

1 **Optimisation of a current generation ICP-QMS and benchmarking against MC-**
2 **ICP-MS spectrometry for the determination of lead isotope ratios in**
3 **environmental samples**

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6 **Abstract**

7 The precision and accuracy of lead (Pb) isotope measurements obtained from quadrupole-based mass
8 spectrometers (ICP-QMS) are considered to be limited by a number of factors originating in different
9 components of the instruments. In this study, experimental and instrumental protocols were
10 optimised for determining lead isotope ratios in urban soil digests. Experimental measures included
11 individual dilution of all samples and isotopic standards (SRM-981, NIST) to a single Pb concentration
12 intended to produce an intensity which was high enough to negate blanks and interferences but low
13 enough to ensure the detector operated only in pulse counting mode. Instrumental protocols included
14 batch dead time correction, optimisation of dwell time and the number of scans employed and
15 correction of mass discrimination by sequential application of both internal ($^{203}\text{Tl}/^{205}\text{Tl}$ ratio) and
16 external (SRM-981, NIST) standards.

17 This optimised methodology was benchmarked against multi-collector mass spectrometer (MC-ICP-
18 MS) measurements of Pb isotope ratios using replicate digest solutions of the same soil; but after
19 these had been subjected to Pb separation using an ion-exchange procedure. On the assumption that
20 MC-ICP-MS measurements are more accurate, small additive and multiplicative differences were
21 observed in only the 4th decimal place. ANOVA was used to compare the precisions of the two
22 techniques demonstrating equal precisions c. 0.08% for $^{207}\text{Pb}/^{206}\text{Pb}$, suggesting a sample heterogeneity
23 limitation. By contrast, for $^{207}\text{Pb}/^{204}\text{Pb}$, the worst-case ratio, ICP-QMS had a 10-fold poorer precision,
24 despite negligible interference from ^{204}Hg , implying an instrumental limitation. The study concludes
25 that ICP-QMS can provide valuable source apportionment information for most Pb isotope ratios but
26 further efforts should focus on improving assay of the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio.

Keywords: ICP-QMS, MC-ICP-MS, lead isotopes, soil, parameter optimisation

27 **Introduction**

28 Lead isotopes can be measured by a range of mass spectrometry techniques. Until fairly recently,
29 thermal ionization mass spectrometry (TIMS) was the preferred choice for precise (0.001-0.01% RSD)
30 measurement of Pb isotope abundances (1, 2). However, TIMS involves laborious sample preparation
31 steps, such as separation of the analyte from the matrix into a highly purified form, involving extensive
32 chemical treatment, and stringent optimisation of vaporisation and ionisation conditions of samples,
33 with long analysis times (~45 minutes). These measurements are not only time consuming but also
34 incur cost, rendering TIMS unsuitable when analysing large numbers of samples (3, 4). Inductively
35 coupled plasma mass spectrometers (ICP-MS) are more appropriate for routine use with large sample
36 numbers and are operationally simpler than TIMS (5); sample introduction is at atmospheric pressure
37 and ionization of most elements is readily achieved. They are widely used for multi-element and
38 isotopic analysis and are routinely capable of a precision (<0.05% RSD) comparable to that of TIMS
39 for Pb isotopes. The term 'ICP-MS' covers a range of instruments which differ in their mass filter and
40 detector systems. These include; those that are quadrupole-based (ICP-QMS) or high resolution,
41 magnetic sector field-based (HR-ICP-MS) and those which can utilize single-collector (SC), multi-
42 collector (MC), array detector (AD) or 'time-of-flight' (TOF) detectors (4, 6).

43 Quadrupole-based inductively coupled plasma - mass spectrometers (ICP-QMS) are the most
44 commonly used ICP-MS instruments principally because they are relatively inexpensive to produce
45 and support, and are fast and simple in terms of sample preparation, handling and operation. As a
46 result, the number and availability of ICP-QMS instruments far outweigh MC-ICP-MS. However, in
47 isotope studies, specifically when high precision ratio measurements are required, MC-ICP-MS is
48 preferred over ICP-QMS and is considered the benchmark for accurate and precise isotope data (7).
49 This is principally due to simultaneous measurement of all relevant isotopes, which effectively cancels
50 out the effects of 'plasma flicker', and the flat-topped peaks produced in MC-ICP-MS, with their
51 inherent resistance to instrument drift. This is in contrast to sequential measurement of isotopes on
52 leptokurtic peaks in ICP-QMS (8-10). The sequential nature of the analysis in any single collector
53 instrument renders the technique susceptible to variations in, for example, sample aerosol transport,
54 RF power fluctuations and physical perturbations within the plasma itself (plasma flicker). In essence,
55 any signal instability results in non-sample related variation in relative isotope abundances from one
56 microsecond to the next. To achieve the ultimate high accuracy and precision that MC-ICP-MS is
57 capable of, does pose some extra constraints, these include the need to separate the element of
58 interest not just to ensure minimising any spectral interferences but also to minimise matrix effects,

59 including mass bias. However, this is rarely used in ICP-QMS studies as the aims in particularly
60 environmental research require the analysis of large numbers of samples, in the minimum time.

61 The accuracy and precision of isotopic ratios measured through ICP-QMS are considered limited by
62 'noise' (variation in signal intensity). This originates from varying conditions throughout the ion
63 pathway, including the ion source (i.e. sample introduction system and the plasma itself), the interface
64 region, the collision/reaction cell (if used), the quadrupole mass filter and the detector (9, 11).
65 Variation in the efficiency of nebulisation and sample transport produces low frequency noise (12); as
66 a result it is common in MC-ICP-MS studies to use manual sample introduction with naturally
67 aspirating nebulisers. In the ICP ion source, noise is produced due to 'plasma flicker' that is caused by
68 changes in energy transfer from plasma to analyte atoms. In addition to mainly random fluctuation
69 caused by these instrumental factors, variation in 'mass bias' is a major source of systematic error,
70 responsible for deviation of measured intensity ratios from true isotopic ratios (5, 13). The largest
71 mass discrimination effect in ICP-MS is observed due to space charge effects (9), which occur between
72 the plasma torch and the skimmer cone, and cause differential deflection of lighter ions (11, 14). Thus
73 the ratio of heavier to lighter isotopes increases in the ion beam passing through the skimmer cone
74 (15); therefore it is common in high precision isotope ratio studies to separate the element of interest
75 to minimise these effects. Woodhead (16) , used this variability in mass bias with matrix to propose
76 an improved Tl bias correction by "calibrating" the small difference in mass bias for Tl and Pb. It also
77 has been reported that mass discrimination induced by space charge effects should be minimal in
78 magnetic sector instruments due to high accelerating voltages however this is not always the case
79 compared to the low extraction voltages, behind the skimmer cone, in a quadrupole instrument.
80 Heumann, Gallus (15) showed that mass discrimination for bromine isotopes was smaller than for a
81 quadrupole but was still significant leading to the suggestion that discrimination can occur between
82 the plasma torch and the skimmer cone. Random noise originating in the ICP ion source and
83 quadrupole mass filter is also responsible for imprecision in measuring isotope ratios because of the
84 sequential measurement required in ICP-QMS and, to a lesser extent, single collector HR-ICP-MS.

85 In ICP-QMS, a discrete dynode detector is normally used which necessitates a compromise between
86 employing large analyte concentrations to improve the counting statistics of minor isotopes while
87 working below the point at which the detector trips to analogue mode for major isotopes. This may
88 push the intensities of high abundance isotopes into the zone in which the detector dead time
89 correction has a significant effect. Therefore, accurate *dead time correction* is necessary for precise
90 measurement of isotopic ratios especially when very different isotope abundances are involved (e.g.

91 $^{208}\text{Pb}/^{204}\text{Pb}$) (15). The age of the detector is also considered an important factor in influencing dead
92 time (8, 10, 17, 18).

93 Different strategies have been employed for precise determination of Pb isotopes using different
94 types of mass spectrometers. To minimise low frequency noise sources, Furuta (19), Begley and Sharp
95 (11) and Monna, Loizeau (20) all recommended cycling the ICP-QMS as rapidly as possible through the
96 measured masses. Quénel, Thomas (9) used a factorial design approach to investigate the
97 simultaneous effects of different factors (dwell time, number of sweeps/replicates, number of
98 replicates/analysis and time factor) on the precise determination of Pb isotopes, including ^{204}Pb . To
99 reduce the effects of mass bias in multi-collector, quadrupole and other mass spectrometers Ingle,
100 Sharp (21) demonstrated mass bias correction by modelling the underlying instrument response
101 function in MC-ICP-MS. Reuer, Boyle (22) revealed the importance of both external and internal
102 correction for mass bias in MC-ICP-MS to improve measurements of Pb isotopes in natural samples,
103 i.e. marine carbonates and sea water. Simultaneous assessment of several optimising parameters
104 have also been undertaken in some studies. For regular monitoring of dead time and mass
105 discrimination, Appelblad and Baxter (13) presented a linear model for the simultaneous
106 determination of dead time and mass bias correction factor in double focusing sector field mass
107 spectrometry (SF-ICP-MS) for regular monitoring of dead time and mass discrimination. This had the
108 advantage of utilizing more time on the isotopes of interest. Different methods for calculating
109 accurate detector dead times have also been demonstrated to improve the accuracy of isotopic ratios
110 (10, 17).

111 In this study, the ability of a current-generation ICP-QMS instrument to determine Pb isotope ratios
112 in urban soil samples was tested through a comparison with MC-ICP-MS analysis. The primary aim of
113 this study was to refine protocols intended to maximise the accuracy and precision of ICP-QMS
114 determination of Pb isotope ratios to enable soil Pb source apportionment. The optimised
115 methodology was benchmarked against MC-ICP-MS measurements on the same sample material.

116 **Experimental**

117 **Preparation of samples**

118 Composite urban surface (0-15 cm) soil samples (n=11) from a range of sites in Wolverhampton and
119 Nottingham were used. These had been sampled previously as part of a Natural Environmental
120 Research Council (NERC) project, under the URGENT programme, conducted by a research consortium
121 from Imperial College, London, NERC Isotope Geosciences Laboratory, British Geological Survey and
122 University of Nottingham between 1999 and 2002 (Table 1).

Table 1 Soil samples from Nottingham (Ng) and Wolverhampton (Wv)

Sample	Total Pb content mg kg ⁻¹	Land use	Grid ref
Ng2	385	Churchyard	455280 338770
Ng5	434	Domestic garden	457360 342370
Ng7	340	Grassland (imported)	458500 339110
Ng8	339	Grassland (racecourse)	459710 339170
Ng9	146	Vegetated colliery spoil heap	453570 344310
Ng12	893	Disused factory	455760 338550
Wv2	47.6	Grassland (Golf course)	388450 300860
Wv12	134	Grassland	388240 295750
Wv19	40.6	Grassland	395150 299140
Wv21	27.9	Brownfield	393960 299860
Wv29	271	Deciduous woodland	391680 300080

123 Soil samples were air-dried and sieved to <2 mm and a small subsample of the archived soil (c. 2.0 g
 124 in triplicate) was ground in an agate ball mill (Model PM400, Retsch GmbH & Co., Germany). Complete
 125 digestion of 0.2 g samples was achieved in PFA vials in a 48-place Teflon-coated graphite block digester
 126 (Model A3, Analysco Ltd, Chipping Norton, UK) using a mixed acid digestion process i.e., HNO₃ (68%),
 127 HClO₄ (70%) and HF (70%). The dried digestate was dissolved in 68% HNO₃ and diluted to 50 mL with
 128 Milli-Q water (18.2 MΩ cm). Prior to analysis of total Pb concentration by ICP-QMS a further 1:10
 129 dilution with 2% HNO₃ was undertaken. Internal standards were introduced to the sample stream via
 130 a separate T-line including Ge (50 µg L⁻¹), Rh (20 µg L⁻¹) and Ir (10 µg L⁻¹) in 2% HNO₃ and multi-element
 131 standards (0, 20, 40, 100 µg L⁻¹) were used to determine the Pb concentration (CLMS-2; CertPrep™).
 132 Three procedural blanks were also included in each digestion batch for quality assurance. All samples
 133 were analysed with the ICP-QMS operating in 'kinetic energy discrimination' (KED) mode, with He as
 134 the cell gas, to eliminate polyatomic interferences e.g. ¹⁹¹Ir¹⁶O, ¹⁶⁷Er⁴⁰O and ²⁰⁶Pb¹H on ²⁰⁷Pb.

135 (i) Dilution of samples for Pb isotopes measurement (ICP-QMS)

136 The precision of Pb isotope ratio measurements generally improves with increasing Pb concentration
 137 as counting statistics improve (19). However, at high concentrations the ion counter detector used
 138 with the ICP-QMS employed in this study trips to an analogue signal, resulting in non-linearity caused

139 by measuring isotopes in different detector modes, with added uncertainty due to the application of
140 a gain correction between the two detector types (20, 23). Thus, individually tailored dilutions of each
141 sample digest were carried out, with 2% HNO₃, using previously quantified total concentrations of Pb.
142 The objective was to work with near identical concentrations (~15 µg L⁻¹) of all samples and reference
143 materials (SRM-981, NIST Pb wire). This approach had the advantages of (i) reducing the effect of any
144 error in the dead time correction factor and (ii) ensuring that the intensity of the ²⁰⁴Pb signal was as
145 high as possible (c. 27 X 10³ cps) while keeping the ²⁰⁸Pb signal below the detector trip point (c. 1 X 10⁶
146 cps). The blank contribution for each isotope although subtracted during analysis was only 0.76% of
147 the sample Pb and had an insignificant effect on results.

148 (ii) **Lead separation method for Pb isotope measurement by MC-ICP-MS.**

149 Variations in mass bias and small interferences are known to impact on data quality in MC-ICP-MS
150 isotope ratio determinations (24). Therefore, prior to the measurement of Pb isotopes in soil digests,
151 a preliminary separation of Pb was performed using an anion exchange (AG1-X80) column (25).
152 Aliquots, containing an estimated 200 ng of Pb from each digest, were heated overnight to dryness in
153 PFA vials on a hotplate. An aliquot of HBr (2 mL) was then added to each vial and left overnight again
154 to solubilise the sample. Sample Pb was separated using anion exchange resin columns (2 mL, AG1-
155 X80). The resin was pre-cleaned with MQ quality (>18 MΩ cm) water followed by 6 M HCl and then
156 equilibrated by washing the column with 2 mL 1 M HBr. All samples were then passed through
157 individual columns adsorbing the sample Pb as PbBr₄²⁻ ions. Major cations were then eluted from the
158 columns with further HBr. The sample Pb was then eluted using 8 mL of 6 M HCl back into its original
159 vial. Concentrated nitric acid (0.2 mL) was added to each vial as an oxidising agent and the contents
160 evaporated to dryness on a hotplate, overnight, at 90°C. Prior to analysis by MC-ICP-MS each sample
161 was diluted to c.5-10 ng mL⁻¹ and spiked with Tl (c. 5-10 ng mL⁻¹) for instrumental mass bias correction
162 with the aim of achieving less than the maximum 10V signal on ²⁰⁸Pb and ²⁰⁵Tl.

163 **Instrumentation and optimisation procedures**

164 ICP-QMS

165 At the University of Nottingham Pb isotope ratios were determined by current generation ICP-QMS
166 (Model iCAP Q; Thermo Scientific, Bremen, Germany). All samples were analysed with the ICP-QMS
167 operating in 'kinetic energy discrimination' (KED) mode, with He as the cell gas, to reduce potential
168 polyatomic interferences. Additionally, in the past it has been suggested that the use of a collision gas
169 may "thermalize" the ion beam and improve isotope ratio precision (26). Samples were introduced
170 from an autosampler incorporating an ASXpress™ rapid uptake module (Cetac ASX-520, Teledyne
171 Technologies Inc., Omaha, NE, USA), with a 5 mL sample loop, through a perfluoroalkoxy (PFA)

172 Microflow PFA-ST nebuliser (Thermo Fisher Scientific, Bremen, Germany). The typical operational
 173 parameters selected for measurement of Pb isotopic ratios are given in Table 2. The settle/idle time
 174 was not optimised as this is hard-wired into the software of this instrument and not readily available
 175 to the user.

Table 2 Operational parameters selected for measurement of Pb isotopic ratios using ICP-QMS

Detector acquisition mode	Pulse counting mode
Dead time	36.8 ns
Dwell time	10 ms
Number of runs	10
Number of scans	10000
Isotopes measured	^{202}Hg , ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{203}Tl and ^{205}Tl
Points per peak	1
Number of replicates	3
Analysis time per sample	16 minutes

176 MC-ICP-MS

177 Lead isotope analysis was conducted at the NERC Isotope Geosciences Laboratory (BGS, Keyworth,
 178 U.K.) using a Nu Instruments, Nu Plasma, MC-ICP-MS (Multi-Collector Inductively Coupled Plasma
 179 Mass Spectrometer). Prior to analysis, each sample was spiked with a Thallium (Tl) solution, to enable
 180 correction of instrument induced mass bias. Samples were then introduced into the instrument via an
 181 ESI PFA50 nebuliser attached to a de-solvating unit, (Nu Instruments DSN 100). For each sample, five
 182 ratios were simultaneously measured ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$)
 183 using the instruments array of Faraday detectors. The collector configuration used is illustrated in
 184 Table 3. Each individual acquisition consisted of 3 blocks of 25 cycles, with a 5-second integration time
 185 per cycle, following a 60 second de-focused baseline (c. 7 min. per acquisition). The measured Tl ratio
 186 was used to make an exponential correction for instrument induced mass bias effects on both Pb and
 187 Hg isotopes, based on an assumed $^{205}\text{Tl}/^{203}\text{Tl}$ ratio of 2.3890. Hg was measured at amu 202 and a
 188 proportionate amount subtracted from the ion beam at amu 204, based on an assumed $^{204}\text{Hg}/^{202}\text{Hg}$
 189 ratio of 0.229883.

190 The precision and accuracy of the method was assessed through repeat analysis of a SRM-981, NIST
 191 Pb reference solution, (also spiked with Tl). The average values obtained for each of the mass bias
 192 corrected SRM-981, NIST ratios were then compared to the known values for this reference material
 193 (27): $^{206}\text{Pb}/^{204}\text{Pb} = 16.9417 \pm 29$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4996 \pm 31$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.724 \pm 09$, $^{207}\text{Pb}/^{206}\text{Pb} =$
 194 0.91488 ± 08 and $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677 \pm 24$; Precision = ppm \pm 2sd. All sample data were subsequently
 195 normalised according to the relative deviation of the measured reference values from the true values.

196 The analytical errors for each of the sample ratios were propagated relative to the reproducibility of
 197 the SRM-981, NIST to take into account the errors associated with the normalisation process.

Table 3 Configuration of the Nu Plasma HR 'Zircon' collector block, used for Pb isotope analysis

High 4	High 3	High 2	High 1	Axial	Low 1	Low 2
²⁰⁸ Pb	²⁰⁷ Pb	²⁰⁶ Pb	²⁰⁵ Tl*2	²⁰⁴ Pb ²⁰⁴ Hg	²⁰³ Tl*2	²⁰² Hg*1

*1 Measured to allow for the correction of the isobaric interference of ²⁰⁴Hg on ²⁰⁴Pb.

*2 Measured to allow for the correction of instrumental mass bias.

198 Procedures for optimising measurement of Pb isotopes using ICP-QMS

199 Evaluation of detector dead time correction factor

200 A dead time correction factor (dtcf) was determined, according to a method described by Nelms,
 201 Quételet (17), for the isotopic ratios: ²⁰⁴Pb/²⁰⁸Pb, ²⁰⁶Pb/²⁰⁸Pb and ²⁰⁷Pb/²⁰⁸Pb. Values of dtcf were
 202 measured from intensity ratios determined across a range of Pb standard solutions (i.e. 0, 2, 4, 6,
 203 8....22 µg L⁻¹) prepared from SRM-981, NIST in 2% HNO₃. Data from samples providing higher count
 204 rates for ²⁰⁸Pb were used so that the detector was more likely to be close to saturation; we also wanted
 205 to investigate the validity of measurements up to the point where the detector tripped to analogue
 206 signals.

207 The dtcf was initially set to zero ns. An isobaric correction factor for ²⁰⁴Hg was determined from
 208 measurement of the signal at m/z = 202 (²⁰²Hg). This correction was negligible for samples as Hg would
 209 be efficiently evaporated from the sample solutions during the high temperatures of the digestion
 210 procedure. Intensity values (cps) were measured using a quadrupole dwell time of 10 ms with 200
 211 sweeps and 20 separate integrations to give 4000 quadrupole visits to each isotope per sample and a
 212 total signal integration time per isotope of 40 seconds. Initially, a blank correction was made to all raw
 213 Pb isotope intensities (I_{sample} - I_{blank}). Sample intensity values were corrected using Eq. 1, following
 214 optimisation of the dtcf value (28).

$$215 \quad I_{\text{corr}} = \frac{(I_{\text{sample}} - I_{\text{blank}})}{1 - (I_{\text{sample}} - I_{\text{blank}})dtcf \cdot 10^{-9}} \quad (1)$$

216 The value of dtcf was optimised by determining the slope of individual isotope intensity ratios
 217 (i.e. $^{204}\text{I}_{\text{corr}}/^{208}\text{I}_{\text{corr}}$) against the intensity signal for ^{208}Pb (cps) and varying the value of dtcf until the value
 218 of the slope squared (slope^2) was minimised. This was undertaken using the Microsoft Excel *Solver*
 219 function. The optimised values of dead time calculated for Pb isotopic ratios were 37.4, 36.7 and 36.3
 220 ns for $^{204}\text{Pb}/^{208}\text{Pb}$, $^{206}\text{Pb}/^{208}\text{Pb}$ and $^{207}\text{Pb}/^{208}\text{Pb}$ ratios respectively. The values of dtcf calculated did not
 221 change systematically with mass difference between the isotopes and they were independent of mass
 222 and analyte concentration as illustrated in Fig. 1 for the isotopic ratio $^{204}\text{Pb}/^{208}\text{Pb}$. An average value of
 223 dead time correction was calculated (i.e., 36.8 ns) and set within the instrument software. Values of
 224 dead time were in good agreement with previous studies (20, 29) and close to the manufacturer's
 225 factory-set value of 40 ns. Subsequently, all analytical sessions were preceded by measurement and
 226 re-setting of detector dead-time.

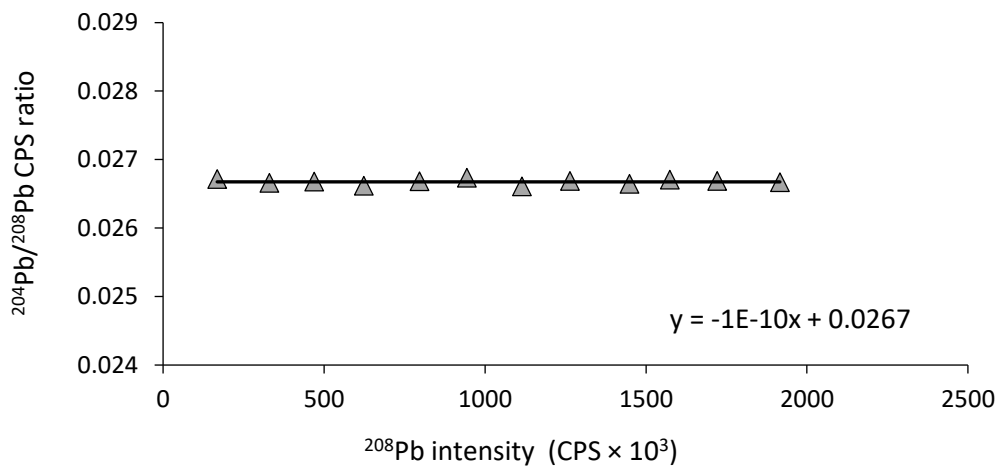


Figure 1. Isotopic count ratios (CR) $^{204}\text{Pb}/^{208}\text{Pb}$ vs ^{208}Pb intensity measurements (cps) at the optimised value of dtcf.

227 Mass bias correction

228 Prior to mass bias correction, Pb isotope intensities were corrected for an isobaric interference from
 229 ^{204}Hg , through measurement of ^{202}Hg , and for operational blanks. The resulting data was then
 230 corrected for mass bias using both *proxy internal* and *external standards*. Thallium ($2 \mu\text{g L}^{-1}$) was used
 231 as an internal standard because its isotopic masses (i.e., ^{203}Tl and ^{205}Tl) are sufficiently close to those
 232 of the Pb isotopes that it can be used as a proxy for continuous monitoring of mass discrimination in
 233 individual samples (22). Thallium was continuously delivered to the nebulizer on a separate line and
 234 the bias per unit mass (ϵ) determined from the measured $^{205}\text{Tl}/^{203}\text{Tl}$, when compared to the known,
 235 'true', value for this ratio i.e., 2.3871 (1).

236 Three equations (i.e., linear, power and exponential models; equations 2-4 below) are generally used
 237 to estimate the mass discrimination correction factor (or 'K-factor') for a pair of Pb isotopes when Tl
 238 is used as an internal standard (15, 30). Most previous studies conducted using MC-ICP-MS have
 239 favoured a power (Eq 3.) or exponential (Eq 4.) equation over a linear relation (Eq. 2) on grounds of
 240 precision for internal standardisation (1, 15, 30). However, a linear model (Eq. 2) is more commonly
 241 used for mass discrimination correction for quadrupole mass analysers as this has been found to be a
 242 sufficiently accurate model as their precision is rarely good enough to discriminate between models
 243 (31).

244
$$K = 1 + (\Delta m \varepsilon) \dots\dots\dots (2)$$

245
$$K = (1 + \varepsilon)^{\Delta m} \dots\dots\dots (3)$$

246
$$K = \exp(\Delta m \varepsilon) \dots\dots\dots (4)$$

247 In equations 2 – 4, Δm is the mass difference between two Pb isotopes; K is the K-factor for the ratio
 248 of those two isotopes and ε is the bias per unit mass determined for the ratio $^{205}\text{Tl}/^{203}\text{Tl}$. Preliminary
 249 data for Pb isotopes were processed using the linear (Eq. 2), power (Eq. 3) and exponential (Eq. 4)
 250 equations to assess the difference in mass bias correction factor, but very similar results were
 251 observed using the three approaches. Therefore, the simplest linear correction was used in this study
 252 and applied to all samples and the NIST SRM-981 Pb reference material.

253 Thallium-corrected data was then further normalised using the NIST SRM-981 Pb reference material
 254 to allow for any element-specific drift in instrument sensitivity during the experiment. The refined K-
 255 factor for each sample was calculated using interpolated values of the K-factor for SRM-981, NIST
 256 samples ($15 \mu\text{g L}^{-1}$) run every 10th sample. The magnitude of the K-factor correction using Tl varied
 257 between 0.5% for the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio to 2% for the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio, reflecting the greater correction
 258 for mass bias for wider spaced isotopes. The subsequent SRM-981 K-factor corrections varied between
 259 0.25% and 0.5% and were not mass dependent, probably reflecting differences in Pb-Tl responses,
 260 that others have addressed using artificially modified Tl isotope ratios. A table of these K-factors for
 261 both correction stages are given in Electronic Appendix Table 1.

262 **Quadrupole dwell time**

263 Improvement in precision of Pb isotope ratio determinations can be achieved by decreasing the
 264 quadrupole dwell time in order to reduce low frequency noise in the plasma (11), but this may result
 265 in inaccurately jumping to the mass peak maximum at extremely fast scanning rates (low dwell times)
 266 (19) and additionally becomes a state of diminishing returns as the quadrupole settle time becomes
 267 large relative to the data acquisition time. This suggests that there should be an optimum isotope

268 dwell time at which counting precision is greatest. The influence of quadrupole dwell time was tested
 269 using a solution of SRM-981, NIST ($5 \mu\text{g L}^{-1}$) spiked with Tl ($1 \mu\text{g L}^{-1}$). The test solution was aspirated
 270 directly and the precision of Pb isotopic ratio measurements (% RDS) determined for a range of dwell
 271 times. Ten separate integrations were set with the number of sweeps changed inversely to increasing
 272 isotope dwell time (1-15 ms) to retain a constant overall signal acquisition time. Values of %RSD for
 273 individual Pb isotopic ratios were plotted against dwell time.

274 Figure 2 shows that the variation in precision across the range of dwell times was neither systematic
 275 nor significantly different between dwell times, with the single outlier of ^{204}Pb ratios at 9 ms. It was
 276 therefore decided to retain a dwell time of 10 ms for further studies as suggested in the literature
 277 (32).

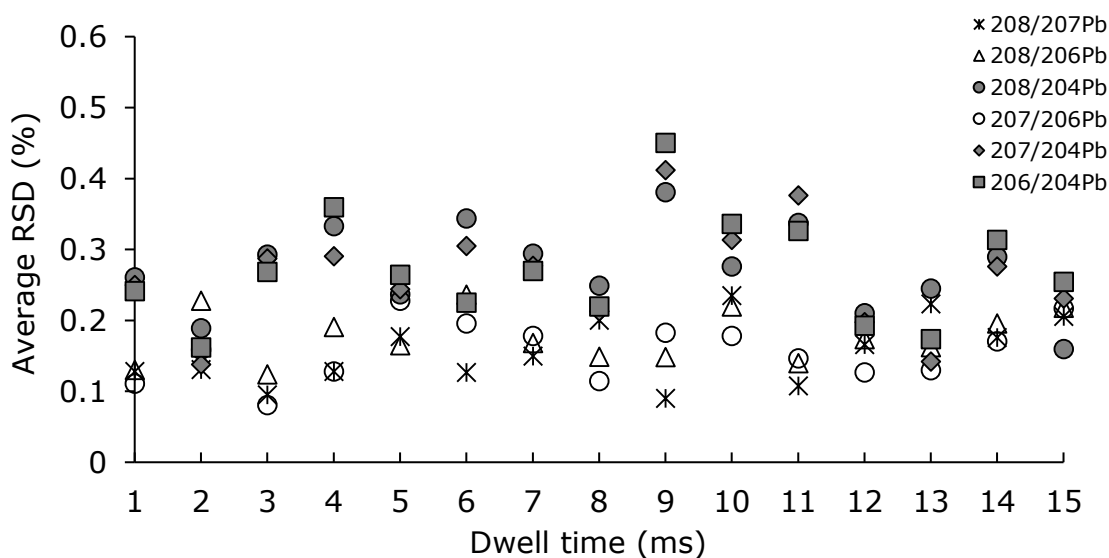


Figure 2. Average residual standard deviation expressed as a proportion (%) of Pb isotope ratios against dwell time (ms) whilst retaining a constant total acquisition time.

278 **Optimising the number of scans (quadrupole peak visits)**

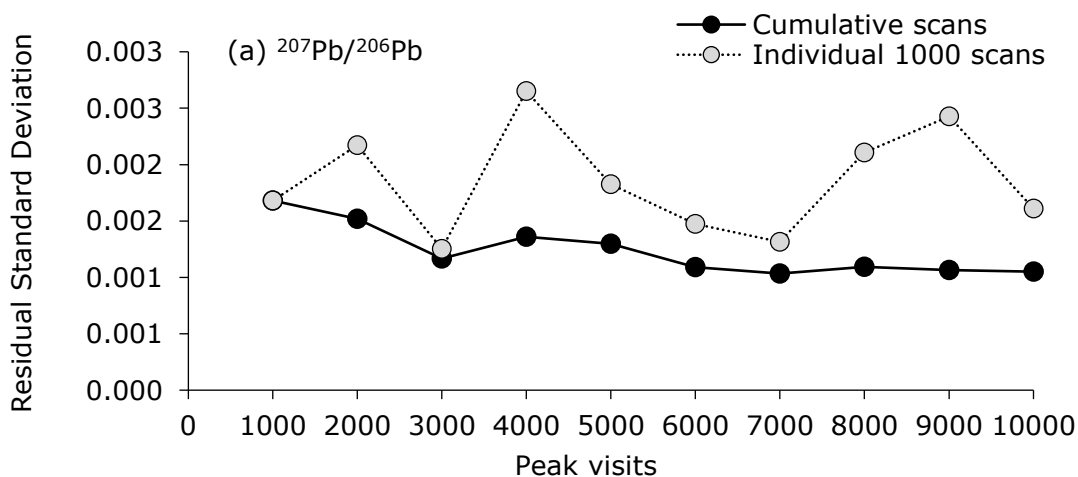
279 To optimise the number of scans (peak visits by the quadrupole), 10 separate runs with 1000 scans
 280 per run was selected and the number of points per peak was set to one (dwell time 10 ms). The total
 281 analysis time for each sample (SRM-981, NIST) was approximately 16 minutes. To determine the
 282 effects of the number of scans on Pb isotopic ratios determination, each of the 10 runs of 1000 scans
 283 was processed (i) separately and (ii) cumulatively i.e. using 1000, 2000 scans etc. A comparison of the
 284 resulting data is shown in Fig 3. The error for different Pb isotopic ratios (i.e., $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$
 285 and $^{208}\text{Pb}/^{204}\text{Pb}$) was assessed by comparing residual standard deviation values against the multi-

286 collector data. Results were calculated by taking 10 measurements of 1000 peak visits and calculating
 287 the residual standard deviation from those 10 values. Residual standard deviation (RSD) was
 288 calculated from multi-collector data Eq. 5,

$$289 \quad RSD = \sqrt{\frac{\sum (IR_{MC} - IR_{Quad})^2}{df}} \quad 5$$

290 where IR_{MC} and IR_{Quad} are isotope ratio measurements from the multi-collector and quadrupole
 291 instruments and df represents degrees of freedom.

292 The data processed using individual groups of 1000 scans showed relatively high and variable residual
 293 standard deviation values for all isotopic ratios (grey circles). By contrast, data processed in a
 294 cumulative way showed better precision and consistency for all three isotopic ratios. Precision
 295 generally increased with increasing number of scans as shown in Fig 3. (a-d). For the current study we
 296 decided to use 10,000 scans to try to minimise variation due to counting statistics, although Fig .3
 297 suggests this could potentially be reduced to 6000 scans to save time without significant loss of
 298 precision. For example, if the precision of the ratios is solely based on counting (Poissonian) based
 299 statistics, then the standard deviation of the number of counts measured is the square root of the
 300 mean number of counts. This would result in a $\sqrt{10} = 3.162$ improvement in ratio precision, when using
 301 10,000 ratios rather than 1,000. Whereas acquiring 10,000 ratios rather than 6,000 would produce a
 302 more modest precision improvement of $\sqrt{(10,000/6,000)} = 1.291$. This potentially being swamped by
 303 other normally distributed noise sources.



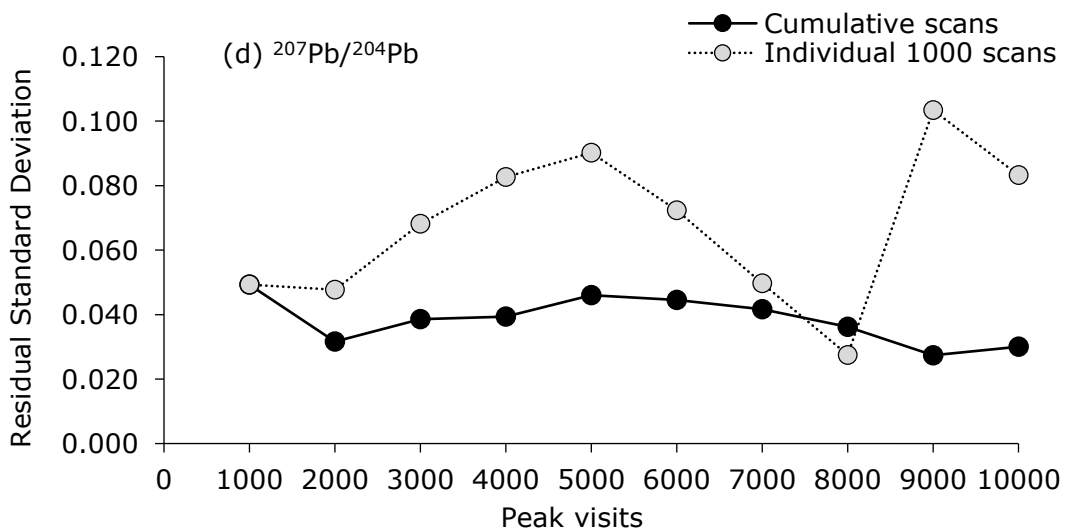
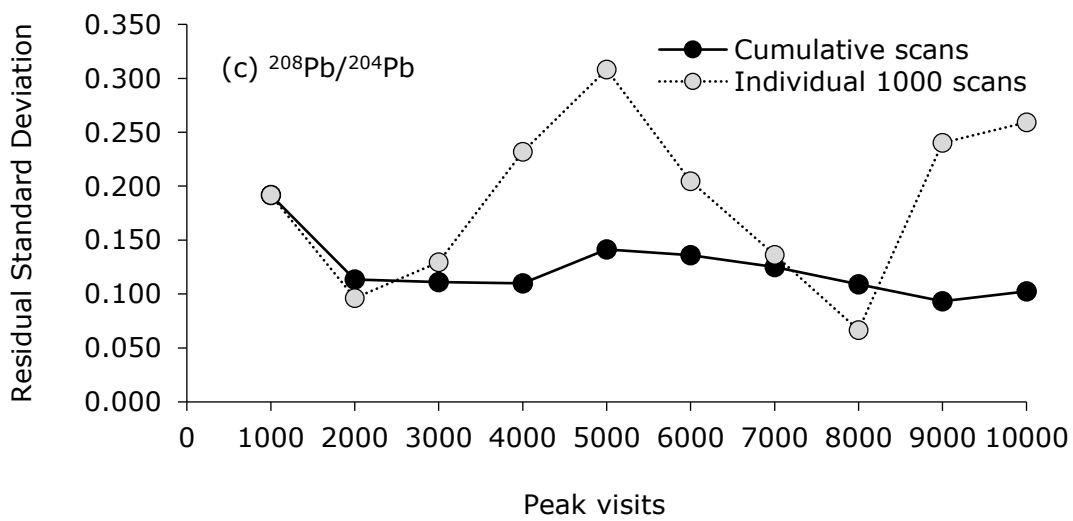
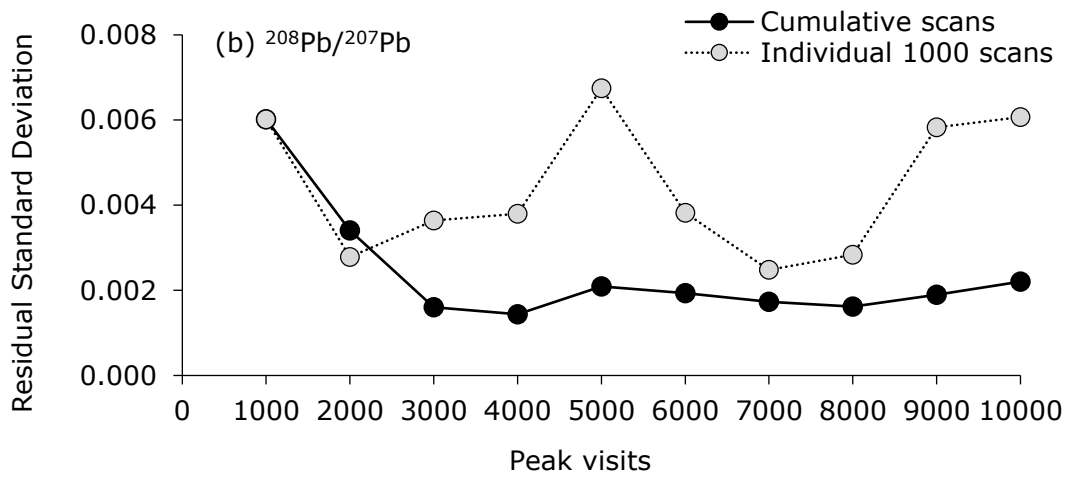
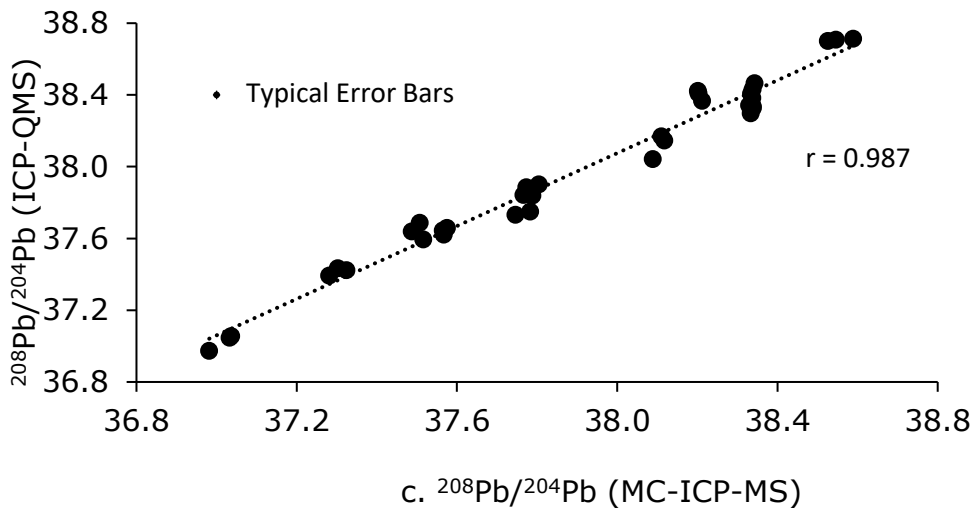
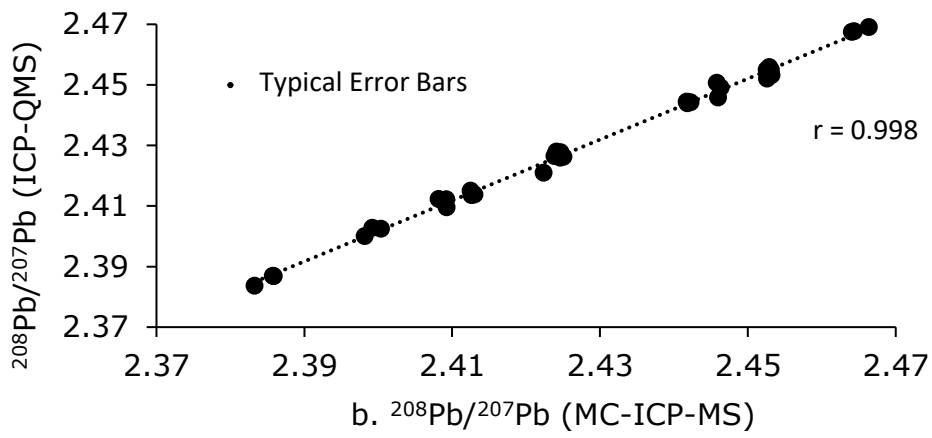
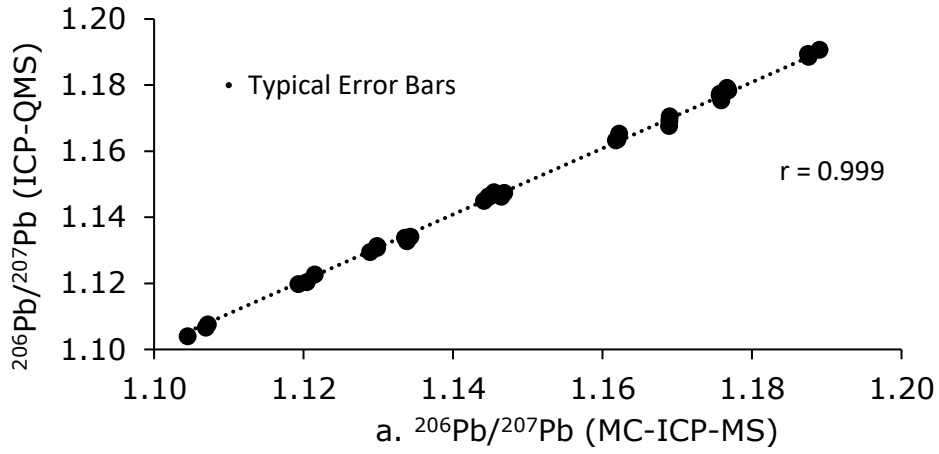


Figure 3. Values of residual standard deviation, comparing ICP-QMS with MC-ICP-MS, for Pb isotope ratios (a) $^{207}\text{Pb}/^{206}\text{Pb}$, (b) $^{208}\text{Pb}/^{207}\text{Pb}$, (c) $^{208}\text{Pb}/^{204}\text{Pb}$, and (d) $^{207}\text{Pb}/^{204}\text{Pb}$ against the number of quadrupole scans (peak visits).

304 **Results and discussion**

305 **Comparison of Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$)**
306 **measured by ICP-QMS and MC-ICP-MS**

307 Following optimisation of the Pb isotopic ratios measurement protocol, the processed data for diluted
308 soil sample digests analysed with ICP-QMS (10,000 scans) were compared to equivalent data for
309 chemically separated Pb measured by MC-ICP-MS. Each of the 3 digestions for an individual sample
310 were treated as a separate data point to achieve the most direct comparison of the two techniques.
311 An excellent correlation ($r=0.999$ and $r=0.998$; $n=36$) was observed for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$
312 isotopic ratios with slope values of 1.0008 and 1.0006 respectively shown in Fig 4. (a and b). The
313 correlation observed for the $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratio was also good, albeit a little weaker than for the
314 other ratios (Fig 4. c; $r=0.987$, slope=1.0017). This is understandable given that: (i) there is a greater
315 dependence on mass bias because of the mass difference of 4 amu; (ii) ^{204}Pb (isotopic abundance =
316 1.4%) produces a lower signal giving poorer counting statistics; (iii) the large difference in isotopic
317 abundance results in increased vulnerability to errors in dead time correction and (iv) the need for Hg
318 correction on ^{204}Pb , which further compromises the measurement uncertainty. Of these potential
319 effects, the dominant and unavoidable one will be number (ii), poorer statistics from the isotopic
320 abundance of ^{204}Pb c.1.4% compared to the next smallest isotope ^{207}Pb c.22.1%; this being a factor of
321 c.3.4. All of the other effects are either minimised by optimisation, (i) and (iii), or, in the case of (iv),
322 insignificant for samples prepared in the current study by HF digestion.



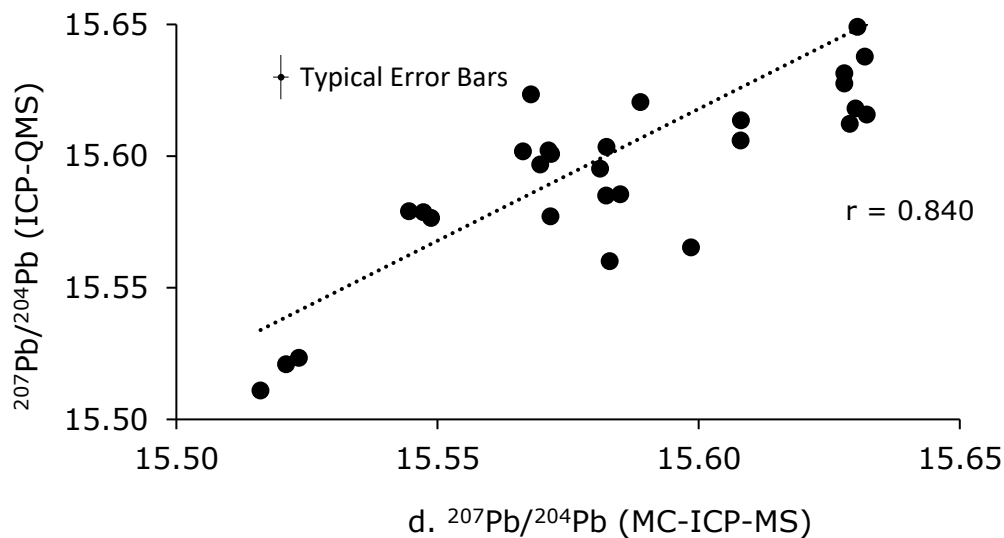


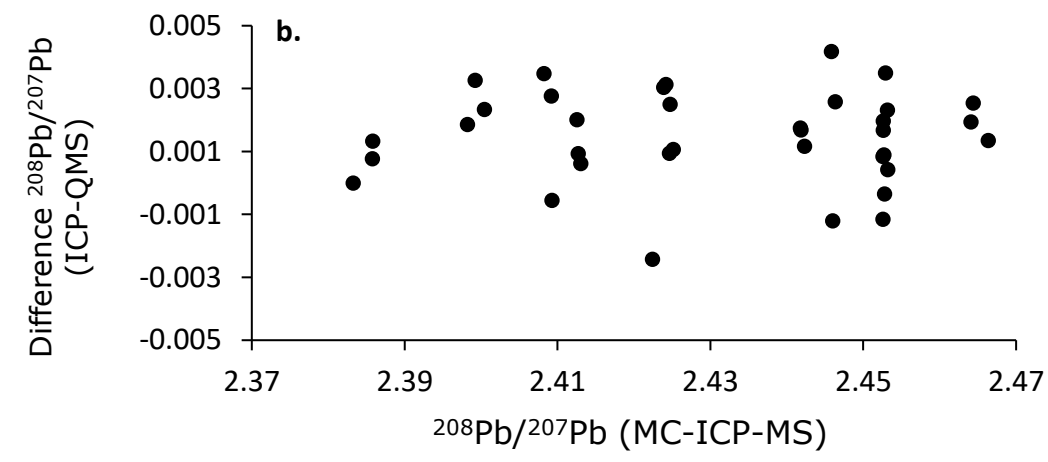
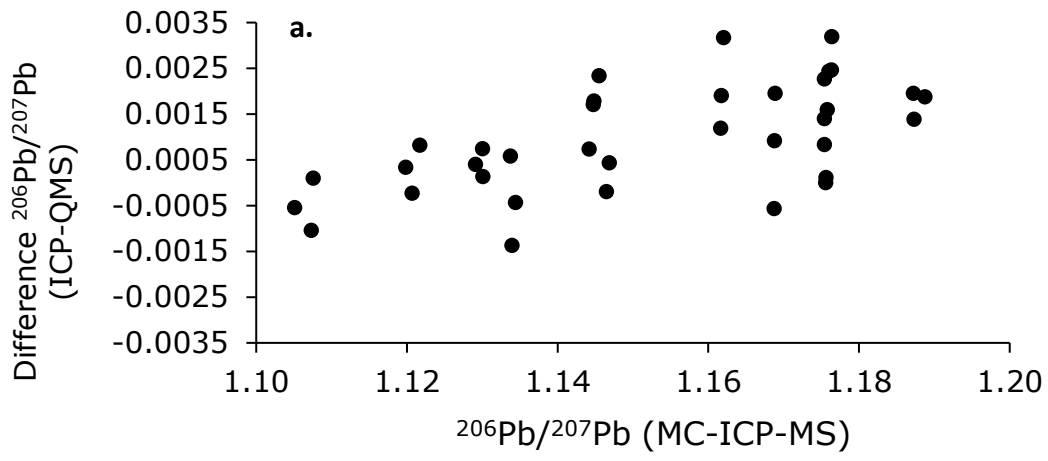
Figure 4. Correlation of Pb isotope ratios (a) $^{206}\text{Pb}/^{207}\text{Pb}$, (b) $^{208}\text{Pb}/^{207}\text{Pb}$, (c) $^{208}\text{Pb}/^{204}\text{Pb}$ and (d) $^{207}\text{Pb}/^{204}\text{Pb}$ measured using quadrupole (ICP-QMS) and multi-collector (MC-ICP-MS) instruments.

323 With such strong correlations it is instructive to examine the difference between the
 324 accuracy/precision of the benchmark MC-ICP-MS and the ICP-QMS data (Fig 5. a- d), assuming that
 325 the MC-ICP-MS has no error for the purposes of this comparison. There may be two sources of error
 326 between the datasets: *additive* i.e. a simple offset value constant for all samples, and *multiplicative*
 327 i.e. a change in value proportional to the isotope ratio measured. For $^{206}\text{Pb}/^{207}\text{Pb}$ (Fig. 5a) there was a
 328 clear increase in error with increasing isotopic ratio, indicating a multiplicative bias between ICP-QMS
 329 and MC-ICP-MS. For $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ this was not apparent. A regression analysis of ICP-
 330 QMS on MC-ICP-MS was made and tested for significance of the slope being different to 1 for all ratios
 331 shown in Table 4. All slope values were statistically different from 1 except $^{208}\text{Pb}/^{206}\text{Pb}$; however only
 332 in the 4th significant figure. To account for the effect of the very narrow range of isotope ratio values,
 333 an intercept between the ICP-QMS and MC-ICP-MS data was estimated by correcting the ICP-QMS
 334 data for the slope, then calculating the difference between the two data sets. The median difference
 335 was calculated (Table 4) to avoid outliers biasing the estimate. In terms of impact, the offset for
 336 $^{208}\text{Pb}/^{204}\text{Pb}$ ratio was the most significant with an absolute value of 0.02, equivalent to approximately
 337 0.04% of the median $^{208}\text{Pb}/^{204}\text{Pb}$ ratio.

338 As each original soil sample was digested and analysed separately 3 times there was an opportunity
 339 to test 'fitness for purpose' for the whole method from digestion to ICP-QMS and MC-ICP-MS
 340 measurement. This was achieved using analysis of variance (ANOVA) to separate the total variance of
 341 the dataset into the analytical variance and the true variance between samples; where the analytical
 342 variance is a combination of the digestion variance and the measurement variance.

343 In evaluating the quality of data produced by the two techniques the first comparison is the within-
344 sample analytical precision (as measured by RSD %) of the ICP-QMS with that of MC-ICP-MS (Table 5).
345 If we assume that the MC-ICP-MS inherently has a better measurement precision but with the within
346 sample precision essentially being equal between the techniques, then we must assume that the
347 digestion process has limited our analytical precision. For example, for $^{207}\text{Pb}/^{206}\text{Pb}$ values of RSD for
348 ICP-QMS and MC-ICP-MS were 0.09% and 0.07%, respectively, which suggests the data were digestion
349 heterogeneity limited. By contrast, for $^{207}\text{Pb}/^{204}\text{Pb}$ the greater values for ICP-QMS (0.13%) compared
350 to MC-ICP-MS (0.02%) suggests that the precision is limited by instrumental factors. This is supported
351 by quantifying if within sample variance is different between ICP-QMS and MC-ICP-MS using the F-
352 statistic. This statistic demonstrated that there was no difference in precision between the two
353 instruments for $^{207}\text{Pb}/^{206}\text{Pb}$; but very significant differences for $^{207}\text{Pb}/^{204}\text{Pb}$ (Table 5). This implies that
354 there is no advantage in using MC-ICP-MS, and chemical separation of Pb, for determination of
355 $^{207}\text{Pb}/^{206}\text{Pb}$ ratios but the converse is true for $^{207}\text{Pb}/^{204}\text{Pb}$. This is qualified by consideration of the mass
356 of Pb required for this comparison. In the current study, typical of many environmental investigations,
357 the mass available is not a limiting factor and the equivalence of capability for $^{207}\text{Pb}/^{206}\text{Pb}$ ratios holds.
358 However, in other applications where the mass of Pb available may be limited, the greater sensitivity
359 of the MC-ICP-MS (a factor of 5-10 fold), provides a clear advantage, even for $^{207}\text{Pb}/^{206}\text{Pb}$ ratios.

360 The ANOVA, via the F-statistic, can be further used to test, for each isotope ratio, the power of the
361 analytical technique to discriminate between samples. The greater the ratio of the “between samples”
362 variance and the “within sample” variance which is the F-statistic, the better the discrimination i.e.
363 when the ratio falls below the F_{crit} value we have no discrimination. For $^{207}\text{Pb}/^{206}\text{Pb}$, a variance ratio of
364 615 for ICP-QMS implies that we can readily discriminate between samples; for $^{207}\text{Pb}/^{204}\text{Pb}$ with a
365 variance ratio of 6, this was not the case, as this is barely above the F_{crit} of 2.78. Thus, values of
366 $^{207}\text{Pb}/^{204}\text{Pb}$ ratio measured by ICP-QMS (the lowest F-value), will have little resolving power between
367 samples and any further analytical improvements should focus on determination of this isotopic ratio.
368 By comparison, the variance ratios for these isotope ratios by MC-ICP-MS were 1123 and 137
369 respectively, suggesting that MC-ICP-MS can be readily used for all isotope ratios to differentiate
370 between samples.



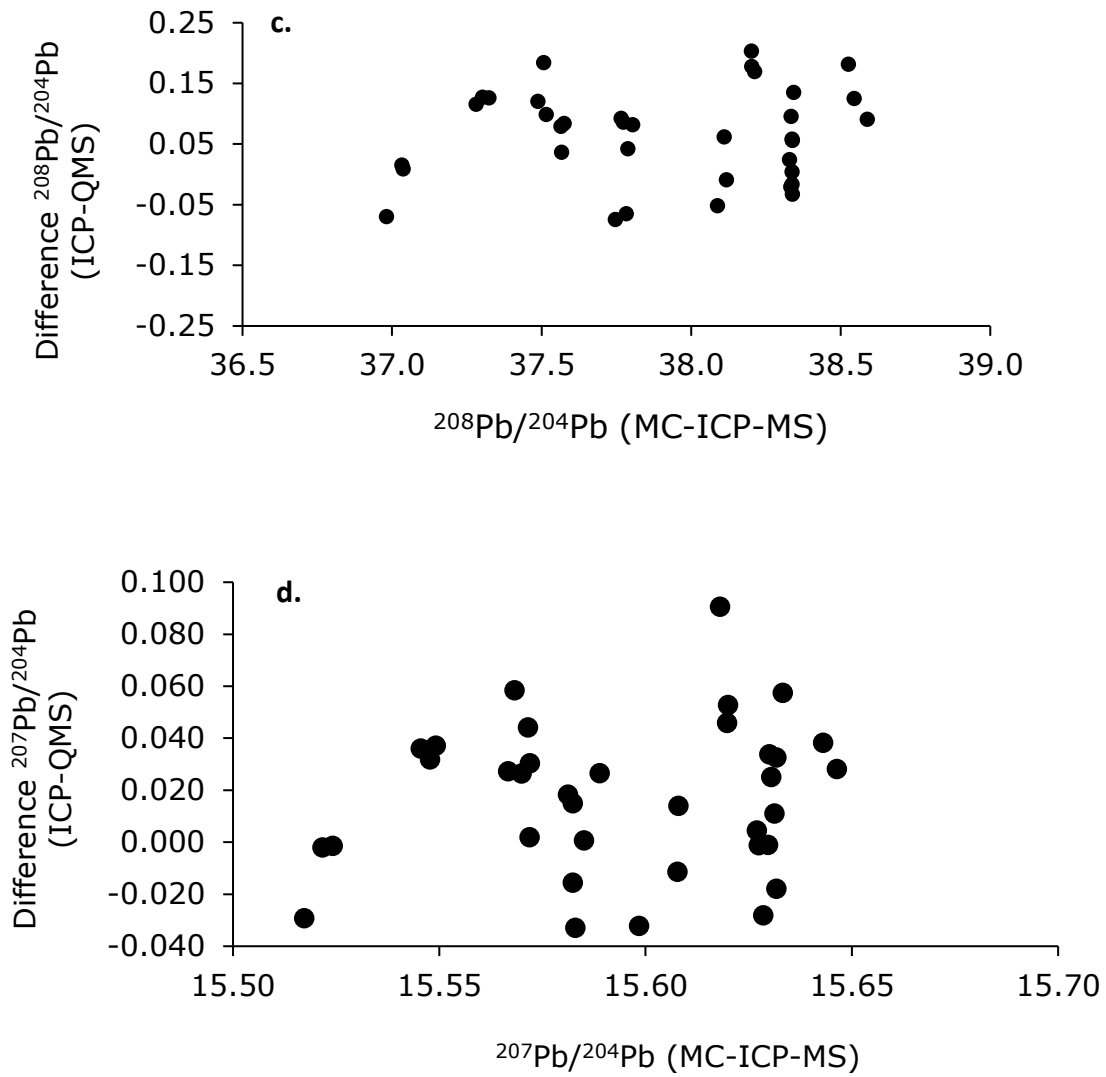


Figure 5. Difference between the benchmark MC-ICP-MS data and the difference between ICP-QMS and MC-ICP-MS (a) $^{206}\text{Pb}/^{207}\text{Pb}$, (b) $^{208}\text{Pb}/^{207}\text{Pb}$, (c) $^{208}\text{Pb}/^{204}\text{Pb}$ and (d) $^{207}\text{Pb}/^{204}\text{Pb}$.

Table 4 Evaluation of significance of slope (multiplicative) and offset (additive) when regressing the difference between measured ICP-QMS and MC-ICP-MS against MC-ICP-MS ratios, showing the significant differences occurring in the offset for ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios.

Ratio	Slope	95% Confidence interval	Median Offset
²⁰⁷ Pb/ ²⁰⁶ Pb	0.9992	0.0003	0.00007
²⁰⁶ Pb/ ²⁰⁷ Pb	1.0009	0.0003	-0.0001
²⁰⁸ Pb/ ²⁰⁶ Pb	0.9998	0.0004	0.0001
²⁰⁸ Pb/ ²⁰⁷ Pb	1.0006	0.0002	0.0002
²⁰⁶ Pb/ ²⁰⁴ Pb	1.0019	0.0006	0.0008
²⁰⁷ Pb/ ²⁰⁴ Pb	1.0011	0.0006	0.0045
²⁰⁸ Pb/ ²⁰⁴ Pb	1.0017	0.0007	0.02

Table 5 Statistical comparison of within sample measurement precision with between sample precision and evaluation for Pb isotope ratios determined both by ICP-QMS and MC-ICP-MS. Note: the greater the F-statistic is over the critical F value, the greater the power of the measurement to discriminate true sample variation from analytical 'noise'.

		²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb
MC-ICP-MS	Within sample RSD%	0.07	0.03	0.08	0.02	0.05	0.07	0.03
MC-ICP-MS	Between sample RSD%	2.27	1.21	2.48	0.24	1.28	2.25	1.04
ICP-QMS	Within sample RSD%	0.09	0.08	0.14	0.13	0.16	0.09	0.08
ICP-QMS	Between sample RSD%	2.34	1.28	2.58	0.31	1.32	2.31	1.04
F _{crit} 1-tail 95% (10df,10df) = 2.98	Within sample F-stat MC-ICP-MS v ICP-QMS	1.94	6.11	3.35	37.30	10.34	2.00	5.40
F _{crit} 1-tail 95% (22df,10df) = 2.78	Between v Within sample F-stat ICP-QMS	615	237	322	6	67	625	167
F _{crit} 1-tail 95% (22df,10df) = 2.78	Between v Within sample F-stat MC-ICP-MS	1123	1302	1001	137	653	1180	902

372 **Comparison of Binary plots**

373 Binary plots were used to attempt soil Pb source apportionment for the three sets of data derived
374 from (i) MC-ICP-MS, (ii) ICP-QMS measured using 10,000 scans, and (iii) ICP-QMS using just the first
375 run of 1,000 scans as an example of acquisition parameters used previously in the literature (33). The
376 first comparison was made using a conventional binary plot ($^{208}\text{Pb}/^{207}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$) as shown in
377 Fig. 6. The MC-ICP-MS data (dark circles) all fell on a single straight trend line, expected from a simple
378 2 isotopic end-member system. Similarly, data analysed by ICP-QMS with 10,000 scans (grey circles)
379 fell very close to the multi-collector data. By contrast, data from ICP-QMS using 1000 scans (white
380 circles) clearly deviated from the multi-collector data and the single mixing line in the binary plot. The
381 standard error at each data point ($n=3$) was also large compared to ICP-QMS data analysed using
382 10,000 scans where reproducibility was very high.

383 A further comparison was made using a second binary plot (Fig. 7) involving the ^{204}Pb isotope ($^{208}/^{204}\text{Pb}$
384 versus $^{206}\text{Pb}/^{207}\text{Pb}$) in an attempt to identify the presence of further end member sources not revealed
385 by Fig. 6; as Ellam (34) has pointed out plots based only on $^{206,207,208}\text{Pb}$ ratio have a limited ability to
386 discriminate more than 2 end-members. Again, all data points determined by MC-ICP-MS fell on a
387 single straight mixing line, providing no evidence of a 'third source' of Pb. The data determined by ICP-
388 QMS using 10000 scans (grey circles) again fell very close to the multi-collector data. However, a few
389 points visibly deviated from the single mixing line and the standard errors were very small, suggesting
390 a small systematic deviation. The largest systematic deviations and standard errors ($n=3$) were
391 observed for ICP-QMS data using 1,000 scans (white circles). It is clear that although a straight line
392 through the data would indicate 2 dominant sources, the substantial scatter around the mixing line
393 could be erroneously interpreted as indicating multiple (> 2) sources of Pb in the current dataset. This
394 highlights the necessity for longer total acquisition time than previously reported (33, 35) and a fuller
395 understanding of causes of error in determination of Pb isotope ratios.

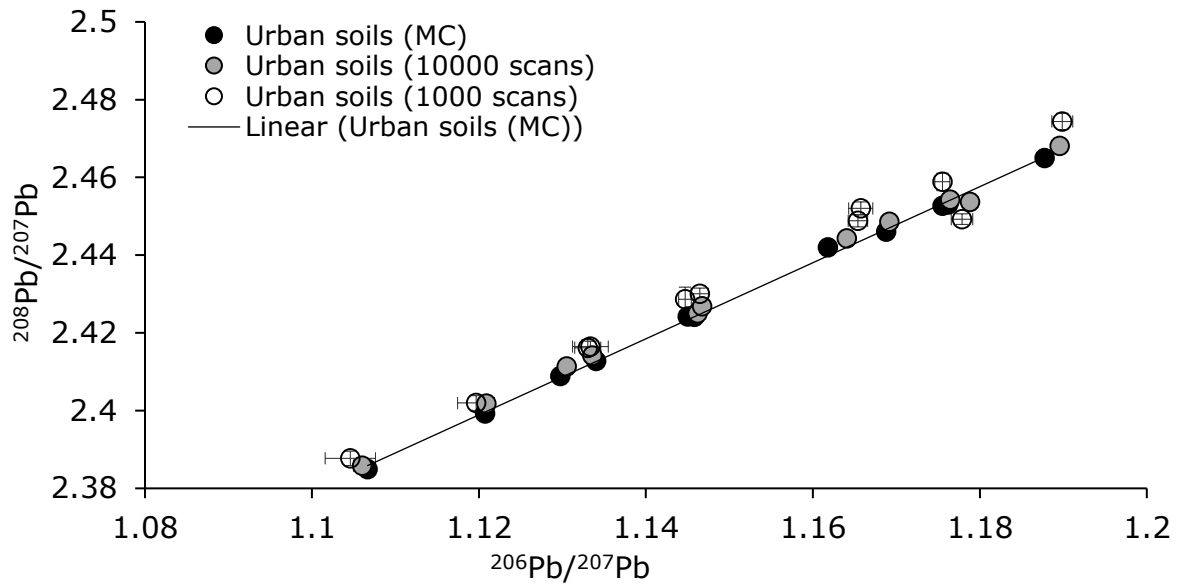


Figure 6. A binary plot using isotopic ratios $^{208}\text{Pb}/^{207}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ for data derived from MC-ICP-MS and ICP-QMS with either 10,000 or 1,000 scans. Note error bars for MC-ICP-MS and ICP-QMS (10000 scans) are smaller than symbols for most samples.

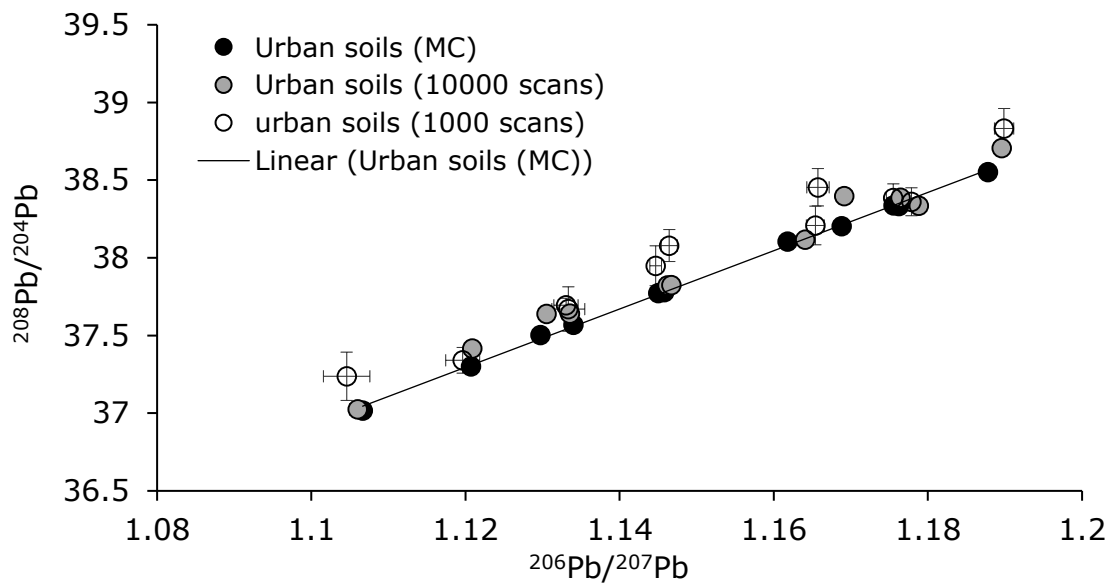


Figure 7. A binary plot using isotopic ratios $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ for data derived from MC-ICP-MS and ICP-QMS with either 10,000 or 1,000 scans.

396 **Conclusions**

397 The use of ICP-QMS for the determination of lead isotope ratios in environmental samples rather than
398 TIMS or MC-ICP-MS is a highly attractive approach. Advantages include greater sample throughput,
399 both as a result of sample introduction at atmospheric pressure and the possibility of avoiding
400 separation of Pb from its matrix. This permits larger scale, more representative and cost-effective
401 applications and has led to its adoption in many laboratories and resulted in numerous publications.
402 Recently, Gulson et al (36) have called into question the quality of data produced by ICP-QMS and
403 conclusions drawn from such data. However, it may be argued that this is not an inherent limitation
404 of the ICP-QMS technique but a lack of attention to detail in making measurements and an
405 understanding of the 'fitness for purpose' of chosen methodologies.

406 Therefore, in this study a protocol is refined for accurate and precise determination of Pb isotope
407 ratios in urban soils using current-generation ICP-QMS. The operating parameters optimised were;
408 individual dilution of soil samples to a single Pb concentration (15 ug L^{-1}), identical to that of an
409 external isotope standard (SRM-981, NIST), determination of dead time correction factor (dtcf = 36.8
410 ns), optimisation of quadrupole dwell time (10 ms), number of scans per sample and use of both
411 internal (TI) and external (SRM-981, NIST) mass bias correction. No dependency of measurement
412 precision on isotope dwell time, was observed compared to that observed in studies with previous
413 generations of ICP-QMS instrument. High reproducibility was observed for data where the number of
414 scans was increased to 10,000 (total analyte time per sample = 16 min). This developed protocol was
415 further compared to Pb isotopic ratios data measured through MC-ICP-MS using the same soil sample
416 digests. An excellent correlation was observed for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios ($r = 0.999$
417 and $r = 0.998$, $n = 35$). The correlation observed for $^{208}\text{Pb} / ^{204}\text{Pb}$ isotope ratio was also strong but
418 weaker than for other ratios ($r=0.987$).

419 Analysis of Variance (ANOVA) was used to test 'fitness for purpose' for the whole method from
420 digestion of samples to ICP-QMS and MC-ICP-MS measurement. No statistical difference was observed
421 for $^{207}\text{Pb}/^{206}\text{Pb}$ (ICP-QMS RSD 0.09%; MC-ICP-MS 0.07%) whereas for determination of the $^{207}\text{Pb}/^{204}\text{Pb}$
422 isotope ratio (ICP-QMS 0.13%; MC-ICP-MS 0.02%) ICP-QMS appeared to be limited by instrumental
423 factors. Comparison of measurement variance with that of the between-sample variance was also
424 undertaken using the F-statistic. It was apparent that the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio determined through ICP-
425 QMS (V.R. = 615) has excellent discriminating power between samples; by contrast utilising the
426 $^{207}\text{Pb}/^{204}\text{Pb}$ ratio (V.R. = 6) for Pb source apportionment would require further analytical
427 improvements, for example a detector with a wider pulse counting dynamic range that would allow
428 the accumulation of better counting statistics within a reasonable time-frame.

429 In summary, although ICP-QMS is not capable of the absolute precision or the full source
430 discrimination power of MC-ICP-MS, it is clearly capable of providing 'fit-for-purpose' Pb isotope ratio
431 data on environmental samples, such as soils, where sample heterogeneity can be a limiting factor.

432 **Conflicts of interest**

433 SN is an employee of Thermo Fisher Scientific but the study was independently designed and
434 executed by the other authors.

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