Iodine soil dynamics and methods of measurement: a review

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Iodine is an essential micronutrient for human health: insufficient intake can have multiple effects on development and growth, affecting approximately 1.9 billion people worldwide. Previous reviews have focussed on iodine analysis in environmental and biological samples, however, no such review exists for the determination of iodine fractionation and speciation in soils. This article reviews the geodynamics of both stable ^{127}I and the long-lived isotope ^{129}I ($t_{½}$ = 15.7 million years), alongside the analytical methods for determining iodine concentrations in soils, including consideration of sample preparation. The ability to measure total iodine concentration in soils has developed significantly from rudimentary spectrophotometric analysis methods to inductively coupled plasma mass spectrometry (ICP-MS). Analysis with ICP-MS has been reported as the best method for determining iodine concentrations in a range of environmental samples and soils due to developments in extraction procedures and sensitivity, with extremely good detection limits typically <μg L^{-1}. The ability of ICP-MS to measure iodine and its capabilities to couple on-line separation tools has the significance to develop the understanding of iodine geodynamics. In addition, nuclear-related analysis and recent synchrotron light source analysis are discussed.

Introduction

Iodine is an essential micronutrient for human health due to its involvement in the production of thyroid hormones; thyroxine (T4) and triiodothyronine (T3), which regulate multiple biochemical processes, including metabolism.[1,2] The recommended daily intake rates of iodine are 120, 150 and 250 μg for children, adults and pregnant/lactating women, respectively.[3] Insufficient iodine intake can have multiple effects on development and growth in mammals, these are collectively known as iodine deficiency disorders (IDD).[4] Approximately 1.9 billion people are at risk of developing IDD, despite the global effort to increase dietary iodine intake in the past decade.[5] The most serious consequences of iodine deficiency (ID) occur during fetal development. Severe ID during pregnancy and infancy increases the risk of stillbirths, impaired cognitive development as well as neurologic and myxedematous cretinism.[3,6-8] Iodine deficiency is often identified from the swelling of the thyroid gland, a condition known as goitre.[4,8] In addition, excessive intake, >300 μg day^{-1}, can also cause hyper/hypo-thyroidism, euthyroid goitre or thyroid autoimmunity.[6,9]

To date, dietary supplementation, by means of iodised salt, has proved to be an efficient method of reducing the global prevalence of IDD.[4] However, this approach is associated with a number of issues including inadequate monitoring of iodine concentrations in fortified salt, as such, approximately one-third of households lack access to adequately iodised salt.[10,11] A concentrated effort by the World Health Organisation (WHO) to reduce salt consumption to alleviate chronic health diseases, such as high blood pressure and other heart complications, could also impair the effectiveness of this prophylaxis.[12-14] Iodine biofortification is an alternative strategy to address ID, as iodine stored in food is readily bioavailable (up to 99%).[15,16] Whilst a number of studies have investigated iodine uptake by crops, significant gaps in knowledge still remain, particularly associated with the effects of soil properties (organic matter content, Fe/Al oxides, soil pH) on iodine solubility and speciation and plant uptake mechanisms.

Further knowledge of how iodine interacts with soils will enable us to better understand the spatial distribution of ID and, therefore, improve active strategies to counter IDD. This paper provides a review of analytical methods associated with the study of iodine-soil dynamics.

Iodine geodynamics

The biogeochemical cycling of iodine in soils is controlled by soil characteristics that affect retention against leaching, such as pH and the concentration of organic matter and metal oxides, and factors related to external iodine inputs, such as proximity of the soil to the coast.[17-20] Partly due to issues regarding the analytical detection of various iodine species, the understanding of soil-iodine reactions and plant uptake mechanisms are still limited.[21,22] The average iodine concentration in the Earth's crust is 0.25-0.45 mg kg^{-1}, whilst the average soil concentration is significantly higher at 5.1 mg kg^{-1}.[17,23,24] Soil iodine concentrations are less dependent on parent material sources than on the wet and dry deposition of volatised iodine compounds from oceans.[25] Biological and photochemical reactions cause both inorganic and organically bound iodine to be volatilised from seawater; volatile organic compounds include methyl iodide, diiodomethane, chloroiodomethane, iodoethane and iodopropane.[26-29] Once released into the atmosphere, the volatilised iodine undergoes photolysis, aerosol formation and finally deposition inland. Soils within close proximity to oceans are generally enriched with iodine as they are directly affected by deposition via rainfall.[30] However, soil-iodine concentrations are also heavily influenced by soil characteristics, which affect retention and iodine

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speciation. Figure 1 highlights the complexity of soil interactions.

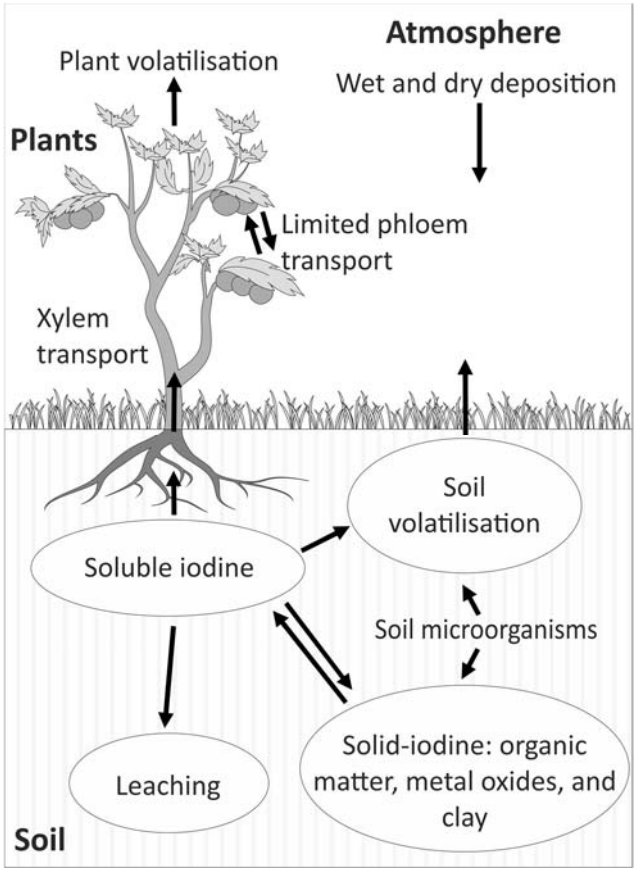

Figure 1 Iodine interactions within the soil-plant-atmosphere system

An important factor that influences iodine biogeochemical dynamics and cycling within the natural environment is pH and Eh (redox potential). Within the literature an inverse relationship between soil-iodine and pH is often found due to lower pH levels increasing the anion exchange capacity of many pH-dependent charge soils,[31] and a desorption of soil iodine into solution when soil Eh falls below 150mV.[32] Under environmental conditions, the speciation of inorganic iodine is generally controlled by pH and Eh.[33] Shetaya*, et al.*[34] reported that soil pH acts mainly on the initial adsorption of iodate in soils while soil organic matter influences time-dependent sorption. Xu*, et al.*[31] showed that Eh was positively correlated to total iodine concentrations in seven urban surface soils collected from Fukushima Prefecture, Japan. However, this trend was not found in the soil depth profiles, suggesting more complex interactions exist and that multiple soil properties influence iodine geodynacmis.[34]

Soil humus and Fe/Al/Mn hydrous oxides are known to influence iodine speciation and fixation into unavailable forms in soils.[31-33] In most soils the majority of iodine is bound to organic matter and soils with high organic matter contents often have higher iodine concentrations.[35-37] A common theme reported within the scientific literature was that organic matter is naturally degraded by biotic and abiotic processes in soil leading to the creation of humic substances (HS), which are composed of the operational fractions: humic acids (HA), fulvic acids (FA) and humin.[38] Both HA and FA are polycarboxylic acids with substituted oxyacid functional groups (COOH and OH). Humic acid has an estimated molecular weight range of 10,000-100,000 g mol^{-1} and is only soluble under neutral – alkaline conditions. Fulvic acid, soluble in acid and alkaline conditions, has a molecular weight range of 1000-10,000 g mol^{-1} and has more reactive, densely spaced carboxyl and hydroxyl groups.[39] Warner*, et al.*[40] proposed that, because of the smaller molecular mass of FA, it is more likely to interact with inorganic species in soils. In the case of oxyanions such as iodide (I^-) and iodate (IO_3^-) however, reactions with FA may be moderated by negative charge repulsion between the inorganic anion and dissociated COO^- groups. However, a new concept was proposed by Lehmann and Kleber[41] whereby organic matter is 'a continuum of progressively decomposing organic compounds towards smaller molecular size'. It is important to note that the terminology such as humic substances and its subsidiary groups, HA and FA, are still commonly used in peer-reviewed papers assessing iodine geodynamics.[18,21,42-44] A more robust understanding of iodine dynamics in soils could be obtained if, instead of studying hypothetical interactions between iodine extracts of 'humic substances', future research were to assess the interactions between organic matter and iodine by investigating the entire soil organic matter or soil solution rather than what is extractable by alkali.[41] Schlegel*, et al.*[43] stated that when iodine enters a soil it can react in at least three ways: (1) methylation of inorganic iodine by microbes, (2) iodination of phenolic moieties and (3) iodination of amines, in addition the adsorption of inorganic iodine by variable-charge oxides, such as Fe oxides, is an important initial reaction.[34]

Soluble iodine exists predominantly as iodate, iodide and org-I: the proportions of these are influenced by soil characteristics and probably contact time.[17-19] There is substantial evidence demonstrating that when iodide and iodate are added to soils they are rapidly converted to org-I within minutes-to-days and days-to-weeks, respectively.[34,36,37,42,45] Within acidic soils, inorganic iodate may be reduced to elemental iodine and iodide; in soils with pH >6, organic matter has a greater influence on iodine sorption compared to Fe/Al oxides.[46,47] Flood events influence iodine speciation and fractionation through changes in soil redox conditions. In flooded anoxic soils iodide is the dominant inorganic species, however, in oxidising conditions iodate is more likely to be the stable inorganic species.[19,48] Once in the terrestrial environment iodine is highly mobile; iodine present in the soil-plant system can be (re-)volatised into the atmosphere. Amiro and Johnston[49] speculated that iodine volatilised from plants is primarily released as methyl iodide, but emissions from living vegetation might only contribute ~0.1% to the stable iodine concentration in the surrounding atmosphere. Current understanding of soil-iodine-plant interactions requires more in-depth analysis regarding uptake mechanisms, transfer rates and the effects of soil properties on plant concentrations.

Radionuclides of iodine, ^{131}I ($t_{½}$ = 8.02 days) and ^{129}I ($t_{½}$ = 15.7 x 10^7 y), are produced during nuclear fission, weapons testing, nuclear fuel reprocessing, nuclear incidents, and from medical research facilities. Radioiodine has the potential to undergo biological accumulation, due to its mobility and volatility, via deposition on crops, consumption of food, drinking and inhalation. Short-lived isotopes (e.g. ^{131}I, $t_{½}$=8 days) move rapidly into the food chain due to their interactions with the soil-plant environment, therefore, it is essential that reaction rates and transport mechanisms are understood. During the Chernobyl accident an estimated 1.7 x 10^9 GBq of ^{131}I was released,[50] this resulted in inadequate thyroid function and tumours to develop in children in Ukraine, Belarus, and Russia.[34,51-53]

Successfully identifying iodine concentrations and species present in soils is critical to understanding its geochemical interactions. Previous review papers have focussed on analytical processes to identify iodine species in various environmental and biological media e.g. waters, sediments, plants/food, tissues, milk, blood serum and urine.[17,54-56] However, in-depth reviews of iodine analysis in soils are limited. The following sections review established methods of analysis for total iodine concentration and speciation in soils, considering both analytical technique and sample preparation.

Analysis of total iodine concentration in soils

Spectrophotometric analysis

The Sandell–Kolthoff (S-K) reaction is a low-cost method for quantifying total iodine in a range of samples including serum, urine, milk, foodstuff, plants and soils. [57-64] The reaction, outlined below, involves the reduction of cerium- Ce^{4+} (yellow) by arsenite (As^{3+}) to Ce^{3+} (colourless) in the presence of an iodide catalyst. Without the iodide catalyst, this reaction in a dilute sulfuric acid medium takes 2–4 days at room temperature, however, with the iodide catalyst the decolourisation occurs within a few minutes [65].

$$2Ce^{4+} + As^{3+} \xrightarrow{I^-} 2Ce^{3+} + As^{5+}$$

The rate of disappearance of the Ce^{4+} yellow colour at 405 – 420 nm is used to determine the iodine concentration.[56] This kinetic colourimetric method is a relatively simple technique for total iodine analysis for which Whitehead[20] defined the critical parameters controlling the procedure, including: (1) the oxidative acid digestion which converts the organic and inorganic iodine compounds to iodate, (2) the conversion from iodate to iodide in the presence of As^{3+} in dilute sulfuric acid, and (3) the spectrophotometric measurement of iodide based on the catalytic effect and colour change compared to a blank sample. A limited number of studies have utilised the S–K reaction to determine iodine concentrations in soils but the majority of reported studies have investigated biological material. This is due, in part, to the number of interferences that can produce significant analytical error. Sandell and Kolthoff[65] identified that osmium and ruthenium acted as catalysts in the reduction of Ce^{4+}, as did manganese and permanganate in the presence of bromides. Cyanide and silver are capable of inhibiting the S–K reaction by chelating with either Ce^{4+}/Ce^{3+} or forming complexes with iodide which directly affects the reaction rate.[65] Fluoride, mercury salts, nitrite, ascorbic acid, and ferrous iron are also capable of inhibiting this reaction. [65,66]

The application of the S-K method for determining iodine concentrations in solid samples is rarely seen in published reports, mainly due to the low sensitivity of the method. Whitehead[67] investigated iodine concentrations of 132 surface soils (0-15 cm) across the UK. Soils were prepared, extracted and analysed using the S-K method and a detection limit of 0.5 mg kg^{-1} I was calculated. The database of global soil-iodine concentrations collated by Johnson[24] suggested that >40% of soil-iodine concentrations were <2.5 mg kg^{-1}. Thus the detection limit presented in Whitehead[67] highlights a limitation in the ability of the S-K method to accurately quantify trace iodine concentrations in soils. Rae and Malik[59] extracted iodine from soil and geological samples using a pyrohydrolysis extraction prior to analysis via the S-K method. The pyrohydrolysis trap solution was analysed and a detection limit of 0.1 mg L^{-1} I was calculated in the solution. In comparison to more sophisticated instruments, such as ICP-MS where the limits of detections (LOD) are typically presented as parts-per-billion (µg kg^{-1}), the detection limit achieved by Rae and Malik[59] further highlights the analytical limitations of the S-K method for iodine in soils. Nevertheless, the S-K method and its application in inexpensive rapid-test kits to detect iodine concentrations in salt have helped to assess the progress of universal salt iodisation initiatives. The rapid-test kits are basic and are capable of detecting iodine in the range 10-90 mg kg^{-1}, they have successfully been used in situations where advanced instruments are unavailable, owing to lack of resources and reliability of analytical utilities e.g. electricity and argon gas. [68] However, the Biomarkers of Nutrition for Development (BOND) review for iodine suggested that biomonitoring results determined by urinary iodine and food composition tables should be calculated using ICP-MS as iodine is typically present in the parts-per-billion (µg kg^{-1}) range and is considered undetectable by less sophisticated analytical methods.[9,69]

Neutron activation analysis (NAA)

In neutron activation analysis, elemental concentrations are determined in a sample based on the release of gamma radiation from the radionuclides formed when the sample is irradiated by neutrons. The type of neutron used to irradiate the sample will determine which radionuclides are released. For example, thermal neutrons will induce the reaction $^{127}I(n,\gamma)^{128}I$, $t_{1/2}$= 25 minutes; alternatively, applying fast neutrons will induce the reaction $^{127}I(n,2n)^{126}I$, $t_{1/2}$= 13 days.[70] Variants on the technique exist, including non-destructive instrumental NAA and radiochemical NAA; the latter includes a chemical separation process prior to analysis. Radiochemical NAA is used to determine soil iodine concentrations due to the complex interferences from other elements; the sample has to undergo chemical separation to remove interfering species and

concentrate the radioisotopes of interest. Iodine separation procedures including an ashing/fusion solvent extraction and a combustion separation method, which have been developed to increase the accuracy and sensitivity of the analysis. Muramatsu*, et al.*[71] used an ashing/fusion solvent extraction before irradiating and purifying the iodine fraction for analysis. The extraction process incurred iodine losses of 5-20%, indicating the difficulties associated with extracting iodine from soils. Further drawbacks included the complexity of the procedure, long irradiation and cool-down periods and post-irradiation handling issues. A combustion method that trapped evaporated iodine in two receiver solutions, with an average chemical yield of 92%, was developed by Muramatsu et al. (1985); the method was a significant improvement compared to previous ashing/fusion extraction techniques. Muramatsu and Yoshida[72] also reported a method that specifically focused on the analysis of ^{127}I using thermal neutrons to create ^{128}I with a half-life of 25 min. No post-irradiation purification was performed, as the sample required immediate analysis, therefore, reducing the handling time of irradiated samples; a detection limit of 0.1 mg kg^{-1} was achieved. Sensitivity is a problem when environmental samples are analysed as sample preparation releases radioactivity from co-existing elements such as Mn, Na, K, Cl and Al that disrupt the background spectrum and interfere with iodine peak detection.[72,73] An advantage of NAA is the ability to simultaneously measure multiple isotopes in a sample, however, this can lead to further interferences, increasing the potential for error in the results. Aumann*, et al.*[74] used ^{130}I and ^{126}I to determine the concentrations of ^{129}I and ^{127}I, respectively. There is the possibility that ^{130}I can be produced when irradiating ^{127}I; triple neutron capture (TNC) could present a theoretical problem when analysing sample matrices with relatively high concentrations of ^{127}I. However, the results of Aumann*, et al.*[74] indicated that TNC interference would produce a negligible amount of ^{130}I activity - less than six times the detection limit. Muramatsu*, et al.*[71] tested several concentrations of ^{129}I and ^{127}I, to investigate the influence of TNC; 5 mg of ^{127}I was irradiated but the concentration of ^{130}I was below detection limits, confirming that it did not influence the measured I concentration. Other interferences can be caused by uranium, caesium, and tellurium which may be present at trace concentrations in the pyrohydrolysis equipment (activated charcoal and quartz tubes); however, there is evidence that these interferences are removed during the alkali fusion/ashing method sample preparation.[17,75]

Accelerator Mass Spectrometry (AMS)

Accelerator mass spectrometry is a well-recognised method for analysing ^{129}I, due to the high sensitivity achieved during analysis. Prior to the analysis of soils, ^{129}I must be extracted and prepared as an AgI precipitate, then dried and mixed with either Ag or Nb powder for AMS analysis. The extraction protocols are similar to those of NAA analysis and involve a series of extractions and back-extractions.[76-82] The AMS consists of an ion source (high-intensity Cs^+), injector and analyser magnets, linked by a tandem accelerator, switching magnet, electrostatic analyser and a detector. The AgI precipitate is injected into the ion source, as a negative ion, by ion sputtering. Whilst I^- ions are easily formed, the main isobaric interference, $^{129}Xe^-$, rapidly decomposes leaving the sample interference free.[17,83] When a sample is passed through the tandem accelerator, several electrons are stripped off: I^- to form I^{3+}, I^{5+} or I^{7+}, this in turn helps to eliminate interferences from $^{128}TeH^-$ and $^{127}IH_2^-$. The ^{129}I is then detected by time-of-flight (TOF) and silicon charged particle detectors or gas ionisation energy detectors.[17,84]

Instrumental background ratios of ^{129}I/^{127}I have previously been reported as low as 10^{-14},[76,80,85] however, the practical detection limit of ^{129}I in soils is affected by: analytical memory effects, the chemical separation procedure and the use of an iodine carrier during analysis. The carrier solution is usually a KI solution, with a concentration of 1-5 mg for soil samples, consequently, the practical detection limit of ^{129}I/^{127}I is slightly higher, typically reported as ~10^{-13}.[76,81,83,85] The concentration of ^{129}I is calculated from the measured ^{129}I/^{127}I ratio and the ^{127}I content of the sample; ICP-MS is often used to determine the ^{127}I concentration

Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry determines the concentration of an analyte in solution on the basis of mass-to-charge ratio (*m/z*). Samples are introduced, as an aerosol, into an ionising argon plasma which converts analytes to singly-charged ions. A subsample of the ion cloud formed is directed through a vacuum unit into a mass analyser and onto a detector – typically an electron multiplier.[86] The majority of ICP-MS instruments use a single quadrupole mass spectrometer, capable of isolating a single *m/z* value at one time, and usually employ some means of removing polyatomic species prior to the ion detector. Inductively coupled plasma mass spectrometry is capable of determining iodine concentrations in soil samples following extraction into solution. Iodine extraction is a critical step for ICP-MS analysis, and there have been significant developments in extraction methods (Table 1).

Table 1 Sample preparation, extraction and observations for total iodine analysis by ICP-MS

Sample	Analyte	Sample preparation	Extraction process	Instrumentation	Observations	Ref
Geological reference materials	^{127}I	Samples were dried for 4 h at 80 °C and stored at room temperature.	Samples were mixed with a flux (Na_2CO_3 and ZnO) and heated at 650 °C for 40 min in a muffle furnace and then dissolved in hot water.	TJA Solutions (USA); PQ ExCell.	Ammonia solution effectively eliminated the memory effects of iodine during analysis. The LOD was 30 μg L^{-1}.	87
Soil, sediment and biological samples	^{127}I	Samples were dried for 4 h at 80 °C and stored at room temperature.	Samples were weighed into a 10 mL PTFE-lined stainless steel bomb, 10% v/v ammonia solution was added and heated at 185 °C for 18 h.	TJA Solutions (USA); PQ ExCell.	This technique is not suitable for total extraction of iodine from mineral structures. The LOD was 0.003 μg L^{-1}. Tellurium-126 was used as the internal standard.	88
Geochemical reference materials	^{127}I	Samples were received in powdered form.	Total I and Br was extracted using the pyrohydrolysis technique outlined by Schnetger and Muramatsu[89]. Slight modification to the trap solution, which contained TMAH (0.5%) and Na_2SO_3 (0.005%).	Yokogawa Analytical Systems (Japan); Agilent 7500a.	All solutions were measured in a final matrix of 0.5% TMAH. Memory effects were significantly reduced by the TMAH (0.5%) wash. Caesium (10 μg L^{-1}) was added to the trap solution as an internal standard. The LOD was 0.13 μg kg^{-1}, in soil material.	90
Clay rock	^{127}I	Samples were powdered in an agate mortar and finely ground in a grinder in the absence of O_2.	(i) Overnight extraction by nitric acid digestion at 90 °C in closed PFA (perfluoroalkoxy) vessel. (ii) Ammonia method.[88]	Thermo Scientific; X Series II ICP-MS.	Iodine was not associated with organic matter but rather carbonate minerals. To stabilise the signal and minimise memory effect, the samples and standards contained 0.25% TMAH.	91
Soils	$^{127}I/^{129}I$	Soils were air-dried and sieved <2 mm, prior to use.	The sample, in a quartz tube, was heated to 1000 °C for 15 min under oxygen flow, and the evaporated iodine was collected by an active carbon column (ACC). The ACC was then heated to 500 °C and the iodine was recaptured in a smaller ACC. Iodine was extracted from the ACC by 20 mL of 24% NaOH, an aliquot was taken for ^{127}I analysis. Benzene, HNO_3 and $NaNO_2$ was added to the remaining solution to extract the iodine as I_2 and then back-extract as I^- into 1 mL TMAH containing 0.02 M $(NH4)_2SO_3$ and analysed for ^{129}I.	PerkinElmer Sciex (Canada); ELAN DRCe ICP-MS.	For ^{127}I samples were diluted in 1% TMAH and rhenium (10 μg L^{-1}) was used as an internal standard. For ^{129}I a 0.5 μg mL^{-1} solution of Rh was added to the TMAH/$(NH4)_2SO_3$ solution prior to the back-extraction. The LOD for ^{129}I was 0.0152 μg L^{-1} in a 1 mg mL^{-1} ^{127}I matrix with an isotope ratio of 1.5 x 10^{-8}. The $^{129}Xe^+$ interference was eliminated by using O_2 as the reaction gas. The $^{127}H_2^+$ interference was reduced by removing traces of H_2 and H_2O from the reaction gas.	92
Austrian soils	^{127}I	Soils were sieved and powdered.	The sample, in a quartz tube, was mixed with V_2O_5, was heated to 1100 °C for 15 min under a wet oxygen flow, the evaporated iodine was collected in a receiver solution containing 7 mL H_2O, 0.4 mL TMAH and 0.1 mL 5000 mg kg^{-1} Na_2SO_3.	Yokogawa (Japan); PMS-2000.	Iodine was positively correlated with organic carbon. Iodine was completely separated from the sample at 1000 °C. The LOD was 5 μg L^{-1}. Caesium-133 was used as the internal standard.	93
Soils	$^{127}I/^{129}I$	No preparation required for soil samples.	Soils were heated ~1000 °C for 20 min, after which oxygen was introduced at a flow rate of 80 mL min^{-1}. The evaporated iodine was transferred into the ICP-CC-QMS for on-line measurement of ^{129}I and ^{127}I and $^{129}I/^{127}I$.	Platform ICP, Micromass Ltd. (Manchester, UK); ICP-CC-QMS.	Oxygen and helium were introduced into the hexapole cell as collision gases to optimise the $^{127}I^+$ ion intensities and improve the LOD for ^{129}I. The LOD for ^{129}I was 0.03 μg kg^{-1} in soil material.	52

Table 1 (Contd.)

Sample	Analyte	Sample preparation	Extraction process	Instrumentation	Observations	Ref
Soil reference materials	^{127}I	Soils were powdered.	Samples were weighed into Savillex vessel and 5 mL of 10% TMAH was added to the soil. The vessel was heated to 80 °C for 6 h.	Perkin-Elmer Sciex; Elan DRC II.	The procedure is capable of successfully analysing iodine concentrations in soils. The LOD was 27 μg L^{-1}.	94
Geological and organic material	^{127}I	Samples were powdered.	The sample, in a quartz tube, was mixed with V_2O_5, was heated to 1100 °C for 15 min under a wet oxygen flow (pyrohydrolysis), the evaporated iodine was collected in a receiver solution containing 7 mL H_2O, 0.4 mL TMAH and 0.1 mL 5000 mg kg^{-1} Na_2SO_3.	Yokogawa (Tokyo, Japan); PMS-2000.	TMAH (1%) solution was integrated into the sample, standard and washing solutions for better reproducibility. The LOD was 0.2 μg L^{-1}. Caesium-133 was used as the internal standard.	95
Soils	$^{127}I/^{129}I$	Soils were powdered.	The sample, in a quartz tube, was mixed with V_2O_5, was heated to 1000 °C for 30 min under a wet oxygen flow, the evaporated iodine was collected in a receiver solution containing 10 mL 1% TMAH and 0.1% Na_2SO_3. An aliquot was taken for ^{127}I analysis. The remaining solution was purified and back-extracted using carbon tetrachloride, 5% $NaNO_2$, 0.3 mL of 20% HNO_3 and Na_2SO_3 and concentrated for ^{129}I analysis.	Agilent Technologies Inc. (Santa Clara); Agilent 8800 (ICP-QQQ).	The $^{129}Xe^+$ interference was suppressed by O_2 as a reaction gas, and the application of a negative voltage gap in the ICP-QQQ between the cell and the quadrupole meant that the ^{127}I intensity was not significantly affected.	96
Soils	$^{127}I/^{129}I$	Soils were powdered.	Iodine was extracted using a modified method outlined by Ohno*, et al.*[97].	Agilent Technologies Inc. (Santa Clara); Agilent 7700x, with an octopole reaction system (ICP-ORS-QMS).	The interference of $^{129}Xe^+$ was suppressed by the introduction of O_2 as a collision gas. The LOD for ^{129}I was 0.0015 μg L^{-1}, this was significantly improved by using the reaction gas. Caesium-133 was added to the samples and standards as an internal standard.	97
Standard reference materials: rock, soil, milk, leaves, tissue	^{127}I	Samples were powdered.	The sample, in a quartz tube, was mixed with V_2O_5, was heated to 1100 °C for 15 min, and the evaporated iodine was collected in a receiver solution containing Na_2SO_3 (50 mg L^{-1}).	Yokogawa (Tokyo, Japan); PMS-2000.	The method successfully extracted iodine from the standard reference materials. The LOD was 0.02 μg L^{-1}.	89
Soils and waters	^{127}I	Soils were dried at 40 °C, sieved <2 mm and milled to <125 μm using an agate ball mill.	Samples were weighed into a PTFE bottle, 5 mL of 5% TMAH was added they were placed in an oven at 70 °C for 3 h and shaken after 1.5 h. DI water was added and the samples which were centrifuged and the supernatant was extracted.	Thermo Fisher ScientiWc (Waltham, MA); Thermo-Electron PQ ExCell ICP-MS.	The accuracy and precision of the method was evaluated using 17 soil- and sediment-certified reference materials, the extraction provided a good comparison between certified data. Rhenium in 1% TMAH was used as the internal standard.	98

Table 1 (Contd.)

Sample	Analyte	Sample preparation	Extraction process	Instrumentation	Observations	Ref
Soils and waters	^{127}I	Soils were dried at 40 °C, sieved <2 mm and then sieved to <125 µm.	Total I was extracted using the method outlined by Watts and Mitchell[98]. Soluble I was extracted by cold water extraction; 12.5 mL of DI water and 1.25 g of soil shaken for 15 min, centrifuged at 2500 rpm for 10 min and adjusted to a matrix of 1%TMAH for analysis.	Agilent (Hemel Hempstead, UK); Agilent 7500 ICP-MS.	Iodine determinations were completed in standard mode and rhenium in 1% TMAH was used as the internal standard.	[99]
Soils, waters and foodstuff	^{127}I	Soil were air-dried, crushed and sieved <2 mm. Samples were then ground to <40 µm in an agate ball mill.	Iodine was extracted using the method outlined by Watts and Mitchell[98] and Watts, *et al.*[99].	Agilent (Hemel Hempstead, UK); Agilent 7500 ICP-MS.	Iodine determinations were completed in no-gas mode with an improved washout time compared to Watts and Mitchell[98] due to the use of an ASXpress loop (CETAC), which introduced 500 µL of sample. The LOD was 0.25 µg L^{-1}.	[9]
Soils	^{127}I	Soils were air-dried and finely powdered.	Samples were placed in a polypropylene centrifuge tube, 5 mL of a 5% TMAH solution was added and heated at 70 °C for 3 h. The mixture was centrifuged and the supernatant was extracted.	Seiko Instruments Inc. (Chiba); Seiko Model SPQ-8000A.	Between each sample, the nebuliser and spray chamber were washed with water, ca. 0.1 mol L^{-1} HNO_3 and 2.5% TMAH solution. Indium-113 was used as the internal standard. The LOD was 0.012 µg L^{-1}.	[100]
Soils	^{127}I	Soils were air-dried, crushed, and sieved <2 mm. Soil were further ground to <32 µm in an agate ball mill for analysis.	Iodine was extracted using the method outlined by Watts and Mitchell[98] and Watts, *et al.*[99].	Agilent 7500cx.	Operating in no-gas mode, tellurium was used as an internal standard. All standards and samples were measured in a final matrix of 0.5% TMAH.	[101]

Over the past 20 years, there have been significant developments in soil-iodine extraction protocols for subsequent ICP-MS analysis. Initial extraction processes were based on methods developed for NAA using pyrohydrolysis extraction procedures.[87-89,93,95] Iodate and org-I are strongly sorbed in soils, therefore, an extraction method capable of mobilising colloidal and molecular organic forms iodine is required, in addition, it must also minimise the adsorption strength of inorganic iodine. Acid digestions cannot be used as iodine volatilises from solution as I_2 following reduction from iodate.[55,95,102] Several alkaline digestions have been developed involving NH_4OH, KOH and NaOH, however, the use of 5% tetramethylammonium hydroxide (TMAH) significantly improved the sample throughput and analytical precision of ICP-MS in determining soil iodine concentrations.[9,20,88,95,98-101,103] The alkaline conditions (c. pH 12) of TMAH prevents iodine from volatilising from solution, ionises humic and fulvic acids making them hydrophilic and desorbs inorganic forms of I (I^-, IO_3^-) from adsorption sites on oxides partly through hydroxyl ion competition.[100] Analytical sensitivity was also improved with TMAH incorporated into the wash and internal standard solutions; this leads to decreased memory effects and lowers the detection limit for iodine.[95,98,100,104]

The first ionisation energy of iodine is relatively high (10.45 eV), which results in poor ionisation efficiency in the argon plasma. Nevertheless, it is possible to measure iodine at concentrations below 1 µg L^{-1} due to the lack of isobaric interferences, doubly charged ions or oxides at *m/z* 127.[100,105,106] Internal standards are analysed simultaneously to correct for signal drift and are selected based on their similarity to the element of interest and absence from typical samples. However, due to the high first ionisation energy of iodine, selecting an appropriate internal standard can be complicated.[107] A range of internal standards for iodine have been tried; for example, caesium (*m/z* = 133) is commonly reported in the literature and has previously been used for soil solutions.[85,89,93,95,108,109] As an alkaline metal, Cs has very different chemical properties compared to iodine. Tagami and Uchida[110] investigated the stability of Cs and I in a range of TMAH concentrations, 0-1.25%, it was observed that whilst the I count remained stable, the Cs count decreased with increasing TMAH concentrations. In order to use Cs as the internal standard, it is necessary to maintain identical TMAH concentrations in the samples and standards; subsequent work has used a concentration of 0.5% TMAH for sample and internal standard preparation to obtain a consistent Cs ion count.[111] Besides Cs, rhenium (*m/z* = 186) has also been used as an

internal standard for iodine analysis.[36,98] To demonstrate the successful extraction of iodine from soils, Watts and Mitchell[98] mixed an internal standard of 10 µg L^{-1} Re with the sample in 1% TMAH. The accuracy and precision of the extraction method was evaluated using 17 soil- and sediment-certified reference materials; good agreement was achieved between the certified materials and analytical results. To a much lesser extent, indium (*m/z* = 113) has also been used as an internal standard, previous studies have incorporated In prepared in a 2.5% TMAH solution.[35,100] The first ionisation energies for Cs, In, Re are 3.89, 5.79 and 7.83 eV, respectively; by contrast, the first ionisation energy of iodine is considerably higher at 10.45 eV. The use of tellurium (*m/z* = 126) as an internal standard is also fairly common.[88,112-114] Tellurium has a similar mass and first ionisation energy (9.01 eV) to iodine. Previous studies have shown that Te has a similar signal response to iodine when exposed to plasma conditions and it remains in solution in alkaline TMAH.[113,114]

Quadrupole mass spectrometers are widely used due to their sensitivity, dynamic range, robustness, and relatively low cost. However, there are limitations associated with particular trace elements and with isotope ratio analysis, especially when the elements or isotopes have disproportionately higher natural concentrations. Achieving high levels of precision is challenging for ^{129}I, partly due to the presence of xenon impurities in the argon plasma gas ($^{129}Xe^+$ interference) in the collision cell and the potential occurrence of $^{127}IH_2^+$ from samples.[52,92,96,97,115,116] Eiden, *et al.*[117] originally investigated the effects of employing oxygen as a reaction gas to eliminate a number of interferences including: Y^+, Zr^+, and Xe^+, achieving greatly improved sensitivity for the elements and isotopes of interest. Izmer, *et al.*[52] employed a mixture of oxygen and helium as reaction and carrier gases in a collision cell thereby reducing $^{129}Xe^+$, and achieving a detection limit of 0.03 µg kg^{-1} for ^{129}I in soil material. This work was further developed with the addition of a cooling finger between the pretreatment oven and the ICP-MS.[116] The cooling finger was able to effectively enrich the evaporated iodine concentrations prior to analysis, achieving a detection limit of 0.0004 µg kg^{-1}, which is 75 times greater than that of Izmer, *et al.*[52]. Recent advances in ICP-MS and the development of triple quadrupole ICP-MS (QQQ-ICP-MS) have further improved analytical capabilities, with detection limits as low as 0.07 ng L^{-1}.[118] The additional quadrupole mass filter, located in front of the collision-reaction cell only allows species with the target analyte mass *m/z* value to enter the cell (e.g. *m/z* = 129).[118] Polyatomic interferences such as $^{127}IH_2^+$, $^{97}MoO_2$ and $^{113}CdO^+$ are then removed within the cell and only ^{129}I at *m/z* 129 then proceeds to the analytical quadrupole, crucially without the creation of new *m/z* 129 species in the cell.[96]

Trends in total iodine analysis

In order to illustrate recent trends in peer-reviewed publications, a systematic review of the literature using the WorldCat library database and NERC library service was conducted. Figure 2 highlights the number of peer-reviewed papers published in each year from 1990-2016 for the following search terms: ("iodine" AND "soil" AND "ICP-MS" OR "neutron activation analysis" OR "AMS" OR "Sandell–Kolthoff"). Within the past 25 years, the number of publications citing ICP-MS has surpassed those using spectrophotometric analysis, AMS and NAA – especially since the year 2000. The surge in publications applying ICP-MS for data analysis coincides with increased use of TMAH as an extractant for soil and other matrices (Table 1). The popularity of AMS has also increased as ICP-MS analysis has improved. The use of the S–K reaction to determine iodine in soil extracts is severely limited by the lack of sensitivity achieved by this method and the high level of uncertainty in the results due to the range of interferences that may be present.[66,69] Figure 2 shows that the application of NAA is not as common as ICP-MS, the reasons for this include: (1) the lack of nuclear research reactors required to provide the neutrons flux, (2) the relatively high cost, (3) the iodine separation procedures required for NAA which are complex and labour intensive, and (4) the substantial advancements in extraction protocols and ICP-MS instrumentation.

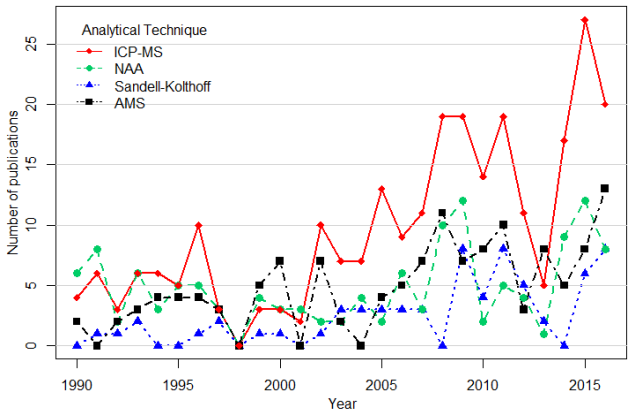

Figure 2 WorldCat library and NERC library service search results for ("iodine" AND "soil" AND "ICP-MS" OR "neutron activation analysis" OR "Sandell–Kolthoff" OR "AMS" from 1990-2016 (date of search: 14/03/2017) (n = 455)

The analytical methods described so far are used simply to measure total iodine concentrations in a sample extract. However, the requirement to identify multiple chemical species is crucial to our understanding of the dynamic interactions of iodine in soils and plants. Therefore, more complex combinations of analytical instruments and fractionation techniques have been developed; the following sections identify the range of methods used to analyse iodine species.

Fractionation analysis of iodine in soils

The sequential extraction procedure developed by Tessier, *et al.*[119] separated soil analytes into multiple fractions defined as (i) water-soluble, (ii) exchangeable, (iii) bound to carbonate, (iv) metal oxides (reducible), (v) organic matter, and a final (vi) residual (mineral bound) phase. The original procedure has been used to investigate various trace metal concentrations in soil using multiple reagents to release the different fractions in sequence. However, due to the volatile nature of iodine in acidic media, modified versions have been adapted to reduce iodine losses during the extraction.[17,35,120,121] Most sequential

extraction procedures are associated with errors caused by re-adsorption, cross-contamination, incomplete dissolution, premature releases and the transformation of chemical species during extraction.[36]

Schmitz and Aumann[120] used a modified sequential extraction protocol to investigate ^{127}I and ^{129}I fractionation using NAA in soils located next to a nuclear reprocessing plant. The extraction procedure involved separating iodine into: (F1) water-soluble iodine, (F2) exchangeable iodine at pH 8.2, (F3) exchangeable iodine at pH 4.8, (F4) iodine adsorbed on metal-oxides, (F5) iodine bound to organic matter, and (F6) residual iodine. The samples had ^{125}I added as a tracer to provide an estimate of chemical yield in the pre-irradiated sample, the iodine was separated from the samples by combustion in a stream of oxygen and analysed using NAA, full description in Aumann*, et al.*[74]. The results indicated that the water-soluble fractions of ^{127}I and ^{129}I were <4% and 39–49%, respectively, potentially demonstrating a greater mobility of the radioisotope compared to native soil iodine. The organic fraction (F5) was consistently low, <4% and 4-14% for ^{127}I and ^{129}I, respectively, with larger proportions found in the residual fraction (F6), 56-71% and 8-26%, respectively. The organically bound iodine (F5) was extracted using hydroxylamine, however, no evidence suggests that hydroxylamine can completely disassociate iodine bound to organic matter, therefore, it is possible that the organic fraction was severely underestimated.[121] Hou*, et al.*[121] investigated ^{129}I in Chernobyl-contaminated soils, using a fractionation procedure modified form that of Schmitz and Aumann[120] in which the organic fraction was extracted using a mixture of 30% H_2O_2 and HNO_3. The samples were then irradiated, purified and analysed using the 536 keV γ-line of ^{130}I produced by neutron activation of ^{129}I and was counted using an high-purity Germanium (HPGe) detector. In contrast to the findings of Schmitz and Aumann[120], approximately 70% of ^{129}I in the Chernobyl-contaminated soil was bound to oxides and organic matter (probably humus), with only 10–20% in the readily-available phase.[121] The significant differences between these two studies may be associated with the different sources or soil properties, however, it is much more likely that the extraction procedure used by Schmitz and Aumann[120] did not successfully separate the organic and residual fractions, a severe limitation to this extraction procedure.

Yamada*, et al.*[35] developed a fractional separation method to determine the inorganic species (I^-, IO_3^-), and iodine bound to FA and HA (I-FA and I-HA) in soils. Total iodine in the soils was extracted using 1.0 g of soil, shaken with 10 mL 5% TMAH for 4 hours at room temperature and centrifuged; F1 = I^- + IO_3^- + I-FA + I-HA. To an aliquot of F1, the I-HA was removed by acidification to pH 1.5 with H_2SO_4, to yield F2 = I^- + IO_3^- + I-FA. To a proportion of the residual solution, ammonium oxalate and calcium acetate were added to form calcium oxalate and incorporate the fulvic acids to give F3= I^- + IO_3^-.[109] The original sample was independently treated with 0.1 M KCl solution, absorbing IO_3^-, so that I^- was in solution; F4= I^-. Subsequently, F4, F3−F4, F1−F2, and F2−F3 correspond to the I^-, IO_3^-, I-HA, and I-FA fractions, respectively. All supernatant solutions were analysed for total iodine using the method described in Yamada*, et al.*[100]. The reproducibility of the extraction and analysis, defined by the relative standard deviations, was poor. There is a large potential for error in the results following this extraction process, and this led to an underestimation of iodine in the results, alternatively in other soils with different properties, an overestimation could also occur. Fractionation studies have a limited scope for iodine analysis in soils as operational procedures do not necessarily yield discrete fractions. A much greater emphasis has been placed on chemical speciation analysis and various methods have been successfully developed for analysing chemical species.

Speciation analysis of iodine in soils

Developing our understanding of iodine geodynamics could improve the strategies currently used to increase iodine concentrations in crops and thereby enable interventions to decrease the incidence of IDD. The identification of iodine species in soil presents significant difficulties, due to the complex nature of soils. Nevertheless, there are a variety of different analytical methods capable of identifying chemical species with various degrees of accuracy. Soluble iodine exists mainly as IO_3^-, I^- and org-I, and the proportions of these species present are significantly influenced by soil properties.[17-19] Iodine speciation analysis, in solution, can be performed by gas chromatography, high performance liquid chromatography, size exclusion chromatography, and electrospray ionisation, whilst synchrotron light source analysis can determine iodine species in a solid matrix.[19,35,37,122,123]

Gas chromatography (GC)

The application of GC-MS to analysis iodine in soils is scarcely used, however, Zhang*, et al.*[124] developed a method using GC-MS capable of directly analysing $^{127/129}I^-$, $^{127/129}IO_3^-$, and calculating the concentration of org-I in soil samples. Soil samples were mixed with V_2O_5, and heated to 300 °C for 4 min before being heated and held at 850 °C for a further 15 minutes under a wet oxygen flow, the evaporated iodine was collected in a receiver solution (H_2O). The concentrations of I^- and IO_3^- were then determined using separated methods. The detection limits were reported as 0.34 nM and 1.11 nM for $^{127}I^-$ and $^{127}IO_3^-$ respectively, whereas the detection limit for both $^{129}I^-$ and $^{129}IO_3^-$ was 0.08 nM (2pCi ^{129}I L^{-1}). All samples were spiked with ^{125}I as a tracer to provide an estimate of chemical yield, the extraction was successful with an average recovery of ~90.0%. The method described in Zhang*, et al.*[124] manages to circumvent the interferences associated with ICP-MS analysis when measuring ^{129}I which has the interferences from Xe impurities in the argon plasma. However, as previously mentioned, the latest advancements in ICP-QQQ-MS analysis successfully removes all polyatomic interferences on the mass charge 129, whilst offering a far higher sample throughput rate and sensitivity.

High performance liquid chromatography (HPLC)

The separation of iodine species in solution using HPLC is well established; HPLC is often coupled to ICP-MS which acts as the

principal, but not necessarily the only detector. The analysis of environmental samples requires three steps: (1) quantitative extraction from the sample matrix that maintains the chemical species; (2) effective separation by liquid chromatography; (3) reliable detection. An overarching requirement is that the iodine species are sufficiently non-labile that neither the extraction procedure nor transition through the chromatography column cause changes to the speciation. Inorganic iodine speciation analysis can be determined by HPLC-ICP-MS in a wide range of environmental and biological samples, however, the majority of samples are waters.[36,54,122,125-127]

Yoshida, *et al.*[128] developed an online separation procedure, followed by ICP-MS to determine the concentrations of I^- and IO_3^- in aqueous solutions, achieving a detection limit 0.1–1 μg L^{-1}. Soil solutions were extracted from flooded andosols during an incubation period of 24-days at different depths (surface, 1 cm, and 10 cm). The concentration of I^- present in the soil solution increased with decreasing Eh and depth over time, the presence of org-I was also observed. The author stated that further study is required with regards to identifying the org-I, and that understanding the chemical forms of iodine in soils is important to understanding the long-term behaviour of ^{129}I released into the environment.

Shimamoto, *et al.*[19] investigated the mobility of iodide and iodate in soil pore water of paddy field soils using HPLC-ICP-MS. Soil columns (10.7 cm) were incrementally packed and pressed with a 2.0 kg weight the ensure uniform bulk density, the treatment consisted of applying 80 mL of Milli-Q water and then 50 mL of a treatment solution. To separate the iodine species, an anion exchange column (TSK-gel Super IC-AP; 7.5 cm, Tosoh) was used at a constant temperature of 40 °C with a mobile phase consisting of 0.25% TMAH and 0.3% methanol with a flow rate of 1.0 mL min^{-1}. One significant benefit of HPLC-ICP-MS is the rapid determination of I^- and IO_3^- peaks, observed at approximately 128 s and 220 s, respectively. In the columns treated with I^-, only I^- was detected, inferring it was stable for the duration of the experiment. In comparison, the IO_3^- column showed that IO_3^- was significantly reduced to I^- with increasing depth in the column. This suggests that IO_3^- is severely affected by adsorption and reduction, as such the mobility of I^- is a dominant factor controlling the fate of iodine in the surface environment. Shimamoto, *et al.*[19] simulated the fate of I^- and IO_3^- in the soil columns using a three-dimensional, transient water flow system. The model was able to successfully simulate the fate of I^-, however, due to the absence of chemical transformation of IO_3^- to I^- in their simulation, a more elaborate model is required to simulate the fate of IO_3^- in soil columns. Speciation analysis can be used to improve the mechanistic credibility of models describing the fate and species transformations of trace elements in soil. This is especially true in complex simulations required to describe soil-iodine interactions; models describing soil-iodine dynamics have subsequently been improved upon by Shetaya, *et al.*[34] by integrating soil characteristics in kinetic model parameters.

Shetaya, *et al.*[34] investigated changes in iodine (^{129}I) solubility and speciation in nine soils with contrasting properties incubated over nine months. Soil extracts were analysed by ICP-MS coupled to a Dionex ICS-3000 ion chromatography system with a Hamilton PRP-X100 anion exchange column (250 x 4.6 mm; 5 μm particle size). The isocratic mobile-phase (flow rate 1.3 mL min^{-1}) consisted of 60 mmol L^{-1} NH_4NO_3, 1 x 10^{-5} mmol L^{-1} Na_2-EDTA, and 2% methanol adjusted to pH 9.5 with TMAH. The results were then modelled with irreversible and reversible first order kinetic models, and a spherical diffusion model, to describe the kinetics of both IO_3^- to I^- loss from the soil solution which required the inclusion of a distribution coefficient (kd) to allow for instantaneous adsorption. A spherical diffusion model was also collectively parameterised in the study by using pH, soil organic carbon concentration and combined Fe and Mn oxide content as all were necessary to describe the fate of iodine in soils. The results from this paper highlight the importance of including soil properties and speciation analysis when attempting to model soil-iodine interactions. The work shows that inorganic iodine quickly transforms into organically bound species forms, with the speed of this reaction being dependent upon its speciation; I^- was lost more rapidly (minutes-hours) than iodate (hours–days) especially in high organic matter soils.

One specific drawback of HPLC separation includes the inability to directly identify org-I compounds. Shimamoto, *et al.*[36] found that org-I dissolved in TMAH remained trapped in the column packing material and did not elute from the column. Quantitative recovery and the potential alteration of chemical speciation during an extraction and species separation can be compensated for by using isotope dilution mass spectrometry (IDMS). IDMS involves spiking solution samples with a known amount of the analyte element in a different isotopic composition. After complete mixing of the sample, 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 and the blended isotope ratio directly reflects the analyte concentration in the sample.[129] Mono-isotopic elements can also be determined if a long-living radionuclide is available; in the case of iodine analysis, ^{129}I can be used.[130,131] This has been used in several studies to accurately determine iodine concentration in environmental and biological samples, including aquatic systems,[132] food samples[133] and urine.[134]

HPLC-ICP-MS has been used to describe the fate of iodine in the surface environment and can successfully separate inorganic iodine species prior to analysis, combined with total I analysis it has been proven that org-I is the main species present in soils. However, other analytical techniques, such as size exclusion chromatography (SEC) and electrospray ionisation (ESI) are required for more complex identification and characterisation of org-I compounds.

Size exclusion chromatography (SEC)

Size exclusion chromatography separates chemical species in aqueous samples according to molecular size: low retention times represent compounds with a large molecular size, excluded from entry to part of the columns porous matrix,

whilst higher retention times denote smaller molecules. When SEC is coupled with both a UV detector and ICP-MS, it provides an effective analytical platform for identifying org-I species in small environmental or biological sample volumes (100 µL), as seen in Table 2.[36,42,126,135]

Table 2 SEC parameters in literature for iodine analysis in environmental samples

Sample	Analysis	Mobile phase parameters	Column	Observations	Ref
Groundwater	SEC, S-K analysis	0.1 M Tris buffer adjusted to pH 7.0. Flow rate of 1.0 mL min^{-1}.	Superose 12 HR 10/30 column (Amersham Pharmacia Biotech, Freiburg, Germany).	Strong correlation between total iodine in groundwater and organic matter.	136
Humic Substances	SEC-ICP-MS	0.1 M Tris adjusted to pH 8.8 using 50% HNO_3. Flow rate of 1.0 mL min^{-1}.	Superose 12 10/300 GL size exclusion chromatography (SEC) column (GE Healthcare).	Inorganic iodine (I^- and IO_3^-) reacted with HA to produce org-I. LOD were 0.047 mg L^{-1} for ^{127}I and 0.014 mg L^{-1} for ^{129}I.	42
Milk	SEC-ICP-MS	30 mM Tris±HCl buffer adjusted to pH 7.0. Flow rate of 0.75 mL min^{-1}.	Superdex-75 and Superdex-200 (10 x 300 mm x 13 µm) columns (Pharmacia Biotech, Uppsala, Sweden).	95% of iodine was found as I^- in all samples. LOD 1.0 µg L^{-1}.	125
Microalgae: *Chlorella vulgaris*	SEC-ICP-MS	30 mM of Tris in MQ water, adjusted to pH 7.0 by HCL (1:10, v/v). Flow rate of 0.75 mL min^{-1}.	Superdex-75 and Superdex-200 (10 x 300 mm x 13 µm) columns (Pharmacia Biotech, Uppsala, Sweden).	The water-soluble fraction represents 66.7% of the total iodine in microalgae: I^- (75%) and IO_3^- (25%).	137
Saline groundwater	SEC-UV/vis-ICP-MS (absorbance measured at 254 nm)	(i) 50 mM Tris-HCl buffer solution adjusted to pH 7.0. (ii) 50 mM NaCl adjusted to pH 7.0. Flow rate of 1 mL min^{-1}.	Pre-column GL-W500 4.0 mmφ × 10 mm (Hitachi High-Technologies Corp). UV (UVeVis) detector (SPD-M20A; Shimadzu Corp). (i) SEC column GL-W540 columns, 10.7 mmφ × 300 mm (Hitachi High-Technologies Corp, Tokyo, Japan) (ii) Superdex 200, 10 mmφ x 300 mm; (GE Healthcare Bio-Sciences AB, Uppsala, Sweden).	>99.9% of the iodine in groundwater was I^-. Unusual as previous studies show org-I and $I-O_3^-$ present.	138
Seawater and urine	SEC-Ion Chromatography and UV/vis (absorbance measured at 254 nm)	Methanol–0.01 mol l^{-1} aqueous phosphoric acid (10:90, v/v). Flow rate of 1.2 mL min^{-1}.	Shim-pack DIOL-150 size exclusion column (250 × 7.9 mm I.D., Shimadzu, Kyoto, Japan).	The method only capable of measuring I^-. LOD 0.2 µg L^{-1}.	139
Groundwater, seepage water from soil and brown water	SEC-UV/vis-ICP-MS (absorbance measured at 254 nm).	Milli-Q water. Constant flow rate.	(i) HEMA-SEC BIO 300 (TosoHaas). (ii) TSK Gel 3000 PW (Alltech).	Described as a sensitive and fast method for characterising halogen-HS species in aquatic systems. Org-I compounds were observed despite the poor separation of iodine species.	135
Humic substances	SEC-UV/vis-ICP-MS (absorbance measured at 254 nm)	Milli-Q water. Constant flow rate.	(i) TSKgel 3000 PW (TosoHaas) – initially used, however, it was abandoned due to poor performance. (ii) HEMA SEC BIO 300 (Alltech).	Unclear peaks, moderate correlation between iodine and organics. Correlation between microbial activity and I^- transformation to org-I.	126
Seaweed: Wakame (*Undaria pinna tifida*) and Kombu (*Laminaria digita japonica*)	SEC-UV-ICP-MS (absorbance measured at 295 nm)	0.03 mol L^{-1} Tris-HCl buffer, adjusted to pH 8.0. Flow rate of 0.6 mL min^{-1}.	Superdex 75 HR (10 mm x 300 mm x 13 um) (Amersham Pharmacia Biotech AB, Uppsala, Sweden)	Iodine in Wakame is incorporated into water-soluble high molecular weight proteins. However, the SEC-ICP-MS results suggest that Kombu does not produce any significant org-I species.	140
Pore water	SEC-ICP-MS, UV/vis (absorbance measured at 260 nm)	20 mM Tris-HCL with 0.3 wt.% ethanol, adjusted to pH 8.0. Flow rate of 0.4 mL min^{-1}.	TSKgel G3000 PWXL (Tosoh, Japan).	Iodine in the pore water was associated with org-I and I^-. It was noted that transformation from inorganic iodine to org-I has a vital role in iodine immobilisation.	36

Table 2 (*Contd.*)

Sample	Analysis	Mobile phase parameters	Column	Observations	Ref
Groundwater	SEC-UV-ICP-MS (absorbance measured at 260 nm)	20 mM Tris–HCl with 0.3 wt.% ethanol, adjusted to pH 8. Flow rate of 0.4 mL min^{-1}. The column temperature was kept at 40 °C.	TSKgel G3000 PWXL column (Tosoh, Japan).	Iodine was predominately (>97%) found as I^- in groundwater samples, org-I was only 0.2–2.7%.	141
Mushroom: *Fungi Porcini*	SEC-UV/vis-ICP-MS (absorbance measured at 230 nm)	10 mmol L^{-1} CAPS buffer, adjusted to pH 10.0. Flow rate of 0.7 mL min^{-1}.	Superdex 75 SEC column (Amersham Biosciences, Inc., Piscataway, NJ).	Iodine was associated with low molecular weight fractions. Samples were successfully extracted with NaOH and hot water. No quantification of org species.	142
Soil humic substances	SEC-UV/vis-ICP-MS (absorbance measured at 230 nm)	(i) 8 mmol L^{-1} $(TMA)_2SO_4$ solution for the FA. (ii) 0.1% TMAH solution for the HA. Flow rate of 0.75 mL min^{-1}.	TSKgel Toyopearl HW-50 (fine) (Toso Co. Ltd., Tokyo) in a stainless steel column (7.6 x 250 mm).	Correlation of humic and fulvic peaks with iodine. Iodine quantified as 'inorganic', HA or FA. No iodate observed.	18
Groundwater	SEC-ICP-MS	0.03 mol L^{-1} ammonium carbonate solution, adjust to pH 9.4.	TSK G3000PW (TOSOH, Japan).	The method described accurately quantifies iodine species in groundwater and quantitatively measures org-I. The LOD for total I was 0.025 µg L^{-1}.	1

Table 2 highlights peer-reviewed publications that have used SEC to assist in iodine speciation analysis in a range of environmental samples. Rädlinger and Heumann[135] investigated halogen species bound to HS in natural waters and seepage water from soils; in addition org-I species were investigated by labelling experiments with a $^{129}I^-$ spike solution, the identification of org-I was confirmed with UV-vis and quantified using on-line IDMS. Both iodine isotopes were analysed by ICP-MS, analytical interferences from $^{129}Xe^+$ ions for ^{129}I, were corrected for using the background signal in the chromatogram. The sample species were separated using SEC-ICP-MS and simultaneously analysed using a UV-vis spectrophotometric detector at wavelength 254 nm. The wavelength was selected to measure organic substances with aromatic and other mesomeric π electron systems rather than aliphatic compounds. The study demonstrated that the source of HS has a significant impact on the halogen distribution. The soil solution chromatogram showed that iodine was eluted as a double-peak, providing evidence of multiple iodine-HS species present. Rädlinger and Heumann[135] also investigated the effects of ageing and filtering samples. The affects of ageing were assessed over a four week period, changes were observed in both the distribution of iodine-HS and UV-vis absorption. New iodine-HS species emerged at lower retention times, indicating that larger iodine-HS molecules had formed, and a greater distribution of I was evident at higher retention times. Filtering to *<45 µ*m significantly reduces biological activity, compared to unfiltered samples: it was clear that biological activity considerably altered which iodine-HS compounds were present; this should be a focus for future work.

Yamada*, et al.*[18] combined SEC with ICP-MS to investigate the binding of iodine to soil HA and FA. Using the same fractionation separation method developed by Yamada*, et al.*[35], the fractionated solutions were then passed through the SEC column and analysed using a UV-vis spectrophotometric detector and ICP-MS: the column separated the HA and FA fractions. Organic components were then measured using UV-vis (absorbance at 230 nm) before being made to 1% TMAH for assay by ICP-MS. Yamada*, et al.*[18] concluded that iodine binds directly to carbon atoms in HS. The process is thought to be an addition reaction of iodine to an unsaturated carbon bond in the HS, which contributes to the high thermal stability of iodine bound to HS.[18,143]

Shimamoto*, et al.*[36] employed ICP-MS and UV-vis spectrophotometry (260 nm) to investigate the concentration of iodine and its molecular weight distribution in pore waters. The results indicated that iodine reacts uniformly with organic matter of all sizes with no particular affiliation to small or large molecules. Despite having a near constant concentration of organic matter throughout the depth of the soil, the results indicated that org-I was the dominant chemical species within the top 0-6 cm, constituting 50-60% of total iodine, however, at lower depths, 9-12 cm, 98% of the iodine was present as I^-. Shimamoto*, et al.*[36] suggested that smaller concentrations of org-I are attributed to reduced microbial activities or the dissociation of iodine from organic matter under suboxic conditions at greater depth in the soil.

Recent work assessed the rate of reaction between purified HA and I^- or IO_3^- using SEC-ICP-MS to investigate changes in speciation with ^{129}I.[42] Both forms of inorganic iodine were found to react with HA, however, I^- reacted much more slowly than IO_3^- and the mixed (I^- and IO_3^-) system. These results contrasted to previous findings that suggested I^- transforms to org-I faster than IO_3^-. Bowley*, et al.*[42] suggested that in the purified HA

substrate the reaction mechanisms thought to govern the interactions of iodine with soils, such as adsorption on metal oxides or enzymatic oxidation and reduction, were absent and this resulted in I^- oxidation and subsequent binding to HA being relatively slow. The use of SEC was able to show that org-^{129}I was present in both high and low molecular weight fractions of HA but there was a slight preference to bind to lower molecular weight fractions.[42]

The use of SEC with an UV detector and ESI-MS has enabled the identification of org-I species according to their molecular mass. By measuring at specific UV wavelengths (254 nm) it has been determined that iodine binds to soil organic matter and interacts with aromatic and other mesomeric π electron systems rather than aliphatic compounds [135]. The reaction between iodine and an unsaturated carbon bond in the HS contributes to the high thermal stability of iodine bound to HS.[18,143] The majority of iodine in soils is strongly bound to organic matter as unavailable forms for plant uptake, the use of SEC has significantly developed our understanding of iodine geodynamics.[18,36] In addition, Bowley*, et al.*[42] was able to show that whilst iodine was capable of binding with both high and low molecular weight fractions of HA, there is a preference to bind to lower molecular weight fractions. When the complexity of org-I species allows a fuller characterisation (e.g. non-humic compounds), more advanced separation techniques are required to investigate the specific iodinated compounds produced in soils.

Electrospray ionisation (ESI)

Electrospray ionisation (ESI) coupled to a mass spectrometer (MS) is capable of providing qualitative and quantitative information on specific identifiable compounds in biological and environmental samples. The application of ESI has previously been used on metal-ligand solution equilibria to characterise org-I compounds.[44,122,144,145] Electrospray ionisation uses electrical energy to assist the transfer of charged ions from solution into the gaseous phase prior to MS analyses. The transfer involves three steps: (1) dispersal of a fine spray of charge droplets, (2) solvent evaporation, and (3) ion ejection from the highly charged droplets [146]. The sample solution is passed through a capillary tube (stainless steel or quartz silica) which is maintained at a relatively high voltage (2.5 - 6.0 kV). A plume of highly charged droplets exit the electrospray tip. The ESI-source temperature (100-300 °C) and/or stream of drying gas (N_2) continuously reduced the size of the charged ions, increasing the surface charge density and a decreasing of the droplet radius. Once the charged droplets are ejected into the gaseous phase, they are transported from the atmospheric pressure ionisation source region into the vacuum and mass analyser of the mass spectrometer for analysis of molecular mass and ion intensity.[146,147] Whilst ionic species in solution can be directly analysed by ESI-MS, neutral compounds require a conversion to an ionic form by a charging mechanism (e.g. protonation, deprotonation, ion attachment). In positive ion mode, the solution is sprayed at a low pH to encourage positive ion formation; cationisation, whilst in negative ion mode the analysis is carried out well above the molecules isoelectric point to deprotonate the molecules. Defined as a low-fragmentation 'soft' ionisation method, ESI is a desirable method for analysing the molecular weight and structural composition of compounds in solution when combined with either a single (MS) or a tandem mass spectrometer (MS/MS).[148]

Moulin*, et al.*[122] utilised ESI to investigate the binding of iodine with FA, analysing the structural features of iodinated compounds coupled to a tandem mass spectrometer. The samples were analysed using a Q-TOF hybrid MS coupled with an electrospray source operating in negative-ion mode with nitrogen gas used as the drying and nebulising gas. The MS/MS analysis of odd-mass ions suggested that aromatic substitution of the FA compounds had occurred, denoted as [RI - H^-] where R describes the FA. One concern highlighted by Moulin*, et al.*[122] is the potential for error in the MS/MS spectra, as it was unable to identify unreacted FA from iodine derivatives due to the similar molecular structure. The distribution of iodinated FA showed an apparent lack of the high molecular mass compounds, which would be expected if iodine had bonded to the FA. Moulin*, et al.*[122] suggested that the interactions between iodine and phenols would lead to aromatic substitutions and further extended oxidation-reduction reactions. The MS/MS results validated previous findings and supported the consensus that iodine binds to FA via aromatic substitutions. Recently, ESI has been coupled with Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS). A number of mass spectrometers have been used in the structural characterisation: FT-ICR MS determines the *m/z* values based on the detection of ion cyclotron motion within a magnetic field, a detailed explanation is provided by Marshall*, et al.*[149]. The analysis of HS using this technique confirmed the complexity and heterogeneity of HA and FA that make up HS. The high-resolution mass spectra allows us to examine molecular-level changes as a function of specific geochemical processes, making it ideal for analysing iodine in HS.[150]

Xu*, et al.*[44] examined the interactions between I^- and IO_3^- and FA extracted from a surface soil using ESI-FT-ICR MS. This study developed the work conducted by Moulin*, et al.*[122] and investigated the iodination process involved in the non-enzymatic reaction between IO_3^- and FA under controlled conditions. Binding sites of I^- and IO_3^- with FA were analysed in an attempt to understand the molecular structure of org-I formed from non-enzymatic and enzymatic processes. The reactions between nitrogen compounds were measured in positive ion mode, whilst HS containing acidic carboxyl and phenolic groups, which are prone to ionise, were analysed in negative ion mode. Xu*, et al.*[44] produced Van Krevelen diagrams for both the non-enzymatic and enzymatic reactions to show the difference between the iodinated FA based on elemental ratios (O/C vs. H/C). The results indicated that non-iodinated FA compounds such as lignins, tannins and carboxylic-rich alicyclic molecules were present in a 'reactive pool', as they were present in the un-iodinated FA but not in the iodinated FA. It is suggested that they were involved in the reduction of IO_3^- to I^- assisting in the formation of the 'produced' org-I species, consisting of condensed aromatics. Xu*, et al.*[44] found >120

different org-I species in positive (n=94) and negative (n=35) ion mode. All the identified compounds contained only one iodine atom, suggesting that the iodination of HS is dominated by mono-substitution. A significant majority (91%) of the identified org-I compounds were covalently bound to the newly produced compounds; the remaining 9% of org-I compounds were formed when an iodine atom replaced one hydrogen atom without modifying the original molecular structure. They reported a distribution preference of org-I from hydrocarbon>lignin>protein with an O/C ratio typically <0.4. The relatively low O/C values of the org-I could provide an explanation as to why org-I has a significantly reduced environmental mobility in soils, as the low oxygen content decreases the hydrophilicity of the molecule, however, further studies are required to prove this. Furthermore, Xu*, et al.*[44] speculated what percentage of carbon present in the FA is available for C-I bonds to occur: they stated that 46% of the FA is organic carbon, and 13.7% of that was characterised as aromatic carbon. Therefore, assuming one out of six carbons is ready for iodine electrophilic substitution based on stoichiometric grounds, 8.75 x 10^{-4} mol C g^{-1} of FA is viable for C-I bonds. Therefore, based on their results, the iodination of FA occurs at unique and very limited sites, approximately 10-88 times lower than what is theoretically available. Interestingly, ~69% of the identified org-I species contained nitrogen, presumably present as -NH_2 or -HNCOR groups, which would enhance the nucleophilicity of the aromatic ring favouring the electrophilic substitution in the HS.[151] This is the first time the molecular reaction mechanism of iodine sequestration into HS has been documented alongside the structure of resulting org-I compounds. One particular challenge highlighted by Xu*, et al.*[44] is correctly defining the molecular structures of the org-I compounds, as one formula might correspond to a number of isomers, however, with other techniques such as tandem MS, which is capable of filtering ions to a specific m/z ratios, it would be possible to correctly identify the structure of org-I compounds.

The application of this low-fragmentation ionisation method has been successfully used to analyse the molecular weight of org-I compounds. The distribution of iodinated organic matter shows a lack of the high molecular mass compounds, which clearly indicates that iodine preferentially bonds to smaller compounds.

Synchrotron light source analysis

In-situ iodine analysis with a synchrotron light source has previously been conducted by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectra (EXAFS); when XANES and EXAFS are combined the entire structured absorption region is observed, this is known as XAFS.[17,19,36,37,109,152] The use of XANES requires a high-intensity monochromatic X-ray beam tuned between a few 10's eV below and approximately 100 eV above the binding energy of a core electron, providing information on the oxidation state of the element and its chemical surrounding.[17] Further information regarding coordination numbers and bond lengths to first, second and even more distant neighbour atoms can be obtained at the same time by extending the energy range ~50–1000 eV above absorption edge by EXAFS.[17]

Shimamoto and Takahashi[153] assessed the application of both K-edge and L_{III}-edge XANES spectra for analysing iodine speciation in natural Japanese soil samples. Both methods encountered issues with high background concentrations; particularly with calcium, a major element in soil. The Ca spectra overlaps with the iodine spectra, however, the background effects of Ca were greater for the L_{III}-edge spectra which was unable to detect iodine concentrations <55 mg kg^{-1}. The K-edge spectra was able to identify KI and org-I: the results indicated that org-I, bound to HS was the most abundant form of iodine in the soil, in accordance with previous findings.[35,122,135] Whilst K-edge XANES was confirmed as the superior method due to the lower detection limits, the application of XANES becomes limited when the analyte of interest has concentrations <10 mg kg^{-1}, due to background interferences. As previously stated, the average iodine concentration in soils is 5.1 mg kg^{-1}, therefore, XANES is unable to provide structural information on native soil iodine or ultra-trace levels of ^{129}I in soils.[153,154]

Yamaguchi*, et al.*[152] investigated the effects of water management on iodine speciation in andosols and gleysols during an incubation study. The distribution coefficient of I^- and IO_3^- was much greater in the andosol compared to the gleysol. This is due to the higher content of poorly-crystalline minerals, such as Al_{ox}, Si_{ox} and Fe_{ox}, which play an important role in the sorption of I^- and IO_3^-, thus reducing the amount of iodine present in the soil solution. After 30 days under anaerobic conditions, the XANES post-edge feature of IO_3^- disappeared; this was thought to be due to a reduction of IO_3^- to I_2 and a further reduction to I^- or org-I. Whilst I^- was found in solution IO_3^-, I_2 and org-I were found bound to the solid phase, Shimamoto*, et al.*[19] also used K-edge XANES to investigate the fate of inorganic iodine added to soils. The XANES results indicate that IO_3^- had a greater rate of absorbance to soils compared to I^- and that the mobility of I^- was mainly controlled by advection and dispersion. The application of XANES and EXAFS can also be used to investigate the molecular structure of org-I. Schlegel*, et al.*[43] used XANES analysis to determine that the structural properties were consistent with the formation of covalent bonds to aromatic rings; this was quantified by EXAFS analysis that showed the bond length was significantly shorter than aliphatic bonds: these results support previous findings by ESI-MS and SEC-MS analysis.[122,135] Yamaguchi*, et al.*[152] demonstrated that in anaerobic soils IO_3^- was first converted to elemental iodine and then to org-I, and that this conversion was substantially retarded when microbial activity was reduced. It is widely acknowledged that microbial activity is involved the biogeochemical cycle of iodine, however, the extent to which microorganisms influence sorption with soil organic matter (SOM) and/or volatilization is poorly understood in terrestrial environments.[155] As there is also evidence which demonstrates in aerobic soils SOM has the ability to transform IO_3^- to org-I suggesting that microbial activity was not necessary for the reduction of iodate by humic substances.[37]

Takeda, *et al.*[123] assessed the chemical form of exogenous iodine added to soil samples collected from pine forests: soil from the organic horizon (O-horizon) and two mineral horizons (A-horizon 0-10cm, C-horizon 20-70cm) were collected and an aliquot of soil was treated with either NaI or $NaIO_3$ to 500 mg I kg^{-1}. At 24 hours and 14 days post-treatment, the soils were analysed using XANES using beamline BL14B2 at Spring-8 (Hyogo, Japan) in transmission and fluorescence modes for standards and soils, respectively. The results indicated the rapid transformation of inorganic iodine to the O-horizon; after 1 d, 29% and 90% of the I^- and IO_3^- added to the soils had transformed to org-I, respectively. After 14 d, the majority of the inorganic iodine added to the O- and A-horizons had been transformed to org-I. However, after 14 d in the C-horizon, where there was significantly less carbon, the chemical species had not significantly changed. This supports the results from Amachi[156] and Yamaguchi, *et al.*[37] who suggested that SOM significantly contributed to the transformation of inorganic iodine to org-I added to soils due to the higher microbial activity. The extracted soil solutions appeared to suggest that the formation of org-I decreases the solubility of iodine.

One major benefit of XANES and EXAFS is its ability to examine the molecular structure of org-I. Schlegel, *et al.*[43] was able to utilise XANES to determine that the structural properties were consistent with the formation of covalent bonds to aromatic rings and confirm this with EXAFS which showed the bond length was significantly shorter than aliphatic bonds. The application of K-edge and L_{III}-edge XANES spectra for analysing iodine speciation in soils was conducted by Shimamoto and Takahashi[153]. The K-edge spectra had greater detection limits compared to L_{III}-edge, however, if iodine concentrations are <10 mg kg^{-1}, then analysis becomes very challenging due to background interferences. Therefore, synchrotron light source analysis struggles to provide structural information on most soils and ultra-trace levels of ^{129}I in soils.

Trends in speciation analysis

Similar to total iodine analysis, it is possible to highlight specific trends in speciation analysis over time. Figure 3 highlights the number of peer-reviewed papers published in each year from 1990-2016 available in the WorldCat library database and NERC library service for the following search term: ("iodine" AND "soil" AND “high performance liquid chromatography” OR “size exclusion chromatography” OR “electrospray ionisation” OR “XANES and/or EXAFS” from 1990-2016.

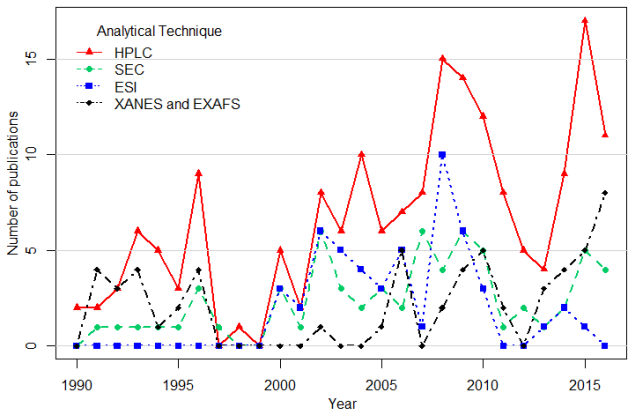

Figure 3 WorldCat library and NERC library service search results for ("iodine" AND "soil" AND “high performance liquid chromatography” OR “size exclusion chromatography” OR “electrospray ionisation” OR “XANES and/or EXAFS” from 1990-2016 (date of search: 14/03/2017) (n = 330)

Iodine speciation analysis has significantly developed since the year 2000 as the ability to perform sensitive analysis has improved. It is evident from Figure 3 that HPLC has been a very popular and successful method for separating inorganic iodine species and has significantly contributed to improving our knowledge of iodine interactions in soils. However, to further improve our knowledge regarding the complex soil-iodine interactions including the mobility of iodine from drainage water, speciation changes and fixation into unavailable forms, all of which are influenced by soil characteristics, more sophisticated analytical techniques are required. With the emergence of in-situ synchrotron light source analysis techniques, such as XANES and EXAFS, which are increasing in use, and the development of more advanced ICP-MS instruments and separation techniques (SEC) and ionisation techniques (ESI), our understanding of iodine dynamics and the structure of org-I bound in soils will improve.

Quality assurance

Iodine analysis for soils, both the determination of total and speciation concentrations, requires a stringent understanding of the elements physiochemical characteristics and specific good laboratory practices. In this final section sampling and analytical protocols for iodine analysis are emphasised.

Sample representativeness

Cross contamination may occur during collection as a process of sampling itself. To ensure that soils are representative of the collection site with no external contamination the operator tasked with collecting soils must ensure that collection equipment is adequately washed between each site and any in-situ measuring equipment or other equipment does not alter the concentration of iodine or the speciation of the natively bound iodine.

Sample preservation

Once collected, soil samples require processing prior to analysis. Total iodine analysis by extraction or direct analysis requires

soils to have been dried, either in an oven or freeze-drier. The critical parameter in this process is that the temperature of the drying apparatus does not exceed 70 °C as there is a risk of iodine volatisation at temperatures higher than this, it is preferable to dry at 30 °C.[9] Once dried the soil requires sieving, which removes extraneous material and ensures sample homogeneity in the disaggregation, milling to an appropriate size fraction, typically <63 µm, prior to a soluble extraction is also recommended. Whilst direct determinations such as synchrotron light source analysis can be performed on fresh soils the sample must still be homogenous and be a true representation of the original sample, and therefore requires sieving. The best practice is based upon the analytical method used to determine either the total and/or the speciation of iodine bound to soils. Prepared soil samples should always be stored sealed and in a dry environment.

Analytical protocols

Control samples and standards, both internal and certified reference materials (CRM's), are required to assure the quality of analysis and sample preparation. Control samples should include; replicates, reagent blanks, calibration standards and analytical blanks as well as quality control samples containing a known concentration of either total, or speciated compounds. Specific challenges associated with solution techniques such as ICP-MS, include the selection of an appropriate internal standard for iodine analysis to ensure that any instrumental drift is corrected and can be scrutinised with the concentration data. For ICP-MS, the high first ionisation energy of iodine requires the use of alkaline matrices to reduce carryover. However, the alkali extraction reagent, usually TMAH, restricts iodine analysis due to high background counts, which affects the limit of detection (LOD ~ 0.02 µg L^{-1}) for total or speciation analysis with online separation tools. Therefore, reagent (extraction stage) and analytical run blanks are crucial to identify poor reagent quality or potential carryover of iodine signal between samples. Calibration standards for iodine analysis are typically first order linear within a 0.5-100 µg L^{-1} range, it is recommended that any sample measurement exceeding the linear dynamic range of the calibration curve should be diluted and reanalysed due to the questionable reliability of calibration models above the highest calibration standard. Sample randomisation is recommended to minimise systematic biases arising from instrumental drift and carry-over effects, in addition, quality control samples should be analysed throughout the analysis to ensure that the instrument is running adequately and to highlight any matrix effects.

Certified reference materials are used as a measure of accuracy and reproducibility, using a CRM of similar matrix to the sample regardless of the analytical technique used is recommended. Govindaraju[157] stated the fact that iodine CRM data is particularly limited. According to GeoReM, an online geochemical database for reference materials[158] lists 30 CRM's for iodine in soils, which include a range of different soil types and iodine concentrations (0.44 - 54 µg g^{-1}). However, many of these CRM's are now discontinued and difficult to source. Certified values are often produced by an analytical method technique providing a 'total' iodine measurement (e.g. NAA, XRF) rather than a panel of methods, resulting in some low comparisons when using solution techniques. In addition, iodine values are often given as indicative values only. A full list of peer reviewed CRM values is listed in electronic supplementary information. Currently there are no CRM's for iodine speciation analysis in soils, however, speciated milk CRM's do exist, highlighting another challenge associated with analysing iodine in soils.

Conclusions

Iodine analysis is very complex and there are a range of methods for determining iodine concentrations in soils, as summarised in Table 3. Knowledge of the iodine geochemical cycle has vastly improved owing to advances in instrumentation capable of analysing environmental samples with improved sensitivity. The development of iodine analysis in soils, from basic spectrophotometric methods to ICP-MS and synchrotron light source analysis has enabled the study of natural soils with trace concentrations of both ^{127}I and ^{129}I. Significant developments in the understanding of inorganic iodine incorporation in soils and the dynamic interactions influenced by soil properties have arisen by coupling instruments with separation techniques, such as: GC, HPLC, SEC and ionisation techniques such as: ESI. There is now evidence that demonstrates the processes in which inorganic iodine, I^- and IO_3^-, are incorporated with HS within minutes-to-days and days-to-weeks, respectively; critically, it has also been possible to identify the existence of org-I substances, however, more work is required to characterise and name the observed org-I.[34,36,37,42,44,45,122] The use of in-situ analysis in the form of XANES and EXAFS is beginning to compliment results from on-line separation techniques, providing information on the oxidation state of the element and its chemical surrounding, without subjecting samples to extraction procedures. It is recognised that when inorganic iodine is added to soils, IO_3^- binds and interacts with soils to a greater extent than I^- and interacts with organic matter to a greater degree, whilst I^- remains mobile and is dispersed to greater depths in soil profiles.[19,36,152] Understanding iodine geodynamics, and the processes that occur during iodine treatments, will enable the development of a appropriate strategies to increase iodine concentrations in soils and crops, thereby, providing suitable agronomic interventions to decrease the incidence of IDD.

Table 3 Summary of methods for iodine analysis in soil samples

Analysis	Positives	Negatives
Spectrophotometric	• Inexpensive. • Technology is used in rapid-test kits to identify the presence of iodine in concentrations between 10-90 mg kg^{-1}.[68]	• The S-K reaction used in spectrophotometric determination is susceptible to a number of interferences.[65] • The analysis is not sensitive enough for determining trace iodine concentrations.[69] • Typical detection limits ~0.5 mg kg^{-1}.[67]
NAA	• Capable of measuring multiple isotopes in the same sample.[74] • Inferences from U, Cs and Te are removed during pyrohydrolysis and alkaline fusion/ashing procedure.[75]	• Expensive. • Complex extractions with limited success, long irradiation and cool-down periods and post-irradiation handling issues. • Sensitivity is a problem in soils with high concentrations of Mn, Na, K, Cl and Al, with typical detection limits ~0.1 mg kg^{-1}.[72,73]
AMS	• High sensitivity, and ability to determine $^{129}I/^{127}I$ ratios with typical detection limits ~10^{-13}.[76,83] • Interferences from $^{129}Xe^-$, $^{128}TeH^-$ and $^{127}IH_2^-$ are eliminated as the sample is introduced and passed the through the tandem accelerator.[17]	• AMS is a relative analytical method, the concentrations are calculated based on stable ^{127}I concentrations determined by ICP-MS.
ICP-MS	• Capable of routine analysis, with extremely good detection limits, typically <µg L^{-1}. • Simple extraction procedure using 5% TMAH eliminating iodine volatilisation in acidic solutions.[98] • Can be coupled with on-line separation techniques to investigate iodine speciation. • New advancements in QQQ-ICP-MS allows for ^{129}I to be directly measured without interferences from $^{127}H^+$ and $^{129}Xe^+$ with a LOD ~0.03 µg kg^{-1}.[96]	• Initial difficulties with selecting an appropriate internal standard, that is suitable for iodine due to its relatively higher first ionisation energy and the requirements for samples to be in alkaline solution.
Fractionation	• Can be used to comment on the mobility of iodine based on soil fractions.[35]	• Susceptible to re-adsorption, cross-contamination, incomplete dissolutions and transformations. • Large potential for error.[121]
GC-MS	• Capable of analysing $^{127/129}I^-$, $^{127/129}IO_3^-$, elemental $^{127/129}I$ and the calculation of org-I in soil samples.[124] • No interferences from ^{129}Xe	• Unable to directly measure org-I. • Limited application for soil analysis.
HPLC-ICP-MS	• Very well established methods for identifying I^- and IO_3^- in a range of environmental samples. • Separation is relatively fast <8 min on average. • Can infer org-I concentrations in a sample by measuring total and inorganic concentrations (org-I= total I – inorganic I).[19]	• Unable to directly measure org-I.
SEC-ICP-MS	• Can separate iodine compounds based on molecular size. • Can identify I^-, IO_3^- and org-I in a solution.[135] • Requires very small sample volume <100 µL. • Been used to identify interactions between iodine and soil components. • Can be used with UV-detector to comment on org-I binding sites.[18]	• Relatively long separation time compared to HPLC-ICP-MS ~30 min. • Unable to identify the structure of org-I.
ESI-ICP-MS	• Minimises fragmentation of org-I compounds, allowing for the analyse of molecular weight and structural composition.[159] • Able to compare the distribution of compounds and binding sites.	• Potential for incorrect identification of compounds due to the heterogeneity of samples.[44]
Synchrotron light source analysis	• In-situ analysis with no need for sample preparation. • Able to determine structural components and oxidations states of org-I in soils.[17] • Able to investigate effects of biological components in soils of binding.[37,152]	• Extremely costly procedure, unable to perform routine analysis. • A limited number of synchrotrons, worldwide. • Sensitivity is a major issue, high background concentrations of Ca, Al, Si, Fe disrupt I signal with a detection limit ~10 mg kg^{-1}.[153]

Conflicts of interest

There are no conflicts to declare.

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