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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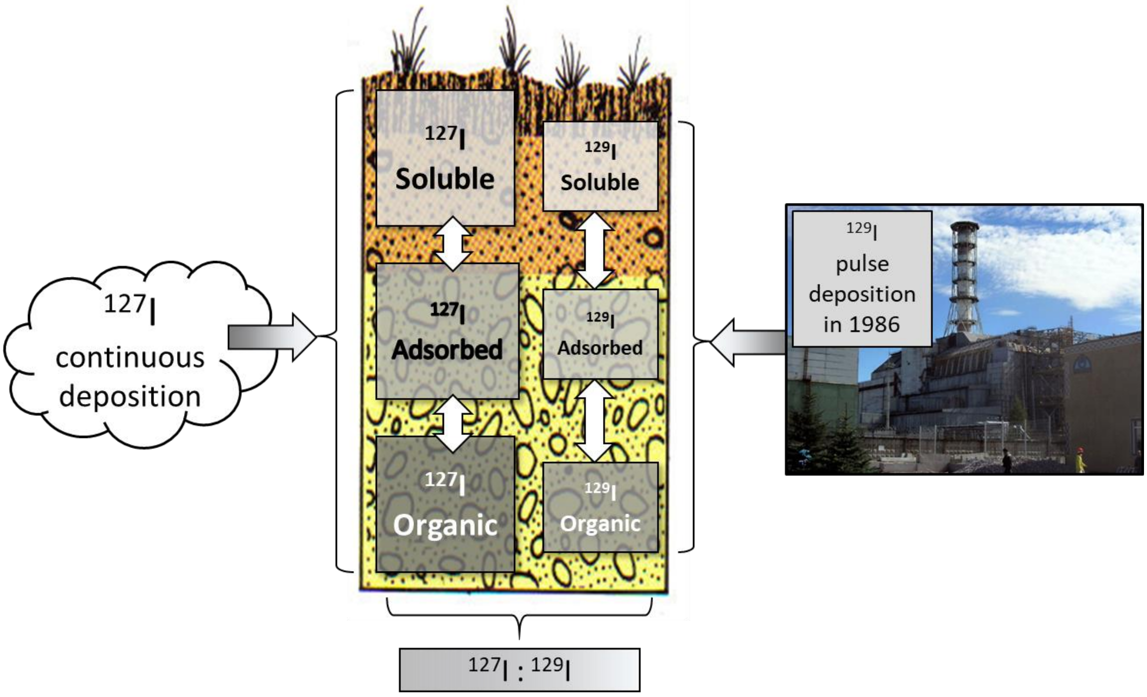

Graphical Abstract

Abstract

The Chernobyl Exclusion Zone (CEZ) represents a unique natural laboratory that received significant ^{129}I contamination across a range of soils and land-use types in a short time period in 1986. Data are presented 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, ^{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 5 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 relatively 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 that is present naturally within the soil? To answer these questions contaminated soils within a 30 km radius of the Chernobyl nuclear power station were investigated. This area 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. The results of analyses of

^{127}I and ^{129}I in these samples are reported, 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 a comprehensive analysis 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 3500 rpm for 30 min. 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 using an orbital shaker. The soil suspensions were centrifuged at 3500 rpm for 30 min 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, 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 3500 rpm for 30 min 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 min. 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 were 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, Tables S1 to S4); 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 S4). 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 taken 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 determined here. 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 that 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 S4). 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 S4). 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 S5) 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 it can be concluded that the ^{129}I measured in the soil samples 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 S5), as well as the highest ^{127}I and ^{129}I concentrations (Table S4). 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) resulting 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 S4). Furthermore, ratios of total ^{129}I/^{127}I were higher in topsoils than in sub-soils at all sites except RF1 (Table S4), 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 indicating 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 S5. 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 (beyond the scope of this study).

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

In this study 10% w/v (2.5 M) NaOH was used 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 that 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) indicated that iodide and iodate were lost from soil solutions due to interactions with reactive surfaces such as hydrous oxides and humic molecules on time scales of min to h and h 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) that 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 humic acid 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 that 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 samples in this study were taken almost 30 years after deposition there was clear autoradiographic evidence (Supplementary Materials, Figure S2) of the existence of hot particles in CEZ soils. 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. The 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 that 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.)

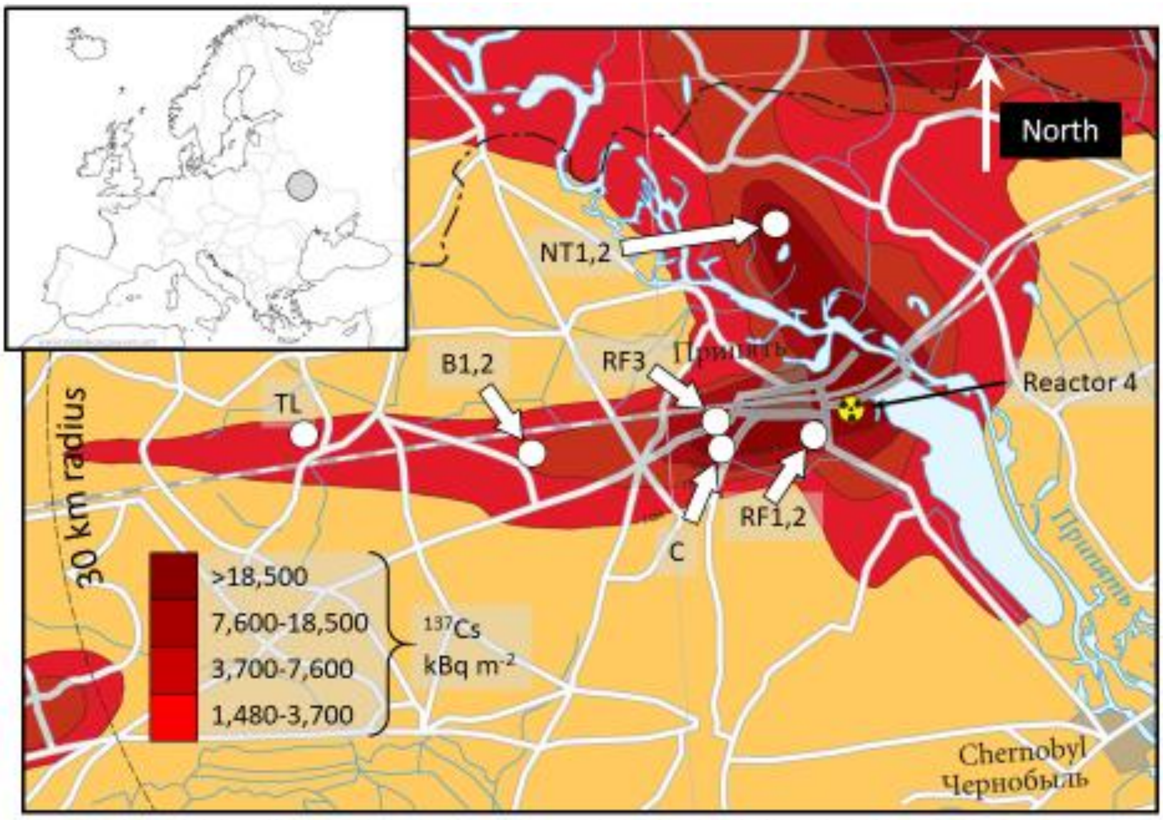

Figure 1: Sampling locations (◯) within the Chernobyl Exclusion Zone (base map from De Cort et al., 1998). The scale is shown by the 30 km radius from the reactor, visible along the western edge of the map. The grey circle in the inset map shows the general location of Chernobyl. Codes for sampling sites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

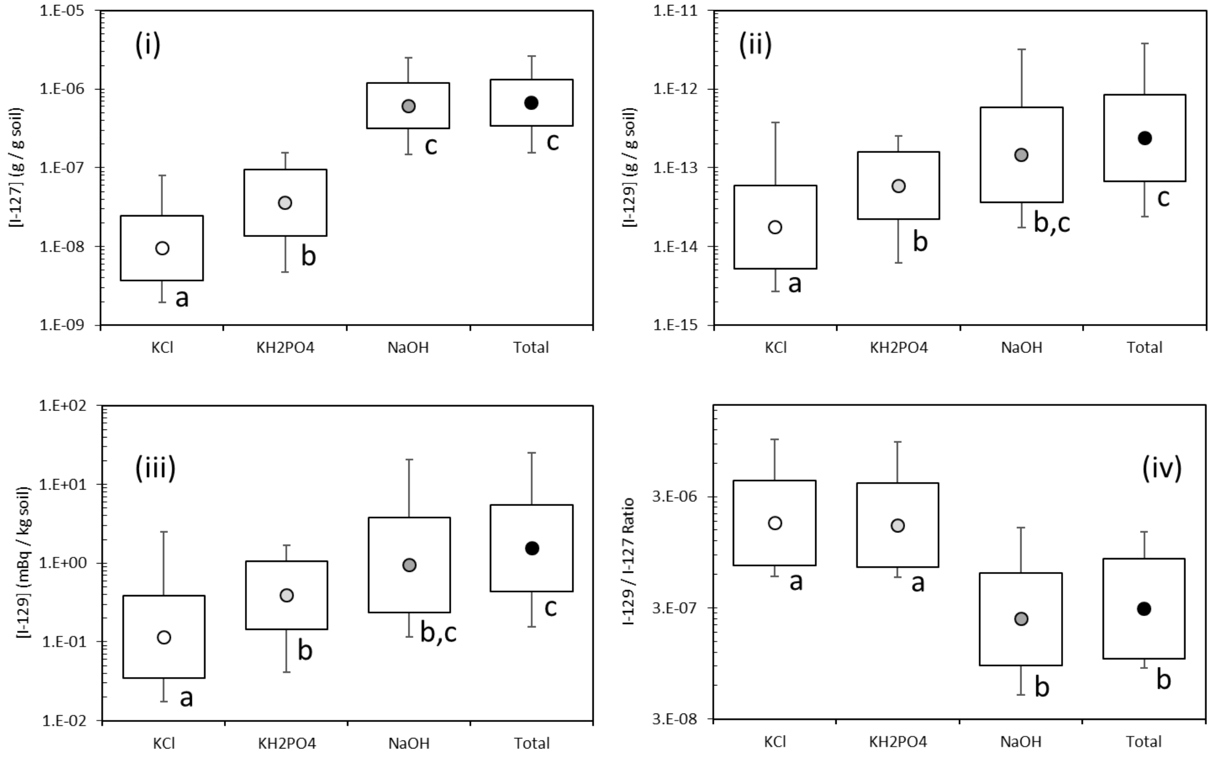

Figure 2: I-127 and ^{129}I concentrations (i, ii and iii) and ^{129}I / ^{127}I ratios (iv) in soil extracts from CEZ. Points represent geometric means, boxes represent ±1 geometric standard deviation and whiskers represent maxima and minima. Points with different letters are significantly different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

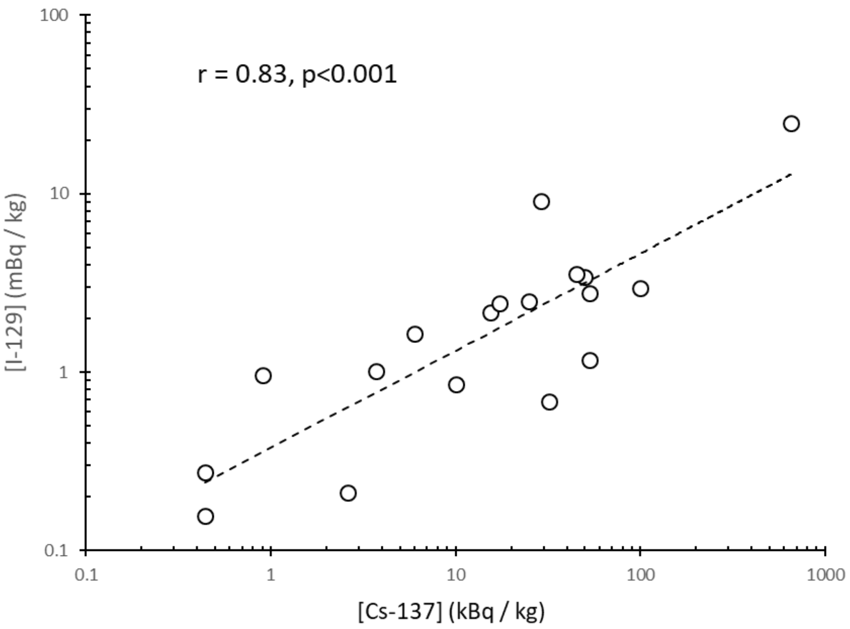

Figure 3: Relationship between ^{129}I and ^{137}Cs activity concentrations in soils from the CEZ. Both Pearson (r=0.83) and Spearman Rank correlations were highly significant (p<0.001 for both).

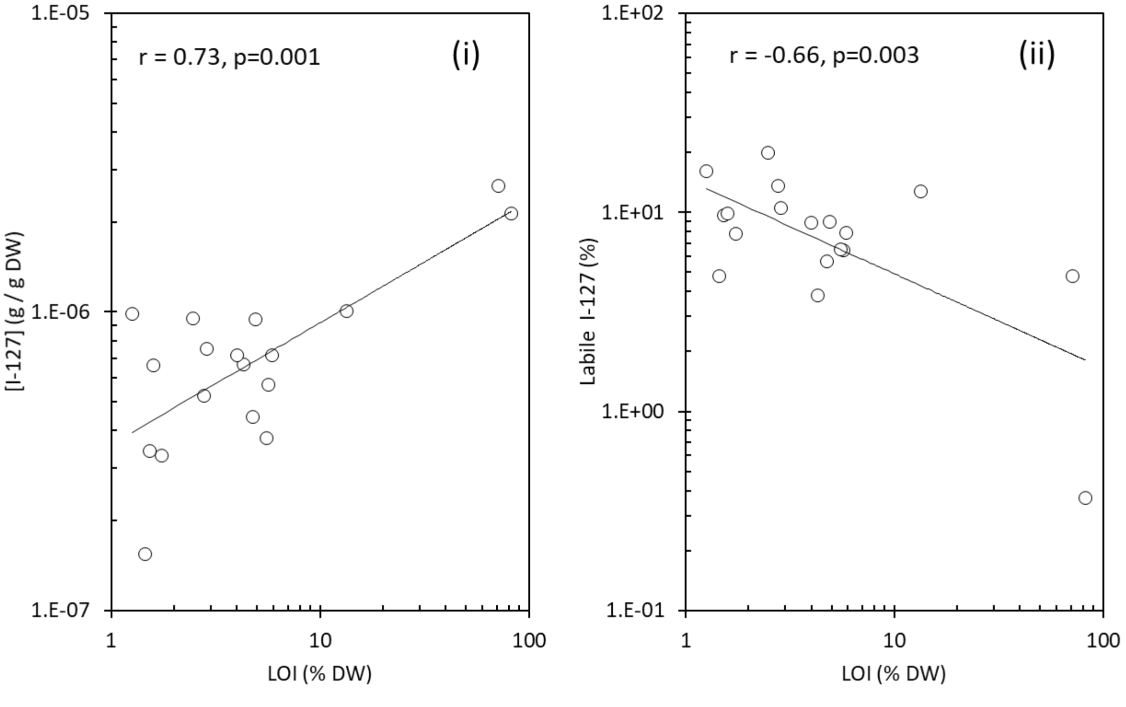

Figure 4: (i) Total concentration of ^{127}I (g g^{-1} DW) vs LOI (as a proxy for organic matter) in soils from the CEZ. The Spearman rank correlation was significant at p = 0.037 (p=0.223 for ^{129}I versus LOI). (ii) Percentage labile (KCl + KH_2PO_4 extractable) ^{127}I vs LOI. Spearman rank correlation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

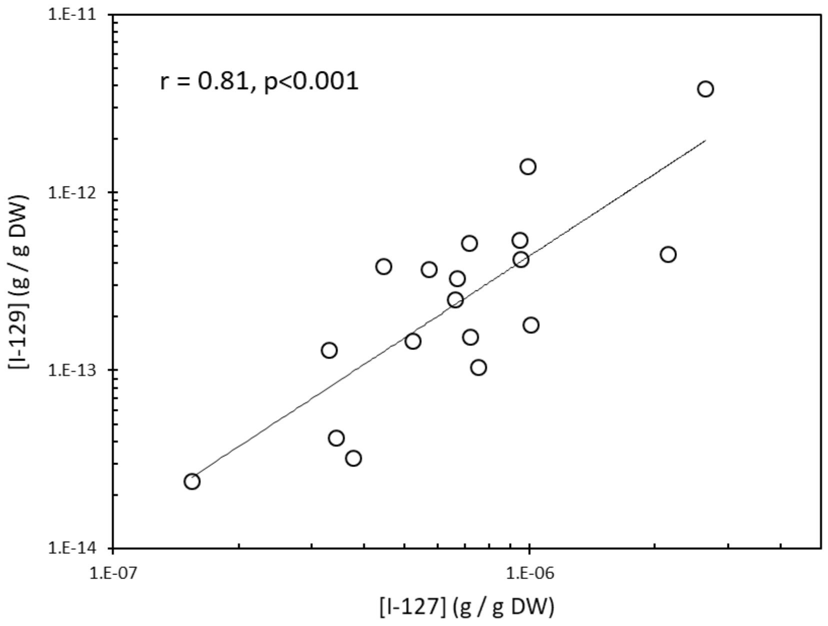

Figure 5: Relationship between TOTAL ^{127}I and ^{129}I (g g^{-1} DW) concentrations in soils from the CEZ. Both Pearson (r=0.81) and Spearman Rank correlations were highly significant (p<0.001 and p=0.001, respectively).

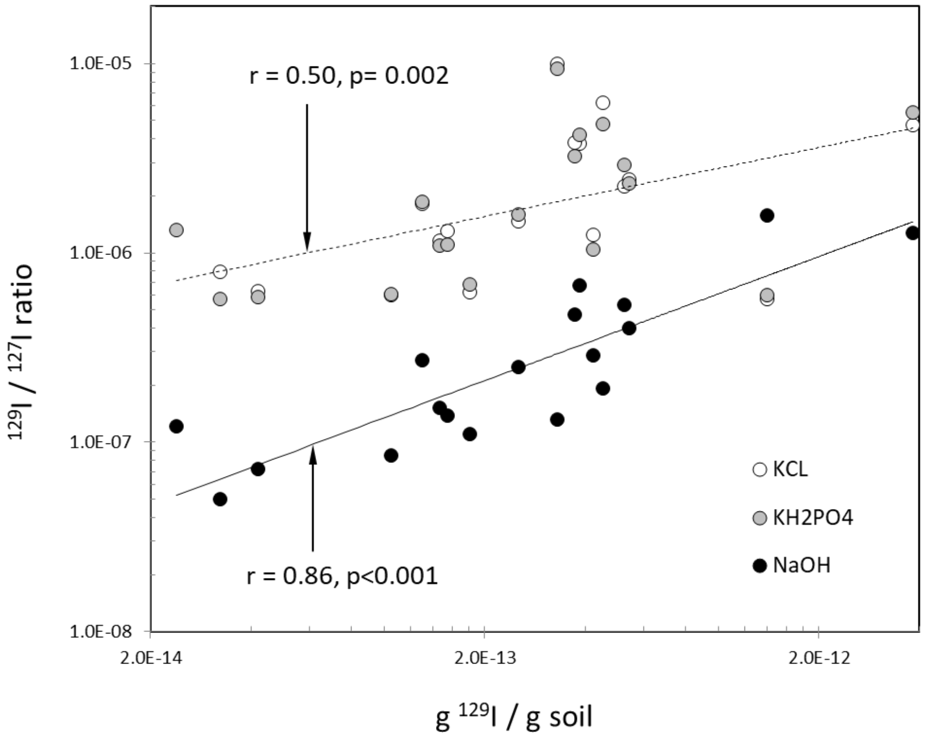

Figure 6: Relationships between ^{129}I / ^{127}I ratios in soil extracts and total ^{129}I concentrations in soils from CEZ. The dashed regression line is for 'labile' (KCl + KH_2PO_4) extracts; the solid regression line is for NaOH extracts. Spearman Rank Correlations: p=0.003 for labile (KCl + KH_2PO_4),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