Analysis of ^{129}I and ^{127}I in soils of the Chernobyl Exclusion Zone, 29 years after the deposition of ^{129}I

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***Responses to Reviewers Comments**

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Dear Dr Gustin

Thank you for your email of 5th June 2019.

On behalf of my co-authors I am submitting responses to the four reviewers' comments …

All responses are listed below. For clarity, in the 'revised manuscript with changes marked', the revisions are highlighted in yellow, green, red or blue according to each reviewer's comments.

We trust these responses and the revisions in the accompanying manuscript are satisfactory.

Yours sincerely,

George Shaw.

Responses to Reviewers' Comments Received 5th June 2019

Reviewer #1: (Revisions to text highlighted in yellow in the manuscript)

General comments:

1: The authors compared behavior of I-129 with stable iodine in the soils. Before comparison, they should discuss whether all of the I-129 deposited on the ground still remain in the soil surface to a depth of 20 cm or not.

> Response: We have added a discussion of this question in the results and discussion, Section 3.3 (p. 12) – please see the response to detailed comment #7, below.

2: The authors discussed the behavior of I-129 and stable iodine in topsoils and subsoils together. Iodine-129 deposited on the surface soil at the accident, however, stable iodine already distributed in the soil at that time. The reviewer thinks that the authors need more careful discussion about the relationship between I-129 and stable iodine in soils.

> Response: We have added the following paragraph in the introduction: "Iodine is a relative active and mobile element in the environment. Although ^{129}I and ^{127}I in soils have different sources, they are expected to behave in a very similar manner. The great majority of ^{129}I in the Chernobyl Exclusion Zone (CEZ) is expected to have originated from rapid localised deposition of Chernobyl-released iodine in 1986, while ^{127}I has accumulated over the long-term (centuries to millennia) from deposition of atmospheric iodine originating from distant marine sources. Weathering of soil parent material can also contribute some ^{127}I to soils (though usually a minor source) and turnover of soil organic matter is a key part of the long-term accumulation and redistribution process of iodine in soils (Roulier et al., 2018). Following deposition on the soil, both ^{129}I and ^{127}I experience similar processes of fixation and leaching. It is expected that anthropogenic ^{129}I, deposited in the very short-term, should reach equilibrium with the numerous chemical species of naturally occurring ^{127}I after some period of time through dynamic chemical and biochemical processes; thereafter the two iodine isotopes would be expected to behave in the same way. This paper aims to investigate if such an equilibrium has been achieved by speciation (fractionation) analysis of these two isotopes of iodine." (page 3, lines 3-16)

3: Sessions of "Materials and Methods" and "Results and discussion" are little bit difficult to understand. Sub-titles are help to understand.

> Response: Sub-sections with sub-titles have been added to the 'Materials and Methods' and 'Results and Discussion' sections. Text in section 2.1 has been rearranged as a result of sub-section numbering.

4: It is better to make a "Conclusion".

> Response: A 'Conclusions' section has been added (Section 4).

Detailed comments:

#1: Graphical abstract

Because the sizes of squares are same, the readers thought that I-129 and stable iodine have same behavior in the environment from this abstract. And this abstract shows not only I-129, but also stable iodine in the soils released from the Chernobyl accident.

> Response: The graphical abstract has been revised.

#2: 2p line 10
Could the authors check the specific activity of I-131?
Is 1.46 x 10^8 Bq g-1 correct?

> Response: This number has been checked and the specific activity of ^{131}I re-calculated to be 4.60 × 10^{15} Bq/g.

#3: 2p lines 11- 17
The authors described that the committed effective dose per unit intake for I-129 (1.1 Ã— 10-7 Sv Bq-1) is five times higher than that of I-131 (2.2 Ã— 10-8 Sv Bq-1) and then the importance of reconstructing I-131 deposition patterns by I-129 data.
However, I think that the most concern of the readers is the reconstructing. So, it is better that the authors described firstly the reconstructing and then the committed effective dose for I-129.

> Response: The sentence describing the doses per unit intake for ^{131}I and ^{129}I has been moved down to lines 18-20.

#4: 4p line 22
Could the authors quote a suitable paper on a sequential extraction procedure?

> Response: We have added a sentence at the beginning of section 2.3 referencing Zhao and McGrath (1994) and Martens and Suarez (1997) on which our iodine extraction method is based: 'The extraction method is based on one published by Zhao and McGrath (1994) for sulphate extraction that was subsequently adapted by Martens and Suarez (1997) for Se extraction.'

#5: 4-5p lines 23 to 15
For better understand of the readers, could the authors show a sequential extraction procedure in a figure?

> Response: A flow diagram illustrating the sequential extraction procedure has been added to the Supplementary Materials (Figure S1: Schematic diagram of three-step sequential extraction procedure applied to CEZ soils). This could be added within the main text if preferred.

#6: 8p lines 2-3
Could the authors show the proof that all of iodine in the soils could be extracted by this sequential extraction procedure?
It is better to quote a suitable paper.

> Response: We have added a sentence in Section 3.4 which cites two relevant studies: "Studies by Watts and Mitchell (2008) and Shetaya et al. (2012) have shown that strongly alkaline extractants such as TMAH and NaOH are effective in quantitatively extracting iodine from soils."

#7: 8p lines 21-22

Table 3 shows that the I-129/Cs-137 atom ratios in topsoils are lower than those in subsoils. This means that the migration rate of I-129 in soil is faster than Cs-137. I am afraid that some amount of I-129 has already leached out from the soil depth 0-20 cm.

It is necessary to estimate the amount of I-129 leached out from 0-20 cm soil layer.

> Response: This is a useful observation by the reviewer. To address it we have added the following sentences to Section 3.3: “This is supported by the observation that the ^{129}I/^{137}Cs atom ratios in topsoils are lower than those in subsoils for 7 of the 9 soils sampled in this study, which indicates that ^{129}I has moved faster than ^{137}Cs from the topsoil to the subsoil. Leaching of a portion of the originally deposited ^{129}I from the upper 20 cm of the soils sampled cannot be excluded, which would partially explain the slightly lower total ^{129}I activity concentrations we measured compared with previous studies, as discussed in section 3.1. Approximate estimates of the magnitude of ^{129}I leaching below a depth of 20 cm may be possible by comparing ^{129}I activity concentrations measured by Sahoo et al. (2009) and in our study. Furthermore, if the rate of ^{137}Cs leaching were known than the comparative rate of ^{129}I could be calculated using the ^{129}I/^{137}Cs atom ratios in Table 3. However, the only reliable way to quantify the degree of ^{129}I leaching deep into the soil profile is to take deeper soil samples for further analysis by AMS, which is beyond the scope of this study.” (page 12, lines 13-23)

#8: 9p line 1

The authors described "the strong and highly significant correlation between ^{129}I and ^{137}Cs activity concentrations in the samples (Figure 3)" in the manuscript.

Because, the migration of radioiodine and Cs-137 in the soils is one of the most interest topics for readers, careful discussion is needed.

Table 3 shows that the ^{129}I/^{137}Cs atom ratios in topsoils are lower than those in subsoils. This means that migration rate of I-129 is different from Cs-137. I think that discussion for relationships between 129I and 137Cs activity concentrations in topsoils and subsoils together lead to a rough estimation.

> Response: Please see the response to the previous question (#7) raised by the reviewer.

#9: 9p lines 9-10

The authors showed that total concentrations of I-127 and I-129 were positively and significantly correlated. What does this correlation mean?

> Response: We have added the underlined text to the sentence: “Total concentrations of ^{127}I and ^{129}I were positively and significantly correlated (Figure 5) which probably results from a similar tendency for retention of both isotopes in soils with similar organic matter contents.” (page 11, lines 17-18)

As authors pointed out in 9p lines 14-15 in the manuscript, total concentrations of 129I in the soils in CEZ were affected by deposited I-129 at the accident, whereas stable iodine in the soils in CEZ were not affected by the accident.

Table 2 shows the ratios of 129I/127I in topsoils and subsoils. Why did authors discuss about the difference between the ratios of topsoils and those of subsoils?

> Response: We think the reviewer means ‘Why did authors NOT discuss about the difference between the ratios of topsoils and those of subsoils?’ We have added a sentence in section 3.3: “Furthermore, ratios of total ^{129}I/^{127}I were higher in topsoils than in sub-soils at all sites except RF1 (Table 2), indicating that proportionally more of the ^{129}I deposited to the soil

surface in 1986 was still present in the topsoil". Just below this we have also added "However, some downwards migration of ^{129}I must have occurred in the 30 year period following the Chernobyl accident" which leads into the discussion added in response to question #7, above.

#10: 9p lines 22-23
The authors pointed out that significant downwards migration of I-129 in CEZ soils may have occurred since initial deposition in 1986. They also described that I-129 remains more mobile and more bioavailable fractions than 127I three decades after the Chernobyl accident. From these descriptions, some of I-129 deposited on the surface soils migrated downwards already, but most of I-129 in the soils remains in more mobile and more bioavailable fractions. Is it true?

Response: Some migration of ^{129}I has almost certainly occurred, based on the evidence we discuss, but it is not true that MOST of the ^{129}I currently in the soil remains in mobile/bioavailable fractions, as shown by Figure (ii) and (iii). The organic (NaOH-extractable) fraction of ^{129}I dominates the total ^{129}I within all the soil we analysed.

Besides, though significant downwards migration of I-129 have occurred, I-129 and Cs-137 activity concentrations in the soil samples show the strong and highly significant correlation (p9, line 1). Do the authors think that significant downwards migration of Cs-137 in CEZ soils may also have occurred since initial deposition in 1986?

Response: Significant downwards migration of Cs-137 in CEZ soils since 1986 is certainly possible, but this is not something we set out to measure in this study. We do have some evidence for one site in the CEZ which was not included in the I-129 study that the major activity concentration of Cs-137 (Bq / kg) remains in the surface litter layer of forest soil (under Pine), but it is likely that the activity inventory (Bq / m^2) is much higher lower down in the soil profile. However, we do not have sufficient information for the sampling sites in the present study to make any further analysis of the comparative rates of migration of Cs-137 and I-129.

#11: 10p line 26
In figure 2, I-129 concentrations in soil extracts were shown. Figure 2 (ii) was I-129 (g/g soil) and figure 2 (iii) was activity. I think that both results were same. So, figure 2 (iii) is not necessary.

Response: Figures 2(ii) and 2(iii) are qualitatively the same, but quantitatively different. It is important to distinguish between activity concentrations (Bq/kg) and mass concentrations (g/g) of radionuclides, especially for very long-lived nuclides such as I-129 which have low specific activities and high mass-activity ratios. So, we prefer to keep all four panels in Figure 2.

#12: 12p lines 21-23
The authors referred Maryon's paper and wrote that volatile radioiodine released to the atmosphere from Chernobyl is thought to have been progressively sorbed to aerosol particles on a time scale of approximately 45-50 days. I think that even volatile radioiodine deposited on ground within a few days in CEZ. What does this time scale mean in this manuscript?

Response: The inclusion of the Maryon et al. (1991) citation is intended to show that the association of radioactive iodine isotopes from the Chernobyl reactor is too slow for this process to have influenced radio-iodine deposition in the CEZ. Therefore, dry deposition of

> was probably the dominant process resulting in deposition of I-129 and I-131 to the CEZ soils. To clarify this we have added the following sentence after the Maryon et al. (1991) citation: "; this is too long for this process to have influenced radio-iodine deposition in the CEZ".

Reviewer #2: (Revisions to text highlighted in green in the manuscript)

1) The graphical abstract could provide some information on 'sampling time' and emphasize the different behavior for the two isotopes.

> Response: The graphical abstract has been revised.

2) Abstract.

-Sentences in Page 1, Lines 6-8: the two sentences appear to contradict each other 'Both 127I and 129Iâ€¦. Whereasâ€¦. 129I was not). Please re-write to clarify.

> Response: We have clarified these contradictory statements by inserting the highlighted text, as follows: "Both ^{127}I and ^{129}I were predominantly associated with alkaline-extractable soil organic matter, established using a three-step sequential extraction procedure. Whereas ^{127}I was significantly correlated with gross soil organic matter (measured by mass loss on ignition), however, ^{129}I was not" (page 1, lines 10-13)

-In my opinion, the sentence in page 1, lines 11-13 'the initial physico-chemical formâ€¦' is not clearly supported by the data presented in this study. I mean, should not one need information on uranium isotope concentrations (e.g. 236U) before formulating such sentence?

> Response: We clearly state that we do not know the initial physico-chemical form of radioiodine deposited to the CEZ soils. In section 3.6 we consider the possible physico-chemical nature of radioiodine deposits and also state that we have autoradiographic evidence of 'hot particles' in the CEZ soils, now shown in Supplementary Material. Please see response to question 5, specifically the part about pages 12 and 13, below.

3) Introduction.

-An overview on what is already known about iodine behavior and composition in soils is needed to provide a good background. There are several articles cited in the discussion and their most meaningful findings could be summarized here.

> Response: A paragraph has been added in the introduction in response to Q2 of Reviewer #1. (page 3, lines 3-16)

-Please highlight what is the novelty of this work.

> Response: The following sentence has been added at the end of the Introduction: "The data set provides the most comprehensive analysis to date of the comparative extractabilities of ^{127}I and ^{129}I in soil of the CEZ, three decades after contamination with ^{129}I." (page 4, lines 4-6)

-The aim and objectives should also be emphasized.

> Response: in the last paragraph of the introduction we have added the following highlighted text: "Our objectives in this study were to answer the following two key questions i) what

are the physico-chemical forms of ^{129}I in soils over the long-term and ii) what is the time scale over which ^{129}I equilibrates with the stable isotope ^{127}I which is present naturally within the environment?" (page 3, lines 17-19) We have also added a hypothesis, highlighted in yellow, in the same paragraph.

-Dividing the introduction in few smaller paragraphs would facilitate the reading and conveying the message more clearly.

Response: the Introduction has been divided into paragraphs.

4) Materials and methods are a bit too long (particularly regarding sample treatment). I would expect such detail for a new method. Not sure if it is the case, but if the authors are adapting a method that was previously published, the author could cite the original work and provide details on the changes/adaptations.

Response: The analyses of the samples in this study involved several complex steps, carried out in four laboratories in four countries (Ukraine, England, Denmark and Scotland). We feel the description of each step of the work is justified and references to originally published methods are provided where appropriate. In response to one of Reviewer #1's comments we have made the Materials and Methods section more digestible by dividing it into numbered sub-sections.

-Page 5 Line 23: 'worst case' contribution. Name this better as 'contamination'.

Response: The text had been changed to "(worst case) contamination"

5) Results and discussion.

-Please consider dividing this section in sub-sections to better define the structure and the main points.

Response: The Results and Discussion section has been divided into numbered sub-sections.

-Add in Figure 1: B, TL, NT in the same way as RF. Like that, the reader will know once they appear in the main body (e.g. page 8, line 15, 'B1').

Response: The names of the sampling sites in Figure 1 have been changed to site codes – the text in the legend to Fig. 1 has been changed to reflect this: "Codes for sampling sites are shown in Table 1."

-Page 8, line 17-19. Why is you range of 129I activity concentrations much narrower than in Sahoo et al., 2009? In general, if you compare your values to those in the literature please provide some more detail on the work that has been cited. For example, are their sampling sites from different locations? or have they different soil composition or vegetation?

Response: The absolute range of our total ^{129}I concentrations is lower than that reported by Sahoo et al. (25 versus 166 mBq/kg, respectively) but the relative range of our measurements, from lowest to highest, is actually higher (150 × versus 100 ×, respectively). In response to Reviewer#1 we have added additional discussion on the possibly loss of ^{129}I from the soil by leaching, which would have resulted in lower concentrations than measured by Sahoo et al. who took their samples as long ago as 1994/5 and, most recently, in 2001.

> Additional explanatory text has been added on p. 10, lines 10-13 : “Sahoo et al. (2009) took soil samples in 1994/95 and 2001 from sites in the CEZ which covered a very similar geographical range to the samples we took in 2015; soils and vegetation types at the sampling sites are almost identical between the two studies. They”.

-Page 9, Lines 16 to 23. Cite corresponding Table or the reader will get lost looking for the data. Consider also representing surface and subsoil results (e.g. by color gradient) for all locations in a single plot or subplot.

> Response: References to Table 2 are now made in section 3.3. Please see response to Q6, below.

-I would suggest the authors to re-formulate/re-organize the paragraph about the physico-chemical form of 129I (pages 12 and 13). It is said that the samples contained hot particles but no data is shown to back up this, nor to provide a correlation or non-correlation with uranium oxides. I find the discussion interesting but it is weak due to lack of data. Try to strengthen this with more data from the literature, or be crystal clear from the beginning using the sentence in lines 3-4, page 13: 'We can only speculate aboutâ€¦'

> Response: We have added an example autoradiograph from one of our soils in the Supplementary Materials (Figure S2) and edited the text in section 3.6 to read: “…we have found clear autoradiographic evidence (Supplementary Materials S2) of the existence of hot particles in our soil samples.” (page 16, lines 1-2) We have edited the first sentence of section 3.6 to read “The initial physico-chemical form of radionuclides deposited from the atmosphere can have a major impact on their long-term behaviour in the environment, but we can only speculate about the exact physico-chemical form of ^{129}I when it first contacted the CEZ soils.” (page 15, lines 21-23) The last sentence of section 3.6 now reads “Although we do not know the exact physico-chemical form of ^{129}I deposited on CEZ soils in 1986 it is highly probable that it was not ‘bound’ within the uranium oxide particles which are a unique characteristic of the CEZ”. (page 16, lines 17-19)

6) Figures. The visualization of the data can be improved by using different symbols for each location (squares, circlesâ€¦) and distinguish between surface vs sub-surface samples (e.g. empty and filled symbols). Please consider doing this for figures 3 to 6. Otherwise, the reader has to go to Tables, which is far more time consuming and less visual.

> Response: Labels have been added to identify individual data points in Figures 3, 4 and 5. The labels are shaded to distinguish topsoil and subsoil samples at a glance. This works quite well for Figures 3 and 5, but Figure 4 is very crowded. The original figures (without labels) have been left for the reviewer and editor to decide which is clearer. No labels have been added to Figure 6 because the data points were already shaded to distinguish the different extractants used – we consider that this figure will become too crowded if data labels are added.

7) Please revise English grammar for several small errors done throughout the text.

> Response: The text has been checked for grammatical and spelling errors and corrected where necessary.

Reviewer #3: (Revisions to text highlighted in red in the manuscript)

Materials and Methods

Line 10, page 4: '1m' should be '1 m' (insert the space).

> Response: space inserted

Line 15, page 4: '10g' should be '10 g' (insert the space).

> Response: space inserted

Line 23, page 4: '6g' should be '6 g' (insert the space).

> Response: space inserted

Line 23, page 4: Is the sequential extraction scheme presented hereinafter developed in the present study? Or, is it an existing analytical scheme that have been previously developed by others? If the latter, the related reference(s) should be provided here, before starting the explanation of the method.

> Response: please see response to comment #4 of Reviewer#1, above. We have added a sentence at the beginning of section 2.3 referencing Zhao and McGrath (1994) and Martens and Suarez (1997) on which our iodine extraction method is based: 'The extraction method is based on one published by Zhao and McGrath (1994) for sulphate extraction that was subsequently adapted by Martens and Suarez (1997) for Se extraction.' (page 6, lines 4-5)

Line 23, page 4: In addition to above comment, it will be helpful for readers to present a flowchart-type figure of the sequential extraction scheme that is presented in this section. I found some nice figures: e.g. Fig. 1 of 'Hou, X et al., 2001. Chemical speciation analysis of 129I in seawater and a preliminary investigation to use it as a tracer for geochemical cycle study of stable iodine. Marine Chem. 74, 145-155', and Fig. 9 of 'Hou, X. et al. 2009. A review on speciation of iodine-129 in the environmental and biological samples. Anal. Chim. Acta 632, 181-196'.

> Response: please see response to comment #5 of Reviewer#1, above. A flow diagram illustrating the sequential extraction procedure has been added to the Supplementary Materials (Figure S1: Schematic diagram of three-step sequential extraction procedure applied to CEZ soils). This could be added within the main text if preferred.

Line 7, page 7: The explanation of iodide (i.e. 'I-')'should appear previously (line 16, page 6), because the first appearance of iodide is in line 16, page 6.

> Response: the explanation of iodide (I-) has now been added when iodide is first mentioned, in section 2.5.

Line 15, page 7: Typo: 'measured 129I/127I'.

> Response: The typo has been corrected.

Results and Discussion

Line 22, page 8: It is better to present the ranges (values) of 129I/137Cs reported by these literatures (Hou et al., 2013; Sahoo et al, 2009).

> Response: the ranges of ^{129}I/^{137}Cs atom ratios from all three studies have been added in the sentence "the range of ^{129}I/^{137}Cs atom ratios in our samples (0.011 – 0.566, Table 3) is lower than the ranges reported by Hou et al. (2003) and Sahoo et al. (2009) (overall range from 0.1 to 7.2)" (pages 10-11, lines 24-1)

Lines 5-7, page 9: It's better to refer the tables by point-by-point, as: 'The RF3 site is a peaty meadow (Table 1) at the â€¦..all samples taken (Table 2), as well as â€¦concentrations (Table 2).'

> Response: the references to the relevant tables have been added in the sentence.

Lines 16-18, page 9: 'Total topsoilâ€¦than for 127I.'; this important result is not found in the presented data (tables and figures). Can the data be added in the tables (maybe in Table 2)?

> Response: Total topsoil concentrations of ^{129}I and ^{127}I are shown in Table 2 – a reference to Table 2 has been added at the end of this sentence in response to a comment from Reviewer#2.

Line 1, page 10: Refer the results (figures), by: 'the NaOH-extractable fraction (Fig. 2 (i) and (ii)) which representsâ€¦'

> Response: a reference to Figures 2(i) and 2(ii) and to the Supplementary Material has been inserted at the end of this sentence.

Line 16, page 10: 'iodide and iodate are lost from soil solutions'. Why are the water-dissolved iodine lost from soil solutions? Do the authors mention the adsorption of the dissolved-iodide and iodate to the soil as the 'loss'? Please specify the mechanism of the 'loss' used here.

> Response: The following text has been added to the sentence: "iodide and iodate are lost from soil solutions due to interactions with reactive surfaces such as hydrous oxides and humic molecules…" (page 13, lines 21-22)

Line 5, page 11: Refer the results, by: 'since this was the dominant fraction of soil iodine (Fig. 2 (i) and (ii))'.

> Response: The reference to Figure 2(i) and 2(ii) has been added to the sentence

Line 19, page 11: Please spell-out or explain the term 'HA'.

> Response: HA has been replaced with 'humic acid'.

Line 21, page 12: Need reference(s), as: 'radioisotopes of iodine constituted major proportions of these release inventories (REF)'.

> Response: References to Crick and Linsley (1984) and Toth et al. (1986) added to the text and in the reference list.

Line 13, page 13: Need reference(s), as: 'some laboratory experiments (REF)'. And, it is recommended to present the value(s) of time scales for iodine to achieve the isotopic equilibrium suggested by the references.

> Response: The wording of this sentence has been revised and two references cited: "… very long-term process. This contrasts with the observations of most laboratory incubation experiments which suggest that interaction of iodine species with organic and inorganic soil components is complete within a period of days (Duborska et al., 2019) to months (Bowley et al., 2016). Our data show …" (page 17, lines 1-5).

Figures
Fig. 1: I think 'RF' can be spelled out as Rad Forest, as the names of other sampling sites shown in this figure are all spelled-out.

> Response: in response to comment 5 by Reviewer#2 the names of all the sampling sites in Figure 1 have been changed to site codes – the text in the legend to Fig. 1 has been changed to reflect this: "Codes for sampling sites are shown in Table 1."

Reviewer #4: (Revisions to text highlighted in blue in the manuscript)

The last two highlights should be removed and eventually should be replaced with something better.

> Response: the 3rd and 4th highlights have been edited and now read:
>
> - ^{129}I not in complete equilibrium with ^{127}I 29 years after the Chernobyl accident
>
> - native ^{127}I only a partial proxy for ^{129}I behaviour in soils even after three decades

Abstract
Row 4
Referee: insert after in soil < samples> collectedâ€¦

> Response: the word ‘samples’ has been inserted as suggested.

To be added : the averaged result of 129I/127 concentration measured at this moment in CEZ and the comparison with rest of the world.

> Response: appropriate sentences have been added to the abstract: “The geometric mean (GM) total concentration of stable iodine (^{127}I) was 6.7×10^{-7} g g^{-1} and the (GM) total concentration of ^{129}I was 2.39×10^{-13} g g^{-1}, equivalent to 1.56 mBq kg^{-1}. GM total ^{127}I concentration is below the European average soil concentration of 3.94×10^{-6} g g^{-1}, while ^{129}I is significantly higher than the pre-Chernobyl activity concentration for ^{129}I of 0.094 mBq kg^{-1}.” (Page 1, lines 5-8)

Introduction
Page 2
Referee: Some description should be added of the outspreading of contamination effects in the World.

> Response: In the opening paragraph of the introduction we describe, briefly, that I-131 was widely dispersed across Europe and beyond, and that, locally (specifically in Belarus), an excess of human thyroid cancers was a result of this contamination. Since the paper is aimed primarily at understanding the physico-chemical behaviour of soil in the very local vicinity of the Chernobyl reactor we do not think it appropriate to add further description of the world-wide contamination with radioiodine, especially because this was extremely low beyond the European continent.

Row 26 -1 on page 3
One can speak about an equilibrium value of 129I/127I for the pre-nuclear era, only. The ratio 129/127 varies and is at reasonable levels or at base line concentration values for restricted different geographic regions. The comparison should be done with the soli values from Europe and Asia. However, from the measurements of this work , concentrations are resorbable (*sic.*) low (page 8 row 14). Therefore, sentence from page 2 row 26 ii) should be removed or rephrased.

> Response: In response to the need to add a hypothesis, and Q3 from Reviewer #2 we added the following text “We hypothesised that, after residing for almost 30 years in the soils of the CEZ, ^{129}I would have achieved a physico-chemical equilibrium with the native, stable ^{127}I present in the soils: it should be possible to demonstrate such an equilibrium by comparing the relative extractabilities of both iodine isotopes from soils”. (page 3, lines 22-25) We

understand that TOTAL ^{129}I/^{127}I ratios vary geographically, but our study uses ^{129}I/^{127}I ratios in different extractants from soil samples in a relatively small (30 km radius), heavily contaminated area – this demonstrates that the extractabilities of ^{129}I and ^{127}I vary significantly, with ^{129}I being more labile (ie. more extractable) than ^{127}I.

Page 3
Row 1-4:
Referee: Nothing is mentioned about the 137 Cs measurements and that it was used.

> Response: A sentence has been added at the end of the introduction: "Activity concentrations of ^{137}Cs and relevant soil properties, especially organic matter, are useful in interpreting the behaviour of iodine isotopes in soil and these are also reported."

Page 4
Referee: Why samples were not collected from larger distances from the reactor to get a comparison to the normal situation of the organic material ?

> Response: As explained above, this study was focussed on addressing a specific question regarding the relative physico-chemical behaviour of ^{129}I and ^{127}I in soil samples in a relatively small (30 km radius) but uniquely contaminated area. Given the widespread dispersion of radioiodine after the Chernobyl accident it is difficult to define a distance from the reactor at which 'normal' radiodine concentrations occur. We have cited studies by Hou et al. (2003) and Mironov et al. (2002) which provide measurements of ^{129}I and ^{127}I further afield which can be used to set our measurements in a wider geographical context.

It should be explained which are the physico chemical forms of iodine that are extracted by KCl , KH2PO4 and NaOH. What is the importance of measuring iodine separately?

> Response: A sentence has been added at the beginning of section 2.3: "The method is designed to extract soluble iodine species using 0.01M KCl, then specifically adsorbed species using 0.18M KH_2PO_4 and finally organically-bound iodine using 2.5M NaOH."

Row 9 :
Referee: Set <.> after word GPS unit(â€¦..) . Air Kerma ratesâ€¦

> Response: the edit has been done.

Row 11-13 :
Referee: Why only 20 cm depth and not deeper. Please explain.

> Response: The maximum sampling depth of 20 cm was chosen partly because we considered it unlikely that ^{129}I would have migrated significantly below this depth but mainly because we needed ^{129}I at sufficiently high activity concentrations to be able to measure it in sub-fractions of the samples, including soluble fractions which we expected to be close to detection limits. We expected, and generally did, find higher ^{129}I activity concentrations in the 'topsoil' which defined as the top 10 cm layer.

Results and Discussions.

Page 9

Row no.1 : further evidence of the source of 219Iâ€¦..
Referee: 129I. 131I and 137 Cs are fission products and their ratio or correlation factor can be used as evidence for the existence of the same production source if the probe sampling is performed at locations situated far away from that source (your citations about Sweden etc). Close to the source or at small distances such correlations are evident and only anomalies could be the issue of an investigation.
I suggest the authors to rephrase this sentence and remove evidence of..

> Response: We consider that the correlation between ^{137}Cs and ^{129}I shown in Figure 3 does, indeed, provide a strong indication that their source is closely related, especially given the geographical location of the sampling area. We have replaced 'Further evidence of' with "A further indication …"

Row 6 :
Referee: Define LOI . Loss of ignition. Explain shortly and tell if you did the measurement.

> Response: the acronym LOI is now given in the title to section 2.2 in which a brief explanation of the measurement is now given. We consider that only a brief description of LOI is needed because this is a very widely used method in soil science.

Row: 16-18:
Referee: Please rephrase.

> Response: it is difficult to know how to rephrase this sentence without a suggestion from the reviewer. We had added a reference to Table 2 in response to a comment from Reviewer #2.

Rows 20-23
Referee: rephrase and make sentence clearer formulated. For example: start the sentence with: The download migration of â€¦ in CEZ occurred after the deposition in 1986 . And then, you can cite the works , without the expression may have occurredâ€¦since is obviously.

> Response: The section in which this sentence occurs has been expanded following comments by Reviewer #1. Section 3.3 now takes into account the evidence provided by ^{129}I/^{127}I ratios and ^{129}I/^{137}Cs atom ratios in topsoils and subsoils.

Row 24:
Referee: Add the year

> Response: We do not understand the comment.

Page 13:
Referee: Add CONCLUSIONS. The paper jumps between many subjects. Therefore, a conclusion chapter should be added

> Response: A 'Conclusions' section has been added (Section 4).

Abstract

The Chernobyl Exclusion Zone (CEZ) represents a unique natural laboratory which received significant ^{129}I contamination across a range of soils and land-use types in a short time period in 1986. We present data on ^{129}I and ^{127}I in soil samples collected from highly contaminated areas in the CEZ in 2015. The geometric mean (GM) total concentration of stable iodine (^{127}I) was 6.7×10^{-7} g g^{-1} and the (GM) total concentration of ^{129}I was 2.39×10^{-13} g g^{-1}, equivalent to 1.56 mBq kg^{-1}. GM total ^{127}I concentration is below the European average soil concentration of 3.94×10^{-6} g g^{-1}, while ^{129}I is significantly higher than the pre-Chernobyl activity concentration for ^{129}I of 0.094 mBq kg^{-1}. Significant differences were found in the extractability of native, stable ^{127}I and ^{129}I almost 30 years after the introduction of ^{129}I to the soils. Both ^{127}I and ^{129}I were predominantly associated with alkaline-extractable soil organic matter, established using a three-step sequential extraction procedure. Whereas ^{127}I was significantly correlated with gross soil organic matter (measured by loss on ignition), however, ^{129}I was not. The ratio of ^{129}I/^{127}I was significantly lower in extracts of soil organic matter than in more labile (soluble and adsorbed) fractions, indicating incomplete equilibration of ^{129}I with native ^{127}I in soil humic substances after 29 years residence time in the CEZ soils. The initial physico-chemical form of ^{129}I in the CEZ soils is unknown, but the widespread presence of uranium oxide fuel particles is unlikely to have influenced the environmental behaviour of ^{129}I. Our findings have implications for long-term radiation dose from ^{129}I in contaminated soils and the use of native, stable ^{127}I as a proxy for the long-term fate of ^{129}I.

1. Introduction

In the aftermath of the Chernobyl accident in 1986 the short-lived radionuclide ^{131}I (half-life 8.02 days) was dispersed widely in the atmosphere, depositing to the land surface across the European continent and beyond. In some areas, notably in Belarus, radiation doses from ^{131}I to the human population were sufficient to induce excess thyroid cancers, predominantly in young people (WHO, 2016). These doses were received over a period of days to weeks, after which ^{131}I activities in the environment became undetectable. A much longer-term legacy of the Chernobyl accident, however, is the presence in the environment of ^{129}I (half-life 15.7×10^{6} years), an estimated 1.3 kg of which were released in 1986 (Paul et al., 1987). Unlike ^{131}I, ^{129}I emits only a very weak gamma ray (39.6 keV) and, due to its long physical half-life, has a low specific activity (6.54×10^{6} Bq g^{-1}, cf. 4.60×10^{15} Bq g^{-1} for ^{131}I). Estimates of exact doses from ^{131}I after the Chernobyl and Fukushima accidents have been hampered by the narrow window of time available for ^{131}I measurements in the environment. Since ^{131}I and ^{129}I are emitted synchronously to the atmosphere during an accidental release, the lingering presence of ^{129}I in environmental media has proved useful in reconstructing ^{131}I deposition patterns and associated doses (Straume et al., 1996; Pietrzak-Flis et al., 2003; Muramatsu et al., 2015).

Despite its usefulness in radiation dose reconstruction, however, ^{129}I is a significant long-term source of radiation exposure due to its extreme persistence in the environment. For adults ingesting contaminated foodstuffs the committed effective dose per unit intake for ^{129}I (1.1×10^{-7} Sv Bq^{-1}) is five times higher than that of ^{131}I (2.2×10^{-8} Sv Bq^{-1}) (ICRP, 2012) and ^{129}I is of specific concern in the context of radioactive waste disposal. In safety assessment calculations, ^{129}I is treated as a poorly sorbed radionuclide which contributes significantly to long-term radiation dose in the biosphere above geological disposal facilities (Posiva, 2013; SKB, 2014). Understanding the long-term environmental behaviour of ^{129}I is, therefore, of considerable importance in quantifying and controlling risks from such facilities and some studies addressing this problem have used ^{127}I as a proxy for ^{129}I (Roulier et al., 2019).

Iodine is a relative active and mobile element in the environment. Although ^{129}I and ^{127}I in soils have different sources, they are expected to behave in a very similar manner. The great majority of ^{129}I in the Chernobyl Exclusion Zone (CEZ) is expected to have originated from rapid, localised deposition of Chernobyl-released iodine in 1986, while ^{127}I has accumulated over the long-term (centuries to millennia) from deposition of atmospheric iodine originating from distant marine sources. Weathering of soil parent material can also contribute some ^{127}I to soils (though usually a minor source) and turnover of soil organic matter is a key part of the long-term accumulation and redistribution process of iodine in soils (Roulier et al., 2018). Following deposition on the soil, both ^{129}I and ^{127}I experience similar processes of fixation and leaching. It is expected that anthropogenic ^{129}I, deposited in the very short-term, should reach equilibrium with the numerous chemical species of naturally-occurring ^{127}I after some period of time through dynamic chemical and biochemical processes; thereafter the two iodine isotopes would be expected to behave in the same way. This paper aims to investigate if such an equilibrium has been achieved by speciation (fractionation) analysis of these two isotopes of iodine.

Our objectives in this study were to answer the following two key questions i) what are the physico-chemical forms of ^{129}I in soils over the long-term and ii) what is the time scale over which ^{129}I equilibrates with the stable isotope ^{127}I which is present naturally within the soil? To answer these questions we investigated contaminated soils within a 30 km radius of the Chernobyl nuclear power station, which presents unique circumstances in which to make measurements of ^{129}I three decades after the world's worst nuclear accident. We hypothesised that, after residing for almost 30 years in the soils of the CEZ, ^{129}I would have achieved a physico-chemical equilibrium with the native, stable ^{127}I present in the soils: it should be possible to demonstrate such an equilibrium by comparing the relative extractabilities of both iodine isotopes from soils. Here we report results of analyses of ^{127}I and ^{129}I in these samples, with an emphasis on the comparative behaviour of both nuclides 29 years after the deposition of ^{129}I. Activity concentrations of ^{137}Cs and relevant soil properties, especially organic matter, are useful in interpreting the behaviour of iodine isotopes in soil and these are also reported. The data set provides the most comprehensive analysis to date of the comparative extractabilities of ^{127}I and ^{129}I in soils of the CEZ, three decades after contamination with ^{129}I.

2. Materials and Methods

2.1 Soil sampling

Soils were sampled within the CEZ on 1st and 2nd September 2015 at the locations shown in Figure 1 and Table 1. Soil samples were taken close to the centre line of the plume of atmospheric deposition which emanated from the explosion in Reactor 4 on 26th April 1986 and extended due west (the 'Western Trace'). The sampling line extended from the 'Red Forest', 2.5 km west of Reactor 4, where the heaviest radioactive deposition occurred, to an abandoned collective farm at Tolsty Les, 22 km west of Reactor 4. Samples were also taken on the 'North Trace', an area of high radionuclide deposition 8 km to the NNW of Reactor 4. Locations of sampling sites were recorded using a hand-held GPS unit (Garmin GPSMAP® 60CSx). Air kerma rates (µGy h^{-1}) were recorded 1 m above the ground surface using a Mini Instruments Environmental Radiation Meter (type 6-80).

At each sampling site a soil pit was dug to a depth of 20 cm. Topsoil samples were taken with a trowel from a depth of 0-10 cm and subsoils from 10-20 cm. Soils were immediately placed in polythene bags, sealed and taken to the *Chornobyl Center for Nuclear Safety, Radioactive Waste and Radioecology* in Slavutych, 47 km NE of the Chernobyl power station. Here, the samples were stored in a cold room before processing.

2.2 Soil moisture content, pH, loss on ignition (LOI) and gamma ray analysis

Sub-samples of field moist soil (5 - 10 g) were used to determine moisture content (by oven drying at 105°C), pH and loss on ignition (LOI – the mass lost after combustion at 550°C as a proxy for total soil organic matter). Air-dried sub-samples (10 g) were used to determine total ^{137}Cs activity concentrations using a Canberra-Packard gamma-spectrometer with a high-purity germanium (HPGe) detector (GC 3019). A standard source (OISN-16; Applied Ecology Laboratory of Environmental Safety Centre, Odessa, Ukraine) containing ^{152}Eu was used to calibrate the efficiency of the detector. Sample count rates were not decay corrected so represent activity concentrations just after the time of sampling. Sub-samples of the remaining field-moist soils were subject to a sequential extraction procedure, as described below.

2.3 Sequential extraction of soils

The extraction method is based on one published by Zhao and McGrath (1994) for sulphate extraction that was subsequently adapted by Martens and Suarez (1997) for Se extraction. The method is designed to extract soluble iodine species using 0.01M KCl, then specifically adsorbed species using 0.18M KH_2PO_4 and finally organically-bound iodine using 2.5M NaOH. A mass of each field moist soil sample equivalent to 6 g oven-dry material was weighed into a polythene centrifuge tube. After adding 30 mL of 0.01M KCl to each tube, the tubes were shaken for approximately 16 h then centrifuged at 3,500 rpm for 30 minutes. The supernatants were carefully removed using a syringe and filtered through a 0.22 µm PTFE filter. A 19.8 mL aliquot of filtered KCl extract was pipetted into a polythene tube and 0.2 mL of 10% w/v NaOH added to stabilise the iodine in the extract. The excess supernatant was carefully removed and 30 mL 0.18M KH_2PO_4 added to the remaining soil pellets. The tubes were shaken vigorously by hand to disaggregate the pellets and then shaken gently for approximately 16 h. The soil suspensions were centrifuged at 3,500 rpm for 30 minutes before removing and filtering the supernatants, as for the first extraction step. An aliquot (19.8 mL) of filtered KH_2PO_4 extract was pipetted into a polythene tube and stabilised with 0.2 mL of 10% w/v NaOH. After removing the excess supernatant the remaining soil pellets were subjected to a third and final extraction in 15 mL of 10% w/v (2.5M) NaOH, added to each centrifuge tube. The tubes were shaken to disaggregate the pellet then loosely capped, placed in a rack and incubated at a maximum temperature of 90°C for approximately 16 hours. After incubation, the tubes were centrifuged at 3,500 rpm for 30 minutes then 2 mL of NaOH extract removed and transferred to a clean polythene tube. The NaOH extracts were diluted with 18 mL of ultrapure water to give a solution of 1% w/v NaOH. After each extraction step the tubes containing the respective extracts were capped and sealed with Parafilm® prior to transport to the UK. A flow diagram illustrating the sequential extraction procedure is provided in Supplementary Materials (Figure S1).

2.4 Analysis of stable iodine (^{127}I) and preparation of reagent blanks for ^{129}I

Small aliquots (<2 mL) of each extract were taken from each sample tube in a laboratory in the UK (*University of Nottingham*); the time during which the vials were open to the laboratory atmosphere was of the order of 2 minutes. These aliquots were used to analyse ^{127}I by ICP-MS (Thermo-Fisher Scientific, iCAP-Q) with Rh and Re (10 mg L^{-1}) as internal standards for drift correction. Stock standards for ^{127}I calibration were prepared at iodine concentrations of 1000 mg L^{-1} from oven-dried KI and KIO_3, and stored at 4°C in 1% tetra methyl ammonium hydroxide (TMAH). Two vials containing 20 mL of 0.5M (2% w/v) NaOH were left open in the laboratory for 48 hours to assess the (worst case) contamination from ^{129}I which had previously been used as a tracer in this laboratory; these were used as reagent blanks when preparing AgI targets for ^{129}I analysis (see below). The remaining soil extracts and reagent blanks were sealed in the polythene tubes and transported to the *Technical University of Denmark* for separation of ^{129}I from each extract and preparation of targets for AMS measurement of ^{129}I.

2.5 Preparation of targets for AMS measurement of ^{129}I

Aliquots of 5.0-18 mL of each extract were transferred to a beaker and the mass of solution recorded. A carrier solution of ^{127}I (1.802 mg mL^{-1}) was prepared by dissolving iodine crystal (Woodward Company, USA; $^{129}I/^{127}I$ ratio $< 2 \times 10^{-14}$) in a solution consisting of 0.4 M NaOH and 0.05 M $NaHSO_3$. A 0.5 mL aliquot of this carrier was added to the sample, followed by 8M NaOH to achieve a NaOH concentration of 0.5 M. The beaker was covered with a watch glass then heated at 60°C for 10-12 h to convert all organic iodine to an inorganic form. After cooling, 0.5 mL of 1M $NaHSO_3$ solution was added and the pH adjusted to <2 using 3M HNO_3, to convert all iodine to iodide. The sample solution was then transferred to a separation funnel to which 20-30 mL of $CHCl_3$ were added, followed by addition of 0.5-0.8 mL of 1M $NaNO_2$ to oxidize iodide to I_2. Iodine as I_2 was extracted into the organic phase which was then separated and collected in a beaker. The organic extraction step was repeated by adding another 15 ml aliquot of $CHCl_3$ to the separation funnel, plus 0.1 ml of 1M $NaNO_2$, and the two organic phase extracts were combined. The $CHCl_3$ phase solution was then transferred to another separation funnel to which were added 0.2 ml of 0.05M $NaHSO_3$ and 15 ml H_2O to reduce I_2 to iodide (I^-) and back extract it into aqueous phase, after which the organic phase was discarded. These organic solvent extraction and back-extraction steps were repeated, leaving an aqueous phase containing iodide. This was transferred from the separation funnel to a 10 mL centrifuge tube. The funnel was then washed three times with water and the washings combined in the centrifuge tube.

A 1 mL aliquot of 3M HNO_3 was added to the centrifuge tube, followed by 0.5 mL of 1M $AgNO_3$ to form a AgI precipitate which was then separated by centrifugation. After washing the AgI precipitate with water it was centrifuged again, then transferred with 0.5 mL water to a 1.4 mL centrifuge tube. The original centrifuge tube was washed and the washings combined with the AgI precipitate. This was centrifuged and the supernatant discarded. Finally, the AgI precipitate was dried at 60°C for 2-3 hours in readiness for AMS measurement of ^{129}I.

2.6 Analysis of ^{129}I by Accelerator Mass Spectrometry

After preparation, the AgI targets were transported to the *Scottish Universities Environmental Research Centre (UK*) where ^{129}I concentrations were determined using a tandem accelerator mass spectrometer (AMS), as previously described by Xu *et al*. (2013). The AgI precipitates from each sample were mixed with high purity Ag powder (100 mesh, 99.95%, Assure) with a mass ratio 1:2 for AgI:Ag and then pressed into an aluminium target holder (1 mm ∅). Iodide (I^-) ions were extracted using a Cs-sputtering ion source. A terminal voltage of 3 MV was used and I^{5+} ions selected for detection. The $^{127}I^{5+}$ ions were detected using a Faraday cup mounted at the exit of a high energy analyzing magnet, while $^{129}I^{5+}$ ions were counted using an ionization chamber detector with a 100 nm thick SiN detector window. Dissociation of MoO_2^- can produce $^{97}Mo^{4+}$ which may interfere with

$^{129}I^{5+}$ measurement due to a similar magnetic rigidity (ME/q^2); however, the two ions can be completely separated in the detector. The measured $^{129}I/^{127}I$ ratios were corrected against a standard material with $^{129}I/^{127}I$ ratio of 1.138×10^{-10} prepared by ^{127}I addition to the NIST 4949B standard. The measured $^{129}/^{127}I$ ratios in the prepared targets ranged from 2.9×10^{-11}–3.5×10^{-9}, which are higher than the mean of the reagent and laboratory blanks (1.1×10^{-11}) and the estimated pre-atomic ratio (1.5×10^{-12}) (Moran et al., 1999). I-129 concentrations in the samples was calculated based on the amount of ^{127}I carrier added to the samples before chemical separation and the measured $^{129}I/^{127}I$ atomic ratios after subtracting the background of the reagent and laboratory blanks. Uncertainties on measured $^{129}I/^{127}I$ ratios in samples ranged from 0.4–2.8%. After subtracting $^{129}I/^{127}I$ ratios attributable to the reagent blank, a limit of detection (LoD) of 2.0×10^5 ^{129}I atoms per sample was calculated. I-129 in all samples was above this LoD, ranging from 7.7×10^7 – 5.3×10^{10} atoms per sample.

3. Results and Discussion

3.1 Total concentrations of ^{127}I and ^{129}I in CEZ soils

Total concentrations of ^{127}I and ^{129}I in our samples were calculated by summing the concentrations determined in KCl, KH_2PO_4 and NaOH extracts (see Supplementary Material); concentrations were expressed as either mass concentrations (for both ^{127}I and ^{129}I) or activity concentrations (for ^{129}I) per unit dry weight of soil. Total concentrations of stable iodine (^{127}I) in the CEZ soils ranged from 1.54×10^{-7} g g^{-1} in the B1 subsoil to 2.64×10^{-6} g g^{-1} in the RF3 topsoil, with a geometric mean (GM) of 6.7×10^{-7} g g^{-1} (Figure 2(i), Table 2). This range is below the average soil concentration of 3.94 mg kg^{-1} (3.94×10^{-6} g g^{-1}) for iodine in European soils (Salminen et al., 2005) and at the lower end of the range for world soils (Fleming, 1980). Sahoo et al. (2009) took soil samples in 1994/95 and 2001 from sites in the CEZ which covered a very similar geographical range to the samples we took in 2015; soils and vegetation types at the sampling sites are almost identical between the two studies. They also reported low ^{127}I concentrations in CEZ soils (mean = 5.4×10^{-7} g g^{-1}) similar to the concentrations we determined. Shiraishi et al. (2006) found that dietary intake of iodine by residents in NW Ukraine was below the WHO recommended value of 150 µg d^{-1} for adults and was linked to increased occurrence of goitre; this probably reflects low mean regional iodine concentrations which are likely to increase exposure to environmental sources of radioactive iodine. Total mass concentrations of ^{129}I in the CEZ soils ranged from 2.40×10^{-14} g g^{-1} in the B1 subsoil to 3.83×10^{-12} g g^{-1} in the RF3 topsoil, with a GM of 2.39×10^{-13} g g^{-1} (Figure 2(ii), Table 2). When expressed as activity concentrations this range was 0.16 to 25 mBq kg^{-1} with a GM of 1.56 mBq kg^{-1} (Figure 2(iii), Table 2). Sahoo et al. (2009) reported a range of 1.7 to 168 mBq kg^{-1} in soils from the CEZ, with the highest activity concentrations in surface soil samples including forest litter and organic horizons. The slightly lower activity concentrations in our study are consistent with the fact that our samples were averaged across soil depths of 0-10 and 10-20 cm. For the same reason, the range of ^{129}I/^{137}Cs atom ratios in our samples (0.011 – 0.566, Table 3) is lower than the ranges reported by Hou et al. (2003) and Sahoo et al. (2009) (overall range from 0.1 to 7.2), though all three ranges overlap. Mironov et al. (2002) determined an average pre-Chernobyl activity concentration for ^{129}I of 0.094 (± 0.014) mBq kg^{-1} in subsoil samples collected 400 km north of Chernobyl in 1985; ^{129}I activity concentrations in all our samples were significantly higher than this and we conclude that the ^{129}I we measured originated from the Chernobyl reactor. A further indication of the source of ^{129}I in our study is given by the strong and highly significant correlation between ^{129}I and ^{137}Cs activity concentrations in the samples (Figure 3); a similar relationship has previously been proposed as a means of estimating ^{131}I deposition densities in areas of Russia, Belarus and Sweden contaminated by the Chernobyl accident (Hou et al., 2003).

3.2 Relationships between ^{127}I, ^{129}I and organic matter in CEZ soils

The RF3 site is a peaty meadow (Table 1) at the western extremity of the Red Forest and the soil here had the highest organic matter content (LOI) of all the samples taken (Table 3), as well as the highest ^{127}I and ^{129}I concentrations (Table 2). Overall, there was a significant positive relationship (Pearson R = 0.73; Spearman rank p = 0.037) between ^{127}I and soil organic matter (Figure 4(i)), as expected from previous studies on soil iodine (eg. Yamada et al., 1999; Xu et al., 2016; Soderlund et al., 2017). Total concentrations of ^{127}I and ^{129}I were positively and significantly correlated (Figure 5) which probably results from a similar tendency for retention of both isotopes in soils with similar organic matter contents. However, the relationship between ^{129}I and soil LOI (not shown) was much weaker (Pearson R = 0.44) than for ^{127}I versus LOI. Spearman rank correlation indicated an insignificant relationship between ^{129}I and soil LOI (p = 0.22); when the RF3 data points were removed the slope of the relationship was effectively zero, suggesting that the variations in ^{129}I concentrations in the soil are due primarily to the initial deposition pattern in 1986 rather than the properties of the soil on which the ^{129}I was deposited.

3.3 Topsoil versus subsoil concentrations of ^{127}I and ^{129}I in CEZ soils

Total topsoil concentrations of ^{129}I and ^{127}I were generally higher than subsoil concentrations, but not at all sampling sites; ^{129}I concentrations were greater in topsoils at more sites than ^{127}I and the differences between top- and subsoil concentrations were higher for ^{129}I than for ^{127}I (Table 2). Furthermore, ratios of total ^{129}I/^{127}I were higher in topsoils than in sub-soils at all sites except RF1 (Table 2), indicating that proportionally more of the ^{129}I deposited to the soil surface in 1986 was still present in the topsoil. Sahoo et al. (2009) reported generally declining ^{127}I and ^{129}I concentrations from the soil surface to a depth of 15-20 cm in samples taken on the North Trace in 2001. However, some downwards migration of ^{129}I must have occurred in the 30 year period following the Chernobyl accident. Independent estimates of ~30 years have been made for the residence half-times of ^{129}I in the upper 30 cm of soil profiles at Savannah River (Boone et al. 1985) and the Karlsruhe reprocessing plant (Robens et al., 1989) suggesting that significant downwards migration of ^{129}I in CEZ soils is possible since initial deposition in 1986. This is supported by the observation that the ^{129}I/^{137}Cs atom ratios in topsoils are lower than those in subsoils for 7 of the 9 soils sampled in this study, which indicates that ^{129}I has moved faster than ^{137}Cs from the topsoil to the subsoil. Leaching of a portion of the originally deposited ^{129}I from the upper 20 cm of the soils sampled cannot be excluded, which would partially explain the slightly lower total ^{129}I activity concentrations we measured compared with previous studies, as discussed in section 3.1. Approximate estimates of the magnitude of ^{129}I leaching below a depth of 20 cm may be possible by comparing ^{129}I activity concentrations measured by Sahoo et al. (2009) and in our study. Furthermore, if the rate of ^{137}Cs leaching were known than the comparative rate of ^{129}I could be calculated using the ^{129}I/^{137}Cs atom ratios in Table 3. However, the only reliable way to quantify the degree of ^{129}I leaching deep into the soil profile is to take deeper soil samples for further analysis by AMS, which is beyond the scope of this study.

3.4 Sequentially-extractable concentrations of ^{127}I and ^{129}I in CEZ soils

We used 10% w/v (2.5 M) NaOH to recover humic matter and associated iodine isotopes from soil samples. Studies by Watts and Mitchell (2008) and Shetaya et al. (2012) have shown that strongly alkaline extractants such as TMAH and NaOH are effective in quantitatively extracting iodine from soils. Total concentrations of both ^{127}I and ^{129}I (defined above) were dominated by the NaOH-extractable fraction which represents iodine associated with soil organic matter (Figures 2(i) and 2(ii); see also Supplementary Material). In the case of ^{127}I, the organically-bound concentrations were significantly higher than both KCl and KH_2PO_4 extractable concentrations (Figure 2(i)) but not significantly different from the total ^{127}I concentration. The organically-bound concentrations of ^{129}I were significantly higher than the KCl extractable concentrations but not the KH_2PO_4 extractable concentrations (Figure 2(ii)). Extraction of soils with a weak electrolyte such as 0.01M KCl accesses the readily soluble pool within the soil; the dominant iodine species expected to reside in this pool are iodide (I^-) and iodate (IO_3^-). Yuita (1992) found that iodate accounted for >80% of the iodine in soil solutions from a brown forest soil under aerobic conditions, but only ~14% when the soil was flooded. In contrast, iodide accounted for ~6% of soluble iodine in non-flooded forest soil, increasing to >80% in flooded soil. At the time of sampling (September 2015) the CEZ soils were generally dry (gravimetric moisture contents ranged from <0.2% in the sandy B1 subsoil to 61% in the highly organic RF3 subsoil). Even though the soils of the CEZ are generally free-draining, they frequently flood after snow melt during early spring or for longer periods (eg. 2013-2014) so it is probable that soluble inorganic iodine species vary throughout the year. Laboratory studies by Shetaya et al. (2012) and Duborska et al. (2018) indicate that iodide and iodate are lost from soil solutions due to interactions with reactive surfaces such as hydrous oxides and humic molecules on time scales of minutes to hours and hours to days, respectively, suggesting that equilibration of inorganic iodine species in soil solution is complete on these time scales. Longer-term kinetics under environmental conditions cannot be ruled out, however.

Iodide interacts with anion-exchanging surfaces in soils by electrostatic interaction, iodate by chemisorption principally to metal hydrous oxides (Yoshida et al., 1995); extraction of soils with KH_2PO_4 provides a measure of iodide and iodate specifically adsorbed to sesquioxides of Fe, Al and Mn. The GM adsorbed ^{127}I concentration was significantly different (higher and lower, respectively) from GM soluble and organic ^{127}I concentrations (Figure 2(i)). However, the GM adsorbed ^{129}I concentration was significantly higher than soluble ^{129}I but not significantly different from organic ^{129}I concentrations (Figure 2(ii), (iii)), indicating a difference in the physico-chemical distribution of native ^{127}I and Chernobyl-derived ^{129}I.

3.5 Comparison of extractabilities of ^{127}I and ^{129}I in CEZ soils

The relationships between ^{127}I and ^{129}I in the soil extracts are summarised graphically as $^{129}I/^{127}I$ ratios in Figure 2(iv) and Figure 6. Figure 2(iv) shows that $^{129}I/^{127}I$ ratios in KCl and KH_2PO_4 extracts were not significantly different from each other, with GMs of 1.74×10^{-6} and 1.66×10^{-6}, respectively. The GM $^{129}I/^{127}I$ ratios in NaOH extracts were significantly lower (2.37×10^{-7}) and, since this was the dominant fraction (Figure 2(i) and 2(ii)), the GM of the total $^{129}I/^{127}I$ ratio was also significantly lower than the KCl and KH_2PO_4 extracts (2.94×10^{-7}). Figure 6 shows that the $^{129}I/^{127}I$ ratios in all soil extracts were positively and significantly related to the total ^{129}I concentrations in the soils. Since $^{129}I/^{127}I$ ratios for KCl and KH_2PO_4 extracts were not significantly different, a single regression line was fitted to these data in Figure 6. It is clear that $^{129}I/^{127}I$ ratios in KCl and KH_2PO_4 extracts are higher than in the NaOH extracts at all ^{129}I concentrations, indicating a preponderance of ^{129}I in more 'labile' soil extracts compared with soil organic matter (extractable with NaOH) which can be considered to be the long-term sink for iodine in soils. Bowley et al. (2016) observed that mixtures of I^- and IO_3^- in suspensions of humic acid were partially transformed to organic iodine over the course of 77 days. Kinetic modelling suggested a short half-time (~15 minutes) for conversion of IO_3^- to organic iodine, though this was balanced by a slower reverse reaction which led to a 'pseudo-steady-state' over a time scale up to 250 days. Size selective analysis of the humic polymer by Xu et al. (2012) showed proportionally less ^{129}I than native ^{127}I in the larger molecular weight humic fraction, attributable to insufficient reaction time for full isotopic equilibration and to partial exclusion of ^{129}I from the complex humic acid structure. Our results from samples collected almost 30 years after ^{129}I deposition in the CEZ suggest that full isotopic equilibration between ^{129}I and ^{127}I in soil humic molecules has not been achieved on a decadal time-scale.

Schmitz and Aumann (1995) found that ^{129}I was proportionally more water-soluble than ^{127}I in soils around the Karlsruhe reprocessing plant, which they explained by the much shorter residence time of ^{129}I in the soil compared with native ^{127}I. Surprisingly, only 4-15% of ^{129}I was found in the organic fractions of the Karlsruhe soils. In contrast, Hou et al. (2003) found approximately 40% of ^{129}I bound to organic matter in a soil sampled in Belarus (Gomel) in September 1999. Englund et al. (2008) found 50-85% of ^{129}I bound to organic matter in a Swedish lake sediment, while the proportion of organically associated ^{129}I in our CEZ soils ranged from 24-94%. The Englund et al. (2008) study found 5-8% of ^{129}I in water-soluble, exchangeable and carbonate fractions, combined. In our study, the combined KCl and KH_2PO_4 extractable fractions of ^{127}I and ^{129}I can be considered to represent 'labile' iodine. For ^{127}I, the magnitude of these combined fractions relative to the total iodine concentration ranged from 0.4% (in RF3 subsoil) to 20% (in RF1 topsoil). For ^{129}I, the range was from 6% (in RF1 and RF3 subsoils) to 76% (in RF2 topsoil). In the case of ^{127}I, the ratio was significantly and negatively correlated with LOI (Figure 4(ii)) whereas for ^{129}I there was no significant relationship with LOI – another indication of differences in behaviour of the two nuclides in the same soils.

3.6 Consideration of the initial physico-chemical form of ^{129}I deposited in 1986

The initial physico-chemical form of radionuclides deposited from the atmosphere can have a major impact on their long-term behaviour in the environment, but we can only speculate about the exact physico-chemical form of ^{129}I when it first contacted the CEZ soils. Radioactive deposits in the highly contaminated western and northern traces of the CEZ were mostly in the form of irradiated reactor fuel fragments, referred to as 'hot particles' (Sandalls et al., 1993). Even though we sampled almost

30 years after deposition we have found clear autoradiographic evidence (Supplementary Materials S2) of the existence of hot particles in our soil samples. When Vapirev et al. (1990) analysed a hot particle from Chernobyl they found it to be depleted of ^{131}I. At the very high temperatures prevalent during the accident in 1986 radioactive iodine would have been released to the atmosphere in the gas phase; indeed, in less severe accidents in which only volatile radionuclides were released from reactor cores (Windscale, Three Mile Island) radioisotopes of iodine constituted major proportions of the release inventories (Crick and Linsley, 1984; Toth et al., 1986). Volatile radioiodine released to the atmosphere from Chernobyl is thought to have been progressively sorbed to aerosol particles on a time scale of approximately 45-50 days (Maryon et al., 1991); this is too long for this process to have influenced radio-iodine deposition in the CEZ. Weather records from Chernobyl indicate that, apart from very slight (0.4 mm) rainfall on 27th April, there was no significant precipitation at the time of the accident and in the following days up to May 3rd when records stop (NOAA, 2018). In the vicinity of the reactor, gaseous ^{129}I would have been subject to dry deposition to vegetation surfaces, followed by weathering and transfer to the underlying soil over the following weeks. In forests close to Fukushima, Xu et al. (2016) have shown that, in comparison to rainwater, ^{127}I is concentrated in throughfall and stemflow and that it is entirely in organic form in these sub-canopy waters. Although we do not know the exact physico-chemical form of ^{129}I deposited on CEZ soils in 1986 it is highly probable that it was not 'bound' within the uranium oxide particles which are a unique characteristic of the CEZ.

4. Conclusions

Contamination of the CEZ can be precisely dated to the 10 day period from 26th April to 5th May 1986. Any delay in the introduction of ^{129}I to soils as deposits were weathered from vegetation canopies, would have been over a period of weeks. The CEZ therefore provides the opportunity to quantify the long-term behaviour of radioactive iodine under real-world conditions following a well-defined pulse injection. Our observation that full isotopic equilibrium between the native ^{127}I and

^{129}I has not been achieved after 29 years indicates that complete mixing between the nuclides is a very long-term process. This contrasts with the observations of most laboratory incubation experiments which suggest that interaction of iodine species with organic and inorganic soil components is complete within a period of days (Duborska et al., 2019) to months (Bowley et al., 2016). Our data show that ^{129}I remains more mobile and more bioavailable than ^{127}I three decades after the Chernobyl accident, which has implications for the use of native, stable iodine as a proxy for assessments of the radiation doses attributable to ^{129}I, certainly on a decadal time scale and perhaps longer.

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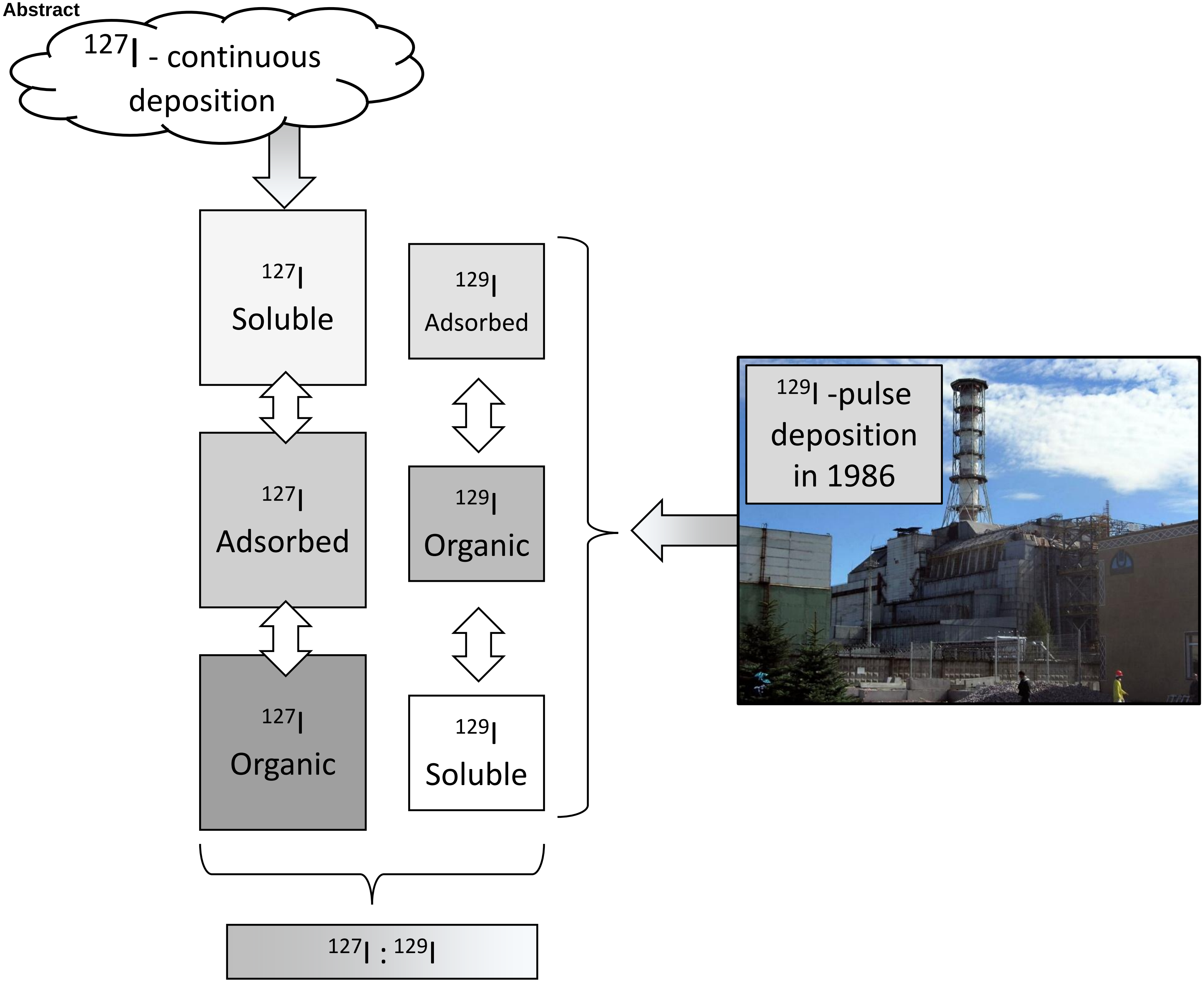
***Graphical Abstract**



^{127}I - continuous deposition

^{127}I Soluble

^{127}I Adsorbed

^{127}I Organic

^{129}I Adsorbed

^{129}I Organic

^{129}I Soluble

^{129}I -pulse deposition in 1986

^{127}I : ^{129}I

***Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

Highlights

- stable iodine concentrations in Chernobyl soils lower than European average
- ^{129}I to ^{127}I ratios significantly lower in organic than in ‘labile’ fractions
- ^{129}I not in complete equilibrium with ^{127}I 29 years after the Chernobyl accident
- native ^{127}I only a partial proxy for ^{129}I behaviour in soils even after three decades

Abstract

The Chernobyl Exclusion Zone (CEZ) represents a unique natural laboratory which received significant ^{129}I contamination across a range of soils and land-use types in a short time period in 1986. We present data on ^{129}I and ^{127}I in soil samples collected from highly contaminated areas in the CEZ in 2015. The geometric mean (GM) total concentration of stable iodine (^{127}I) was 6.7×10^{-7} g g^{-1} and the (GM) total concentration of ^{129}I was 2.39×10^{-13} g g^{-1}, equivalent to 1.56 mBq kg^{-1}. GM total ^{127}I concentration is below the European average soil concentration of 3.94×10^{-6} g g^{-1}, while ^{129}I is significantly higher than the pre-Chernobyl activity concentration for ^{129}I of 0.094 mBq kg^{-1}. Significant differences were found in the extractability of native, stable ^{127}I and ^{129}I almost 30 years after the introduction of ^{129}I to the soils. Both ^{127}I and ^{129}I were predominantly associated with alkaline-extractable soil organic matter, established using a three-step sequential extraction procedure. Whereas ^{127}I was significantly correlated with gross soil organic matter (measured by loss on ignition), however, ^{129}I was not. The ratio of ^{129}I/^{127}I was significantly lower in extracts of soil organic matter than in more labile (soluble and adsorbed) fractions, indicating incomplete equilibration of ^{129}I with native ^{127}I in soil humic substances after 29 years residence time in the CEZ soils. The initial physico-chemical form of ^{129}I in the CEZ soils is unknown, but the widespread presence of uranium oxide fuel particles is unlikely to have influenced the environmental behaviour of ^{129}I. Our findings have implications for long-term radiation dose from ^{129}I in contaminated soils and the use of native, stable ^{127}I as a proxy for the long-term fate of ^{129}I.

1. Introduction

In the aftermath of the Chernobyl accident in 1986 the short-lived radionuclide ^{131}I (half-life 8.02 days) was dispersed widely in the atmosphere, depositing to the land surface across the European continent and beyond. In some areas, notably in Belarus, radiation doses from ^{131}I to the human population were sufficient to induce excess thyroid cancers, predominantly in young people (WHO, 2016). These doses were received over a period of days to weeks, after which ^{131}I activities in the environment became undetectable. A much longer-term legacy of the Chernobyl accident, however, is the presence in the environment of ^{129}I (half-life 15.7×10^{6} years), an estimated 1.3 kg of which were released in 1986 (Paul et al., 1987). Unlike ^{131}I, ^{129}I emits only a very weak gamma ray (39.6 keV) and, due to its long physical half-life, has a low specific activity (6.54×10^{6} Bq g^{-1}, cf. 4.60×10^{15} Bq g^{-1} for ^{131}I). Estimates of exact doses from ^{131}I after the Chernobyl and Fukushima accidents have been hampered by the narrow window of time available for ^{131}I measurements in the environment. Since ^{131}I and ^{129}I are emitted synchronously to the atmosphere during an accidental release, the lingering presence of ^{129}I in environmental media has proved useful in reconstructing ^{131}I deposition patterns and associated doses (Straume et al., 1996; Pietrzak-Flis et al., 2003; Muramatsu et al., 2015).

Despite its usefulness in radiation dose reconstruction, however, ^{129}I is a significant long-term source of radiation exposure due to its extreme persistence in the environment. For adults ingesting contaminated foodstuffs the committed effective dose per unit intake for ^{129}I (1.1×10^{-7} Sv Bq^{-1}) is five times higher than that of ^{131}I (2.2×10^{-8} Sv Bq^{-1}) (ICRP, 2012) and ^{129}I is of specific concern in the context of radioactive waste disposal. In safety assessment calculations, ^{129}I is treated as a poorly sorbed radionuclide which contributes significantly to long-term radiation dose in the biosphere above geological disposal facilities (Posiva, 2013; SKB, 2014). Understanding the long-term environmental behaviour of ^{129}I is, therefore, of considerable importance in quantifying and controlling risks from such facilities and some studies addressing this problem have used ^{127}I as a proxy for ^{129}I (Roulier et al., 2019).

Iodine is a relative active and mobile element in the environment. Although ^{129}I and ^{127}I in soils have different sources, they are expected to behave in a very similar manner. The great majority of ^{129}I in the Chernobyl Exclusion Zone (CEZ) is expected to have originated from rapid, localised deposition of Chernobyl-released iodine in 1986, while ^{127}I has accumulated over the long-term (centuries to millennia) from deposition of atmospheric iodine originating from distant marine sources. Weathering of soil parent material can also contribute some ^{127}I to soils (though usually a minor source) and turnover of soil organic matter is a key part of the long-term accumulation and redistribution process of iodine in soils (Roulier et al., 2018). Following deposition on the soil, both ^{129}I and ^{127}I experience similar processes of fixation and leaching. It is expected that anthropogenic ^{129}I, deposited in the very short-term, should reach equilibrium with the numerous chemical species of naturally-occurring ^{127}I after some period of time through dynamic chemical and biochemical processes; thereafter the two iodine isotopes would be expected to behave in the same way. This paper aims to investigate if such an equilibrium has been achieved by speciation (fractionation) analysis of these two isotopes of iodine.

Our objectives in this study were to answer the following two key questions i) what are the physico-chemical forms of ^{129}I in soils over the long-term and ii) what is the time scale over which ^{129}I equilibrates with the stable isotope ^{127}I which is present naturally within the soil? To answer these questions we investigated contaminated soils within a 30 km radius of the Chernobyl nuclear power station, which presents unique circumstances in which to make measurements of ^{129}I three decades after the world's worst nuclear accident. We hypothesised that, after residing for almost 30 years in the soils of the CEZ, ^{129}I would have achieved a physico-chemical equilibrium with the native, stable ^{127}I present in the soils: it should be possible to demonstrate such an equilibrium by comparing the relative extractabilities of both iodine isotopes from soils. Here we report results of analyses of ^{127}I and ^{129}I in these samples, with an emphasis on the comparative behaviour of both nuclides 29 years after the deposition of ^{129}I. Activity concentrations of ^{137}Cs and relevant soil properties, especially organic matter, are useful in interpreting the behaviour of iodine isotopes in soil and these are also reported. The data set provides the most comprehensive analysis to date of the comparative extractabilities of ^{127}I and ^{129}I in soils of the CEZ, three decades after contamination with ^{129}I.

2. Materials and Methods

2.1 Soil sampling

Soils were sampled within the CEZ on 1st and 2nd September 2015 at the locations shown in Figure 1 and Table 1. Soil samples were taken close to the centre line of the plume of atmospheric deposition which emanated from the explosion in Reactor 4 on 26th April 1986 and extended due west (the 'Western Trace'). The sampling line extended from the 'Red Forest', 2.5 km west of Reactor 4, where the heaviest radioactive deposition occurred, to an abandoned collective farm at Tolsty Les, 22 km west of Reactor 4. Samples were also taken on the 'North Trace', an area of high radionuclide deposition 8 km to the NNW of Reactor 4. Locations of sampling sites were recorded using a hand-held GPS unit (Garmin GPSMAP® 60CSx). Air kerma rates (µGy h^{-1}) were recorded 1 m above the ground surface using a Mini Instruments Environmental Radiation Meter (type 6-80).

At each sampling site a soil pit was dug to a depth of 20 cm. Topsoil samples were taken with a trowel from a depth of 0-10 cm and subsoils from 10-20 cm. Soils were immediately placed in polythene bags, sealed and taken to the *Chornobyl Center for Nuclear Safety, Radioactive Waste and Radioecology* in Slavutych, 47 km NE of the Chernobyl power station. Here, the samples were stored in a cold room before processing.

2.2 Soil moisture content, pH, loss on ignition (LOI) and gamma ray analysis

Sub-samples of field moist soil (5 - 10 g) were used to determine moisture content (by oven drying at 105°C), pH and loss on ignition (LOI – the mass lost after combustion at 550°C as a proxy for total soil organic matter). Air-dried sub-samples (10 g) were used to determine total ^{137}Cs activity concentrations using a Canberra-Packard gamma-spectrometer with a high-purity germanium (HPGe) detector (GC 3019). A standard source (OISN-16; Applied Ecology Laboratory of Environmental Safety Centre, Odessa, Ukraine) containing ^{152}Eu was used to calibrate the efficiency of the detector. Sample count rates were not decay corrected so represent activity concentrations just after the time of sampling. Sub-samples of the remaining field-moist soils were subject to a sequential extraction procedure, as described below.

2.3 Sequential extraction of soils

The extraction method is based on one published by Zhao and McGrath (1994) for sulphate extraction that was subsequently adapted by Martens and Suarez (1997) for Se extraction. The method is designed to extract soluble iodine species using 0.01M KCl, then specifically adsorbed species using 0.18M KH_2PO_4 and finally organically-bound iodine using 2.5M NaOH. A mass of each field moist soil sample equivalent to 6 g oven-dry material was weighed into a polythene centrifuge tube. After adding 30 mL of 0.01M KCl to each tube, the tubes were shaken for approximately 16 h then centrifuged at 3,500 rpm for 30 minutes. The supernatants were carefully removed using a syringe and filtered through a 0.22 µm PTFE filter. A 19.8 mL aliquot of filtered KCl extract was pipetted into a polythene tube and 0.2 mL of 10% w/v NaOH added to stabilise the iodine in the extract. The excess supernatant was carefully removed and 30 mL 0.18M KH_2PO_4 added to the remaining soil pellets. The tubes were shaken vigorously by hand to disaggregate the pellets and then shaken gently for approximately 16 h. The soil suspensions were centrifuged at 3,500 rpm for 30 minutes before removing and filtering the supernatants, as for the first extraction step. An aliquot (19.8 mL) of filtered KH_2PO_4 extract was pipetted into a polythene tube and stabilised with 0.2 mL of 10% w/v NaOH. After removing the excess supernatant the remaining soil pellets were subjected to a third and final extraction in 15 mL of 10% w/v (2.5M) NaOH, added to each centrifuge tube. The tubes were shaken to disaggregate the pellet then loosely capped, placed in a rack and incubated at a maximum temperature of 90°C for approximately 16 hours. After incubation, the tubes were centrifuged at 3,500 rpm for 30 minutes then 2 mL of NaOH extract removed and transferred to a clean polythene tube. The NaOH extracts were diluted with 18 mL of ultrapure water to give a solution of 1% w/v NaOH. After each extraction step the tubes containing the respective extracts were capped and sealed with Parafilm® prior to transport to the UK. A flow diagram illustrating the sequential extraction procedure is provided in Supplementary Materials (Figure S1).

2.4 Analysis of stable iodine (^{127}I) and preparation of reagent blanks for ^{129}I

Small aliquots (<2 mL) of each extract were taken from each sample tube in a laboratory in the UK (*University of Nottingham*); the time during which the vials were open to the laboratory atmosphere was of the order of 2 minutes. These aliquots were used to analyse ^{127}I by ICP-MS (Thermo-Fisher Scientific, iCAP-Q) with Rh and Re (10 mg L^{-1}) as internal standards for drift correction. Stock standards for ^{127}I calibration were prepared at iodine concentrations of 1000 mg L^{-1} from oven-dried KI and KIO_3, and stored at 4°C in 1% tetra methyl ammonium hydroxide (TMAH). Two vials containing 20 mL of 0.5M (2% w/v) NaOH were left open in the laboratory for 48 hours to assess the (worst case) contamination from ^{129}I which had previously been used as a tracer in this laboratory; these were used as reagent blanks when preparing AgI targets for ^{129}I analysis (see below). The remaining soil extracts and reagent blanks were sealed in the polythene tubes and transported to the *Technical University of Denmark* for separation of ^{129}I from each extract and preparation of targets for AMS measurement of ^{129}I.

2.5 Preparation of targets for AMS measurement of ^{129}I

Aliquots of 5.0-18 mL of each extract were transferred to a beaker and the mass of solution recorded. A carrier solution of ^{127}I (1.802 mg mL^{-1}) was prepared by dissolving iodine crystal (Woodward Company, USA; $^{129}I/^{127}I$ ratio $< 2 \times 10^{-14}$) in a solution consisting of 0.4 M NaOH and 0.05 M $NaHSO_3$. A 0.5 mL aliquot of this carrier was added to the sample, followed by 8M NaOH to achieve a NaOH concentration of 0.5 M. The beaker was covered with a watch glass then heated at 60°C for 10-12 h to convert all organic iodine to an inorganic form. After cooling, 0.5 mL of 1M $NaHSO_3$ solution was added and the pH adjusted to <2 using 3M HNO_3, to convert all iodine to iodide. The sample solution was then transferred to a separation funnel to which 20-30 mL of $CHCl_3$ were added, followed by addition of 0.5-0.8 mL of 1M $NaNO_2$ to oxidize iodide to I_2. Iodine as I_2 was extracted into the organic phase which was then separated and collected in a beaker. The organic extraction step was repeated by adding another 15 ml aliquot of $CHCl_3$ to the separation funnel, plus 0.1 ml of 1M $NaNO_2$, and the two organic phase extracts were combined. The $CHCl_3$ phase solution was then transferred to another separation funnel to which were added 0.2 ml of 0.05M $NaHSO_3$ and 15 ml H_2O to reduce I_2 to iodide (I^-) and back extract it into aqueous phase, after which the organic phase was discarded. These organic solvent extraction and back-extraction steps were repeated, leaving an aqueous phase containing iodide. This was transferred from the separation funnel to a 10 mL centrifuge tube. The funnel was then washed three times with water and the washings combined in the centrifuge tube.

A 1 mL aliquot of 3M HNO_3 was added to the centrifuge tube, followed by 0.5 mL of 1M $AgNO_3$ to form a AgI precipitate which was then separated by centrifugation. After washing the AgI precipitate with water it was centrifuged again, then transferred with 0.5 mL water to a 1.4 mL centrifuge tube. The original centrifuge tube was washed and the washings combined with the AgI precipitate. This was centrifuged and the supernatant discarded. Finally, the AgI precipitate was dried at 60°C for 2-3 hours in readiness for AMS measurement of ^{129}I.

2.6 Analysis of ^{129}I by Accelerator Mass Spectrometry

After preparation, the AgI targets were transported to the *Scottish Universities Environmental Research Centre (UK*) where ^{129}I concentrations were determined using a tandem accelerator mass spectrometer (AMS), as previously described by Xu *et al*. (2013). The AgI precipitates from each sample were mixed with high purity Ag powder (100 mesh, 99.95%, Assure) with a mass ratio 1:2 for AgI:Ag and then pressed into an aluminium target holder (1 mm ∅). Iodide (I^-) ions were extracted using a Cs-sputtering ion source. A terminal voltage of 3 MV was used and I^{5+} ions selected for detection. The $^{127}I^{5+}$ ions were detected using a Faraday cup mounted at the exit of a high energy analyzing magnet, while $^{129}I^{5+}$ ions were counted using an ionization chamber detector with a 100 nm thick SiN detector window. Dissociation of MoO_2^- can produce $^{97}Mo^{4+}$ which may interfere with

$^{129}I^{5+}$ measurement due to a similar magnetic rigidity (ME/q^2); however, the two ions can be completely separated in the detector. The measured $^{129}I/^{127}I$ ratios were corrected against a standard material with $^{129}I/^{127}I$ ratio of 1.138×10^{-10} prepared by ^{127}I addition to the NIST 4949B standard. The measured $^{129}/^{127}I$ ratios in the prepared targets ranged from 2.9×10^{-11}–3.5×10^{-9}, which are higher than the mean of the reagent and laboratory blanks (1.1×10^{-11}) and the estimated pre-atomic ratio (1.5×10^{-12}) (Moran et al., 1999). I-129 concentrations in the samples was calculated based on the amount of ^{127}I carrier added to the samples before chemical separation and the measured $^{129}I/^{127}I$ atomic ratios after subtracting the background of the reagent and laboratory blanks. Uncertainties on measured $^{129}I/^{127}I$ ratios in samples ranged from 0.4–2.8%. After subtracting $^{129}I/^{127}I$ ratios attributable to the reagent blank, a limit of detection (LoD) of 2.0×10^5 ^{129}I atoms per sample was calculated. I-129 in all samples was above this LoD, ranging from 7.7×10^7 – 5.3×10^{10} atoms per sample.

3. Results and Discussion

3.1 Total concentrations of ^{127}I and ^{129}I in CEZ soils

Total concentrations of ^{127}I and ^{129}I in our samples were calculated by summing the concentrations determined in KCl, KH_2PO_4 and NaOH extracts (see Supplementary Material); concentrations were expressed as either mass concentrations (for both ^{127}I and ^{129}I) or activity concentrations (for ^{129}I) per unit dry weight of soil. Total concentrations of stable iodine (^{127}I) in the CEZ soils ranged from 1.54×10^{-7} g g^{-1} in the B1 subsoil to 2.64×10^{-6} g g^{-1} in the RF3 topsoil, with a geometric mean (GM) of 6.7×10^{-7} g g^{-1} (Figure 2(i), Table 2). This range is below the average soil concentration of 3.94 mg kg^{-1} (3.94×10^{-6} g g^{-1}) for iodine in European soils (Salminen et al., 2005) and at the lower end of the range for world soils (Fleming, 1980). Sahoo et al. (2009) took soil samples in 1994/95 and 2001 from sites in the CEZ which covered a very similar geographical range to the samples we took in 2015; soils and vegetation types at the sampling sites are almost identical between the two studies. They also reported low ^{127}I concentrations in CEZ soils (mean = 5.4×10^{-7} g g^{-1}) similar to the concentrations we determined. Shiraishi et al. (2006) found that dietary intake of iodine by residents in NW Ukraine was below the WHO recommended value of 150 µg d^{-1} for adults and was linked to increased occurrence of goitre; this probably reflects low mean regional iodine concentrations which are likely to increase exposure to environmental sources of radioactive iodine. Total mass concentrations of ^{129}I in the CEZ soils ranged from 2.40×10^{-14} g g^{-1} in the B1 subsoil to 3.83×10^{-12} g g^{-1} in the RF3 topsoil, with a GM of 2.39×10^{-13} g g^{-1} (Figure 2(ii), Table 2). When expressed as activity concentrations this range was 0.16 to 25 mBq kg^{-1} with a GM of 1.56 mBq kg^{-1} (Figure 2(iii), Table 2). Sahoo et al. (2009) reported a range of 1.7 to 168 mBq kg^{-1} in soils from the CEZ, with the highest activity concentrations in surface soil samples including forest litter and organic horizons. The slightly lower activity concentrations in our study are consistent with the fact that our samples were averaged across soil depths of 0-10 and 10-20 cm. For the same reason, the range of ^{129}I/^{137}Cs atom ratios in our samples (0.011 – 0.566, Table 3) is lower than the ranges reported by Hou et al. (2003) and Sahoo et al. (2009) (overall range from 0.1 to 7.2), though all three ranges overlap. Mironov et al. (2002) determined an average pre-Chernobyl activity concentration for ^{129}I of 0.094 (± 0.014) mBq kg^{-1} in subsoil samples collected 400 km north of Chernobyl in 1985; ^{129}I activity concentrations in all our samples were significantly higher than this and we conclude that the ^{129}I we measured originated from the Chernobyl reactor. A further indication of the source of ^{129}I in our study is given by the strong and highly significant correlation between ^{129}I and ^{137}Cs activity concentrations in the samples (Figure 3); a similar relationship has previously been proposed as a means of estimating ^{131}I deposition densities in areas of Russia, Belarus and Sweden contaminated by the Chernobyl accident (Hou et al., 2003).

3.2 Relationships between ^{127}I, ^{129}I and organic matter in CEZ soils

The RF3 site is a peaty meadow (Table 1) at the western extremity of the Red Forest and the soil here had the highest organic matter content (LOI) of all the samples taken (Table 3), as well as the highest ^{127}I and ^{129}I concentrations (Table 2). Overall, there was a significant positive relationship (Pearson R = 0.73; Spearman rank p = 0.037) between ^{127}I and soil organic matter (Figure 4(i)), as expected from previous studies on soil iodine (eg. Yamada et al., 1999; Xu et al., 2016; Soderlund et al., 2017). Total concentrations of ^{127}I and ^{129}I were positively and significantly correlated (Figure 5) which probably results from a similar tendency for retention of both isotopes in soils with similar organic matter contents. However, the relationship between ^{129}I and soil LOI (not shown) was much weaker (Pearson R = 0.44) than for ^{127}I versus LOI. Spearman rank correlation indicated an insignificant relationship between ^{129}I and soil LOI (p = 0.22); when the RF3 data points were removed the slope of the relationship was effectively zero, suggesting that the variations in ^{129}I concentrations in the soil are due primarily to the initial deposition pattern in 1986 rather than the properties of the soil on which the ^{129}I was deposited.

3.3 Topsoil versus subsoil concentrations of ^{127}I and ^{129}I in CEZ soils

Total topsoil concentrations of ^{129}I and ^{127}I were generally higher than subsoil concentrations, but not at all sampling sites; ^{129}I concentrations were greater in topsoils at more sites than ^{127}I and the differences between top- and subsoil concentrations were higher for ^{129}I than for ^{127}I (Table 2). Furthermore, ratios of total ^{129}I/^{127}I were higher in topsoils than in sub-soils at all sites except RF1 (Table 2), indicating that proportionally more of the ^{129}I deposited to the soil surface in 1986 was still present in the topsoil. Sahoo et al. (2009) reported generally declining ^{127}I and ^{129}I concentrations from the soil surface to a depth of 15-20 cm in samples taken on the North Trace in 2001. However, some downwards migration of ^{129}I must have occurred in the 30 year period following the Chernobyl accident. Independent estimates of ~30 years have been made for the residence half-times of ^{129}I in the upper 30 cm of soil profiles at Savannah River (Boone et al. 1985) and the Karlsruhe reprocessing plant (Robens et al., 1989) suggesting that significant downwards migration of ^{129}I in CEZ soils is possible since initial deposition in 1986. This is supported by the observation that the ^{129}I/^{137}Cs atom ratios in topsoils are lower than those in subsoils for 7 of the 9 soils sampled in this study, which indicates that ^{129}I has moved faster than ^{137}Cs from the topsoil to the subsoil. Leaching of a portion of the originally deposited ^{129}I from the upper 20 cm of the soils sampled cannot be excluded, which would partially explain the slightly lower total ^{129}I activity concentrations we measured compared with previous studies, as discussed in section 3.1. Approximate estimates of the magnitude of ^{129}I leaching below a depth of 20 cm may be possible by comparing ^{129}I activity concentrations measured by Sahoo et al. (2009) and in our study. Furthermore, if the rate of ^{137}Cs leaching were known than the comparative rate of ^{129}I could be calculated using the ^{129}I/^{137}Cs atom ratios in Table 3. However, the only reliable way to quantify the degree of ^{129}I leaching deep into the soil profile is to take deeper soil samples for further analysis by AMS, which is beyond the scope of this study.

3.4 Sequentially-extractable concentrations of ^{127}I and ^{129}I in CEZ soils

We used 10% w/v (2.5 M) NaOH to recover humic matter and associated iodine isotopes from soil samples. Studies by Watts and Mitchell (2008) and Shetaya et al. (2012) have shown that strongly alkaline extractants such as TMAH and NaOH are effective in quantitatively extracting iodine from soils. Total concentrations of both ^{127}I and ^{129}I (defined above) were dominated by the NaOH-extractable fraction which represents iodine associated with soil organic matter (Figures 2(i) and 2(ii); see also Supplementary Material). In the case of ^{127}I, the organically-bound concentrations were significantly higher than both KCl and KH_2PO_4 extractable concentrations (Figure 2(i)) but not significantly different from the total ^{127}I concentration. The organically-bound concentrations of ^{129}I were significantly higher than the KCl extractable concentrations but not the KH_2PO_4 extractable concentrations (Figure 2(ii)). Extraction of soils with a weak electrolyte such as 0.01M KCl accesses the readily soluble pool within the soil; the dominant iodine species expected to reside in this pool are iodide (I^-) and iodate (IO_3^-). Yuita (1992) found that iodate accounted for >80% of the iodine in soil solutions from a brown forest soil under aerobic conditions, but only ~14% when the soil was flooded. In contrast, iodide accounted for ~6% of soluble iodine in non-flooded forest soil, increasing to >80% in flooded soil. At the time of sampling (September 2015) the CEZ soils were generally dry (gravimetric moisture contents ranged from <0.2% in the sandy B1 subsoil to 61% in the highly organic RF3 subsoil). Even though the soils of the CEZ are generally free-draining, they frequently flood after snow melt during early spring or for longer periods (eg. 2013-2014) so it is probable that soluble inorganic iodine species vary throughout the year. Laboratory studies by Shetaya et al. (2012) and Duborska et al. (2018) indicate that iodide and iodate are lost from soil solutions due to interactions with reactive surfaces such as hydrous oxides and humic molecules on time scales of minutes to hours and hours to days, respectively, suggesting that equilibration of inorganic iodine species in soil solution is complete on these time scales. Longer-term kinetics under environmental conditions cannot be ruled out, however.

Iodide interacts with anion-exchanging surfaces in soils by electrostatic interaction, iodate by chemisorption principally to metal hydrous oxides (Yoshida et al., 1995); extraction of soils with KH_2PO_4 provides a measure of iodide and iodate specifically adsorbed to sesquioxides of Fe, Al and Mn. The GM adsorbed ^{127}I concentration was significantly different (higher and lower, respectively) from GM soluble and organic ^{127}I concentrations (Figure 2(i)). However, the GM adsorbed ^{129}I concentration was significantly higher than soluble ^{129}I but not significantly different from organic ^{129}I concentrations (Figure 2(ii), (iii)), indicating a difference in the physico-chemical distribution of native ^{127}I and Chernobyl-derived ^{129}I.

3.5 Comparison of extractabilities of ^{127}I and ^{129}I in CEZ soils

The relationships between ^{127}I and ^{129}I in the soil extracts are summarised graphically as $^{129}I/^{127}I$ ratios in Figure 2(iv) and Figure 6. Figure 2(iv) shows that $^{129}I/^{127}I$ ratios in KCl and KH_2PO_4 extracts were not significantly different from each other, with GMs of 1.74×10^{-6} and 1.66×10^{-6}, respectively. The GM $^{129}I/^{127}I$ ratios in NaOH extracts were significantly lower (2.37×10^{-7}) and, since this was the dominant fraction (Figure 2(i) and 2(ii)), the GM of the total $^{129}I/^{127}I$ ratio was also significantly lower than the KCl and KH_2PO_4 extracts (2.94×10^{-7}). Figure 6 shows that the $^{129}I/^{127}I$ ratios in all soil extracts were positively and significantly related to the total ^{129}I concentrations in the soils. Since $^{129}I/^{127}I$ ratios for KCl and KH_2PO_4 extracts were not significantly different, a single regression line was fitted to these data in Figure 6. It is clear that $^{129}I/^{127}I$ ratios in KCl and KH_2PO_4 extracts are higher than in the NaOH extracts at all ^{129}I concentrations, indicating a preponderance of ^{129}I in more 'labile' soil extracts compared with soil organic matter (extractable with NaOH) which can be considered to be the long-term sink for iodine in soils. Bowley et al. (2016) observed that mixtures of I^- and IO_3^- in suspensions of humic acid were partially transformed to organic iodine over the course of 77 days. Kinetic modelling suggested a short half-time (~15 minutes) for conversion of IO_3^- to organic iodine, though this was balanced by a slower reverse reaction which led to a 'pseudo-steady-state' over a time scale up to 250 days. Size selective analysis of the humic polymer by Xu et al. (2012) showed proportionally less ^{129}I than native ^{127}I in the larger molecular weight humic fraction, attributable to insufficient reaction time for full isotopic equilibration and to partial exclusion of ^{129}I from the complex humic acid structure. Our results from samples collected almost 30 years after ^{129}I deposition in the CEZ suggest that full isotopic equilibration between ^{129}I and ^{127}I in soil humic molecules has not been achieved on a decadal time-scale.

Schmitz and Aumann (1995) found that ^{129}I was proportionally more water-soluble than ^{127}I in soils around the Karlsruhe reprocessing plant, which they explained by the much shorter residence time of ^{129}I in the soil compared with native ^{127}I. Surprisingly, only 4-15% of ^{129}I was found in the organic fractions of the Karlsruhe soils. In contrast, Hou et al. (2003) found approximately 40% of ^{129}I bound to organic matter in a soil sampled in Belarus (Gomel) in September 1999. Englund et al. (2008) found 50-85% of ^{129}I bound to organic matter in a Swedish lake sediment, while the proportion of organically associated ^{129}I in our CEZ soils ranged from 24-94%. The Englund et al. (2008) study found 5-8% of ^{129}I in water-soluble, exchangeable and carbonate fractions, combined. In our study, the combined KCl and KH_2PO_4 extractable fractions of ^{127}I and ^{129}I can be considered to represent 'labile' iodine. For ^{127}I, the magnitude of these combined fractions relative to the total iodine concentration ranged from 0.4% (in RF3 subsoil) to 20% (in RF1 topsoil). For ^{129}I, the range was from 6% (in RF1 and RF3 subsoils) to 76% (in RF2 topsoil). In the case of ^{127}I, the ratio was significantly and negatively correlated with LOI (Figure 4(ii)) whereas for ^{129}I there was no significant relationship with LOI – another indication of differences in behaviour of the two nuclides in the same soils.

3.6 Consideration of the initial physico-chemical form of ^{129}I deposited in 1986

The initial physico-chemical form of radionuclides deposited from the atmosphere can have a major impact on their long-term behaviour in the environment, but we can only speculate about the exact physico-chemical form of ^{129}I when it first contacted the CEZ soils. Radioactive deposits in the highly contaminated western and northern traces of the CEZ were mostly in the form of irradiated reactor fuel fragments, referred to as 'hot particles' (Sandalls et al., 1993). Even though we sampled almost

30 years after deposition we have found clear autoradiographic evidence (Supplementary Materials S2) of the existence of hot particles in our soil samples. When Vapirev et al. (1990) analysed a hot particle from Chernobyl they found it to be depleted of ^{131}I. At the very high temperatures prevalent during the accident in 1986 radioactive iodine would have been released to the atmosphere in the gas phase; indeed, in less severe accidents in which only volatile radionuclides were released from reactor cores (Windscale, Three Mile Island) radioisotopes of iodine constituted major proportions of the release inventories (Crick and Linsley, 1984; Toth et al., 1986). Volatile radioiodine released to the atmosphere from Chernobyl is thought to have been progressively sorbed to aerosol particles on a time scale of approximately 45-50 days (Maryon et al., 1991); this is too long for this process to have influenced radio-iodine deposition in the CEZ. Weather records from Chernobyl indicate that, apart from very slight (0.4 mm) rainfall on 27th April, there was no significant precipitation at the time of the accident and in the following days up to May 3rd when records stop (NOAA, 2018). In the vicinity of the reactor, gaseous ^{129}I would have been subject to dry deposition to vegetation surfaces, followed by weathering and transfer to the underlying soil over the following weeks. In forests close to Fukushima, Xu et al. (2016) have shown that, in comparison to rainwater, ^{127}I is concentrated in throughfall and stemflow and that it is entirely in organic form in these sub-canopy waters. Although we do not know the exact physico-chemical form of ^{129}I deposited on CEZ soils in 1986 it is highly probable that it was not ‘bound’ within the uranium oxide particles which are a unique characteristic of the CEZ.

4. Conclusions

Contamination of the CEZ can be precisely dated to the 10 day period from 26th April to 5th May 1986. Any delay in the introduction of ^{129}I to soils as deposits were weathered from vegetation canopies, would have been over a period of weeks. The CEZ therefore provides the opportunity to quantify the long-term behaviour of radioactive iodine under real-world conditions following a well-defined pulse injection. Our observation that full isotopic equilibrium between the native ^{127}I and

^{129}I has not been achieved after 29 years indicates that complete mixing between the nuclides is a very long-term process. This contrasts with the observations of most laboratory incubation experiments which suggest that interaction of iodine species with organic and inorganic soil components is complete within a period of days (Duborska et al., 2019) to months (Bowley et al., 2016). Our data show that ^{129}I remains more mobile and more bioavailable than ^{127}I three decades after the Chernobyl accident, which has implications for the use of native, stable iodine as a proxy for assessments of the radiation doses attributable to ^{129}I, certainly on a decadal time scale and perhaps longer.

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Site Name	Site Code	Brief description	Dose rate* (μGy h^{-1})	Latitude & Longitude (decimal degrees)
Red Forest 1	RF1	Regenerated birch forest	66	51.3851°N 30.0621°E
Red Forest 2	RF2	Pine forest	8	51.3867°N 30.0623°E
Red Forest 3	RF3	Peaty meadow	45	51.3823°N 30.0280°E
North Trace 1	NT1	Pine forest	6	51.4585°N 30.0534°E
North Trace 2	NT2	Peaty meadow	6	51.4560°N 30.0520°E
Chistogalovka	C	Abandoned meadow	-	51.3765°N 30.0239°E
Bourakovka 1	B1	Birch forest	6	51.3799°N 30.9138°E
Bourakovka 2	B2	Pine forest	6	51.3799°N 30.9112°E
Tolsty Les	TL	Abandoned meadow	2	51.3844°N 29.7901°E

Table 1: Sampling locations and characteristics. (* Air kerma rate determined 1 m above ground level at the time of sampling.)

Sample code	^{127}I g g^{-1} soil	^{129}I g g^{-1} soil	^{129}I mBq kg^{-1} soil	^{129}I / ^{127}I Ratio ‡
RF1$_{top}$	9.52×10^{-7}	4.23×10^{-13}	2.76	4.44×10^{-7}
RF1$_{sub}$	9.89×10^{-7}	1.40×10^{-12}	9.14	1.41×10^{-6}
RF2$_{top}$	6.68×10^{-7}	3.29×10^{-13}	2.15	4.93×10^{-7}
RF2$_{sub}$	6.62×10^{-7}	2.52×10^{-13}	1.65	3.80×10^{-7}
RF3$_{top}$	2.64×10^{-6}	3.83×10^{-12}	25.0	1.45×10^{-6}
RF3$_{sub}$	2.14×10^{-6}	4.52×10^{-13}	2.95	2.11×10^{-7}
NT1$_{top}$	7.14×10^{-7}	5.23×10^{-13}	3.42	7.33×10^{-7}
NT1$_{sub}$	7.51×10^{-7}	1.05×10^{-13}	0.69	1.40×10^{-7}
NT2$_{top}$	1.00×10^{-6}	1.80×10^{-13}	1.18	1.80×10^{-7}
NT2$_{sub}$	3.77×10^{-7}	3.23×10^{-14}	0.21	8.56×10^{-8}
C$_{top}$	5.71×10^{-7}	3.74×10^{-13}	2.44	6.55×10^{-7}
C$_{sub}$	7.18×10^{-7}	1.55×10^{-13}	1.01	2.16×10^{-7}
B1$_{top}$	4.45×10^{-7}	3.84×10^{-13}	2.51	8.63×10^{-7}
B1$_{sub}$	1.54×10^{-7}	2.40×10^{-14}	0.16	1.55×10^{-7}
B2$_{top}$	9.44×10^{-7}	5.42×10^{-13}	3.54	5.74×10^{-7}
B2$_{sub}$	5.23×10^{-7}	1.47×10^{-13}	0.96	2.81×10^{-7}
TL$_{top}$	3.29×10^{-7}	1.30×10^{-13}	0.85	3.95×10^{-7}
TL$_{sub}$	3.43×10^{-7}	4.20×10^{-14}	0.27	1.22×10^{-7}
Geometric Means	6.70×10^{-7}	2.39×10^{-13}	1.56	3.56×10^{-7}

Table 2: Total concentrations of ^{127}I and ^{129}I in soil samples from the Chernobyl Exclusion Zone (September 2015) calculated by summing concentrations determined in KCl, KH_2PO_4 and NaOH extracts. ‡ ^{129}I / ^{127}I ratios were calculated using the total mass concentrations (g g^{-1}) of ^{129}I and ^{127}I in soils expressed on a dry weight basis. All of the ^{129}I concentrations were above the pre-Chernobyl background ^{129}I concentration for the region (of 0.094 mBq kg^{-1} determined by Mironov et al., 2002).

Site Name	**Sample Code**	**^{137}Cs (kBq / kg)**	**^{129}I / ^{137}Cs atom ratio**	**LOI (% DW)**	**pH (H_2O)**
Red Forest 1	$RF1_{top}$	53.0	0.028	2.5	5.04
	$RF1_{sub}$	29.0	0.167	1.3	4.62
Red Forest 2	$RF2_{top}$	15.5	0.074	4.3	4.18
	$RF2_{sub}$	6.0	0.145	1.6	5.57
Red Forest 3	$RF3_{top}$	656	0.020	71.7	4.66
	$RF3_{sub}$	100	0.016	82.1	4.16
North Trace 1	$NT1_{top}$	50.0	0.036	4.0	4.49
	$NT1_{sub}$	32.0	0.011	2.9	4.95
North Trace 2	$NT2_{top}$	53.0	0.012	13.3	5.69
	$NT2_{sub}$	2.6	0.043	5.5	5.39
Chistogalovka	C_{top}	17.2	0.075	5.7	4.84
	C_{sub}	3.7	0.145	5.9	4.91
Bourakovka 1	$B1_{top}$	25.0	0.053	4.7	3.91
	$B1_{sub}$	0.4	0.189	1.4	4.03
Bourakovka 2	$B2_{top}$	45.0	0.042	4.9	4.02
	$B2_{sub}$	0.9	0.566	2.8	4.15
Tolsty Les	TL_{top}	10.0	0.045	1.7	4.86
	TL_{sub}	0.4	0.331	1.5	4.35

Table 3: Total activity concentrations of ^{137}Cs (expressed on a dry weight basis), loss on ignition (LOI – a proxy for soil organic matter) and pH in soil samples. The ^{129}I / ^{137}Cs atom ratios were calculated using total ^{137}Cs activity concentrations and the total ^{129}I activity concentrations reported in Table 2.

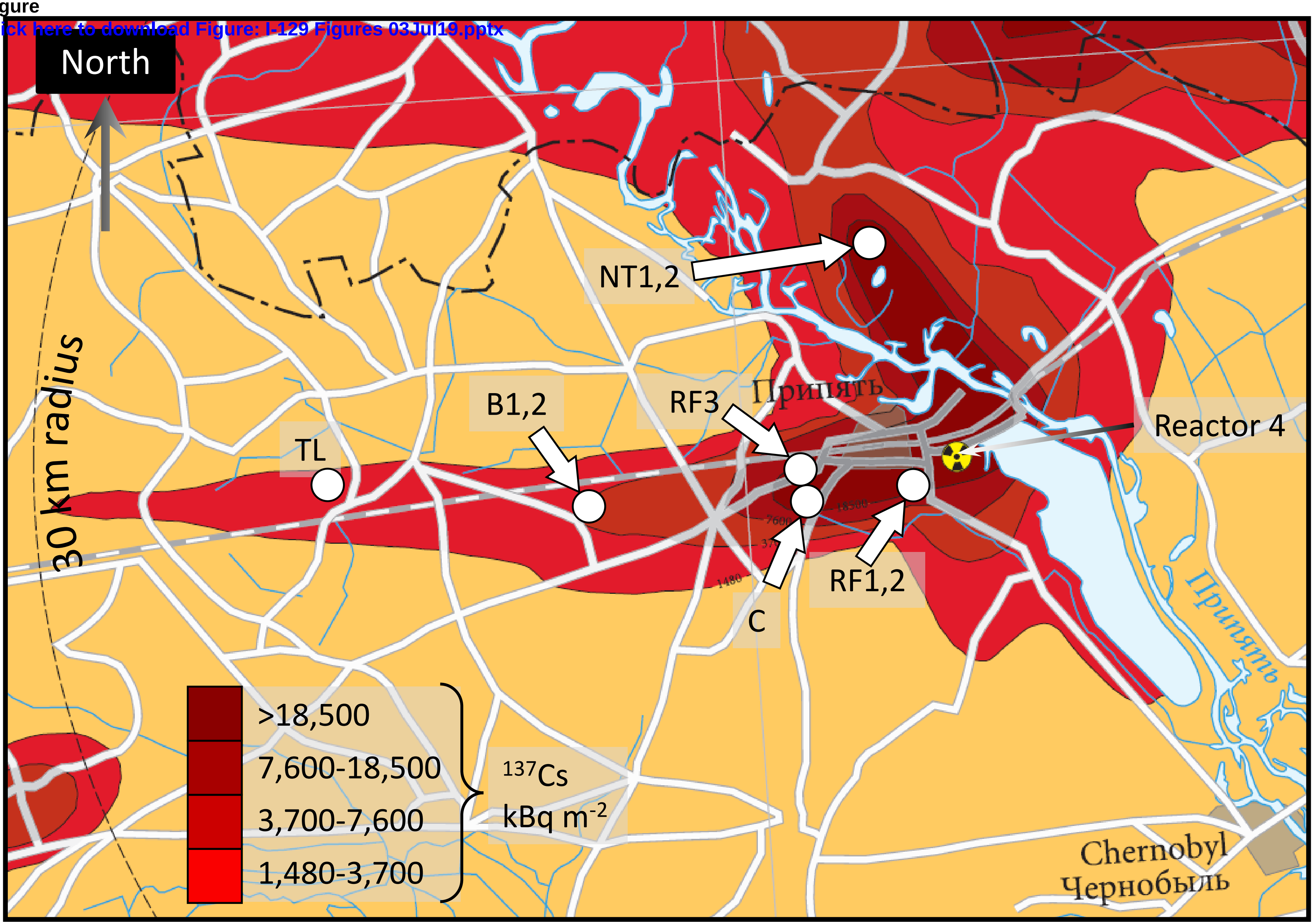


Figure 1: Sampling locations (◯) within the Chernobyl Exclusion Zone (base map from De Cort et al., 1998). The scale is shown by the 30 km radius from the reactor, visible along the western edge of the map. Codes for sampling sites are shown in Table 1.

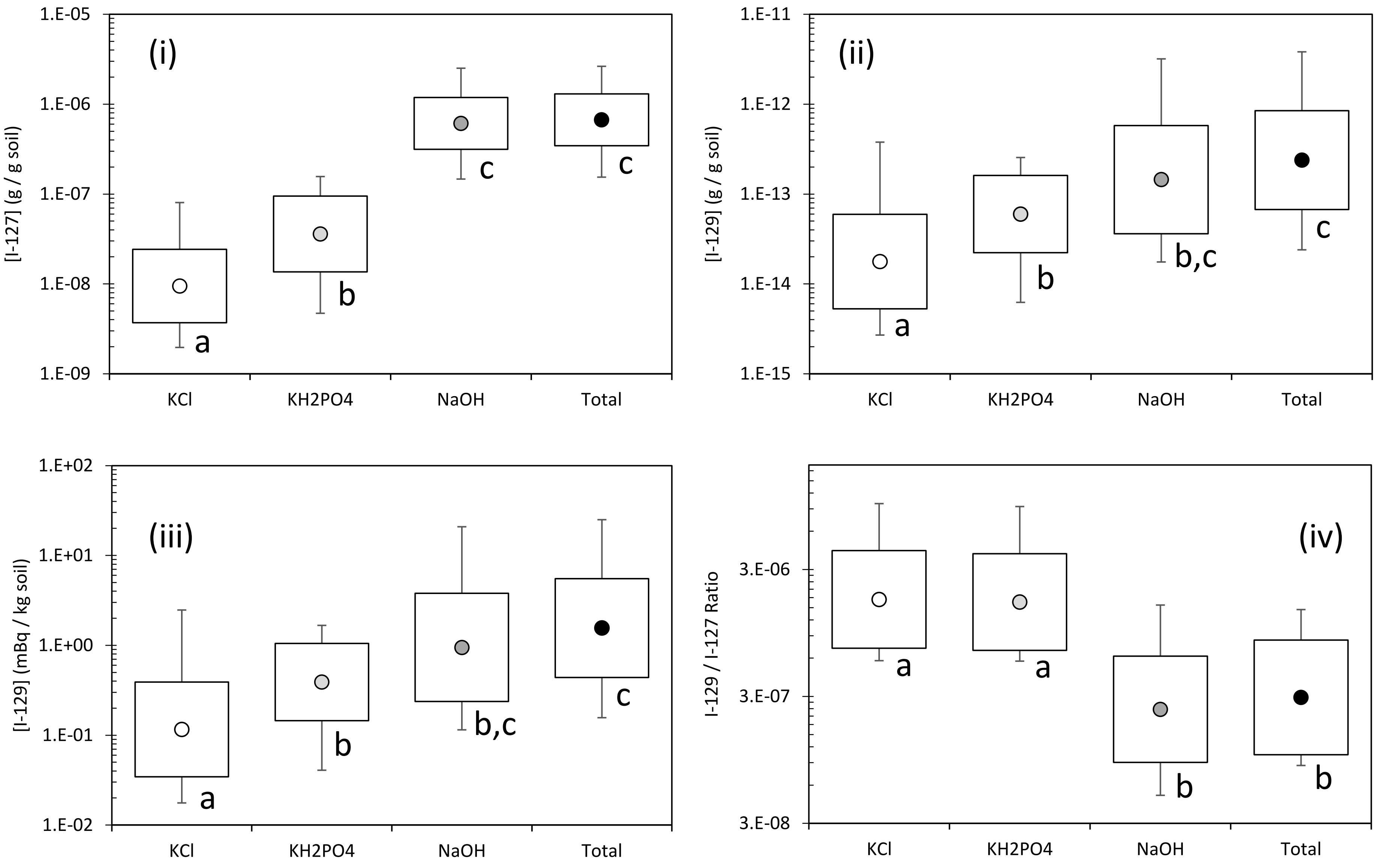


Figure 2: I-127 and ^{129}I concentrations (i, ii and iii) and ^{129}I / ^{127}I ratios (iv) in soil extracts from CEZ. Points represent geometric means, boxes represent ±1 geometric standard deviation and whiskers represent maxima and minima. Points with different letters are significantly different based on Tukey pairwise comparisons following ANOVA of Ln-transformed data.

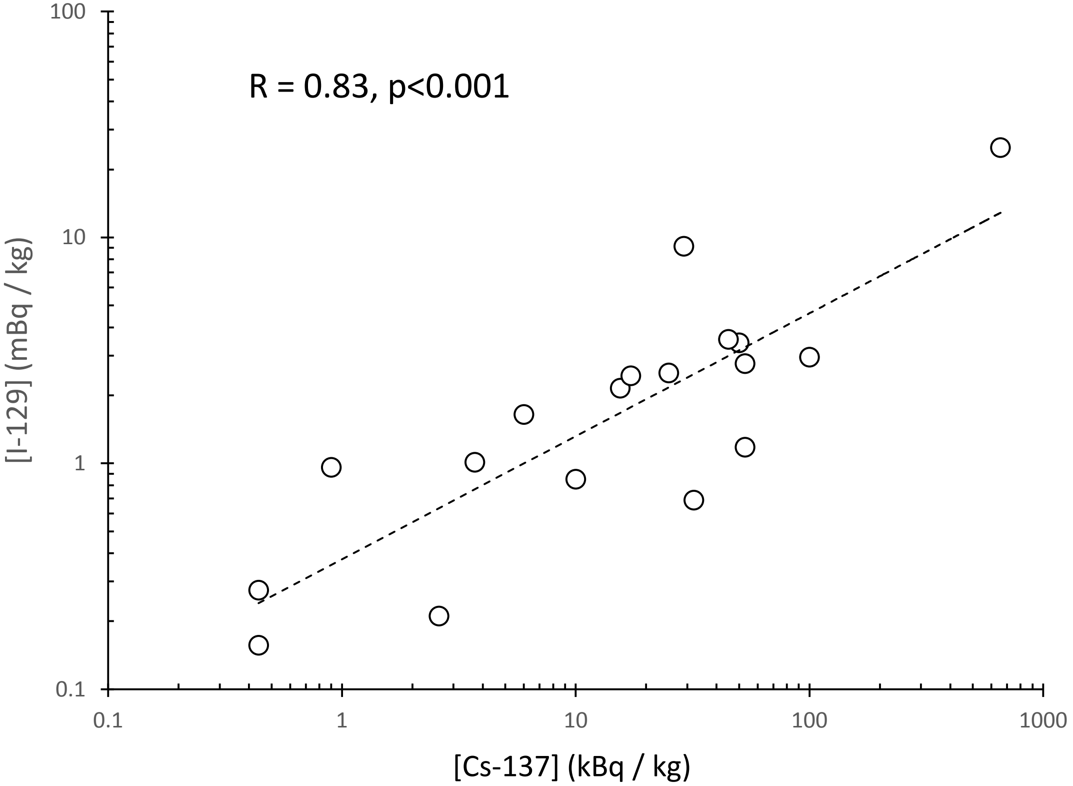


Figure 3: Relationship between ^{129}I and ^{137}Cs activity concentrations in soils from the CEZ. Both Pearson (R=0.83) and Spearman Rank correlations were highly significant (p<0.001 for both).

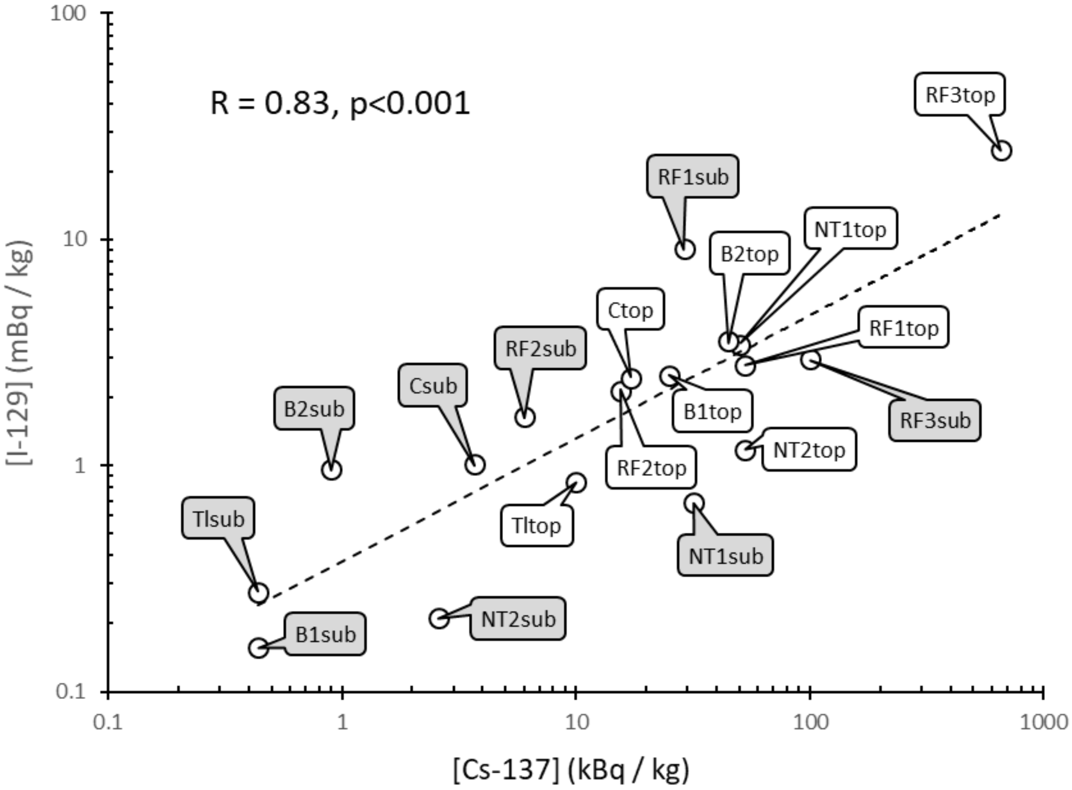


Figure 3: Relationship between ^{129}I and ^{137}Cs activity concentrations in soils from the CEZ. Both Pearson (R=0.83) and Spearman Rank correlations were highly significant (p<0.001 for both).

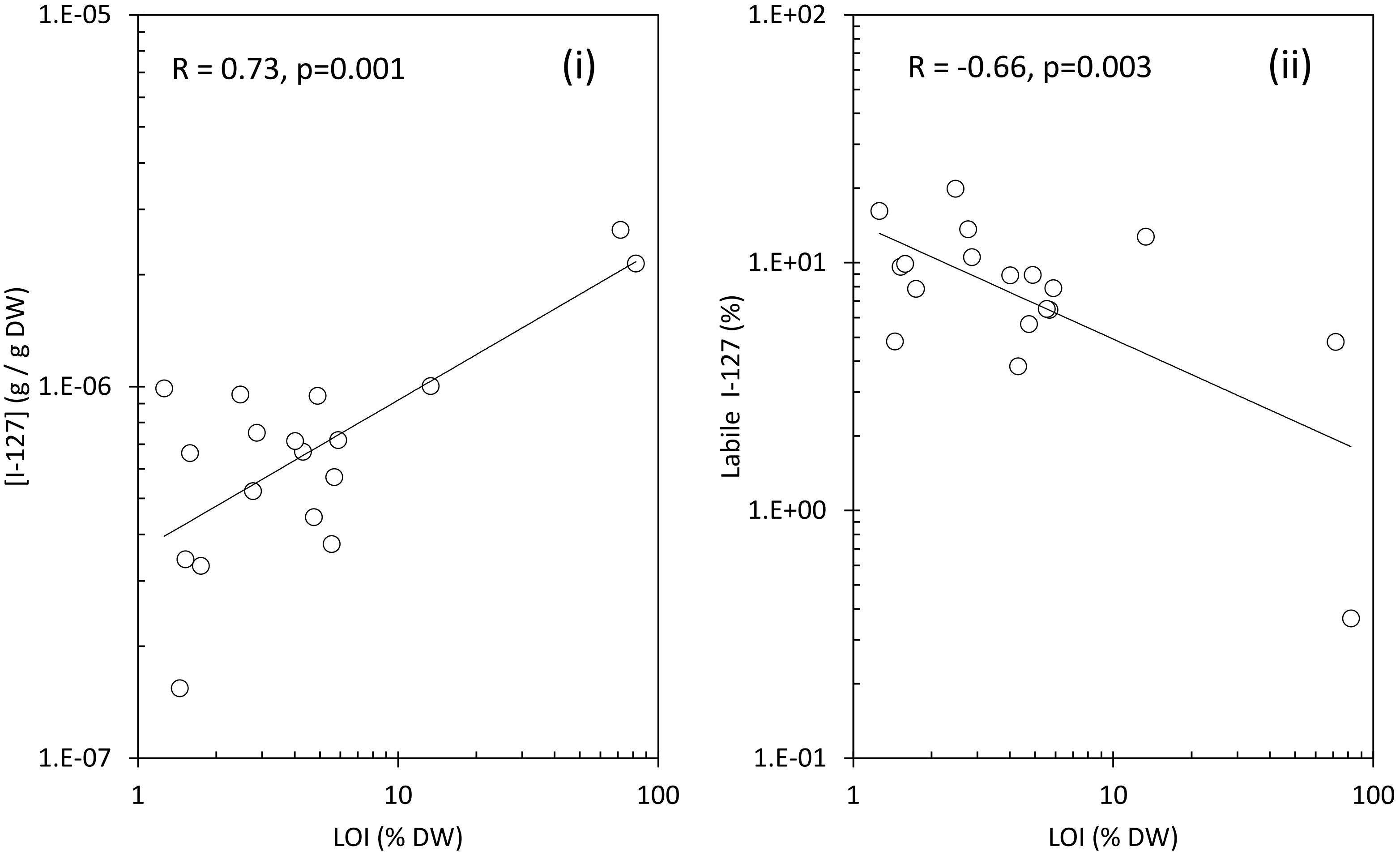
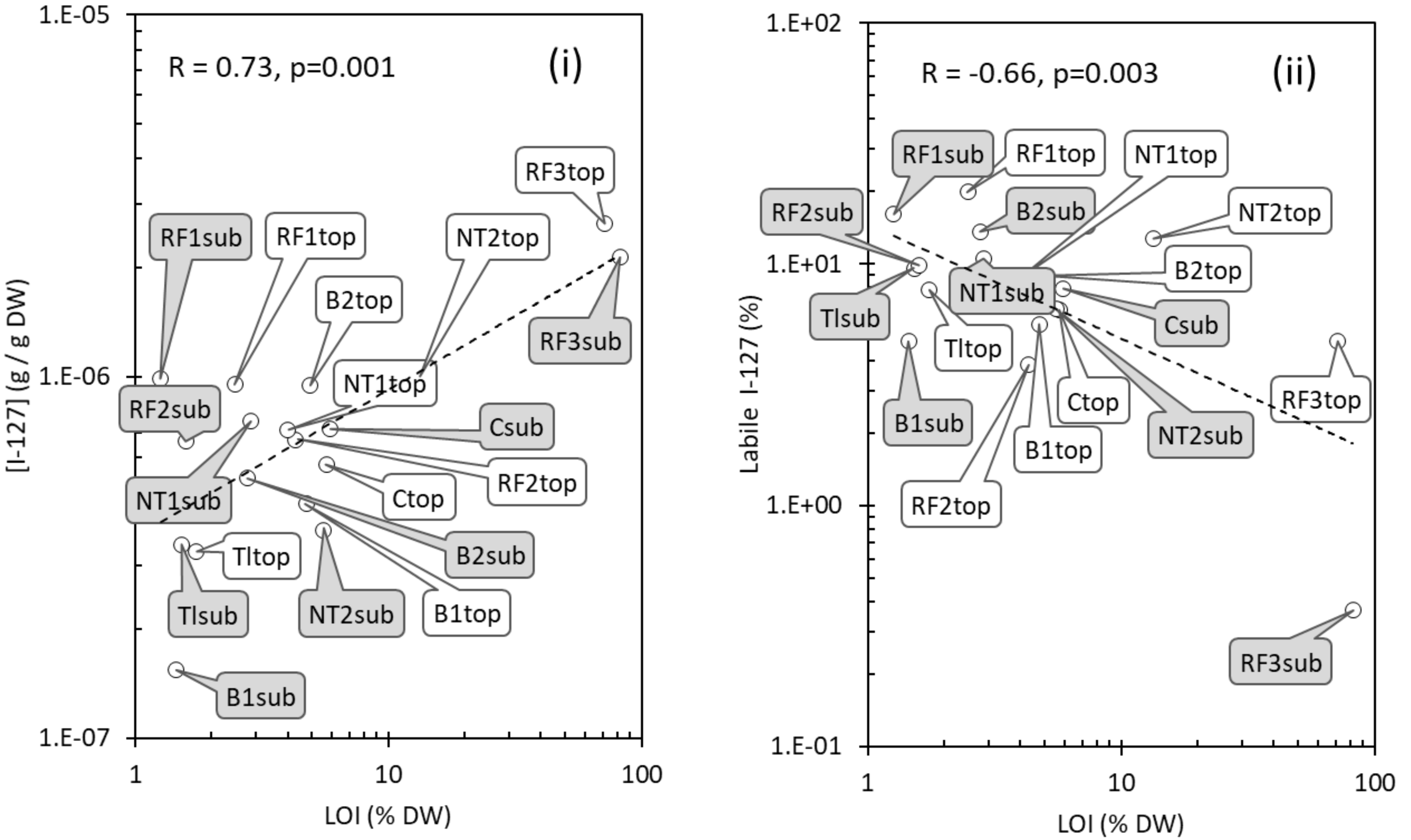


Figure 4: (i) Total concentration of ^{127}I (g g^{-1} DW) vs LOI (as a proxy for organic matter) in soils from the CEZ. The Spearman rank correlation was significant at p = 0.037 (p=0.223 for ^{129}I versus LOI). (ii) Percentage labile (KCl + KH_2PO_4 extractable) ^{127}I vs LOI. Spearman rank correlation was p = 0.054 (p = 0.94 for ^{129}I ratio vs LOI).



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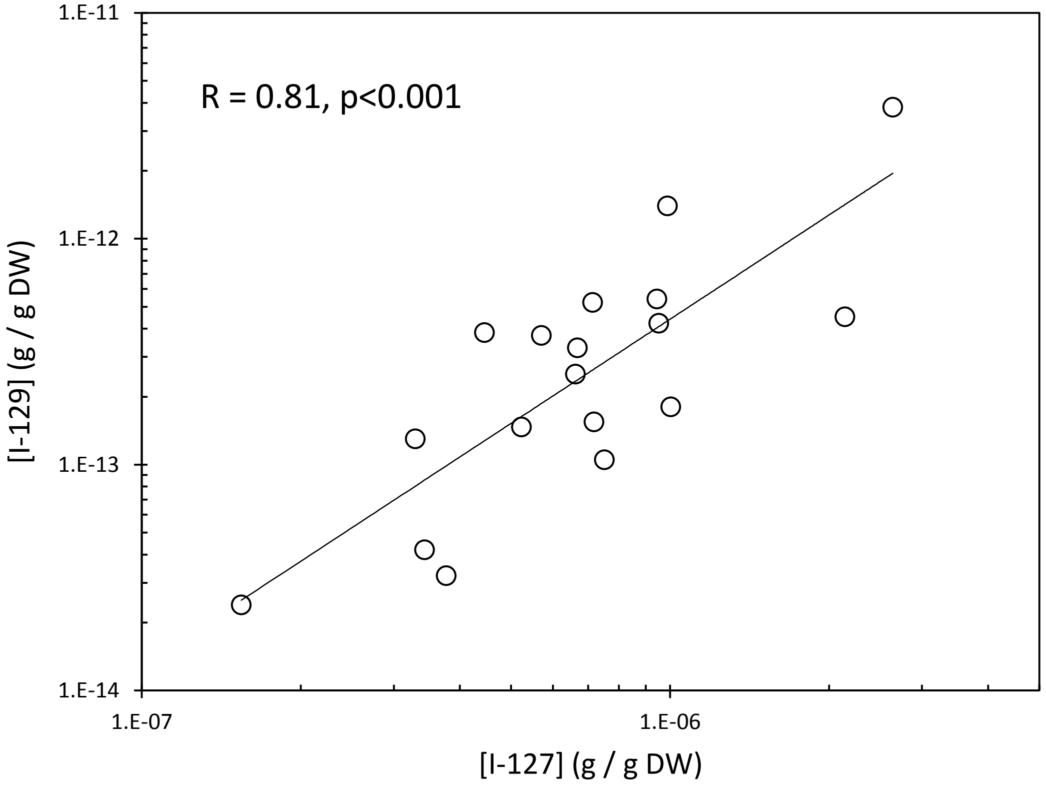

Figure 5: Relationship between TOTAL ^{127}I and ^{129}I (g g^{-1} DW) concentrations in soils from the CEZ. Both Pearson (R=0.81) and Spearman Rank correlations were highly significant (p<0.001 and p=0.001, respectively).

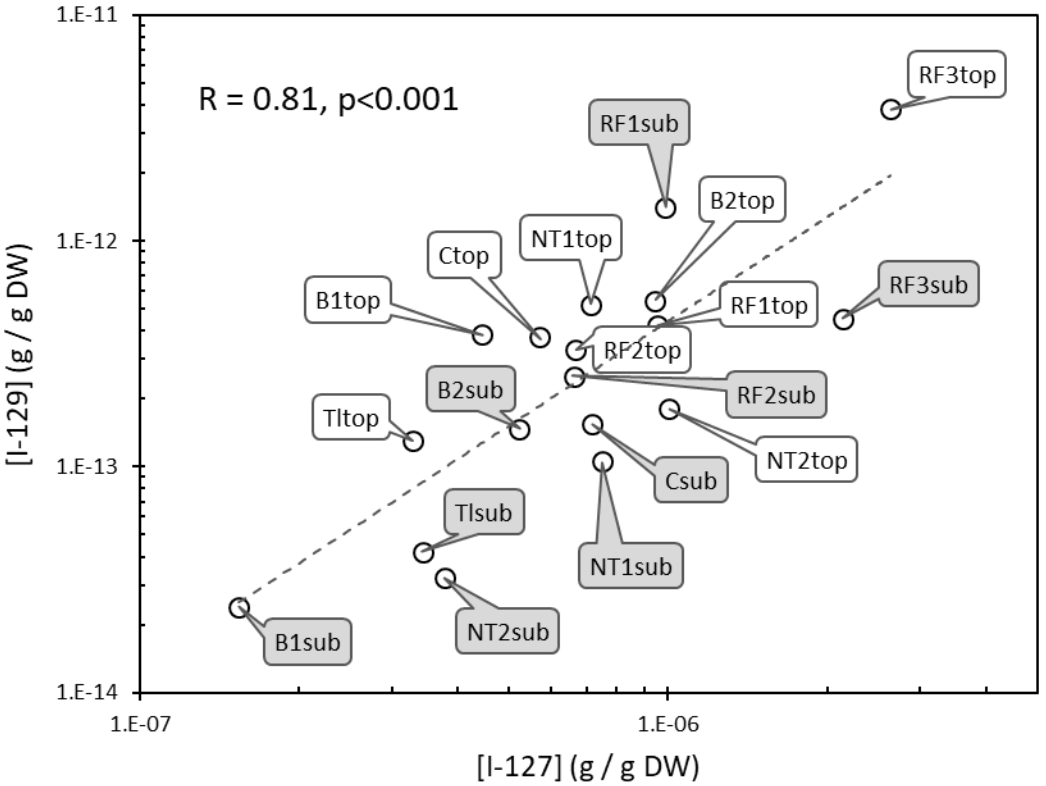

Figure 5: Relationship between TOTAL ^{127}I and ^{129}I (g g^{-1} DW) concentrations in soils from the CEZ. Both Pearson (R=0.81) and Spearman Rank correlations were highly significant (p<0.001 and p=0.001, respectively).

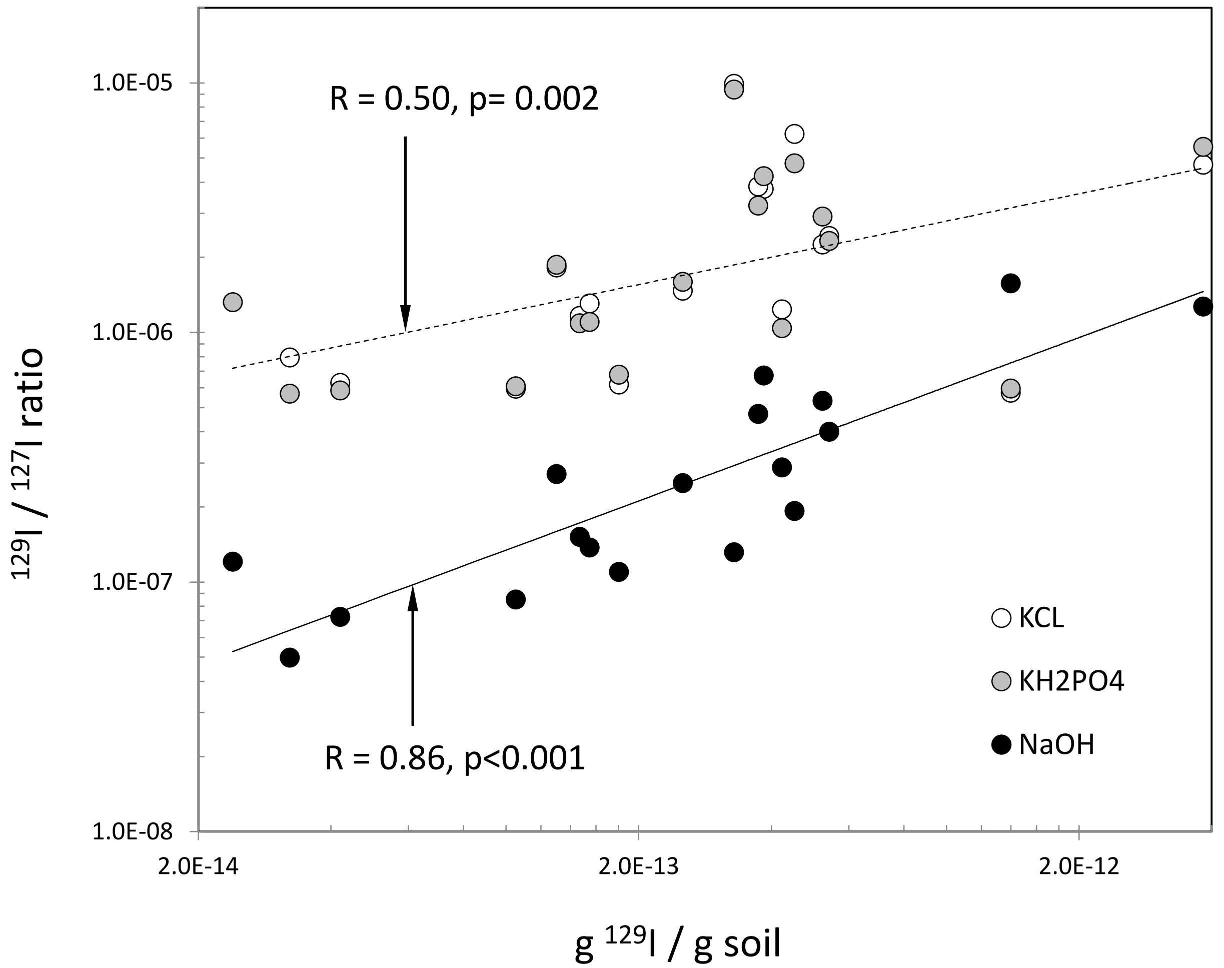

Figure 6: Relationships between ^{129}I / ^{127}I ratios in soil extracts and total ^{129}I concentrations in soils from CEZ. The dashed regression line is for 'labile' (KCl + KH_2PO_4) extracts; the solid regression line is for NaOH extracts. Spearman Rank Correlations: p=0.003 for labile (KCl + KH_2PO_4), p<0.001 for NaOH.