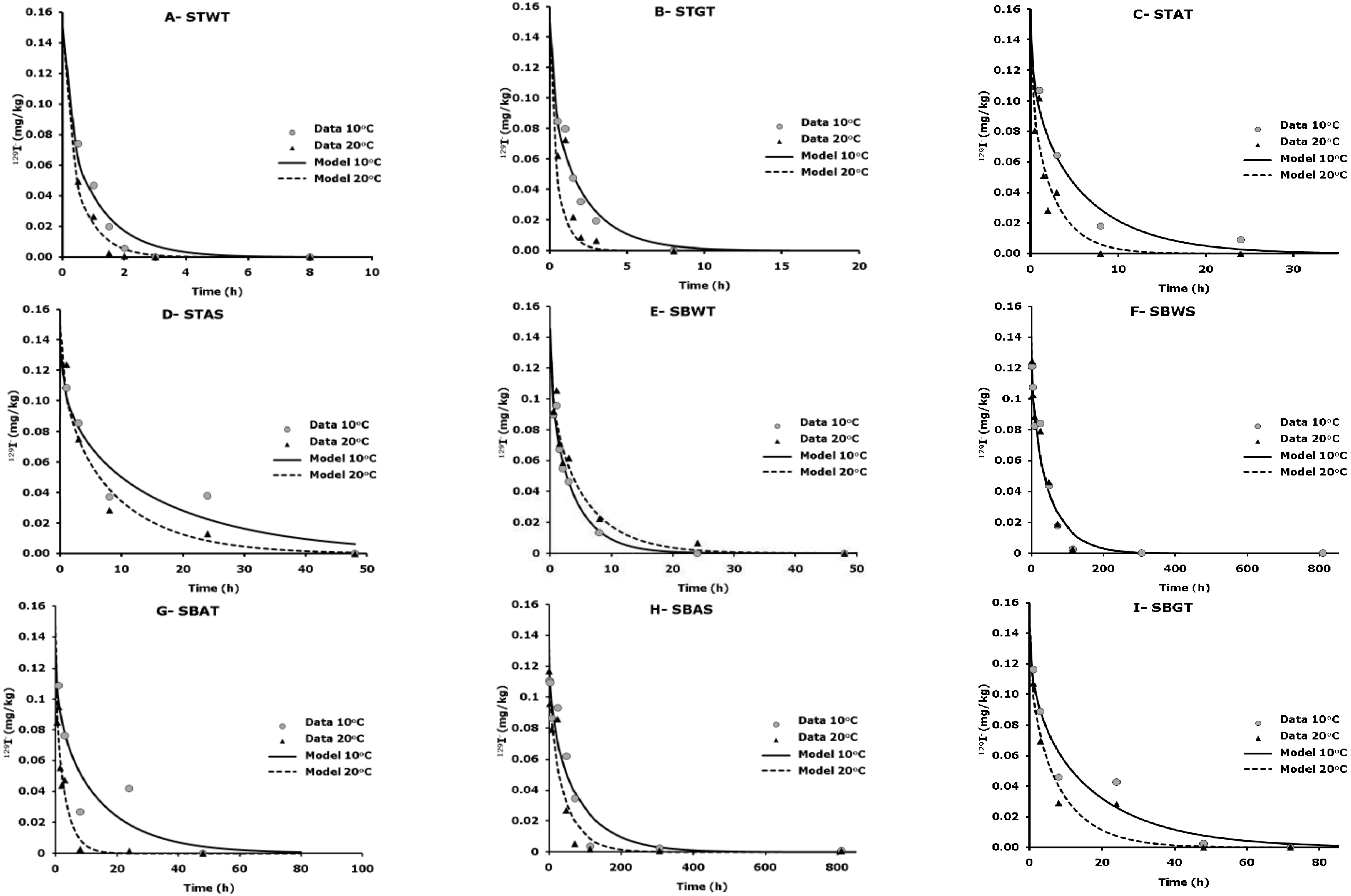


Figure 6.7 Iodide sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}I^-$ spike added to soils and incubated at 10^{o}C and 20^{o}C with model predictions for that soil fitted using a spherical diffusion model with K_d (Sph-Diffn+K_d)

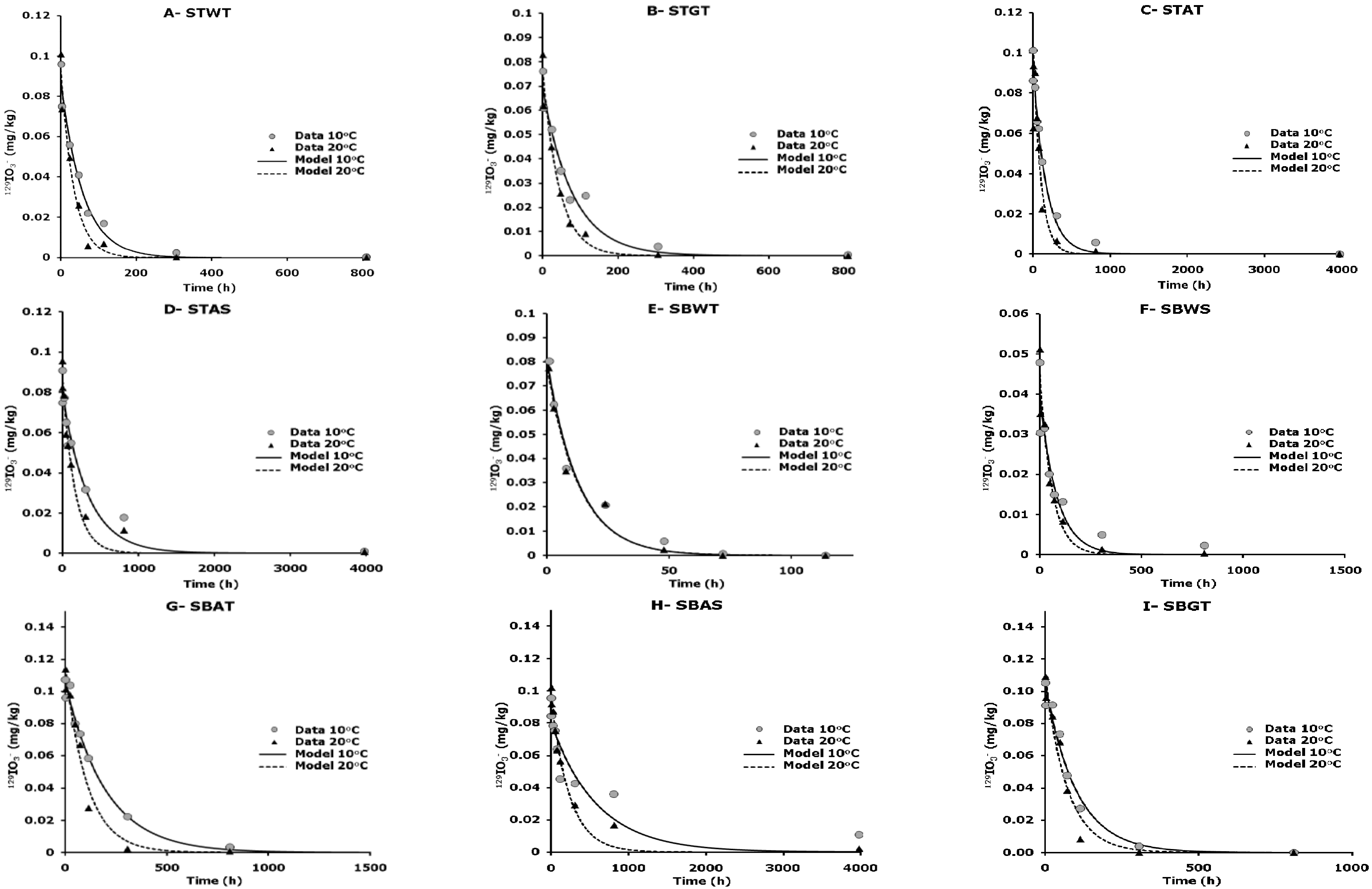


Figure 6.8 Iodate sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}IO_3^-$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using an irreversible 1st order model with K_d (IFO+K_d)

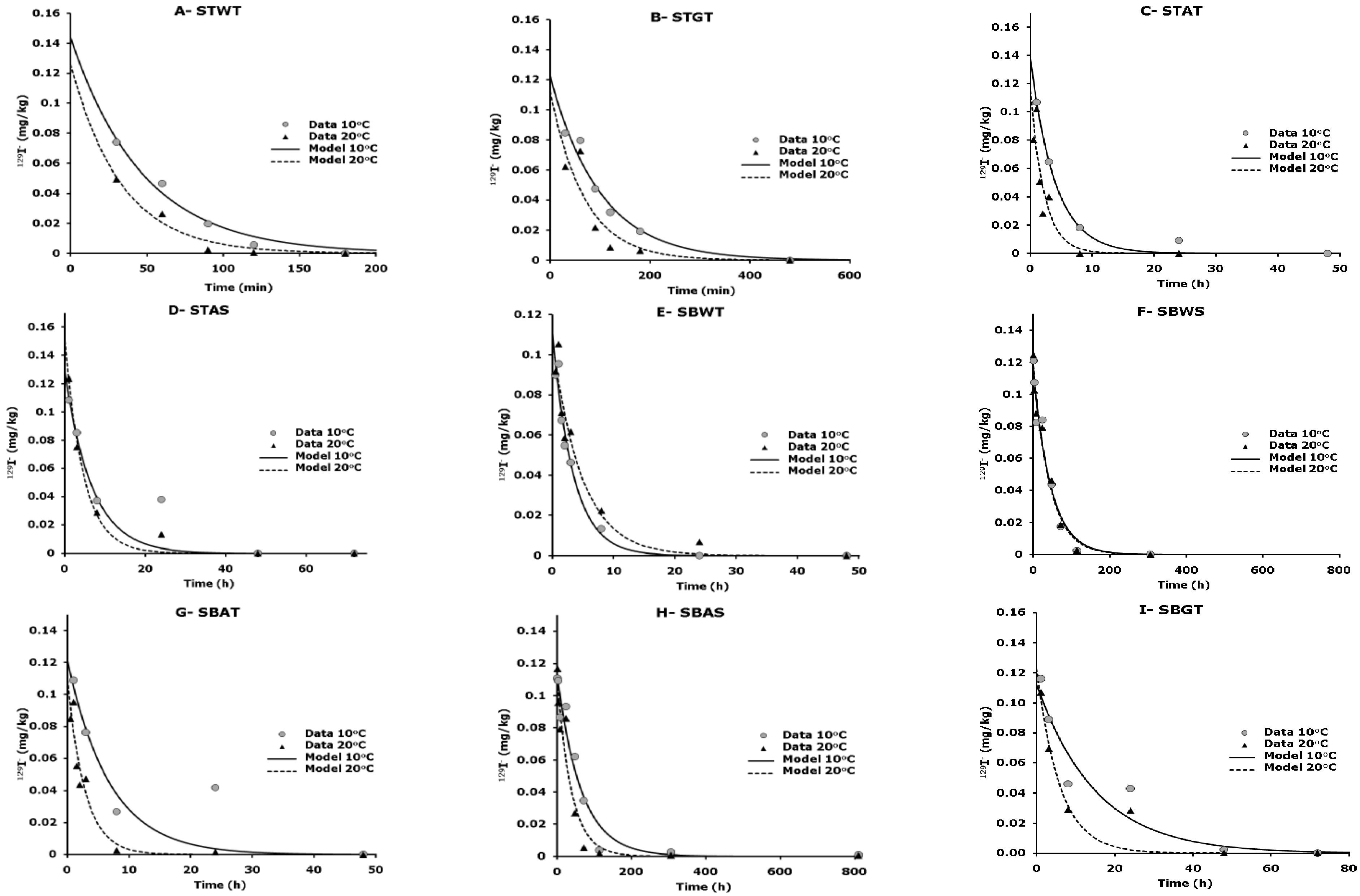


Figure 6.9 Iodide sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}I^{-}$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using an irreversible 1st order model with K_d (IFO+K_d)

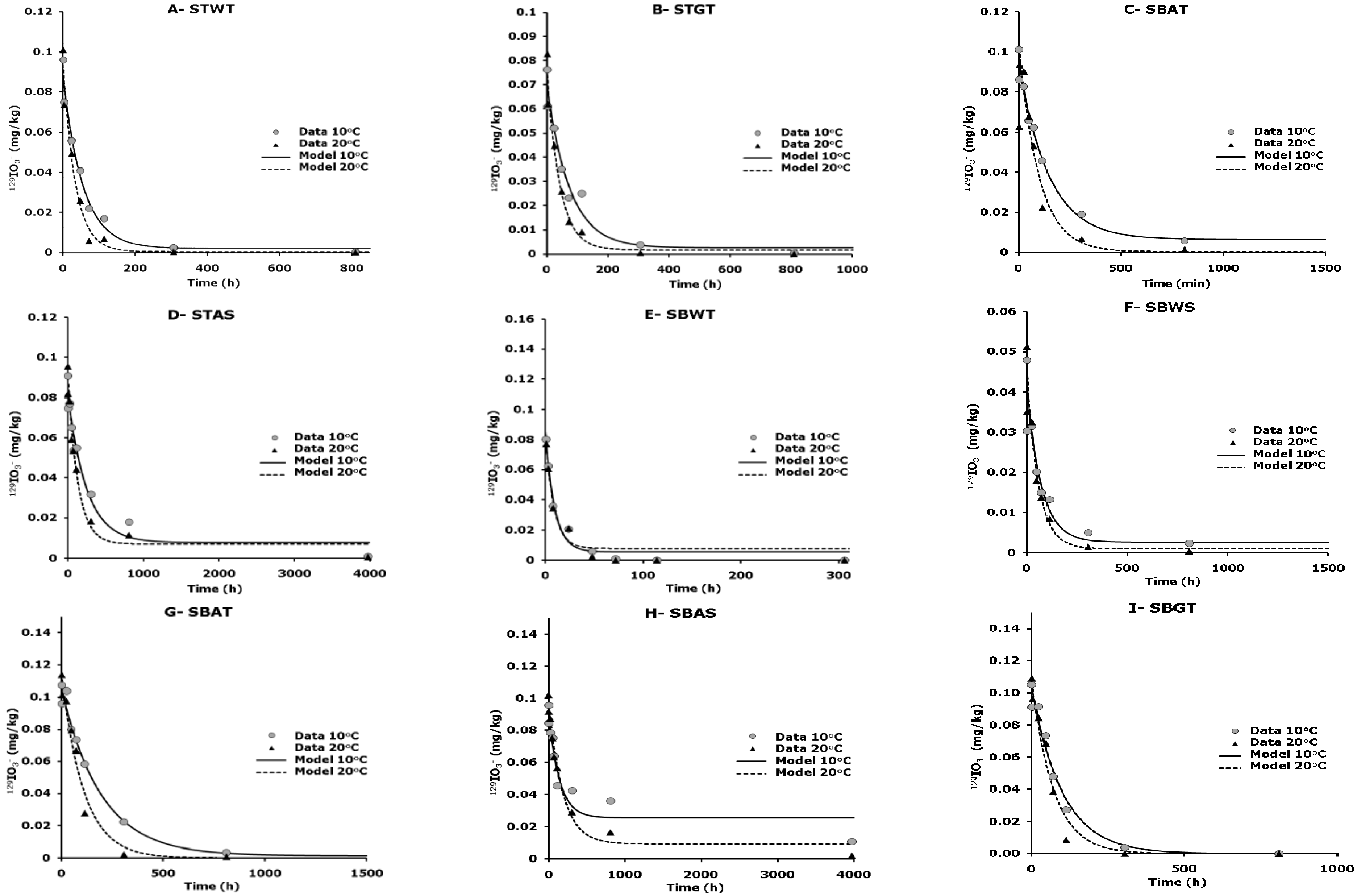


Figure 6.10 Iodate sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}IO_3^-$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using a reversible 1st order model with K_d (RFO+K_d)

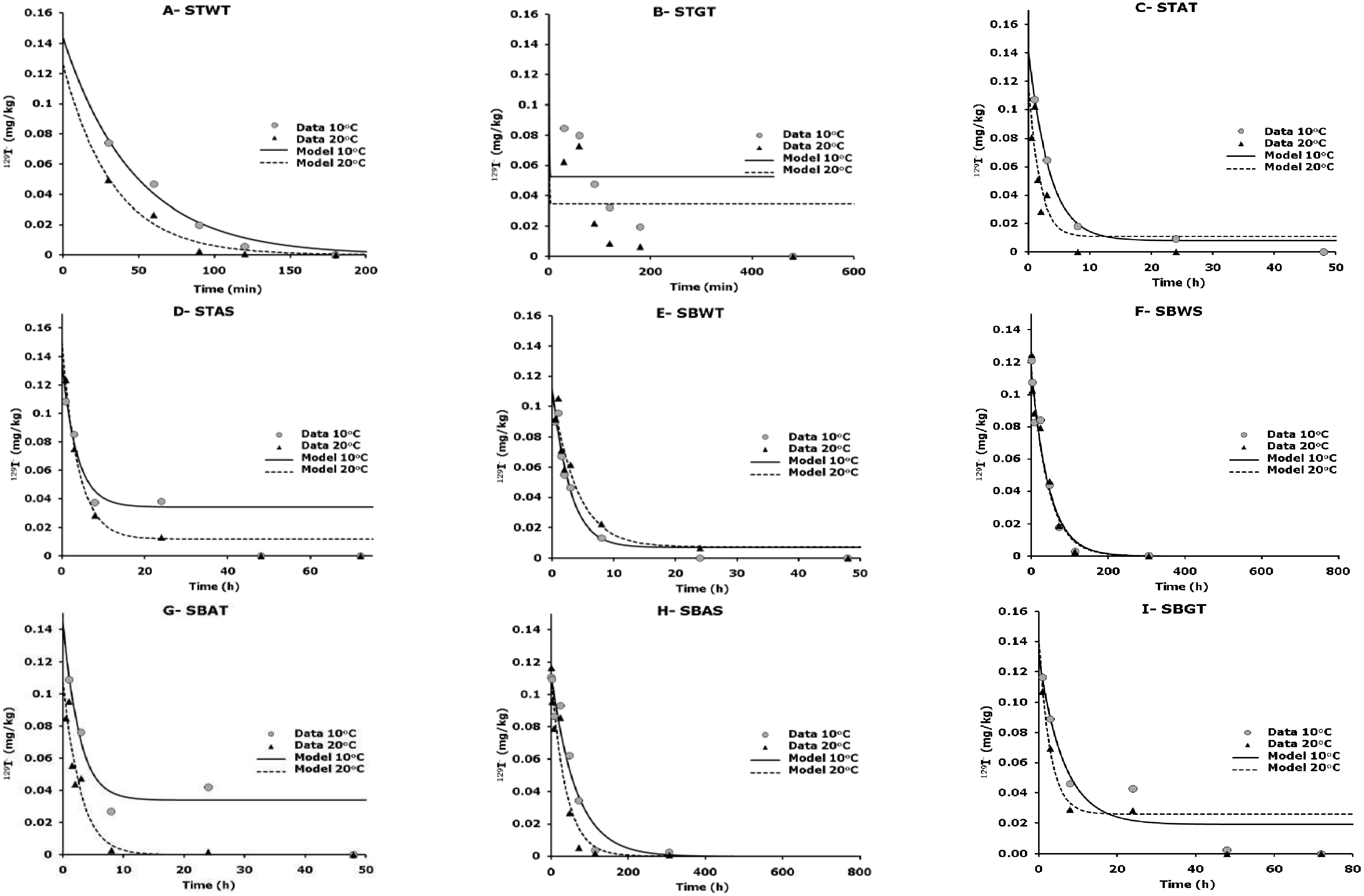


Figure 6.11 Iodide sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}I^-$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using a reversible 1st order model with K_d (RFO+K_d)

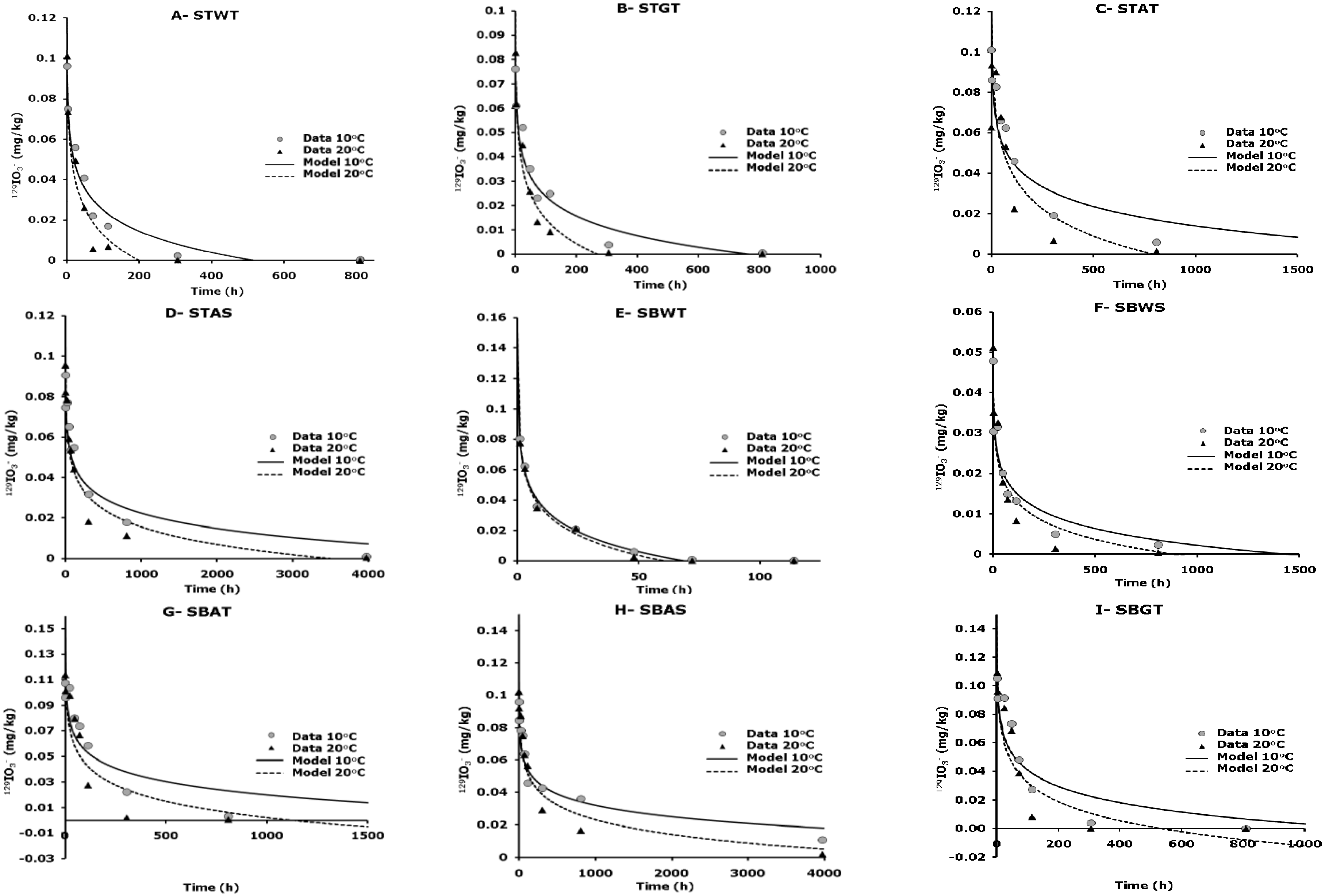


Figure 6.12 Iodate sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}IO_3^-$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using Elovich model

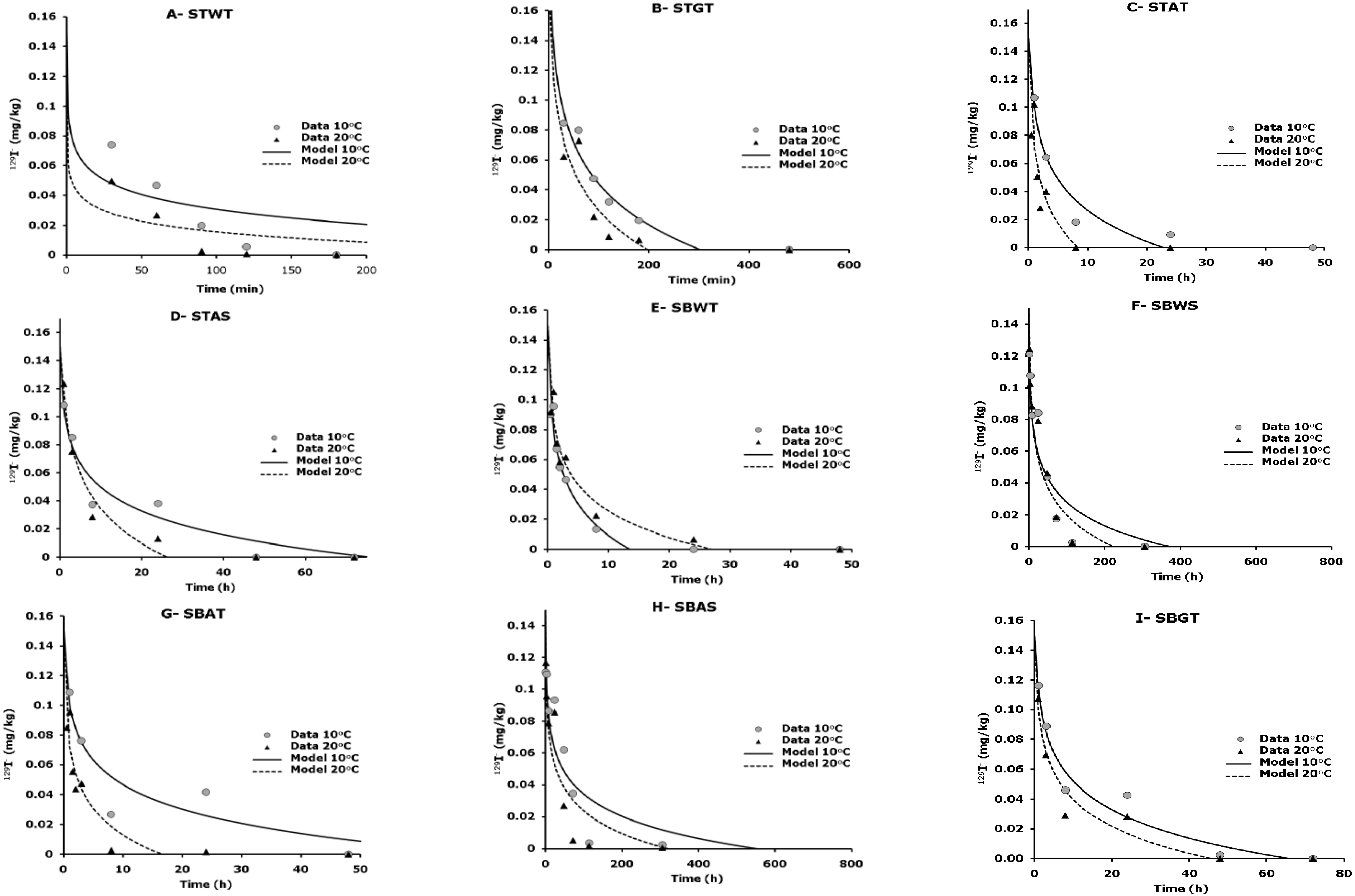


Figure 6.13 Iodide sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}I^-$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using Elovich model

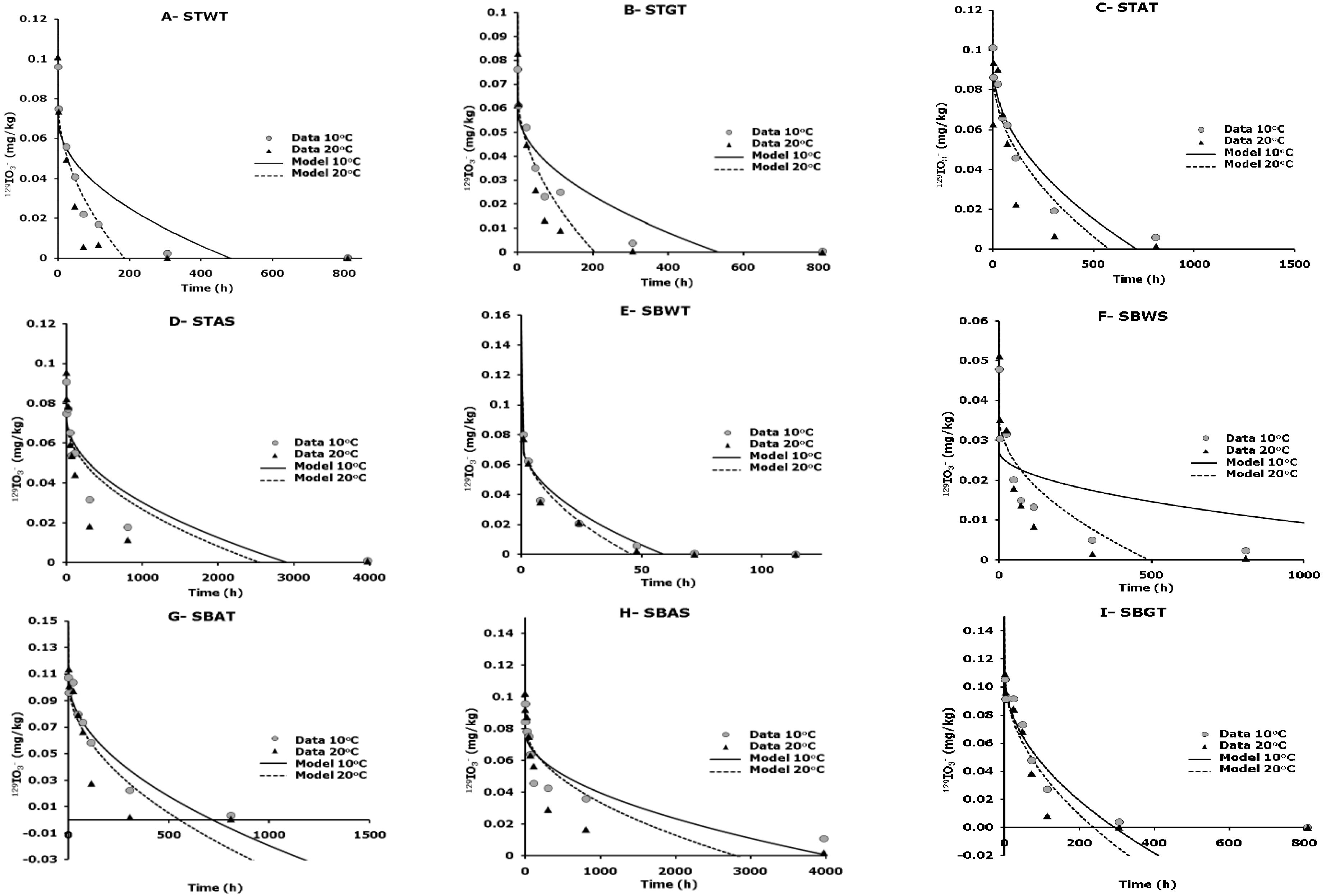


Figure 6.14 Iodate sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}IO_3^-$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using a parabolic diffusion model

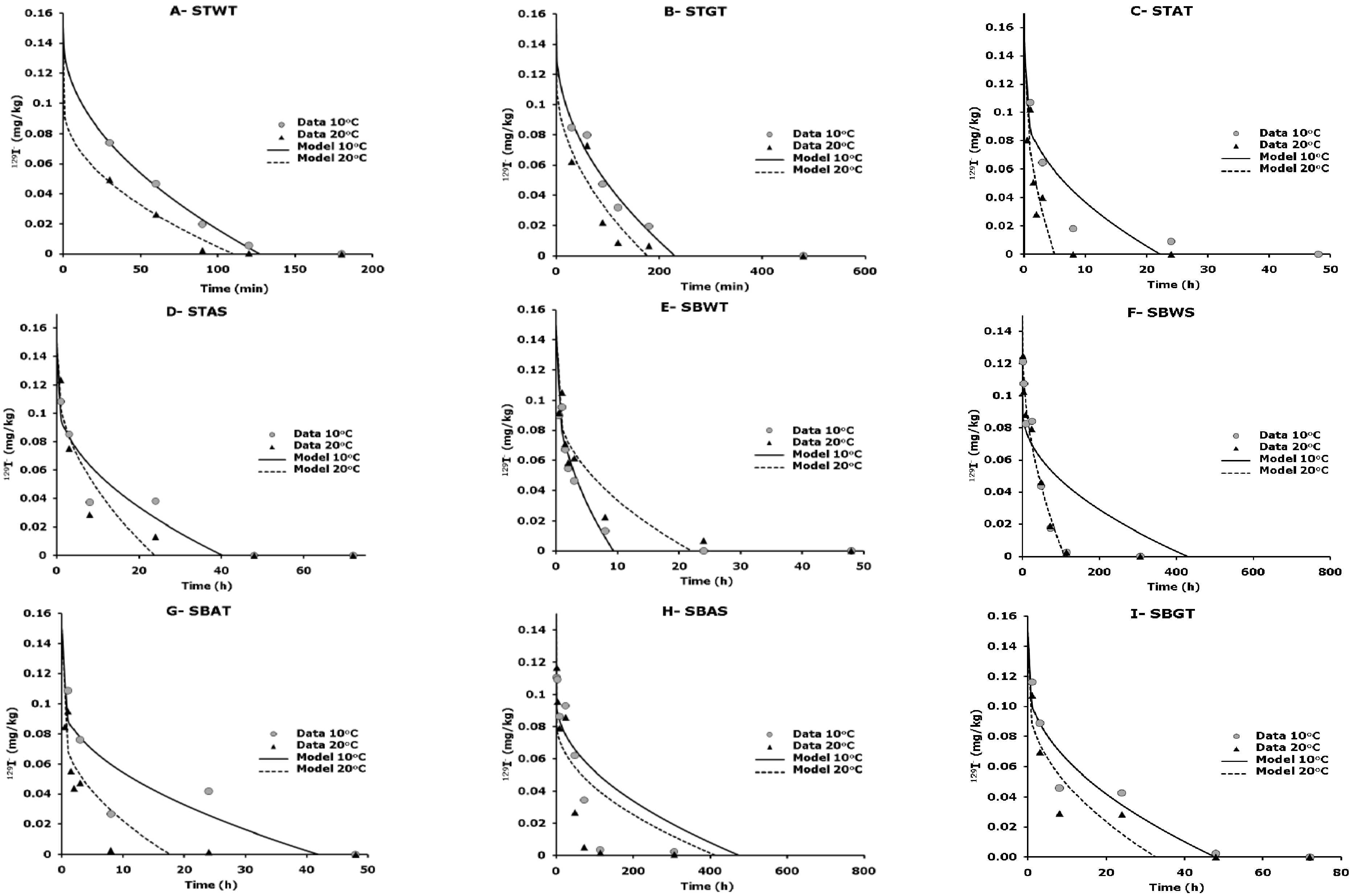


Figure 6.15 Iodide sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} ^{129}I^{-} spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using a parabolic diffusion

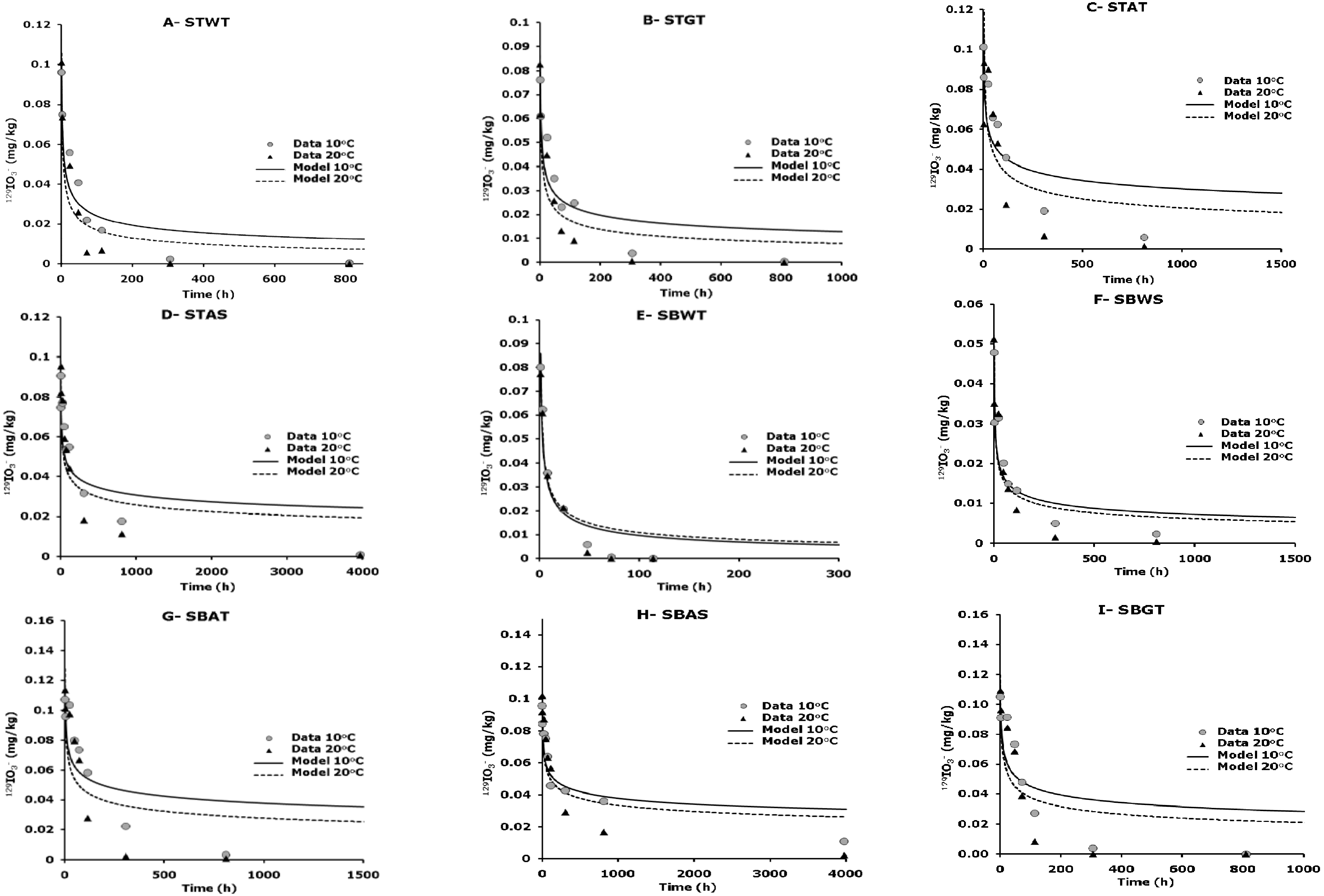


Figure 6.16 Iodate sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} $^{129}IO_3^-$ spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using an infinite series exponential model + K_d (ISE+K_d)

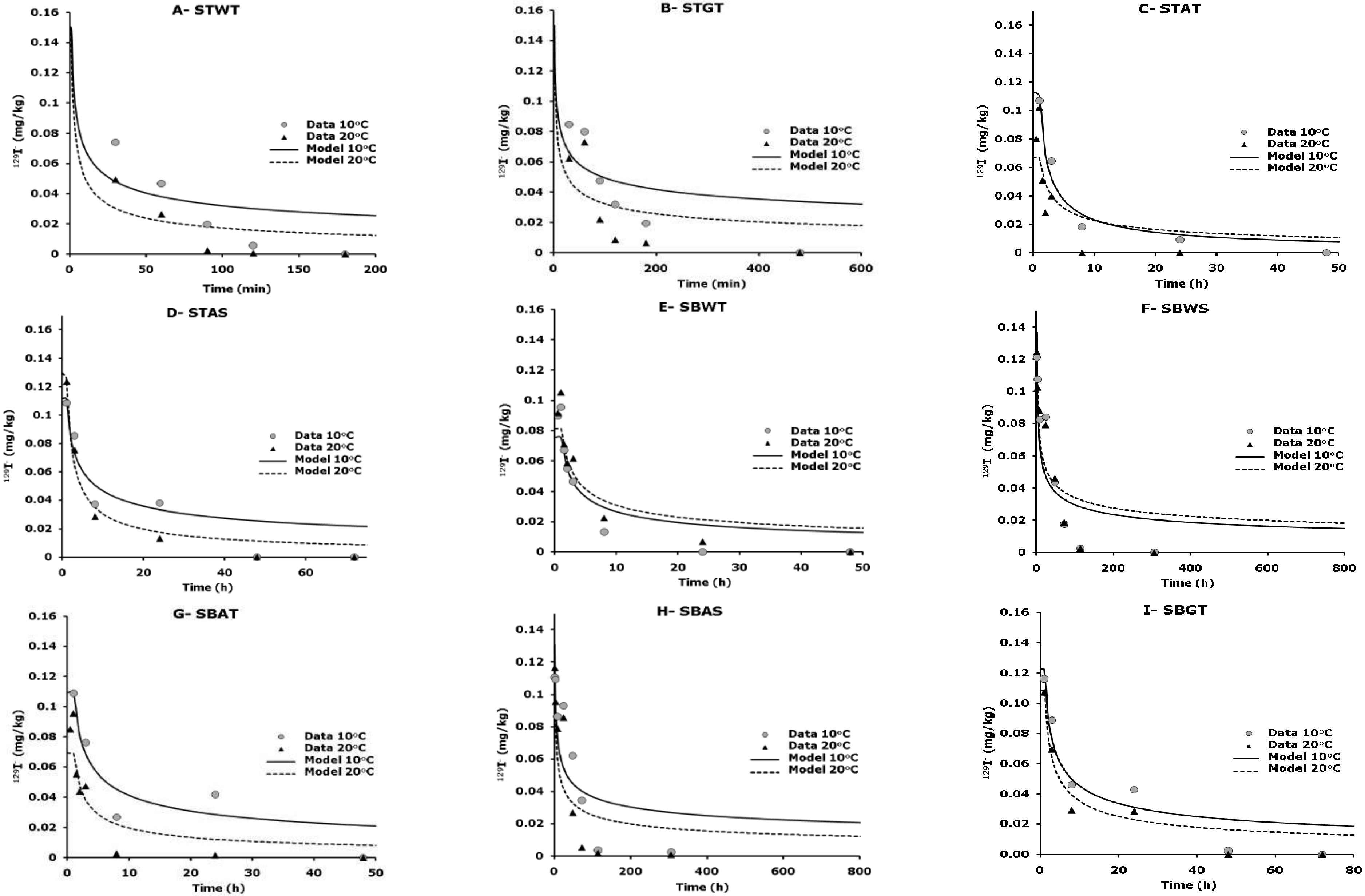


Figure 6.17 Iodide sorption kinetics: comparison of the measured loss from solution of a 0.15 mg kg^{-1} ^{129}I^{-} spike added to soils and incubated at 10°C and 20°C with model predictions for that soil fitted using an infinite series exponential model (ISE+K$_d$).

6.3.6 Parameterising the Spherical Diffusion Model from Soil Variables

An attempt was made to describe iodate sorption by all the soils based on a single spherical diffusion model parameterised from the soil variables judged most likely to influence the reaction with iodine: pH, soil organic carbon concentration (%SOC) and combined Fe+Mn oxide content (%Ox). The two controlling parameters in equation 6.7 (Table 6.1), K_d and D/r^2, were expressed as functions of pH, %SOC and %Ox. The only apparent trends from single parameter fits of equation 6.7 (Table 6.1) to individual soils were a linear relationship between –log (D/r^2) ($p(D/r^2)$) and %SOC and a weak exponential relation between K_d and pH.

For incubations at 10°C:

$$p\left(\frac{D}{r^2}\right) = 3.8 - 0.13\,(\%\text{SOC});\quad r^2 = 0.67 \qquad 6.8$$

and

$$K_d = 17\exp(-\,0.28\,\text{pH});\ r^2 = 0.3 \qquad 6.9$$

The diffusion parameter, $p(D/r^2)$ was therefore expressed as a linear function of the three soil variables and the distribution coefficient (K_d) as an exponential function of pH in which the value of K_d at pH = 0 (K_0) was itself a linear function of %SOC and %Ox:

$$p\left(\frac{D}{r^2}\right) = K_0 + K_{pH}\,(\text{pH}) + K_c\,(\%\text{SOC}) + K_{Ox}\,(\%\text{Ox}) \qquad 6.10$$

$$K_d = [K_0 + K_c\,(\%\text{SOC}) + K_{Ox}\,(\%\text{Ox})]\ \exp(K_{pH}\,\text{pH}) \qquad 6.11$$

A single model fit was made (simultaneously) to all soils at each temperature (10°C and 20°C). Four combinations of the coefficients (K_0, K_{pH}, K_c and K_{ox}) were tested, in the sequence listed, and overall values of RSD calculated (Table 6.6).

Table 6.6

Residual standard deviations for the single spherical diffusion model implemented with all soils simultaneously

Soil variables	Number of model coefficients	RSD (mg kg^{-1}) (x 10^{-2})
K_0	4	1.98
K_0, K_{pH}	8	1.56
K_0, K_{pH}, K_c	12	1.09
K_0 (p(D/r^2), K_{pH}, K_C, K_{ox}	14	0.0850

In Table 6.6 the number of model parameters increases by four with each soil variable added because both p(D/r^2) and K_d were calculated from the soil variables and the two temperature datasets were treated separately. Thus, with only K_0 implemented all the soils at a given temperature are effectively ascribed average values for p(D/r^2) and K_d in which case the model fit was then optimised with four fitted coefficients (for two temperatures). The two model parameters (p(D/r^2) and K_d) were also parameterised independently (holding one at an average value), producing model coefficient numbers between 4, 8, 12 and 16, but this produced broadly intermediate RSD values. Sequential addition of pH, %SOC and %Ox into the model produced significant model improvements ($P<0.001$) in all cases. However, the inclusion of %SOC and %Ox in the calculation of K_d value (Equation 6.11) does produce a potential instability in that it is possible to derive negative values for the distribution coefficient at very large soil humus contents. Also, it was found that K_0 applied to K_d was reduced to zero when both %SOC and %Ox were included as variables to give 14, rather than 16, as the number of model coefficients required to give the best fit (Table 6.5).

Table 6.7 shows the values of the soil coefficients used to derive the model parameters $p(D/r^2)$ and K_d for each incubation temperature (Equations 6.10 and 6.11). For prediction of K_d value, the soil coefficients are broadly in line with expectation in that K_d declined with increasing pH (K_{pH} is a negative exponential factor) and increases with Fe/Mn oxide content. This may reinforce the suggestion that the rapid initial adsorption of iodate is as an inorganic species on hydrous oxides. Similarly, the negative values of K_c (for calculation of K_d values) in Table 6.6 suggest that humus restricts the initial adsorption of iodate – possibly through competition for oxide sites and electrostatic repulsion of iodate. Table 6.8 shows $p(D/r^2)$ and K_d values calculated for all the nine soils used in the current study using the optimised soil coefficients in Table 6.7. The highest K_d values at 10°C and 20°C were observed in the low organic acidic soil SBWS (see Table 6.2 for soil properties) indicating the importance of acidic conditions for the initial sorption of iodate unless the sorption sites on soil oxyhydroxides are blocked by large concentrations of organic matter as may apply in the acidic topsoil SBWT which showed one of the lowest K_d values calculated (Table 6.8). The second highest K_d values were observed in the STGT soil which is slightly acidic and has the highest oxides content of all the soils (Tables 6.2 and 6.8). This initial adsorption behaviour agrees with the more general observation of Dai et al. (2004) who observed iodate adsorption to be positively correlated with free Fe-oxide content and negatively correlated with soil organic matter content.

Table 6.7

Values of optimised soil coefficients (K_0, K_{pH}, K_C, K_{Ox}) for the single spherical diffusion model implemented with all soils simultaneously

Soil coefficients	10°C incubation		20°C incubation	
	K_d; Eq .12	p(D/r^2); Eq. 6.11	K_d; Eq 6.12	p(D/r^2); Eq 6. 11
K_0	0	4.13	0	4.11
K_{pH}	-0.814	-0.0876	-0.878	-0.113
K_C	-38.4	-0.181	-47.4	-0.160
K_{Ox}	419	0.253	478	0.179

Table 6.8

Individual p(D/r^2) and K_d calculated for each soil, using the optimised soil coefficients (K_0, K_{pH}, K_C, K_{Ox}) (Table 6.6), and parameterised from the soil variables: pH, %SOC and %Ox.

Soil	10°C incubation		20°C incubation	
	K_d	p(D/r^2)	K_d	p(D/r^2)
STWT	2.54	3.10	1.79	2.82
STGT	4.57	2.94	3.30	2.64
STAT	2.00	3.51	1.41	3.20
STAS	3.60	3.81	2.60	3.44
SBWT	1.79	2.18	0.75	2.18
SBWS	15.82	3.75	13.89	3.59
SBAT	1.88	3.50	1.36	3.24
SBAS	2.46	3.73	1.85	3.47
SBGT	1.51	3.37	1.10	3.15

Figure 6.18 shows the fit of the soil-parameterised spherical diffusion model to iodate sorption. The overall simulation was reasonable across the range of soils examined with most soils falling wholly within ±1 RSD of the 1:1 relation. However, some individual soils produced systematic deviation from the model trend. For example, iodate persisted in solution in the SBAS, a sandy arable subsoil with low soil organic carbon (%SOC) content, for longer than predicted by the model (at low iodate concentrations); similar behavior was observed for the SBAT soil but at high iodate concentrations. The grassland topsoil from the same site showed the reverse trend with more rapid sorption from solution than predicted.

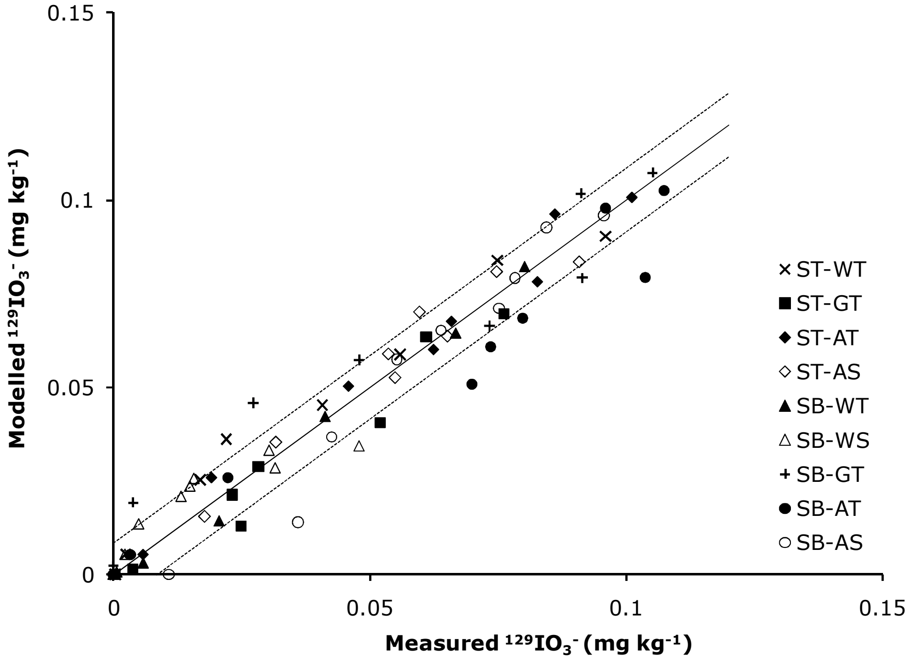


Figure 6.18 Comparison of measured and modeled iodate concentration in solution (mg kg^{-1} soil) modelled for all soils incubated at 10°C with a spherical diffusion model (Equation 6.7, Table 6.1). Model parameters (p(D/r^2) and K_d) were estimated from the soil variables pH, %SOC and %Ox (Equations 6.10 and 6.11). The solid line as a 1:1 relation and the dashed lines represent a displacement of one residual standard deviation (RSD).

Table 6.9. shows the apparent activation energies (Ea, kJ mol^{-1}) for each soil determined from the slope of a plot ln(D/r^2) against T^{-1} (Equation 6.12).

$$\ln\left(\frac{D}{r^2}\right) = \ln\left(\frac{D_o}{r^2}\right) - \frac{E_a}{RT} \qquad 6.12$$

Table 6.9
Apparent activation energies for all nine soils calculated from slope of a plot ln(D/r^2) against T^{-1} (Equation 6.12)

Soil	E_a (kJ mol^{-1})
STWT	44.4
STGT	46.3
STAT	49
STAS	58
SBWT	0.37
SBWS	25.7
SBAT	42.3
SBAS	41.8
SBGT	34.3

The average value for eight of the soils was 42.7 ±3.4 kJ mol^{-1} with no significant relationship with %SOC (Figure 6.19), or soil pH value (Figure 6.20). The acidic woodland topsoil from Sutton Bonington (SBWT), had extremely rapid reaction kinetics which showed very little temperature-dependence (Ea ≈ zero); very low Ea values normally characterise diffusion in free solution or physical adsorption processes (Sparks, 2003). Sparks (2003) presents approximate ranges for activation energies associated with different soil reaction-diffusion processes. A value for Ea just over 40 kJ mol^{-1} suggests a reaction process which is slower than simple pore diffusion (Ea ≈ 20 – 40 kJ mol^{-1}) or physical adsorption (8 – 25 kJ mol^{-1}) but at the lower end of surface reaction mechanisms.

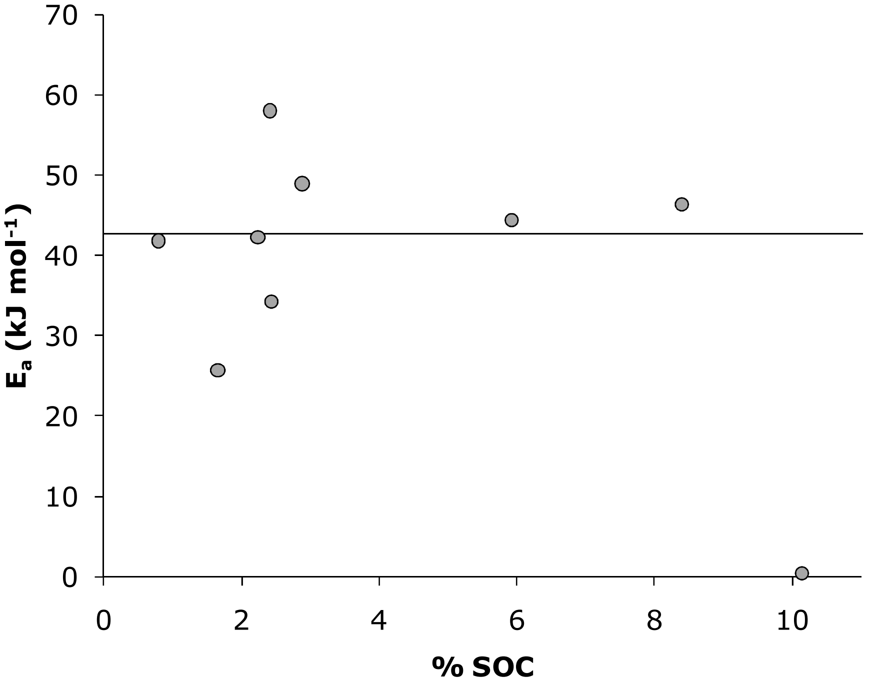


Figure 6.19 Apparent activation energies (Ea, kJ mol^{-1}) from spherical diffusion model as a function of soil organic carbon content (%); solid line represents the average value.

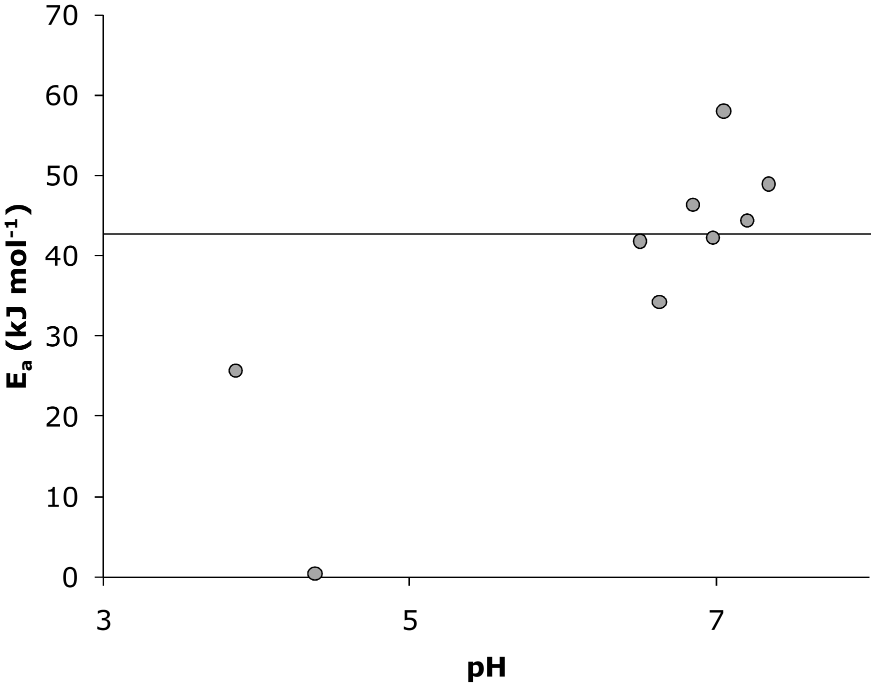
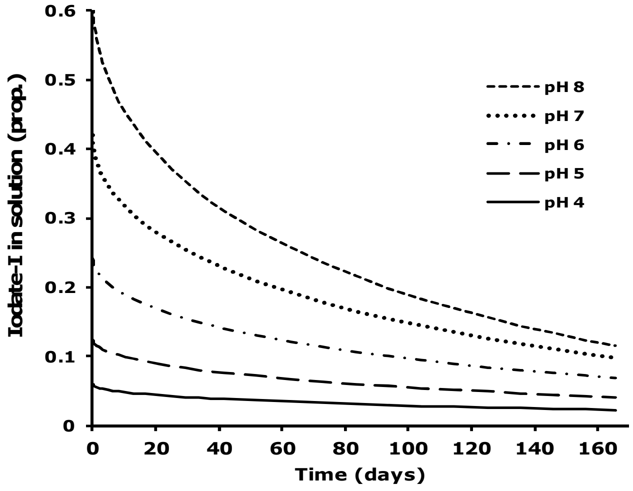
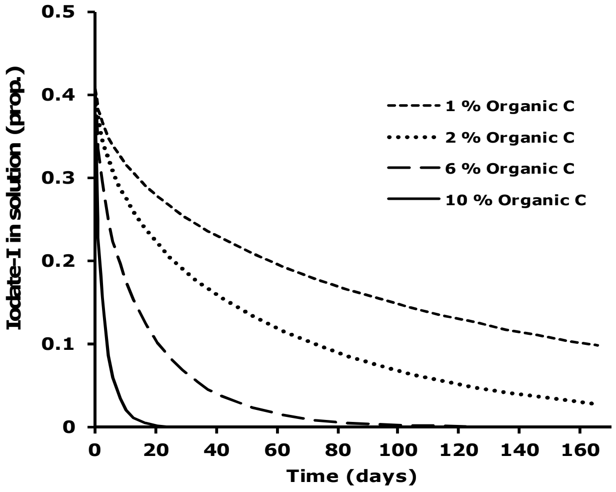


Figure 6.20 Apparent activation energies (Ea, kJ mol^{-1}) from spherical diffusion model as a function of soil pH; solid line represents the average value.

The overall influence of soil characteristics (pH and SOC content) on the pattern of iodate sorption is illustrated in Figure 6.21 for a ‘model’ soil with variable pH (a), % organic C (b) and Fe oxide content (c). Figure 6.21 a mainly shows the effect of soil pH value (pH 4 - pH 8) on the instantaneous sorption of iodate; whether this is through rapid reduction of iodine to organic forms or adsorption of IO_3 on Fe/Mn oxides remains unresolved. By contrast, Figure 6.21 b shows that the primary influence of SOC content (at fixed pH) is to control the rate of the time dependent sorption process, with only a minor effect on the level of instantaneous iodine sorption. Finally, increasing the Fe oxide content in the soil (Figure 6.21 c) causes a greater initial loss of soluble iodate but also appears to delay the conversion of iodate to organic iodine forms. Taken together, the model output presented in Figures 6.21 a - c present a pattern that is compellingly consistent with initial (inorganic) IO_3 adsorption on (Fe) oxides, followed by progressive transfer to organic forms, and with longer retention of inorganic iodate in soils with larger Fe oxide content.


a. Iodate: Effect of pH


b. Iodate: Effect of % organic C

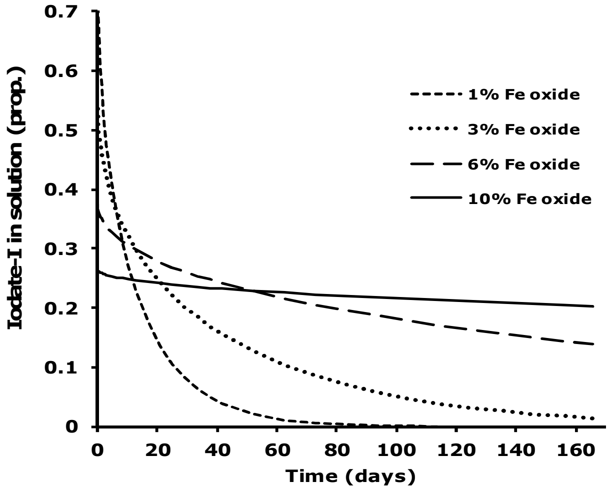

c. Iodate: effect of Fe oxide

Figure 6.21 Simulation of iodate sorption at 10°C, on a hypothetical soil with using the parameterised spherical diffusion model. The proportion of iodate remaining in solution is shown (a) for a range of soil pH values assuming 1% organic C and 5% Fe oxide (b) for a range of organic C concentrations at pH 7 and 5% Fe oxide and (c) for a range of Fe oxide contents at 1% SOC and pH 7

7. CONCLUSIONS

7.1 IODINE SPECIATION ANALYSIS BY HPLC-ICP-MS

The IC mobile-phase used for iodine speciation in the present study was 60 mM L^{-1} NH_4NO_3 with 10^{-5} mmol L^{-1} Na_2-EDTA and 2% methanol; pH was adjusted to 9.4 with TMAH. The chromatographic separation and elemental analysis was undertaken using HPLC-ICP-MS with a Hamilton anion exchange column (model PRP-X100, 250 x 4.6 mm). Peaks for $^{127,129}IO_3^-$ and $^{127,129}I^-$ were detected at ~2.5 min and ~8.5 min after injection. Using a shorter column (50 x 4.6 mm) iodate and iodide peaks were detected at ~0.5 and ~2.25 min, respectively. The same mobile-phase was successfully used for simultaneous speciation of other elements: Selenium (Se^{IV}, Se^{VI}), Chromium (Cr^{III}, Cr^{VI}), Arsenic (As^{III}, As^{V}), and Antimony (Sb^{III}, Sb^{V}).

7.2 SOIL IODINE EXTRACTION AND FRACTIONATION

Results showed that changing TMAH concentration, extraction time, extraction temperature or soil particle size did not significantly affect the concentrations of total iodine extracted, with the possible exception of a neutral arable subsoil where sensitivity toward changing TMAH concentration was observed ($P<<0.05$). The iodide to total iodine ratio in the TMAH extracts varied with the extraction conditions which has led to the conclusion that part or all of the measured iodide is possibly produced by hydrolysis of organic iodine forms. This conclusion was also confirmed by the detection of high concentrations of iodide in the TMAH extracts of humic acid where 100% organic iodine forms is expected. Moreover, iodate spiked on humic acid or soil was totally transformed to other iodine forms when soils/humic acid were extracted with TMAH. It was then concluded that the extraction of soil iodine with TMAH is not suitable to extract soil iodine without inevitably altering the original speciation.

No iodate was measured in the phosphate extracts of acidic woodland subsoil and alkaline arable topsoil; only iodide was measured and it constituted only 13% - 33% of total iodine (in KH_2PO_4 extracts) which indicates that most of the iodine mobilized by KH_2PO_4 is organic. When soil/KH_2PO_4 suspensions were spiked with $^{129}I^-$ and $^{129}IO_3^-$, at least 50% of $^{129}I^-$ and 15% of $^{129}IO_3^-$ were recoverable after 72 hours of reaction. The lowest recoveries were observed with the highest extracting KH_2PO_4 concentrations (highest concentrations of DOC mobilised). This means that although KH_2PO_4 is capable of releasing sorbed iodide and iodate in soil, but it may also catalyse iodide and iodate reaction with soil organic matter by mobilising soil organic matter to soil solution. Therefore, data obtained from KH_2PO_4 extraction is not conclusive about iodine speciation in soil; however, extraction with KH_2PO_4 could be utilised as a second extraction step after separation of soluble iodine forms.

The concentrations of total iodine extracted from soil samples after they were fumigated with chloroform were only marginally higher than iodine concentration in the control (non-fumigated) samples indicating that microbial biomass iodine constitutes only small fraction of total soil iodine.

7.3 SORPTION OF IODINE ON SOIL

Iodide and iodate adsorption data were well fitted to Freundlich adsorption isotherm. Sorption of iodate was greater than iodide in the acidic woodland soils whereas iodide was more strongly adsorbed in the arable neutral soils. The greater sorption of iodate than iodide, particularly in acidic soils with low organic matter contents was attributed to the greater intrinsic strength of iodate sorption on iron and aluminium hydrous oxides. Although iodide and iodate were measured only as total iodine in solution so possible chemical transformations could not be followed, the greater apparent sorption of iodate on the highly organic woodland topsoil than in the more acidic (but less organic) woodland subsoil strongly suggests iodine incorporation into soil organic matter. The equilibrium concentration of both iodide and iodate in soil solution was found to be around 10 μg L^{-1}.

Isotopically exchangeable (labile) soil iodine pool (E-value) varied with different ^{129}I adsorption suggesting irreversible adsorption of the isotope $^{129}I^-$ such as would be expected by chemical reaction with SOM. In general, the level of the isotopically exchangeable iodine was very low indicating that the majority of the native iodine is chemically fixed particularly in SOM and non-reactive.

7.4 IODINE TRANSFORMATIONS AND KINETICS IN SOIL

Results obtained demonstrate that iodine added to soil is rapidly transformed from inorganic to organic forms. Transformation of inorganic iodine into organic forms occurs rapidly in the soil solution and the rate of loss of iodine from the soil solution is dependent upon its speciation, with iodide being lost more rapidly (minutes-hours) than iodate (hours-days) especially in high organic matter soils. The ultimate fate of iodine added to soil appears to be incorporation into soil organic matter via formation of intermediates e.g. HOI or I_2. Abiotic reduction of IO_3^-, or oxidation of I^- by solid or aqueous organic matter (and soil metal oxides in case of iodide oxidation) are likely to be the main mechanisms by which these intermediates are formed. The reaction rates observed are probably too fast for biological processes to play a significant role and the microbial biomass iodine pool appears to be insignificant. It appears that inorganic adsorption of iodide and iodate plays only a minor, and probably transient, role in retention of iodine in soils. Rates of iodine loss are greater at higher temperatures with the rate almost doubling as temperatures increase from 10 to 20°C. The range of rate constants observed suggests that iodine reactions in the topsoil are rapid enough for the majority of the iodine to be retained in the top layer, especially in acidic organic soils. Considering the reactions rates against the likely range of rainfall residence times in topsoil, it is possible that iodine is leached into the subsoil. However, there is field evidence that the limited amount of organic matter, even in sandy subsoils, may be able to effectively scavenge iodine, depending on drainage rate and rainfall intensity. It was found that the iodine:carbon ratio increased with depth in both soils demonstrating that whilst the majority of iodine is retained in the top soil the smaller amounts of humus present at depth have a high iodine concentration compared to the more abundant organic matter in the topsoil. Thus iodine moving beyond the topsoil during rainfall or drainage events appears to be effectively retained in the deeper soil horizons by the substantial adsorption capacity provided by relatively small amounts of humus.

Iodide and iodate sorption kinetics were successfully modelled using a spherical diffusion modelling approach suggesting that their sorption in soil may be controlled by diffusion into spherical humic acid colloidal aggregates. The optimised spherical diffusion model successfully predicts the effect of acidic conditions in soil in causing pronounced instantaneous sorption of iodate, whether this is through rapid reduction of iodine to organic forms or adsorption of IO_3^- on Fe/Mn oxides. It also successfully describes the subsequent slower assimilation rate (relatively faster in organic-rich soils) following the initial sorption. Simulations also include the influence of temperature on the kinetic reaction but with temperature produced minimal effect on the level of instantaneous sorption. The average value of apparent activation energies (Ea, kJ mol^{-1}) for eight of the soils, individually parameterised, was 43 kJ mol^{-1} suggesting reactions that are slower than pore diffusion or physical adsorption; possibly slow surface reaction mechanisms.

7.5 RECOMMENDATIONS AND FUTURE WORK

Two major areas of uncertainty remain:

(i) fully understanding the reaction sequence for iodide and iodate added to soils and, in particular the balance of the initial reaction between inorganic adsorption on oxides and rapid reduction/oxidation leading to carbon bonding in humus;

(ii) the significance of iodine fractionation and speciation for bioavailability to plants.

Whitehead (1975) suggested that iodine was likely to be most bioavaioable in alkaline soils with low organic matter content, partly because iodate would remain bioavailable for a longer period of time. However, it has also been repeatedly reported that plants uptake iodide more readily than iodate (Whitehead, 1973c; Zhu et al., 2003; Voogt et al., 2010), so although iodate may survive longer in soil solution its uptake by plants may be hindered by the physiological preference of plants roots for iodide. Moreover, the distribution of iodine within plants (including edible parts) may differ between plant species (Whitehead, 1973c; Muramatsu et al., 1993; Zhu et al., 2004; Tsukada et al., 2008; Weng et al., 2008; Voogt et al., 2010; Landini et al., 2011).

Some future work is therefore suggested as a continuation of the current 'soil-based' project.

First, it would be important to directly investigate the temporal change in solubility and speciation of iodide and iodate suspended with pure soil materials, which are likely candidates for iodine adsorption, such as goethite, gibbsite, birnessite and humic acid. This could be supported by a spectroscopic study of the surface adsorbed complexes, through time, using EXAFS/XANES. It may also be possible to follow time-dependent changes in the nature of humic-iodine complexes using, for example, size-exclusion chromatography (linked to ICP-MS) to determine whether initial adsorption was on lower molecular weight molecules with progressive incorporation into larger humic aggregates/colloids.

Secondly, it would be useful to try and close the gap between understanding the kinetics of iodine speciation and solubility, and the change in bioavailability of iodine following adsorption. We know that iodide and iodate and quickly converted to organic (humus) forms in soil, but there has been very little work to investigate possible time-dependent changes in bioavailability or lability following transformation to organic-I. One approach, which would also have direct practical significance for possible biofortification programmes, would be to follow plant uptake of an ^{129}I label as a time series trial over several months or even over several growing seasons.

8. REFERENCE

ABDEL-MOATI, M. A. R. (1999) Iodine speciation in the Nile River estuary. *Marine Chemistry,* 65**,** 211-225.

ABOUSHAKRA, F. R., RAYMAN, M. P., WARD, N. I., HOTTON, V. & BASTIAN, G. (1997) Enzymatic digestion for the determination of trace elements in blood serum by inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry,* 12**,** 429-433.

AGILENT-TECHNOLOGIES (2007) Handbook of Hyphenated ICP-MS Applications. *Agilent Technologies,* http://www.chem.agilent.com/temp/rad29FAD/00001681.pdf**,** Date Acessed: August, 08, 2008.

ALBERTS, J. J., SCHINDLE.JE, MILLER, R. W. & NUTTER, D. E. (1974) ELEMENTAL MERCURY EVOLUTION MEDIATED BY HUMIC ACID. *Science,* 184**,** 895-896.

ALDAHAN, A., ALFIMOV, V. & POSSNERT, G. (2007) I-129 anthropogenic budget: Major sources and sinks. *Applied Geochemistry,* 22**,** 606-618.

ALLARD, S., VON GUNTEN, U., SAHLI, E., NICOLAU, R. & GALLARD, H. (2009) Oxidation of iodide and iodine on birnessite (delta-MnO2) in the pH range 4-8. *Water Research,* 43**,** 3417-3426.

ALTFELDER, S. & STRECK, T. (2006) Capability and limitations of first-order and diffusion approaches to describe long-term sorption of chlortoluron in soil. *Journal of Contaminant Hydrology,* 86**,** 279-298.

AMACHI, S., FUJII, T., SHINOYAMA, H. & MURAMATSU, Y. (2005) Microbial Influences on the Mobility and Transformation of Radioactive Iodine in the Environment. *Journal of Nuclear and Radiochemical Sciences,* 6**,** 21-24.

ANIK, M. (2004) Reduction characteristics of iodate ion on copper: Application to copper chemical mechanical polishing. *Journal of Applied Electrochemistry,* 34**,** 963-969.

ANSCHUTZ, P., ZHONG, S. J., SUNDBY, B., MUCCI, A. & GOBEIL, C. (1998) Burial efficiency of phosphorus and the geochemistry of iron in continental margin sediments. *Limnology and Oceanography,* 43**,** 53-64.

ASHWORTH, D. J. & SHAW, G. (2006) A comparison of the soil migration and plant uptake of radioactive chlorine and iodine from contaminated groundwater. *Journal of Environmental Radioactivity,* 89**,** 61-80.

ASHWORTH, D. J., SHAW, G., BUTLER, A. P. & CICIANI, L. (2003) Soil transport and plant uptake of radio-iodine from near-surface groundwater. *Journal of Environmental Radioactivity,* 70**,** 99-114.

ASSEMI, S. & ERTEN, H. N. (1994) Sorption of radioiodine on organic rich soil, clay minerals and alumina. *Journal of Radioanalytical and Nuclear Chemistry-Articles,* 178**,** 193-204.

ASTDR (2003) Toxological profile for selenium. *Agency for Toxic Substances and Disease Registry, US department of health and human services,* http://www.atsdr.cdc.gov/toxprofiles/tp92.pdf**,** Date Accessed: August, 22, 2008.

ATARASHI-ANDOH, M., SCHNABEL, C., COOK, G., MACKENZIE, A. B., DOUGANS, A., ELLAM, R. M., FREEMAN, S., MADEN, C., OLIVE, V., SYNAL, H. A. & XU, S. (2007) I-129/I-127 ratios in surface waters of the English Lake District. *Applied Geochemistry,* 22**,** 628-636.

ATKINSON, R. J., HINGSTON, F. J., POSNER, A. M. & QUIRK, J. P. (1970) Elovich equation for kinetics of isotopic exchange reactions at solid-liquid interfaces. *Nature,* 226**,** 148-149.

BEJEY, A. M., ALAMIN, M. B., MIZERA, J. & KUCERA, J. (2006) Determination of iodine in foodstuffs consumed in Libya using instrumental and radiochemical neutron activation analysis. *Czechoslovak Journal of Physics,* 56**,** D159-D163.

BICHSEL, Y. & VON GUNTEN, U. (1999) Oxidation of iodide and hypoiodous acid in the disinfection of natural waters. *Environmental Science & Technology,* 33**,** 4040-4045.

BICHSEL, Y. & VON GUNTEN, U. (2000) Formation of iodo-trihalomethanes during disinfection and oxidation of iodide containing waters. *Environmental Science & Technology,* 34**,** 2784-2791.

BING, L., MA, X. R., HAN, L. R. & YANG, H. X. (2004) Pressurised extraction using dilute ammonia: A simple method for determination of iodine in soil, sediment and biological samples by inductively coupled plasma-mass spectrometry. *Geostandards and Geoanalytical Research,* 28**,** 317-323.

BIRD, G. A. & SCHWARTZ, W. (1997) Distribution coefficients, K(d)s, for iodide in Canadian Shield lake sediments under oxic and anoxic conditions. *Journal of Environmental Radioactivity,* 35**,** 261-279.

BLODAU, C., BAUER, M., REGENSPURG, S. & MACALADY, D. (2009) Electron accepting capacity of dissolved organic matter as determined by reaction with metallic zinc. *Chemical Geology,* 260**,** 186-195.

BONHOURE, I., SCHEIDEGGER, A. M., WIELAND, E. & DAHN, R. (2002) Iodine species uptake by cement and CSH studied by I K-edge X-ray absorption spectroscopy. *Radiochimica Acta,* 90**,** 647-651.

BORGGAARD, O. K., RABEN-LANGE, B., GIMSING, A. L. & STROBEL, B. W. (2005) Influence of humic substances on phosphate adsorption by aluminium and iron oxides. *Geoderma,* 127**,** 270-279.

BORS, J. & MARTENS, R. (1992) The contribution of microbial biomass to the adsorption of radioiodine in soil. *Journal of Environmental Radioactivity,* 15**,** 35-49.

BROWN, L. M., SHERRY, H. S. & KRAMBECK, F. J. (1971) Mechanism and kinetics of isotopic exchange in zeolites .1. Theory. *Journal of Physical Chemistry,* 75**,** 3846-3855.

BRUMMER, J. G. & FIELD, R. J. (1979) Kinetics and mechanism of the oxidation of ferrous ion by iodate ion in strong perchloric acid, aqueous media. *Journal of Physical Chemistry,* 83**,** 2328-2335.

BUENO, M. E., PANNIER, F. & POTIN-GAUTIER, M. (2007) Determination of organic and inorganic selenium species using HPLC-ICP-MS. *Handbook of Hyphenated ICP-MS Applications, Agilent Technologies 5989-6160EN, p: 18-19,* http://www. chem. agilent. com/temp/rad29fad/00001681.pdf**,** Date Accessed: August, 19, 2008.

BYRDY, F. A., OLSON, L. K., VELA, N. P. & CARUSO, J. A. (1995) Chromium Speciation by Anion-Exchange High-Performance Liquid-Chromatography with Both Inductively-Coupled Plasma-Atomic Emission Spectroscopic and Inductively-Coupled Plasma-Mass Spectrometric Detection. *Journal of Chromatography A,* 712**,** 311-320.

CHEN, J., GU, B. H., ROYER, R. A. & BURGOS, W. D. (2003) The roles of natural organic matter in chemical and microbial reduction of ferric iron. *Science of The Total Environment,* 307**,** 167-178.

CHEN, J. H., WANG, K. E. & JIANG, S. J. (2007) Determination of iodine and bromine compounds in foodstuffs by CE-inductively coupled plasma MS. *Electrophoresis,* 28**,** 4227-4232.

CHIEN, S. H. & CLAYTON, W. R. (1980) Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Science Society of America Journal,* 44**,** 265-268.

CHUTE, J. H. & QUIRK, J. P. (1967) DIFFUSION OF POTASSIUM FROM MICA-LIKE CLAY MINERALS. *Nature,* 213**,** 1156-&.

CLIFF, J. B., BOTTOMLEY, P. J., HAGGERTY, R. & MYROLD, D. D. (2002) Modeling the effects of diffusion limitations on nitrogen-15 isotope dilution experiments with soil aggregates. *Soil Science Society of America Journal,* 66**,** 1868-1877.

COBLE, Y., DAVIS, J., SCHULERT, A., HETA, F. & AWAD, A. Y. (1968) Goiter and Iodine Deficiency in Egyptian Oases. *American Journal of Clinical Nutrition,* 21**,** 277-&.

COCKER, J., MORTON, J., WARREN, N., WHEELER, J. P. & GARROD, A. N. I. (2006) Biomonitoring for chromium and arsenic in timber treatment plant workers exposed to CCA wood preservatives. *Annals of Occupational Hygiene,* 50**,** 517-525.

COLLINS, R. N., TRAN, N. D., BAKKAUS, E., AVOSCAN, L. & GOUGET, B. (2006) Assessment of isotope exchange methodology to determine the sorption coefficient and isotopically exchangeable concentration of selenium in soils and sediments. *Environmental Science & Technology,* 40**,** 7778-7783.

CROUCH, W. H. (1962) A spectorphotometric determination of iodine in silicate rocks. *Analytical Chemistry,* 34**,** 1698-&.

CULLEN, W. R. & REIMER, K. J. (1989) Arsenic Speciation in the Environment. *Chemical Reviews,* 89**,** 713-764.

DAI, J. L., ZHANG, M., HU, Q. H., HUANG, Y. Z., WANG, R. Q. & ZHU, Y. G. (2009) Adsorption and desorption of iodine by various Chinese soils: II. Iodide and iodate. *Geoderma,* 153**,** 130-135.

DAI, J. L., ZHANG, M. & ZHU, Y. G. (2004) Adsorption and desorption of iodine by various Chinese soils - I. Iodate. *Environment International,* 30**,** 525-530.

DELFOSSE, T., DELMELLE, P., GIVRON, C. & DELVAUX, B. (2005) Inorganic sulphate extraction from SO2-impacted andosols. *European Journal of Soil Science,* 56**,** 127-133.

DORMAN, J. W. & STEINBERG, S. M. (2010) Analysis of iodide and iodate in Lake Mead, Nevada using a headspace derivatization gas chromatography-mass spectrometry. *Environmental Monitoring and Assessment,* 161**,** 229-236.

EBIHARA, M., OZAKI, H., KATO, F. & NAKAHARA, H. (1997) Determination of chlorine, bromine and iodine in rock samples by radiochemical neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry,* 216**,** 107-112.

ECHEVARRIA, G., MOREL, J. L., FARDEAU, J. C. & LECLERC-CESSAC, E. (1998) Assessment of phytoavailability of nickel in soils. *Journal of Environmental Quality,* 27**,** 1064-1070.

ENDO, S., TOMITA, J., TANAKA, K., YAMAMOTO, M., FUKUTANI, S., IMANAKA, T., SAKAGUCHI, A., AMANO, H., KAWAMURA, H., KAWAMURA, H., APSALIKOV, K. N., GUSEV, B. I., WHITEHEAD, N. E., SHINKAREV, S. & HOSHI, M. (2008) Iodine-129 measurements in soil samples from Dolon village near the Semipalatinsk nuclear test site. *Radiation and Environmental Biophysics,* 47**,** 359-365.

ENGLUND, E., ALDAHAN, A., HOU, X. L., PETERSEN, R. & POSSNERT, G. (2010) Speciation of iodine (I-127 and I-129) in lake sediments. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 268**,** 1102-1105.

FECHER, P. A., GOLDMANN, I. & NAGENGAST, A. (1998) Determination of iodine in food samples by inductively coupled plasma mass spectrometry after alkaline extraction. *Journal of Analytical Atomic Spectrometry,* 13**,** 977-982.

FERNANDEZ SANCHEZ, L. & SZPUNAR, J. (1999) Speciation analysis for iodine in milk by size-exclusion chromatography with inductively coupled plasma mass spectrometric detection (SEC-ICP MS). *Journal of Analytical Atomic Spectrometry,* 14**,** 1697-1702.

FITOUSSI, C. & RAISBECK, G. M. (2007) Chemical procedure for extracting I-129, Fe-60 and Al-26 from marine sediments: Prospects for detection of a similar to 2.8 My old supernova. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 259**,** 351-358.

FLEMING, G. A. (1980) Essential micronutrients II: Iodine and selenium. *in Applied Soil Trace Elements,* B.E. Davies, ed., pp. 199-234**,** John Wiley & Sons, Chichester.

FLORENCE, T. M. (1989) Trace element speciation in biologicl systems. *Trace Element Speciation: Analytical Methods and Problems, CRC Press,Boca Raton, FL., p: 319-343*

FOX, P. M., DAVIS, J. A. & LUTHER, G. W. (2009) The kinetics of iodide oxidation by the manganese oxide mineral birnessite. *Geochimica Et Cosmochimica Acta,* 73**,** 2850-2861.

FRANCOIS, R. (1987a) The influence of humic substances on the geochemistry of iodine nearshore and Hemipelagic marine sediments. *Geochimica Et Cosmochimica Acta,* 51**,** 2417-2427.

FRANCOIS, R. (1987b) IIodine in marine sedimentary humic substances. *Science of The Total Environment,* 62**,** 341-342.

FRECHOU, C. & CALMET, D. (2003) I-129 in the environment of the La Hague nuclear fuel reprocessing plant from sea to land. *Journal of Environmental Radioactivity,* 70**,** 43-59.

FUGE, R. (2005) Soils and iodine deficiency. *Essentials of Medical Geology: Impacts of the Natural Environment on Public Health***,** 417 - 433.

FUGE, R. (2007) Iodine deficiency: An ancient problem in a modern world. *Ambio,* 36**,** 70-72.

FUGE, R. (1996) Geochemistry of iodine in relation to iodine deficiency diseases. IN APPLETON, J. D. F. R. M. G. J. H. (Ed.) Environmental Geochemistry and Health, with Special Reference to Developing Countries.

FUGE, R. & JOHNSON, C. C. (1986) The Geochemistry of Iodine - a Review. *Environmental Geochemistry and Health,* 8**,** 31-54.

FUGE, R., JOHNSON, C. C. & PHILLIPS, W. J. (1978) IODINE IN GRANITIC AND ASSOCIATED ROCKS. *Chemical Geology,* 22**,** 347-352.

FUHRMANN, M., BAJT, S. & SCHOONEN, M. A. A. (1998) Sorption of iodine on minerals investigated by X-ray absorption near edge structure (XANES) and I-125 tracer sorption experiments. *Applied Geochemistry,* 13**,** 127-141.

FUKUI, M., FUJIKAWA, Y. & SATTA, N. (1996) Factors affecting interaction of radioiodide and iodate species with soil. *Journal of Environmental Radioactivity,* 31**,** 199-216.

GABLER, H. E., BAHR, A., HEIDKAMP, A. & UTERMANN, J. (2007) Enriched stable isotopes for determining the isotopically exchangeable element content in soils. *European Journal of Soil Science,* 58**,** 746-757.

GALLARD, H., ALLARD, S., NICOLAU, R., VON GUNTEN, U. & CROUE, J. P. (2009) Formation of Iodinated Organic Compounds by Oxidation of Iodide-Containing Waters with Manganese Dioxide. *Environmental Science & Technology,* 43**,** 7003-7009.

GAN, D., KOTOB, S. I. & WALIA, D. S. (2007) Evaluation of a Spectrophotometric Method for Practical and Cost Effective Quantification of Fulvic Acid. *Annals of Environmental Science,* 1**,** 11-15.

GANTHER, H. E. & LAWRENCE, J. R. (1997) Chemical transformations of selenium in living organisms. Improved forms of selenium for cancer prevention. *Tetrahedron,* 53**,** 12299-12310.

GAO, Y. C., GAO, Q. F., SUN, M. X., ZHU, Z. X. & CHEN, Z. H. (2007) Simultaneous determination of arsenic, bromine, iodine in coal and coke by inductively coupled plasma-mass spectrometry with microwave digestion. *Chinese Journal of Analytical Chemistry,* 35**,** 1175-1178.

GEELHOED, J. S., HIEMSTRA, T. & VANRIEMSDIJK, W. H. (1997) Phosphate and sulfate adsorption on goethite: Single anion and competitive adsorption. *Geochimica Et Cosmochimica Acta,* 61**,** 2389-2396.

GERKE, J. (1993) PHOSPHATE ADSORPTION BY HUMIC/FE-OXIDE MIXTURES AGED AT PH-4 AND PH-7 AND BY POORLY ORDERED FE-OXIDE. *Geoderma,* 59**,** 279-288.

GERZABEK, M. H., MURAMATSU, Y., STREBL, F. & YOSHIDA, S. (1999) Iodine and bromine contents of some Austrian soils and relations to soil characteristics. *Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde,* 162**,** 415-419.

GILFEDDER, B. S., ALTHOFF, F., PETRI, M. & BIESTER, H. (2007a) A thermo extraction-UV/Vis spectrophotometric method for total iodine quantification in soils and sediments. *Analytical and Bioanalytical Chemistry,* 389**,** 2323-2329.

GILFEDDER, B. S., PETRI, M. & BIESTER, H. (2007b) Iodine and bromine speciation in snow and the effect of orographically induced precipitation. *Atmospheric Chemistry and Physics,* 7**,** 2661-2669.

GILFEDDER, B. S., PETRI, M. & BIESTER, H. (2007c) Iodine speciation in rain and snow: Implications for the atmospheric iodine sink. *Journal of Geophysical Research-Atmospheres,* 112**,** 1-7.

GURLEYUK, H. & WALLSCHLAGER, D. (2001) Determination of chromium(III) and chromium(VI) using suppressed ion chromatography inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry,* 16**,** 926-930.

HAGENDORFER, H. & GOESSLER, W. (2008) Separation of chromium(III) and chromium(VI) by ion chromatography and an inductively coupled plasma mass spectrometer as element-selective detector. *Talanta,* 76**,** 656-661.

HALDIMANN, M., ZIMMERLI, B., ALS, C. & GERBER, H. (1998) Direct determination of urinary iodine by inductively coupled plasma mass spectrometry using isotope dilution with iodine-129. *Clinical Chemistry,* 44**,** 817-824.

HAMON, R. E., LOMBI, E., FORTUNATI, P., NOLAN, A. L. & MCLAUGHLIN, M. J. (2004) Coupling speciation and isotope dilution techniques to study arsenic mobilization in the environment. *Environmental Science & Technology,* 38**,** 1794-1798.

HAVLIN, J. L., WESTFALL, D. G. & OLSEN, S. R. (1985) Mathematical models for potassium release kinetics in calcareous soils. *Soil Science Society of America Journal,* 49**,** 371-376.

HETZEL, B. S. (1986) Bridging the knowledge application gap - The international council for control of iodine deficiency disorders. *International Journal of Epidemiology,* 15**,** 153-154.

HEUMANN, K. G. (1992) Isotope-Dilution Mass-Spectrometry. *International Journal of Mass Spectrometry and Ion Processes,* 118**,** 575-592.

HOU, X., HANSEN, V., ALDAHAN, A., POSSNERT, G., LIND, O. C. & LUJANIENE, G. (2009a) A review on speciation of iodine-129 in the environmental and biological samples. *Analytica Chimica Acta,* 632**,** 181-196.

HOU, X. L., ALDAHAN, A., NIELSEN, S. P. & POSSNERT, G. (2009b) Time Series of I-129 and I-127 Speciation in Precipitation from Denmark. *Environmental Science & Technology,* 43**,** 6522-6528.

HOU, X. L., CHAI, C. F., QIAN, Q. F., YAN, X. J. & FAN, X. (1997) Determination of chemical species of iodine in some seaweeds .1. *Science of the Total Environment,* 204**,** 215-221.

HOU, X. L., FOGH, C. L., KUCERA, J., ANDERSSON, K. G., DAHLGAARD, H. & NIELSEN, S. P. (2003) Iodine-129 and Caesium-137 in Chernobyl contaminated soil and their chemical fractionation. *Science of the Total Environment,* 308**,** 97-109.

IAEA (2007) Speciation Analysis of Arsenic, Chromium and Selenium in Aquatic Media. *International Atomic Energy Agency, IAEA-TECDOC-1542,* http://www-pub. iaea. org/ MTCD/ publications/ PDF/ te_1542_web.pdf**,** Date Acessed: August, 26, 2008.

INOUE, Y., SAKAI, T. & KUMAGAI, H. (1995) Simultaneous Determination of Chromium(Iii) and Chromium(Vi) by Ion Chromatography with Inductively-Coupled Plasma-Mass Spectrometry. *Journal of Chromatography A,* 706**,** 127-136.

ISHIKAWA, N. K., UCHIDA, S. & TAGAMI, K. (2011) Iodide sorption and partitioning in solid, liquid and gas phases in soil samples collected from Japanese paddy fields. *Radiation protection dosimetry,* 146**,** 155-8.

IZNAGA, I. R., PETRANOVSKII, V., FUENTES, G. R., MENDOZA, C. & AGUILAR, A. B. (2007) Exchange and reduction of Cu2+ ions in clinoptilolite. *Journal of Colloid and Interface Science,* 316**,** 877-886.

JARDINE, P. M. & SPARKS, D. L. (1984) Potassium-calcium exchange in a multi-reactive soil ystem .1. KINETICS. *Soil Science Society of America Journal,* 48**,** 39-45.

JENKINSON, D. S., BROOKES, P. C. & POWLSON, D. S. (2004) Measuring soil microbial biomass. *Soil Biology & Biochemistry,* 36**,** 5-7.

JOHNSON, C. C. (2003) The geochemistry of iodine and its application to environmental strategies for reducing the risks from iodine defficiency disorders (IDD). British geological survey, department for international development, DFID KAR Project R7411**,** Commissioned Report CR/03/057N.

JOHNSON, C. C., BREWARD, N., ANDER, E. L. & AULT, L. (2005) G-BASE: baseline geochemical mapping of great Britain and northern Ireland. *Geochemistry-Exploration Environment Analysis,* 5**,** 347-357.

JOHNSON, C. C., STRUTT M H, HMEURRAS M & MOUNIR M (2002) Iodine in the environment of the high atlas mountain area of Morocco. British geological survey*,* department for international development, DFID KAR Project R7411**,** Commissioned Report CR/02/196N.

KAPLAN, D. I., SERNE, R. J., PARKER, K. E. & KUTNYAKOV, I. V. (2000) Iodide sorption to subsurface sediments and illitic minerals. *Environmental Science & Technology,* 34**,** 399-405.

KAZAKOV, V. S., DEMIDCHIK, E. P. & ASTAKHOVA, L. N. (1992) Thyroid cancer after Chernobyl. *Nature,* 359**,** 21-21.

KELLER, J. K., WEISENHORN, P. B. & MEGONIGAL, J. P. (2009) Humic acids as electron acceptors in wetland decomposition. *Soil Biology & Biochemistry,* 41**,** 1518-1522.

KOCH, J. T., RACHAR, D. B. & KAY, B. D. (1989) Microbial participation in iodine removal from solution by organic soil. *Canadian Journal of Soil Science,* 69**,** 127-135.

KODAMA, S., TAKAHASHI, Y., OKUMURA, K. & URUGA, T. (2006) Speciation of iodine in solid environmental samples by iodine K-edge XANES: Application to soils and ferromanganese oxides. *Science of the Total Environment,* 363**,** 275-284.

KOSTKA, J. E. & LUTHER, G. W. (1994) Partitioning and speciation of solid phase iron in salt-march sediments. *Geochimica Et Cosmochimica Acta,* 58**,** 1701-1710.

KUCERA, J., IYENGAR, G. V., RANDA, Z. & PARR, R. M. (2004) Determination of iodine in Asian diets by epithermal and radiochemical neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry,* 259**,** 505-509.

LANDINI, M., GONZALI, S. & PERATA, P. (2011) Iodine biofortification in tomato. *Journal of Plant Nutrition and Soil Science,* 174**,** 480-486.

LEFFLER, P., GERHARDSSON, L., BRUNE, D. & NORDBERG, G. F. (1984) Lung Retention of Antimony and Arsenic in Hamsters after the Intratracheal Instillation of Industrial Dust. *Scandinavian Journal of Work Environment & Health,* 10**,** 245-251.

LEIST, M., LEISER, R. & TOMS, A. (2006) Low-Level Speciation of Chromium in Drinking Waters Using LC–ICP-MS. *Varian, Inc. The Application Notebook,* http:// spectroscopymag. findpharma.com/ spectroscopy/ data/ articlestandard// spectroscopy/ 262006/ 352912/ article. pdf**,** Date Acessed: August, 27, 2008.

LEITERER, M., TRUCKENBRODT, D. & FRANKE, K. (2001) Determination of iodine species in milk using ion chromatographic separation and ICP-MS detection. *European Food Research and Technology,* 213**,** 150-153.

LIKHTAREV, I. A., SOBOLEV, B. G., KAIRO, I. A., TRONKO, N. D., BOGDANOVA, T. I., OLEINIC, V. A., EPSHTEIN, E. V. & BERAL, V. (1995) Thyroid cancer in the Ukraine. *Nature,* 375**,** 365-365.

LINDEMANN, T., PRANGE, A., DANNECKER, W. & NEIDHART, B. (1999) Simultaneous determination of arsenic, selenium and antimony species using HPLC/ICP-MS. *Fresenius Journal of Analytical Chemistry,* 364**,** 462-466.

LIU, W., YANG, H. X., LI, B., CHEN, D. Y. & ZHANG, H. J. (2007) Study on speciation stabilities of iodine in underground water by high performance liquid chromatography-inductively coupled plasma mass spectrometry. *Chinese Journal of Analytical Chemistry,* 35**,** 571-574.

MANI, D., RAO, T. G., BALARAM, V., DAYAL, A. M. & KUMAR, B. (2007) Rapid determination of iodine in soils using inductively coupled plasma mass spectrometry. *Current Science,* 93**,** 1219-1221.

MARCHETTI, A. A., ROSE, L. & STRAUME, T. (1994) A Simple and Reliable Method to Extract and Measure Iodine in Soils. *Analytica Chimica Acta,* 296**,** 243-247.

MARSHALL, S. J., YOUNG, S. D. & GREGSON, K. (1995) Humic acid proton equilibria - A comparison of 2 models assessment of titration error. *European Journal of Soil Science,* 46**,** 471-480.

MARTIN, H. W. & SPARKS, D. L. (1983) Kinetics of non-exchangeable potassium release from coastal plain soils. *Soil Science Society of America Journal,* 47**,** 883-887.

MELICHERCIK, M., OLEXOVA, A. & TREINDL, L. (1997) Kinetics of the oxidation of iodine by hydrogen peroxide catalyzed by MoO_4^{2-} ions. *Journal of Molecular Catalysis a-Chemical,* 127**,** 43-47.

MESKO, M. F., MELLO, P. A., BIZZI, C. A., DRESSLER, V. L., KNAPP, G. & FLORES, E. M. M. (2010) Iodine determination in food by inductively coupled plasma mass spectrometry after digestion by microwave-induced combustion. *Analytical and Bioanalytical Chemistry,* 398**,** 1125-1131.

MICHALKE, B. (2002) The coupling of LC to ICP-MS in element speciation: I. General aspects. *Trac-Trends in Analytical Chemistry,* 21**,** 142-153.

MICHEL, R., HANDL, J., ERNST, T., BOTSCH, W., SZIDAT, S., SCHMIDT, A., JAKOB, D., BELTZ, D., ROMANTSCHUK, L. D., SYNAL, H. A., SCHNABEL, C. & LOPEZ-GUTIERREZ, J. M. (2005) Iodine-129 in soils from Northern Ukraine and the retrospective dosimetry of the iodine-131 exposure after the Chernobyl accident. *Science of The Total Environment,* 340**,** 35-55.

MILES, C. J. & BREZONIK, P. L. (1981) Oxygen consumption in humic-coloured waters by a photochemical ferrous-ferric catalytic cycle. *Environmental Science & Technology,* 15**,** 1089-1095.

MORITA, Y., KOBAYASHI, T., KUROIWA, T. & NARUKAWA, T. (2007) Study on simultaneous speciation of arsenic and antimony by HPLC-ICP-MS. *Talanta,* 73**,** 81-86.

MURAMATSU, Y. & OHMOMO, Y. (1986) Iodine-129 and iodine-127 in environmental samples collected from Tokaimura/Ibaraki, Japan. *Science of The Total Environment,* 48**,** 33-43.

MURAMATSU, Y., TAKADA, Y., MATSUZAKI, H. & YOSHIDA, S. (2008) AMS analysis of I-129 in Japanese soil samples collected from background areas far from nuclear facilities. *Quaternary Geochronology,* 3**,** 291-297.

MURAMATSU, Y., UCHIDA, S. & OHMOMO, Y. (1993) Root-Uptake of Radioiodine by Rice Plants. *Journal of Radiation Research,* 34**,** 214-220.

MURAMATSU, Y., UCHIDA, S., SRIYOTHA, P. & SRIYOTHA, K. (1990) Some Considerations on the Sorption and Desorption Phenomena of Iodide and Iodate on Soil. *Water Air and Soil Pollution,* 49**,** 125-138.

MURAMATSU, Y., YOSHIDA, S., FEHN, U., AMACHI, S. & OHMOMO, Y. (2004) Studies with natural and anthropogenic iodine isotopes: iodine distribution and cycling in the global environment. *Journal of Environmental Radioactivity,* 74**,** 221-232.

MURAMATSU, Y., YOSHIDA, S., UCHIDA, S. & HASEBE, A. (1996) Iodine desorption from rice paddy soil. *Water Air and Soil Pollution,* 86**,** 359-371.

NAGATA, T., FUKUSHI, K. & TAKAHASHI, Y. (2009) Prediction of iodide adsorption on oxides by surface complexation modeling with spectroscopic confirmation. *Journal of Colloid and Interface Science,* 332**,** 309-316.

NEAL, C., NEAL, M., WICKHAM, H., HILL, L. & HARMAN, S. (2007) Dissolved iodine in rainfall, cloud, stream and groundwater in the Plynhmon area of mid-Wales. *Hydrology and Earth System Sciences,* 11**,** 283-293.

NOLAN, A. L., MA, Y. B., LOMBI, E. & MCLAUGHLIN, M. J. (2004) Measurement of labile Cu in soil using stable isotope dilution and isotope ratio analysis by ICP-MS. *Analytical and Bioanalytical Chemistry,* 380**,** 789-797.

ORLEMANN, E. F. & KOLTHOFF, I. M. (1942) The reduction of iodate and bromate in acid medium at the dropping mercury electrode. *Journal of the American Chemical Society,* 64**,** 1044-1052.

OSTERC, A., JACIMOVIC, R. & STIBILJ, V. (2007) Development of a method for I-129 determination using radiochemical neutron activation analysis. *Acta Chimica Slovenica,* 54**,** 273-283.

PIPER, C. S. (1954) Soil and Plant Analysis : A Laboratory Manual of Methods for the Examination of Soils and the Determination of the Inorganic Constituents of Plants. *International Science Publisher Inc., New York*.

RADLINGER, G. & HEUMANN, K. G. (1997) Determination of halogen species of humic substances using HPLC/ICP-MS coupling. *Fresenius Journal of Analytical Chemistry,* 359**,** 430-433.

RADLINGER, G. & HEUMANN, K. G. (1998) Iodine determination in food samples using inductively coupled plasma isotope dilution mass spectrometry. *Analytical Chemistry,* 70**,** 2221-2224.

RADLINGER, G. & HEUMANN, K. G. (2000) Transformation of iodide in natural and wastewater systems by fixation on humic substances. *Environmental Science & Technology,* 34**,** 3932-3936.

RAE, J. E. & MALIK, S. A. (1996) The determination of iodine in geochemical samples: The use of pyrohydrolytic decomposition. *Chemosphere,* 33**,** 2121-2128.

RAYMAN, M. P. (2000) The importance of selenium to human health. *Lancet,* 356**,** 233-241.

REED, W. A., MAY, I., LIVENS, F. R., CHARNOCK, J. M., JEAPES, A. P., GRESLEY, M., MITCHELL, R. M. & KNIGHT, P. (2002) XANES fingerprinting of iodine species in solution and speciation of iodine in spent solvent from nuclear fuel reprocessing. *Journal of Analytical Atomic Spectrometry,* 17**,** 541-543.

REILLER, P., MERCIER-BION, F., GIMENEZ, N., BARRE, N. & MISERQUE, F. (2006) Iodination of humic acid samples from different origins. *Radiochimica Acta,* 94**,** 739-745.

REN, Q., FAN, J., ZHANG, Z. Z., ZHENG, X. Y. & DELONG, G. R. (2008) An environmental approach to correcting iodine deficiency: Supplementing iodine in soil by iodination of irrigation water in remote areas. *Journal of Trace Elements in Medicine and Biology,* 22**,** 1-8.

ROMAN, R. & DUNFORD, H. B. (1972) pH dependence of oxidation of iodide by compound I of horseradish-peroxidase. *Biochemistry,* 11**,** 2076-&.

ROMARIS-HORTAS, V., MOREDA-PINEIRO, A. & BERMEJO-BARRERA, P. (2009) Microwave assisted extraction of iodine and bromine from edible seaweed for inductively coupled plasma-mass spectrometry determination. *Talanta,* 79**,** 947-952.

ROTRUCK, J. T., POPE, A. L., GANTHER, H. E., SWANSON, A. B., HAFEMAN, D. G. & HOEKSTRA, W. G. (1973) Selenium - Biochemical Role as a Component of Glutathione Peroxidase. *Science,* 179**,** 588-590.

SAHOO, S. K., MURAMATSU, Y., YOSHIDA, S., MATSUZAKI, H. & RUHM, W. (2009) Determination of I-129 and I-127 Concentration in Soil Samples from the Chernobyl 30-km Zone by AMS and ICP-MS. *Journal of Radiation Research,* 50**,** 325-332.

SASAKURA, C. & SUZUKI, K. T. (1998) Biological interaction between transition metals (Ag, Cd and Hg), selenide/sulfide and selenoprotein P. *Journal of Inorganic Biochemistry,* 71**,** 159-162.

SCHLEGEL, M. L., REILLER, P., MERCIER-BION, F., BARRE, N. & MOULIN, V. (2006) Molecular environment of iodine in naturally iodinated humic substances: Insight from X-ray absorption spectroscopy. *Geochimica Et Cosmochimica Acta,* 70**,** 5536-5551.

SCHMITZ, G. (2001) The oxidation of iodine to iodate by hydrogen peroxide. *Physical Chemistry Chemical Physics,* 3**,** 4741-4746.

SCHNABEL, C., OLIVE, V., ATARASHI-ANDOH, M., DOUGANS, A., ELLAM, R. M., FREEMAN, S., MADEN, C., STOCKER, M., SYNAL, H. A., WACKER, L. & XU, S. (2007) I-129/I-127, ratios in Scottish coastal surface sea water: Geographical and temporal responses to changing emissions. *Applied Geochemistry,* 22**,** 619-627.

SCHNETGER, B. & MURAMATSU, Y. (1996) Determination of halogens, with special reference to, iodine, in geological and biological samples using pyrohydrolysis for preparation and inductively coupled plasma mass spectrometry and ion chromatography for measurement. *Analyst,* 121**,** 1627-1631.

SCHUMACHER, B. A., SHINES, K. C., BURTON, J. V. & PAPP, M. L. (1990) A comparison of soil sample homogenisation Techniques, *Environmental monitoring system laboratory, Office of research and development, U.S. Environmental protection agency Las Vegas*, http:// www. epa. gov/ esd/ cmb/ research/ papers/ bs120.pdf**,** Date Accessed: 13 September 2010.

SCHWEHR, K. A. & SANTSCHI, P. H. (2003) Sensitive determination of iodine species, including organo-iodine, for freshwater and seawater samples using high performance liquid chromatography and spectrophotometric detection. *Analytica Chimica Acta,* 482**,** 59-71.

SCHWEHR, K. A., SANTSCHI, P. H., KAPLAN, D. I., YEAGER, C. M. & BRINKMEYER, R. (2009) Organo-Iodine Formation in Soils and Aquifer Sediments at Ambient Concentrations. *Environmental Science & Technology,* 43**,** 7258-7264.

SHARPLEY, A. N. (1983) Effect of soil properties on the kinetics of phosphorous detection. *Soil Science Society of America Journal,* 47**,** 462-467.

SHEPPARD, M. I. & HAWKINS, J. L. (1995) Iodine and microbial interactions in an organic soil. *Journal of Environmental Radioactivity,* 29**,** 91-109.

SHEPPARD, M. I., HAWKINS, J. L. & SMITH, P. A. (1996) Linearity of iodine sorption and sorption capacities for seven soils. *Journal of Environmental Quality,* 25**,** 1261-1267.

SHEPPARD, M. I. & THIBAULT, D. H. (1992) Chemical Behavior of Iodine in Organic and Mineral Soils. *Applied Geochemistry,* 7**,** 265-272.

SHEPPARD, S. C., SHEPPARD, M. I., TAIT, J. C. & SANIPELLI, B. L. (2006) Revision and meta-analysis of selected biosphere parameter values for chlorine, iodine, neptunium, radium, radon and uranium. *Journal of Environmental Radioactivity,* 89**,** 115-137.

SHIMAMOTO, Y. S., ITAI, T. & TAKAHASHI, Y. (2010) Soil column experiments for iodate and iodide using K-edge XANES and HPLC-ICP-MS. *Journal of Geochemical Exploration,* 107**,** 117-123.

SHIMAMOTO, Y. S. & TAKAHASHI, Y. (2008) Superiority of K-edge XANES over L-III-edge XANES in the speciation of iodine in natural soils. *Analytical Sciences,* 24**,** 405-409.

SHIMAMOTO, Y. S., TAKAHASHI, Y. & TERADA, Y. (2011) Formation of Organic Iodine Supplied as Iodide in a Soil-Water System in Chiba, Japan. *Environmental Science & Technology,* 45**,** 2086-2092.

SINAJ, S., MACHLER, F. & FROSSARD, E. (1999) Assessment of isotopically exchangeable zinc in polluted and nonpolluted soils. *Soil Science Society of America Journal,* 63**,** 1618-1625.

SIVRY, Y., RIOTTE, J., MUNOZ, M., SAPPIN-DIDIER, V. & DUPRE, B. (2006) Study of labile Cd pool in contaminated soil using stable isotope analysis, radioactive isotope dilution and sequential extraction. *Geochimica Et Cosmochimica Acta,* 70**,** A594-A594.

SMITH, J. D. & BUTLER, E. C. V. (1979) Speciation of dissolved iodine in estuarine waters. *Nature,* 277**,** 468-469.

SMITH, L. M., MAHER, W. A., CRAIG, P. J. & JENKINS, R. O. (2002) Speciation of volatile antimony compounds in culture headspace gases of Cryptococcus humicolus using solid phase microextraction and gas chromatography-mass spectrometry. *Applied Organometallic Chemistry,* 16**,** 287-293.

SMYTH, D. & JOHNSON, C. C. (2011) Distribution of iodine in soils of Northern Ireland. *Geochemistry-Exploration Environment Analysis,* 11**,** 25-39.

SPARKS, D. L. (1989) Kinetics of soil chemical processes. *Academic Press, INC.,* San Diego, California 92101, USA.

SPARKS, D. L. (2003) Environmental Soil Chemistry. *Academic Press, INC.,* San Diego, California, 92101-4495, USA.

STEINBERG, S. M., BUCK, B., MORTON, J. & DORMAN, J. (2008a) The speciation of iodine in the salt impacted Black Butte soil series along the Virgin river, Nevada, USA. *Applied Geochemistry,* 23**,** 3589-3596.

STEINBERG, S. M., KIMBLE, G. M., SCHMETT, G. T., EMERSON, D. W., TURNER, M. F. & RUDIN, M. (2008b) Abiotic reaction of iodate with sphagnum peat and other natural organic matter. *Journal of Radioanalytical and Nuclear Chemistry,* 277**,** 185-191.

STEINBERG, S. M., SCHMETT, G. T., KIMBLE, G., EMERSON, D. W., TURNER, M. F. & RUDIN, M. (2008c) Immobilization of fission iodine by reaction with insoluble natural organic matter. *Journal of Radioanalytical and Nuclear Chemistry,* 277**,** 175-183.

STROUD, J. L., BROADLEY, M. R., FOOT, I., FAIRWEATHER-TAIT, S. J., HART, D. J., HURST, R., KNOTT, P., MOWAT, H., NORMAN, K., SCOTT, P., TUCKER, M., WHITE, P. J., MCGRATH, S. P. & ZHAO, F. J. (2010) Soil factors affecting selenium concentration in wheat grain and the fate and speciation of Se fertilisers applied to soil. *Plant and Soil,* 332**,** 19-30.

SUZUKI, T., BANBA, S., KITAMURA, T., KABUTO, S., ISOGAI, K. & AMANO, H. (2007) Determination of I-129 in environmental samples by AMS and NAA using an anion exchange resin disk. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 259**,** 370-373.

TAGAMI, K., UCHIDA, S., HIRAI, I., TSUKADA, H. & TAKEDA, H. (2006) Determination of chlorine, bromine and iodine in plant samples by inductively coupled plasma-mass spectrometry after leaching with tetramethyl ammonium hydroxide under a mild temperature condition. *Analytica Chimica Acta,* 570**,** 88-92.

TAGAMI, K., UCHIDA, S., TAKEDA, A., YAMASAKI, S.-I. & TSUCHIYA, N. (2010) Estimation of Plant-Unavailable Iodine Concentrations in Agricultural Fields. *Soil Science Society of America Journal,* 74**,** 1562-1567.

TAKATERA, K. & WATANABE, T. (1993) Speciation of iodo-amino acids by high-performance liquid-chromatography with inductively coupled plasma mass spectrometric detection. *Analytical Chemistry,* 65**,** 759-762.

TESSIER, A., CAMPBELL, P. G. C. & BISSON, M. (1979) Sequential Extraction Procedure for the Speciation of Particulate Trace-Metals. *Analytical Chemistry,* 51**,** 844-851.

THERMO-ELECTRON (2008) X Series ICP-MS Clinical Applications Note 2: Determination of Cu, Zn and Se in human serum samples. *Thermo Electron Co., Application Note: AN_EO604,* http:// www. thermo. com/ eThermo/ CMA/ PDFs/ Articles/ articlesFile_24876. pdf**,** Date Accessed: September, 3, 2008.

TONGTAVEE, N., SHIOWATANA, J., MCLAREN, R. G. & GRAY, C. W. (2005) Assessment of lead availability in contaminated soil using isotope dilution techniques. *Science of the Total Environment,* 348**,** 244-256.

TROTTER, W. R. (1960) The Association of Deafness with Thyroid Dysfunction. *British Medical Bulletin,* 16**,** 92-98.

TRUESDALE, V. W. & JONES, S. D. (1996) The variation of iodate and total iodine in some UK rainwaters during 1980-1981. *Journal of Hydrology,* 179**,** 67-86.

TSUKADA, H., TAKEDA, A., HASEGAWA, H., UEDA, S. & IYOGI, T. (2005) Comparison of NAA and ICP-MS for the determination of major and trace elements in environmental sample. *Journal of Radioanalytical and Nuclear Chemistry,* 263**,** 773-778.

TSUKADA, H., TAKEDA, A., TAGAMI, K. & UCHIDA, S. (2008) Uptake and Distribution of Iodine in Rice Plants. *Journal of Environmental Quality,* 37**,** 2243-2247.

ULLMAN, W. J. & ALLER, R. C. (1985) The geochemistry of iodine near-shore carbonate sediments. *Geochimica Et Cosmochimica Acta,* 49**,** 967-978.

UM, W., SERNE, R. J. & KRUPKA, K. M. (2004) Linearity and reversibility of iodide adsorption on sediments from Hanford, Washington under water saturated conditions. *Water Research,* 38**,** 2009-2016.

UMALY, R. C. & POEL, L. W. (1970) Effects of various concentrations of iodine as potassium iodide on growth of barley, tomato and pea in nutrient solution cultures. *Annals of Botany,* 34**,** 919-&.

UNDERWOOD, E. J. (1977) Iodine, *Trace elements in human and animals.* 4th ed. Nueva York, Academic Press, p:271-301.

USDOE (2005) Iodine. *Human Health Fact Sheet, Argonne National Laboratory, EVS,* United States Department of Energy, http:// www. ead. anl. gov/ pub/ doc/ iodine. pdf, Date Acessed: 27 November 2008.

USEPA (2007) Method 6800: Elemental and speciated isotope dilution mass spectrometry. *United States Environmental Protection Agency,* Date Accessed: November, 20, 2008.

VANCE, E. D., BROOKES, P. C. & JENKINSON, D. S. (1987) An extraction method for measuring soil microbial biomass C. *Soil Biology & Biochemistry,* 19, 703-707.

VOOGT, W., HOLWERDA, H. T. & KHODABAKS, R. (2010) Biofortification of lettuce (Lactuca sativa L.) with iodine: the effect of iodine form and concentration in the nutrient solution on growth, development and iodine uptake of lettuce grown in water culture. *Journal of the Science of Food and Agriculture,* 90, 906-913.

WANG, K. E. & JIANG, S. J. (2008) Determination of iodine and bromine compounds by ion chromatography/dynamic reaction cell inductively coupled plasma mass spectrometry. *Analytical Sciences,* 24, 509-514.

WARNER, J. A., CASEY, W. H. & DAHLGREN, R. A. (2000) Interaction kinetics of I-2(aq) with substituted phenols and humic substances. *Environmental Science & Technology,* 34, 3180-3185.

WATTS, M. J. & MITCHELL, C. J. (2009) A pilot study on iodine in soils of Greater Kabul and Nangarhar provinces of Afghanistan. *Environmental Geochemistry and Health,* 31, 503-509.

WEDEPOHL, K. H. (1995) The Composition of the Continental-Crust. *Geochimica Et Cosmochimica Acta,* 59, 1217-1232.

WELS, B. R., AUSTINHARRISON, D. S. & JOHNSON, D. C. (1991) Electrocatalytic reduction of iodate at platinum-electrodes in 0.5 M H_2SO_4. *Langmuir,* 7, 559-566.

WENG, H. X., YAN, A. L., HONG, C. L., XIE, L. L., QIN, Y. C. & CHENG, C. Q. (2008) Uptake of different species of iodine by water spinach and its effect to growth. *Biological Trace Element Research,* 124, 184-194.

WHITEHEAD, D. C. (1973a) Sorption of Iodide by Soils as Influenced by Equilibrium Conditions and Soil Properties. *Journal of the Science of Food and Agriculture,* 24, 547-556.

WHITEHEAD, D. C. (1973b) Studies on Iodine in British Soils. *Journal of Soil Science,* 24, 260-270.

WHITEHEAD, D. C. (1973c) Uptake and Distribution of Iodine in Grass and Clover Plants Grown in Solution Culture. *Journal of the Science of Food and Agriculture,* 24**,** 43-50.

WHITEHEAD, D. C. (1974a) Influence of organic matter, chalk and sesquioxides on solubility of iodide, elemental iodine, and iodate incubated with soil. *Journal of Soil Science,* 25**,** 461-470.

WHITEHEAD, D. C. (1974b) Sorption of Iodide by Soil Components. *Journal of the Science of Food and Agriculture,* 25**,** 73-79.

WHITEHEAD, D. C. (1975) Uptake by perennial ryegrass of iodide, elemental iodine and iodate added to soil as influenced by various amendments. *Journal of the Science of Food and Agriculture,* 26**,** 361-367.

WHITEHEAD, D. C. (1978) Iodine in Soil Profiles in Relation to Iron and Aluminum-Oxides and Organic-Matter. *Journal of Soil Science,* 29**,** 88-94.

WHITEHEAD, D. C. (1979) Iodine in the Uk Environment with Particular Reference to Agriculture. *Journal of Applied Ecology,* 16**,** 269-279.

WHITEHEAD, D. C. (1984) The Distribution and Transformations of Iodine in the Environment. *Environment International,* 10**,** 321-339.

WHO (2004) Iodine status worldwide. *Department of Nutrition for Health and Development, World Health Organization.* 20 Avenue Appia, 1211 Geneva 27, Switzerland.

WHO, UNICEF & ICCIDD (2007) Assessment of iodine deficiency disorders and monitoring their elimination : a guide for programme managers. – 3rd ed. WHO Press, World Health Organization, 20 Avenue Appia, 1211 Geneva 27, Switzerland.

WILSON, S. A. & WEBER, J. H. (1979) EPR study of reduction of vanadium (V) to vanadium (IV) by fulvic acid. *Chemical Geology,* 26**,** 345-354.

YAMADA, H., KIRIYAMA, T., ONAGAWA, Y., HISAMORI, I., MIYAZAKI, C. & YONEBAYASHI, K. (1999) Speciation of iodine in soils. *Soil Science and Plant Nutrition,* 45**,** 563-568.

YAMADA, H., KIRIYAMA, T. & YONEBAYASHI, K. (1996a) Determination of total iodine in soils by inductively coupled plasma mass spectrometry. *Soil Science and Plant Nutrition,* 42**,** 859-866.

YAMADA, H., SUGAHARA, M., KOSAKA, H., KATAYAMA, A., TAKAHASHI, K. & YONEBAYASHI, K. (1996b) Determination of total and water soluble iodine in soil by high performance liquid chromatography. *Soil Science and Plant Nutrition,* 42**,** 367-374.

YAMAGUCHI, N., NAKANO, M., TAKAMATSU, R. & TANIDA, H. (2010) Inorganic iodine incorporation into soil organic matter: evidence from iodine K-edge X-ray absorption near-edge structure. *Journal of Environmental Radioactivity,* 101**,** 451-457.

YAMAGUCHI, N., NAKANO, M., TANIDA, H., FUJIWARA, H. & KIHOU, N. (2006) Redox reaction of iodine in paddy soil investigated by field observation and the IK-edge XANES fingerprinting method. *Journal of Environmental Radioactivity,* 86**,** 212-226.

YANG, H. X., LIU, W., LI, B., ZHANG, H. J., LIU, X. D. & CHEN, D. Y. (2007) Speciation analysis for iodine in groundwater using high performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS). *Geostandards and Geoanalytical Research,* 31**,** 345-351.

YIOU, F., RAISBECK, G. M., ZHOU, Z. Q. & KILIUS, L. R. (1994) I-129 from Nuclear-Fuel Reprocessing - Potential as an Oceanographic Tracer. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 92**,** 436-439.

YNTEMA, L. F. & FLEMING, T. (1939) Volumetric oxidation of iodide to iodate by sodium chlorite. *Industrial and Engineering Chemistry-Analytical Edition,* 11**,** 0375-0377.

YONEHARA, N., YOSHIDA, M. & IWASAKI, I. (1970) The photometric determination of minute amounts of iodine in silicate rocks. *Bulletin of the Chemical Society of Japan,* 43**,** 3796-3800.

YOSHIDA, S., MURAMATSU, Y., KATOU, S. & SEKIMOTO, H. (2007) Determination of the chemical forms of iodine with IC-ICP-MS and its application to environmental samples. *Journal of Radioanalytical and Nuclear Chemistry,* 273**,** 211-214.

YOSHIDA, S., MURAMATSU, Y. & UCHIDA, S. (1992) Studies on the Sorption of I-(Iodide) and Io3-(Iodate) onto Andosols. *Water Air and Soil Pollution,* 63**,** 321-329.

YOSHIDA, S., MURAMATSU, Y. & UCHIDA, S. (1998) Soil-solution distribution coefficients, K(d)s, of I^- and IO_3^- for 68 Japanese soils. *Radiochimica Acta,* 82**,** 293-297.

YOUNG, S. D., CROUT, N., HUTCHINSON, J., TYE, A., TANDY, S. & NAKHONE, L. (2007) Techniques for Measuring Attenuation: Isotopic Dilution Methods, Natural Attenuation of Trace Element Availability in Soils, TheSociety of Environmental Toxicology and Chemistry (SETAC).

YOUNG, S. D., TYE, A., CARSTENSEN, A., RESENDE, L. & CROUT, N. (2000) Methods for determining labile cadmium and zinc in soil. *European Journal of Soil Science,* 51**,** 129-136.

YU, Z. S., WARNER, J. A., DAHLGREN, R. A. & CASEY, W. H. (1996) Reactivity of iodide in volcanic soils and noncrystalline soil constituents. *Geochimica Et Cosmochimica Acta,* 60**,** 4945-4956.

YUITA, K. (1992) Dynamics of Iodine, Bromine, and Chlorine in Soil .2. Chemical Forms of Iodine in Soil Solutions. *Soil Science and Plant Nutrition,* 38**,** 281-287.

YUITA, K., AKABE, S., SHIBUYA, M. & ASO, S. (1982) Iodine, Bromine and Chlorine Contents in Soils and Plants of Japan .2. Iodine, Bromine and Chlorine Contents in Soils and Plants of the Basin of the Nagara River. *Soil Science and Plant Nutrition,* 28**,** 499-515.

YUITA, K. & KIHOU, N. (2005) Behavior of iodine in a forest plot, an upland field, and a paddy field in the upland area of Tsukuba, Japan: Vertical distribution of iodine in soil horizons and layers to a depth of 50 m. *Soil Science and Plant Nutrition,* 51**,** 455-467.

YUITA, K., TANAKA, T., ABE, C. & ASO, S. (1991) Dynamics of Iodine, Bromine, and Chlorine in Soil .1. Effect of Moisture, Temperature, and Ph on the Dissolution of the Triad from Soil. *Soil Science and Plant Nutrition,* 37**,** 61-73.

ZABLOTSKA, L. B., RON, E., ROZHKO, A. V., HATCH, M., POLYANSKAYA, O. N., BRENNER, A. V., LUBIN, J., ROMANOV, G. N., MCCONNELL, R. J., O'KANE, P., EVSEENKO, V. V., DROZDOVITCH, V. V., LUCKYANOV, N., MINENKO, V. F., BOUVILLE, A. & MASYAKIN, V. B. (2011) Thyroid cancer risk in Belarus among children and adolescents exposed to radioiodine after the Chornobyl accident. *British Journal of Cancer,* 104**,** 181-187.

ZHU, Y. G., HUANG, Y. Z., HU, Y. & LIU, Y. X. (2003) Iodine uptake by spinach (Spinacia oleracea L.) plants grown in solution culture: effects of iodine species and solution concentrations. *Environment International,* 29**,** 33-37.

ZHU, Y. G., HUANG, Y. Z., HU, Y., LIU, Y. X. & CHRISTIE, P. (2004) Interactions between selenium and iodine uptake by spinach (Spinacia oleracea L.) in solution culture. *Plant and Soil,* 261**,** 99-105.