Electronic supplementary information for ***Analytical Methods***

Sequential Inductively Coupled Plasma Quadrupole Mass-spectrometric Quantification of Radioactive Strontium-90 Incorporating Cascade Separation Step for Radioactive Contamination Rapid Survey

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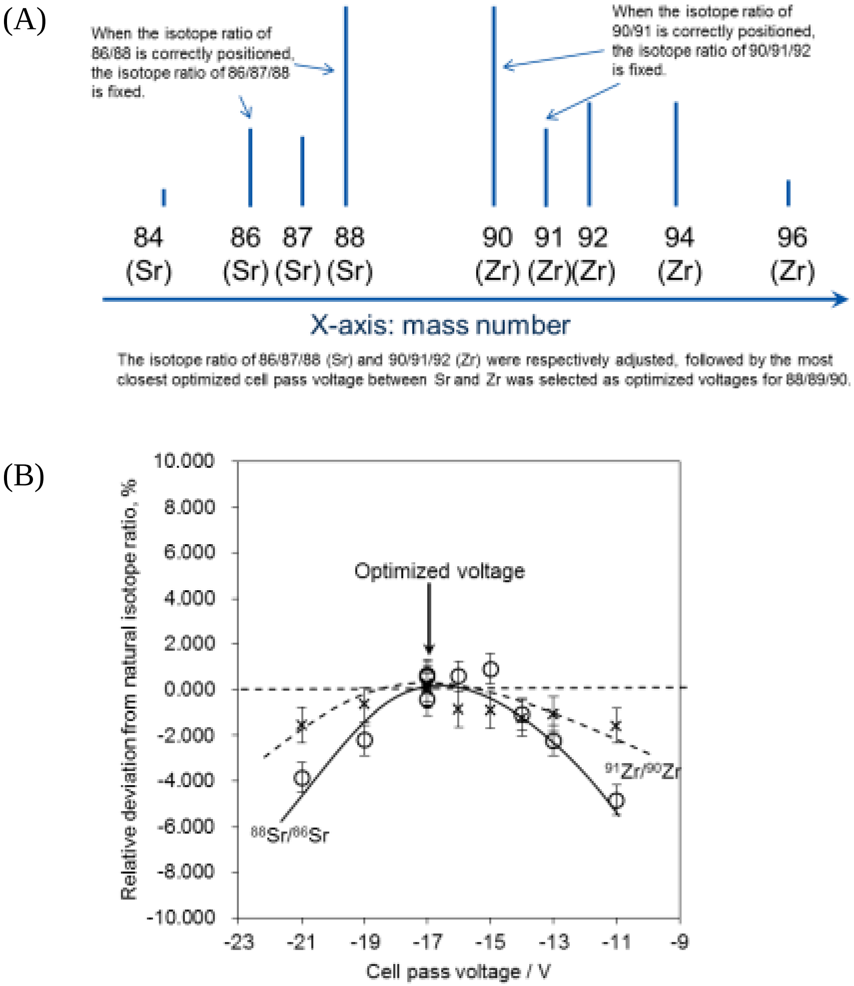
Mass-spectrometric alignment of mass bias and mass precision in ICP-QMS

The alignment of cell pass voltage is controlled using two elements. A parameter of the reaction cell in ICP-QMS specifies the way in which elements are passed though the cell; accordingly, the cell pass voltage is needed to adjust to ensure natural isotope ratio, using a stable isotope material that captures the analytical target mass number. Appropriate stable isotopes (requiring mass numbers between 89 and 91) are not available for mass number 90 (the available mass numbers 84–88, 89, and 90–96 are suitable for stable isotopes of Sr, Y, and Zr, respectively). In this study, alignment was conducted using two stable isotopes between Sr (86 and 88) and Zr (90 and 91) (for illustration, see Fig. S1-(A) in ESI). In this study, the lens voltage was typically set at −17 V, where the detected isotope ratios of the two elements (Sr and Zr) corresponded to their natural isotope ratios, as shown in Fig. S1-(B) (Note: the voltage may be varied to suit the machine conditions and should be individually reset during each measurement).



The isotope ratio of 86/87/88 (Sr) and 90/91/92 (Zr) were respectively adjusted, followed by the most closest optimized cell pass voltage between Sr and Zr was selected as optimized voltages for 88/89/90.

Fig. S1 Adjustment of the cell pass voltages in the QMS detector; (A) Alignment using double elements (Sr and Zr) for adjusting the mass bias to between 88 and 90; (B) Cell pass voltages profiles of the Sr and Zr isotope ratios. Relative deviation from natural isotope ratio (%) is calculated as {1-(detected isotope ratio/natural isotope ratio reported in the literature)} × 100; at 0 % , the detected value equals the reported value. The solid line and circles represent strontium isotope ratios (^{88}Sr/^{86}Sr); dotted-line and crosses represent (^{91}Zr/^{90}Zr); error bars show the RSD (n = 5).

Reagents. Standard stock solutions of metal ions (stable isotopes; concentration 1000 ppm) were obtained from Nacalai Tesque (Kyoto, Japan) and used as received for ICP-MS measurements. Working solutions were prepared by appropriate serial dilution of this metal ion solution in water or ultrapure nitric acid. Other purchased chemicals were a standard stock solution of radioactive strontium 90, supplied as 10 μg/g $SrCl_2$ and 10μg/g YCl_3 (stabilizer) in 0.1 M HCl (>99.9% purity) with an activity of 3.26 kBq/mL (certificated on February 8, 2012 with1.5% uncertainty). The radioactive chemicals were obtained from the Japan Isotope Association (Tokyo, Japan).The ^{90}Sr solution contained other elements such as ^{90}Y and ^{90}Zr, resulting from radioactive decay. The appropriate concentrations of the calibration standards were calculated from the decay curve of ^{90}Sr and prepared by appropriate serial dilution of ^{90}Sr ion in water or ultrapure nitric acid (typically prepared as 50 ppt ^{90}Sr stock solution (255 Bq/mL)). The concentrated HNO_3 (high-purity electric grade, 61w/w%) was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan) and diluted to appropriate concentrations in ultrapure water. In-house ultrapure water was obtained from DIRECT-Q 3 UV Ultrapure water supply system (Millipore SAS, Molsheim, France). An Eichrom Sr resin (particle diameter 50–100 μm; chemical component 4,4'(5')-di-t-butylcyclohexano 18-crown-6, purchased from Eichrom Tech) was used for strontium trapping. The powder (50 mg) was packed into the empty plastic ion chromatography column (length 50 mm; inner diameter 4.6 mm). As a pre-treatment option, the same chemical component in the form of a Sr resin cartridge (for use as a disposable syringe) was also obtained from (Eichrom Tech). A JG-1a certificated geochemical reference material (granodiorite, average diameter 4.80 μm, prepared by Geological Survey of Japan, The National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan) was used for tuning both the Q-mass spectrometric mass bias and the mass-precision of the Sr and Zr isotope ratios (m/z = 88–93). The geochemical reference was obtained from NIMS (Tukuba, Japan). All other reagents were purchased from Wako Chemical Co., Ltd. (Tokyo, Japan).

Procedures: *Sample preparation of soil using microwave digestion.* One gram of dried sample (containing soil and sediments) was placed in a special Teflon vessel for microwave digestion, followed by 10 ml of 10v/v% HNO_3. The vessels were then tightly capped. Because six vessels were prepared under the same conditions, a total of 6 g of soil was digested by microwave. We caution that 1 g in 10 ml 10v/v% HNO_3 is the upper limit to the sample capacity of the vessels used to avoid risks of bursting the digestion vessles under the pressure of gases liberated by reactions between the soil sample and HNO_3 in the microwave. In the typical microwave digestion program, the electric power was ramped from 90 W/min to 900 W (with 5.0 min hold), then gradually ramped at 50 W/min up to 1400 W (with 15 min hold). The upper limit of the instrument was set to 140°C and 1.0 MPa (10 bar). Once the digestion program was complete, power generation was ramped down to zero, and the sample units were left for 20 min to cool to room temperature. The digested sample solutions (6 vessels; total 60 mL) were placed in disposable plastic vials and centrifuged at 2500 rpm for 10 min to separate the supernatant from the sediment. After centrifugation, the solution with residue was filtered through a disposable plastic syringe and a DISMIC-25AS disposable syringe filter (0.45 μm, mixed cellulose ester, ADVANTEC, Tokyo, Japan) to remove the (chiefly silicate) residue. The filtrates were injected into the ICP-MS. An optional additional procedure is available to reduce the run time of analysis using the ICP-QMS protocol (this is not essential, but is helpful in sequential analysis) and to extend the column lifetime. Prior to injection, the filtrates were concentrated from 60 mL to 10 mL through an Eichrom Sr resin cartridge (length 1cm; particle diameter 50–100 μm; Eichrom Tech) using a disposable plastic syringe. All 60 mL of the filtrate was passed though the cartridge filter and the Sr trapped on the resin was eluted by 8 mL of ultrapure water. The HNO_3 concentration was adjusted to 20v/v% HNO_3 aq. sol by adding 2 mL concentrated HNO_3 to the eluted fraction. These solutions were also used as ICP-MS samples.

Table S1 Pump routine program for on-line pre-concentration and analysis

Step numbers	Duration /sec	Pump #1 / rpm	Pump #2 /rpm	Valve position number(1)
Pre-run	60	0	75	2
Step 1	10	120	0	1
Step 2(2)	325	75	30	2
Step 3	90	30	75	2
Step 4	30	75	0	1
Step 5	90	30	75	2
Step 6	30	75	0	1
Step 7	90	30	75	2
Step 8(3)	152	0	75	1
Post-run	-	0	75	1

1) See Figure 1 in main text. 2) Step 2 is a process for sample loading and the time is depended on sample volume. 3) ICP-MS measurement is programmed to start at the time that step #8 is operated.

Table S2 ICP-QMS parameters used in the analysis

ICP-MS parameters	Manual setting value
Nebulizer gas [L/min]	1.08
Aux gas [L/min]	1.1
Plasma gas [L/min]	15
RF power [W]	1400
Cell pass voltage [V]	−17
Analysis Method	Manual setting value
Sweeps/Reading	5
Readings/Replicate	320
Replicates	1
Dwell time per AMU [ms]	15
Reading time[s]	152
Auto lens	ON
Cell gas [mL/min]	1.2 for O_2
RPq	0.70
Analyte [m/z]	^{86}Sr, ^{88}Sr, ^{89}Y, ^{90}Sr, ^{94}Zr
Total run time	14.6 min

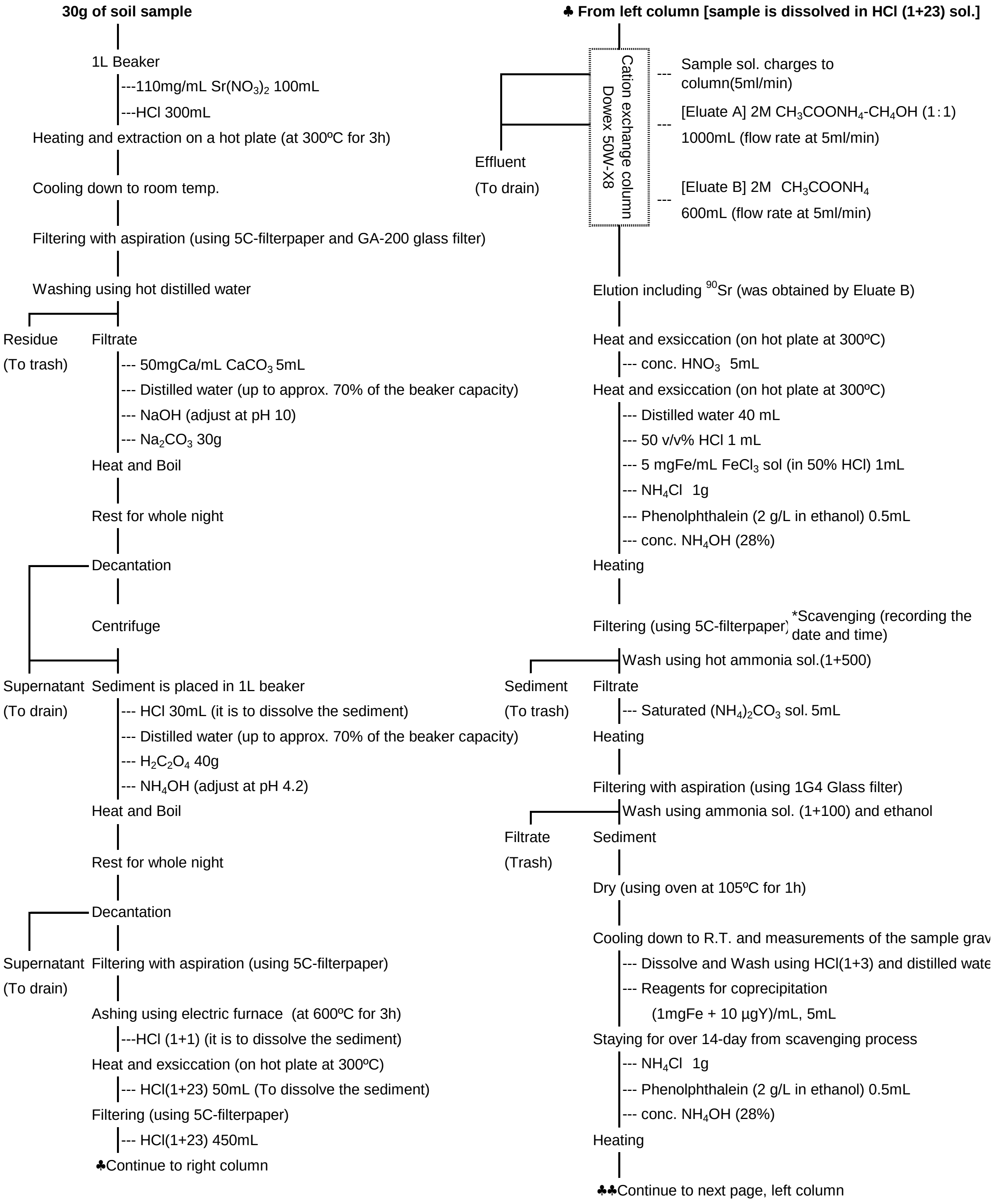
Unit conversion from mass concentration (ppq) to radioactivity (Bq/kg): The mass concentration of the nuclide (pg/kg; ppq) was converted to activity concentration (Bq/kg) as follows:

$$\mathrm{A} = \left(\frac{\ln 2}{t_{\left(\frac{1}{2}\right)}} \times \frac{m}{M_n} \times N_A\right) \Big/ 1kg$$

where A, $t_{(1/2)}$, m, M_n, and N_A denote the activity concentration (Bq kg^{-1}), half-life of the nuclide (s), objective nuclide (i.e. ^{90}Sr) weight (g) per 1kg of sample (the value from mass concentration), mass number of the nuclide, and Avogadro's constant, respectively.

Sampling: Soil was sampled from two sites of high air-radiation level (40 μSv/h and over), 10 km and 20 km north–west (straight distance) from Fukushima Daiichi nuclear power plant. Surface soil (100–150 g, to a depth of 2 cm) was collected into plastic containers (U8 size container: diameter 47 mm; height 60 mm). The soil samples in their plastic containers were carried to the laboratory and transferred to sterile plastic bags. [Note: use of plastic containers enabled measurement of the gamma radiation emitted by the sample using a germanium detector. The plastic containers were wrapped in another clean polythene layer to manage cross contamination and to avoid accumulating a varying background in the laboratory and gamma spectrometry]. The soil samples in plastic bags were crumpled by hand and homogenized as much as possible. The homogenized soil was dried and digested by microwave.

^{90}Sr concentional analytical protocol for soil



30g of soil sample

1L Beaker
---110mg/mL $Sr(NO_3)_2$ 100mL
---HCl 300mL
Heating and extraction on a hot plate (at 300ºC for 3h)
Cooling down to room temp.
Filtering with aspiration (using 5C-filterpaper and GA-200 glass filter)
Washing using hot distilled water
Residue (To trash)
Filtrate
--- 50mgCa/mL $CaCO_3$ 5mL
--- Distilled water (up to approx. 70% of the beaker capacity)
--- NaOH (adjust at pH 10)
--- Na_2CO_3 30g
Heat and Boil
Rest for whole night
Decantation
Centrifuge
Supernatant (To drain)
Sediment is placed in 1L beaker
--- HCl 30mL (it is to dissolve the sediment)
--- Distilled water (up to approx. 70% of the beaker capacity)
--- $H_2C_2O_4$ 40g
--- NH_4OH (adjust at pH 4.2)
Heat and Boil
Rest for whole night
Decantation
Supernatant (To drain)
Filtering with aspiration (using 5C-filterpaper)
Ashing using electric furnace (at 600ºC for 3h)
---HCl (1+1) (it is to dissolve the sediment)
Heat and exsiccation (on hot plate at 300ºC)
--- HCl(1+23) 50mL (To dissolve the sediment)
Filtering (using 5C-filterpaper)
--- HCl(1+23) 450mL
♣Continue to right column

♣ From left column [sample is dissolved in HCl (1+23) sol.]

Cation exchange column
Dowex 50W-X8
--- Sample sol. charges to column(5ml/min)
--- [Eluate A] 2M CH_3COONH_4-CH_4OH (1:1) 1000mL (flow rate at 5ml/min)
--- [Eluate B] 2M CH_3COONH_4 600mL (flow rate at 5ml/min)
Effluent (To drain)
Elution including ^{90}Sr (was obtained by Eluate B)
Heat and exsiccation (on hot plate at 300ºC)
--- conc. HNO_3 5mL
Heat and exsiccation (on hot plate at 300ºC)
--- Distilled water 40 mL
--- 50 v/v% HCl 1 mL
--- 5 mgFe/mL $FeCl_3$ sol (in 50% HCl) 1mL
--- NH_4Cl 1g
--- Phenolphthalein (2 g/L in ethanol) 0.5mL
--- conc. NH_4OH (28%)
Heating
Filtering (using 5C-filterpaper) *Scavenging (recording the date and time)
Wash using hot ammonia sol.(1+500)
Sediment (To trash)
Filtrate
--- Saturated $(NH_4)_2CO_3$ sol. 5mL
Heating
Filtering with aspiration (using 1G4 Glass filter)
Wash using ammonia sol. (1+100) and ethanol
Filtrate (Trash)
Sediment
Dry (using oven at 105ºC for 1h)
Cooling down to R.T. and measurements of the sample grav
--- Dissolve and Wash using HCl(1+3) and distilled wate
--- Reagents for coprecipitation (1mgFe + 10 µgY)/mL, 5mL
Staying for over 14-day from scavenging process
--- NH_4Cl 1g
--- Phenolphthalein (2 g/L in ethanol) 0.5mL
--- conc. NH_4OH (28%)
Heating
♣♣Continue to next page, left column

Fig. S2 continues to next page.

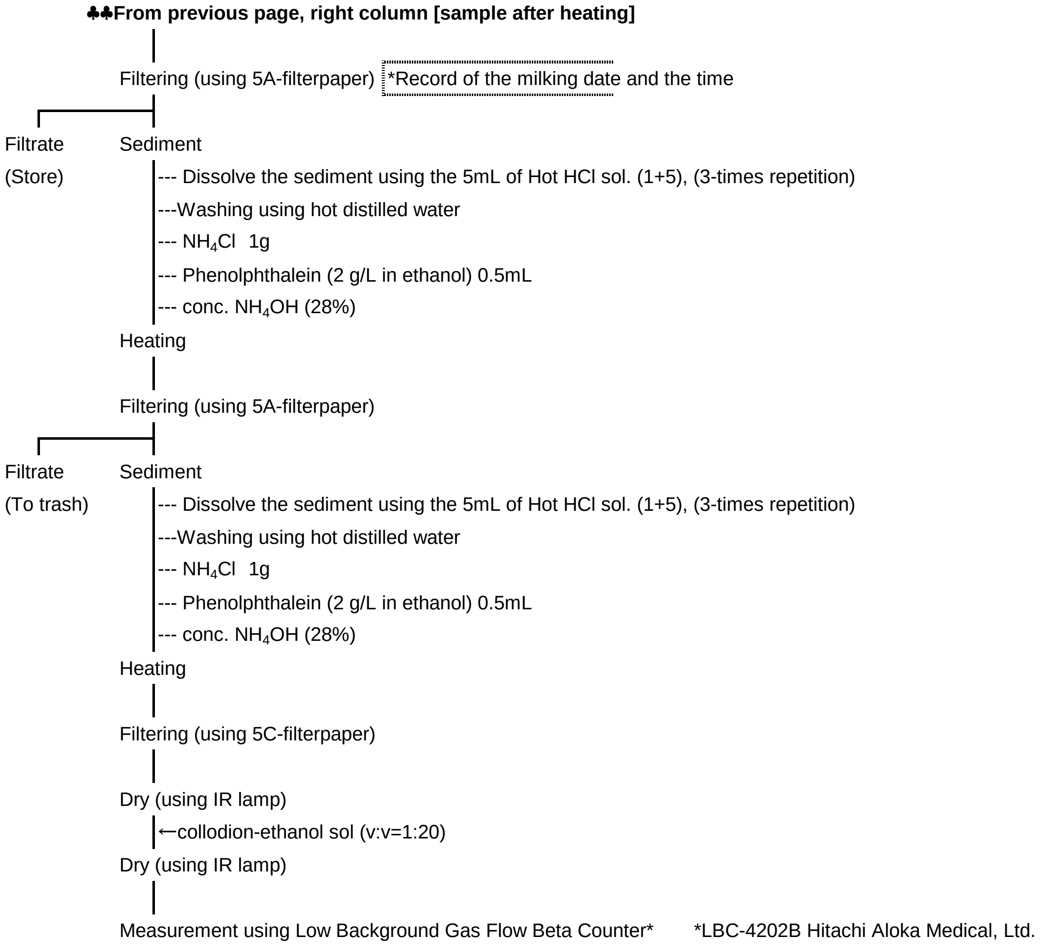


Fig. S2 Gas flow detector with conventional pre-treatment, used to cross-check the presented method in contaminated soil analysis: The analytical protocols followed the manual of environmental radiation monitoring method compiled by the Japanese government [Ministry of Education, Culture, Sports, Science & Technology in Japan, Research and Development Bureau, Atomic Energy Division. "Analytical methods of the radioactive strontium" 2003. http://www.kankyo-hoshano.go.jp/series/lib/No2.pdf (in Japanese)]. Pre-treatment usually takes 2 weeks to one month to complete. Data obtained by the proposed method were cross-checked using a LBC-4202B gas flow detector for low-background beta-ray detection (Hitachi Aloka Medical, Ltd., Tokyo, Japan).

The Sr elution efficiency of microwave digestion, determined from the addition and recovery test

The percentage recovery of digested, eluted Sr was measured as follows: 1 mL of 2.5 mg/L natural Sr with ^{88}Sr (2.5 μg) stable isotope was added to 1.0 g of A JG-1a certificated geochemical reference material. The material was thoroughly mixed and completely dried in an oven. Next, the spiked and standard reference materials were both digested in the microwave, and the quantity of ^{88}Sr in the solution was measured by ICP-QMS. The elution efficiency of Sr in microwave digestion was calculated from the concentration difference between the plain reference and that spiked with ^{88}Sr.

Table S3 The elements and their concentrations eluted from soil samples following microwave digestion[1].

No.	Measurement elemrnt	Mass number	D.L. [µg/kg]	Eluted concentration from soil [mg/kg][2]		No.	Measurement elemrnt	Mass number	D.L. [µg/kg]	Eluted concentration from soil [mg/kg][2]	
				Location#1	Location#2					Location#1	Location#2
1	Li	7	0.80	24	10	35	Cd	114	0.097	0.072	0.19
2	Be	9	2.0	0.58	0.58	36	In	115	0.049	0.027	0.039
3	B	11	1.8	2.0	4.5	37	Sn	120	0.13	0.70	0.059
4	Na	23	2.2	147	237	38	Sb	121	0.091	0.014	< D.L.
5	Mg	24	2.2	2020	3638	39	Te	130	0.59	0.76	0.69
6	Al	27	0.96	20101	15714	40	Cs	133	0.038	3.4	1.3
7	Si	28	0.19	27	23	41	Ba	138	0.50	45	43
8	P	31	18	329	196	42	La	139	0.015	14	14
9	K	39	7.6	1408	1332	43	Ce	140	0.0076	32	30
10	Ca	40	2.1	1447	8393	44	Pr	141	0.0036	3.1	3.3
11	Sc	45	2.9	8.9	12	45	Nd	142	0.026	17	17
12	Ti	48	1.5	1202	662	46	Sm	152	0.065	2.4	2.9
13	V	51	1.1	37	47	47	Eu	153	0.054	0.30	0.56
14	Cr	52	0.22	7.1	28	48	Gd	158	0.038	2.5	3.1
15	Mn	55	0.060	352	340	49	Tb	159	0.0070	0.36	0.45
16	Fe	56	0.49	14187	14993	50	Dy	164	0.020	2.0	2.6
17	Co	59	0.019	5.6	8.4	51	Ho	165	0.004	0.39	0.52
18	Ni	60	0.30	5.5	14	52	Er	166	0.011	1.1	1.5
19	Cu	63	0.10	12	64	53	Tm	169	0.014	0.16	0.21
20	Zn	66	0.44	70	104	54	Yb	174	0.029	1.0	1.3
21	Ga	69	0.049	7.5	7.0	55	Lu	175	0.016	0.15	0.19
22	Ge	74	0.079	0.85	1.24	56	Hf	180	0.050	0.28	0.39
23	As	75	2.7	6.4	9.1	57	Ta	181	0.042	0.0024	0.0032
24	Se	78	3.2	1.1	1.5	58	W	184	0.073	0.012	0.0088
25	Rb	85	0.040	30	13	59	Re	187	0.044	< D.L.	< D.L.
26	Sr	88	0.082	8.4	26	60	Ir	193	0.097	< D.L.	< D.L.
27	Y	89	0.0071	10	13	61	Pt	195	0.12	0.0024	0.0040
28	Zr	90	0.022	6.5	11	62	Au	197	0.18	< D.L.	0.022
29	Nb	93	0.018	0.48	0.0016	63	Hg	202	8.8	< D.L.	0.45
30	Mo	98	0.10	0.28	0.053	64	Tl	205	0.048	0.21	0.10
31	Ru	102	0.075	< D.L.	0.0008	65	Pb	208	0.32	6.8	32
32	Rh	103	0.030	< D.L.	0.0012	66	Bi	209	0.042	0.15	0.18
33	Pd	106	0.050	0.16	0.26	67	Th	232	0.030	8.1	3.4
34	Ag	107	0.077	0.04	0.09	68	U	238	0.013	1.5	0.69

1) Procedure of microwave digestion was followed by the description of "Procedures: *Sample preparation of soil using microwave digestion*" in text. 2) Location number corresponds to the sampling location of Table 1 in the text. ICP-MS measurement conditions are shown in right table.

ICP-QMS	ELAN DRC-II
Torch	Quartz torch
Injector	Quartz injector
Nebulizer unit	Glass concentric nebulizer
Chamber	Cyclone chamber
Sampling cone	Ni cone
Skimmer cone	Ni cone
Nebulizer gas [L/min]	0.9
Aux gas [L/min]	1.1
Plasma gas [L/min]	15
RF power [W]	1400
Sweeps/Reading	20
Readings/Replicate	1
Replicates	3
Dwell time per AMU [ms]	25
Reading time[s]	221
Auto lens	ON
Cell gas	CH_4
No.9 K to No.24 Se	DRC mode

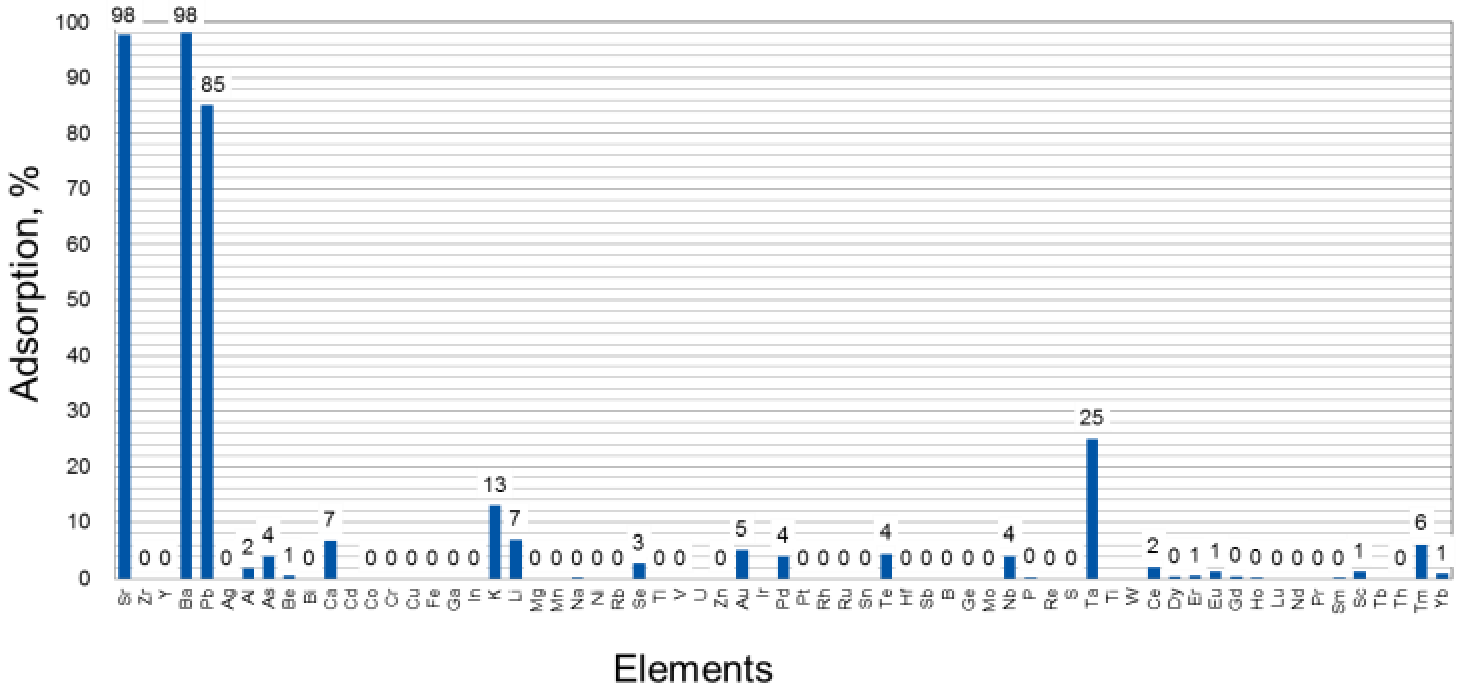


Fig. S3 Percentage adsorption of various metal cation mixtures onto the on-line Sr chelate resin column. Conditions: [metal ion]$_T$ = 250 µg/L (dissolved in 20v/v% HNO_3), 10 mL of sample was injected at flow rate 1.9 mL/min (cleaned by10 mL of 20v/v% HNO_3), eluate = water, Sr resin = 50 mg.

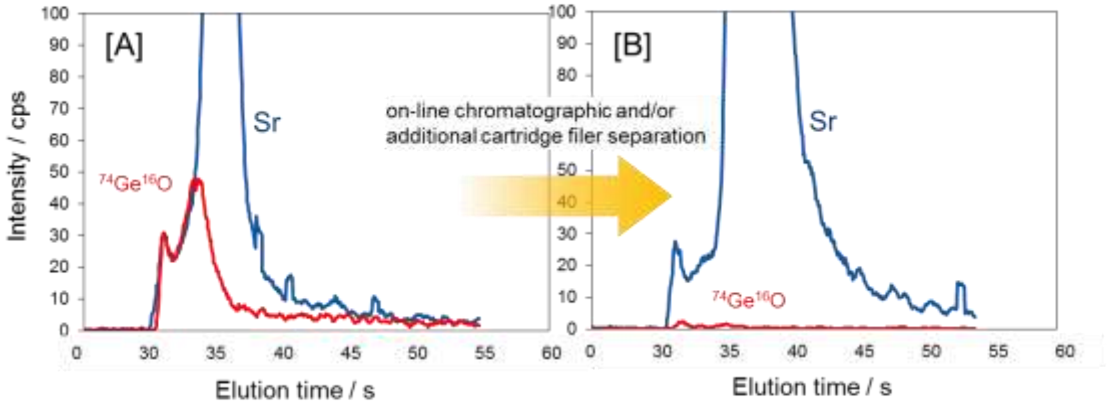


Fig.S4 chromatographic GeO interference peaks and their removal. When the proposed system was operated without on-line chelate column separation, ^{74}Ge inhibited Sr quantification at ppq levels. In Figure S4-[A], Ge and Fe (present at 10 µg and 1 mg, respectively) give rise to significant quantities of $^{74}Ge^{16}O^{+}$ and $^{54}Fe^{36}Ar^{+}$, which present as interference peaks. Figure S4-[B] shows the effect of on-line separation (proposed method). The chromatographic appearance is very similar between the case of $^{54}Fe^{36}Ar^{+}$ and $^{74}Ge^{16}O^{+}$ (Fig.S4-[A] and -[B]). Thence, the peak profile for the case of $^{54}Fe^{36}Ar^{+}$ was not shown in Figure.