

1 **Characterising the stable ( $\delta^{88/86}\text{Sr}$ ) and radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotopic**  
2 **composition of strontium in rainwater**

3

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22

23 **Abstract**

24 Rainwater plays a major role in determining the transfer of elements and pollutants to  
25 soils and hydrological catchments, with compositional variations reflecting the extent

26 of mixing between marine (sea-salt), terrestrial (dust and vegetation) and  
27 anthropogenic aerosols. While the radiogenic strontium isotope system ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) is  
28 often used to help constrain the different sources of atmospheric Sr, the degree of  
29 variability in the stable strontium isotope system ( $\delta^{88/86}\text{Sr}$ ) remains unresolved. In  
30 order to determine how atmospheric Sr affects the  $\delta^{88/86}\text{Sr}$  composition of water  
31 entering the hydrological cycle this study analysed a suite of rainwater samples  
32 collected over the course of a year in central Paris. Rainwater  $\delta^{88/86}\text{Sr}$  compositions  
33 were found to range from 0.13 ‰ to 0.32 ‰, with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios varying between  
34 0.70796 and 0.71093. No seasonality was observed in  $\delta^{88/86}\text{Sr}$ , whereas  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios  
35 were observed to be generally more radiogenic in the summer and less radiogenic in  
36 the winter. Strontium enrichment factors significantly above seawater implied a  
37 predominantly terrestrial (non sea-salt) origin of Sr in rainwater, with the  $\delta^{88/86}\text{Sr}$  and  
38  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of this terrestrial fraction consistent with a mixture of Sr derived  
39 from carbonate dust and agricultural fertiliser. Evidence for a  $\sim 0.1$  ‰ decrease in the  
40  $\delta^{88/86}\text{Sr}$  composition of the River Seine as it passes through Paris suggests that  
41 anthropogenic pollutants may contribute to significant regional variations in the  
42 composition of Sr in the hydrological cycle. Together these results demonstrate that  
43 there is significant potential for both temporal and spatial variations in the  $\delta^{88/86}\text{Sr}$  and  
44  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of rainwater that need to be taken into consideration when  
45 studying  $\delta^{88/86}\text{Sr}$  variations in localised catchments.

46

#### 47 **Keywords**

48 Strontium; Rainwater; Continental dust; Anthropogenic contamination

49

#### 50 **1. Introduction**

51 There is significant interest in understanding how different atmospheric sources affect  
52 the composition of rainwater as variations in the extent of material contributed by sea-  
53 salt dissolution, terrestrial sources (including dust and vegetation) and anthropogenic  
54 emissions have a major impact on the transfer of elements and pollutants to soils and  
55 hydrological catchments (e.g. Derry and Chadwick, 2007; Négrel and Roy, 1998;  
56 Négrel *et al.*, 2007). Dissolved cation concentrations are commonly used to assess the  
57 relative contribution from these aerosols, but they can be affected by fractionation  
58 processes that occur during the precipitation event (Dupré *et al.*, 1994) thus it can be  
59 difficult to differentiate between locally and externally derived material using  
60 concentration data alone (Négrel and Roy, 1998). The isotopic composition of  
61 rainwater is consequently increasingly being used to establish how the mixing of  
62 atmospheric aerosols varies both spatially and temporally (Anderson *et al.*, 1990,  
63 Artaxo *et al.*, 1988; Chabaux *et al.*, 2005; Dupré *et al.*, 1994; Graustein and  
64 Armstrong, 1983; Négrel and Roy, 1998; Négrel *et al.*, 2007; Seimbille *et al.*, 1989).

65

66 Radiogenic strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) are a particularly useful tracer of  
67 atmospheric aerosols as the globally homogenous  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of seawater  
68 (0.70917; Hodell *et al.*, 1990) enables the contribution of sea-salt to be readily  
69 distinguished from terrestrial and anthropogenic components that have more variable  
70  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (e.g. Derry and Chadwick, 2007; Négrel and Roy, 1998; Négrel *et al.*,  
71 2007). In addition to varying between regions as function of different aerosol  
72 contributions (Aberg *et al.*, 1989; Anderson *et al.*, 1990; Chabaux *et al.*, 2005;  
73 Graustein and Armstrong, 1983; Négrel *et al.*, 2007; Seimbille *et al.*, 1989), the  
74  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of rainwater has been demonstrated to vary within a single rain

75 event (Dupré *et al.*, 1994) and between seasons (Négrel *et al.*, 2007), confirming the  
76 high sensitivity of this system to changing atmospheric conditions.

77

78 Recent analytical advances mean that in addition to  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, the stable  
79 strontium ( $\delta^{88/86}\text{Sr}^1$ ) isotopic composition of rainwater can also be measured (e.g.  
80 Fietze and Eisenhauer, 2006; Krabbenhöft *et al.*, 2009; Neymark *et al.*, 2014; Pearce  
81 *et al.*, 2015; Shalev *et al.*, 2013). The sensitivity of  $\delta^{88/86}\text{Sr}$  to mass dependent  
82 fractionation processes enables combined  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  analyses to be used to  
83 identify sources of material not distinguishable using  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios alone (e.g.  
84 carbonates and seawater), as well as the potential influence of biological and chemical  
85 weathering processes on the composition of atmospheric Sr. Rainwater samples from  
86 the Azores, Congo and China have previously been shown to have  $\delta^{88/86}\text{Sr}$   
87 compositions that vary between 0.05 ‰ and 0.32 ‰ (Pearce *et al.*, 2015), which are  
88 significantly lower than the  $\delta^{88/86}\text{Sr}$  composition of seawater (0.39 ‰; Krabbenhöft *et*  
89 *al.*, 2009; Neymark *et al.*, 2014) and other local water sources (Krabbenhöft *et al.*,  
90 2010; Pearce *et al.*, 2015). Although it is possible that these lighter rainwater  $\delta^{88/86}\text{Sr}$   
91 values represent mass dependent fractionation processes that occur during evaporation  
92 and transportation, Pearce *et al.* (2015) hypothesised that the  $\delta^{88/86}\text{Sr}$  composition of  
93 rainwater was driven to lower values as a result of interaction with isotopically light  
94 atmospheric dust (with reported  $\delta^{88/86}\text{Sr}$  compositions between 0.18 ‰ and 0.29 ‰)  
95 and/or anthropogenic sources.

96

97 The aim of this study was consequently to establish the primary controls on the  
98  $\delta^{88/86}\text{Sr}$  composition of rainwater, and to determine how variations in atmospheric Sr

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<sup>1</sup>  $\delta^{88/86}\text{Sr} = ((^{88}\text{Sr}/^{86}\text{Sr})_{\text{sample}} / (^{88}\text{Sr}/^{86}\text{Sr})_{\text{standard}} - 1) \times 1000$

99 sources may affect the  $\delta^{88/86}\text{Sr}$  composition of water entering the hydrological cycle.  
100 To achieve this annual variations in the  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of rainwater  
101 were determined for a suite of samples collected from Paris, France, which had  
102 previously been demonstrated to contain both sea-salt and terrestrial (non sea-salt)  
103 aerosol components (Chetelat *et al.*, 2009). These rainwater compositions were  
104 subsequently compared to samples taken from the River Seine as well as several  
105 agricultural fertilisers in order to assess how varying atmospheric Sr sources may  
106 influence the  $\delta^{88/86}\text{Sr}$  composition of the local hydrological cycle.

107

## 108 **2. Materials and Methods**

### 109 *2.1 Sampling sites and protocols*

110 Rainwater samples were collected on the roof of the Jussieu Campus University in  
111 central Paris between January and December 2002. The sampling protocol (described  
112 in full in Chetelat *et al.*, 2009) included opening and washing the sampling Teflon  
113 funnel with ultra-pure  $\text{H}_2\text{O}$  immediately before the rain event, rinsing the funnel with  
114 the initial rainwater, then collecting the sample in a pre-cleaned polypropylene bottle.  
115 All samples were filtered immediately after collection through 0.2  $\mu\text{m}$  cellulose  
116 acetate filters and were stored at  $\sim 4^\circ\text{C}$  until analysis. Most samples represent a single  
117 rain event that lasted anywhere from an hour to a day, but in some instances rain  
118 events on two or more consecutive days were combined in order to obtain sufficient  
119 sample for analysis (Table 1). In addition to these rainwater samples, one snowfall  
120 event in Paris was analysed together with two river water samples from the River  
121 Seine; sample ‘SP30’ was taken just before the river entered Paris whereas ‘Rouen’  
122 came from  $\sim 180$  km downstream at the hydrological station of Poses, near the town of  
123 Rouen. These river samples were filtered on collection through 0.2  $\mu\text{m}$  filters before

124 being acidified and stored in a cool (<7 °C) environment until analysis. Three  
125 common agricultural fertiliser samples were also analysed in order to help compare  
126 our results to potential anthropogenic pollutants in the Paris Basin. These samples  
127 were initially dissolved in MQ H<sub>2</sub>O before being acidified and further digested in  
128 HNO<sub>3</sub>. Once dissolved they were chemically purified prior to isotopic analysis in the  
129 same manner as the rainwater and river water samples.

130

## 131 2.2 Analytical methods

132 Elemental abundances were determined using an Agilent inductively coupled plasma  
133 mass spectrometer (ICP-MS), while both radiogenic and stable Sr isotopic analyses  
134 were performed by thermal ionisation mass spectrometry using a ThermoFisher Triton  
135 mass spectrometer in positive ionisation mode. These measurements followed the  
136 analytical protocols described in Pearce *et al.* (2015) and involved the addition of an  
137 <sup>84</sup>Sr-<sup>87</sup>Sr double spike to the stable Sr sample to facilitate the deconvolution of  
138 chemical and instrumental mass dependant fractionation effects (c.f. Krabbenhöft *et*  
139 *al.*, 2009; Neymark *et al.*, 2014; Shalev *et al.*, 2013). 500 ng of Sr was loaded onto  
140 single outgassed zone-refined Re filaments for both the radiogenic and stable Sr  
141 measurements, which were subsequently analysed by running a stable <sup>88</sup>Sr beam  
142 intensity of ~8V for 54 cycles of 10 block ratio measurements with a 16.2 second  
143 integration time. Radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr ratios were determined by normalising the  
144 unspiked sample data to a fixed <sup>86</sup>Sr/<sup>88</sup>Sr ratio of 0.1194 (Nier, 1938), while stable Sr  
145 ratios were resolved by combining the unspiked and spiked filament data and  
146 deconvolving using the exponential fractionation law. The <sup>87</sup>Sr/<sup>86</sup>Sr reproducibility of  
147 the NIST987 international Sr standard over the course of this study was 14 ppm,  
148 while normalised δ<sup>88/86</sup>Sr standards gave a long-term reproducibility of 0.025 ‰ (see

149 Pearce *et al.*, 2015 for more details). The average total procedural blank measured via  
150 isotopic dilution using a pure  $^{84}\text{Sr}$  spike during all rainwater analyses was 28 pg,  
151 <0.01 % of the total amount of Sr processed on each filament.

152

### 153 **3. Results**

#### 154 *3.1 Elemental concentrations and Sr enrichment*

155 The Parisian rainwaters analysed in this study display a strong correlation between Cl  
156 and Na concentrations ( $R^2 = 0.989$ ) and have a Cl/Na regression line that is similar to  
157 the seawater ratio of 1.16 (Fig. 1a; Millero *et al.*, 2008). This agrees with  
158 concentration data previous determined for these samples (Chetelat *et al.*, 2009) and  
159 implies that both elements are predominantly of marine origin (i.e. they are derived  
160 from the dissolution of sea-salt aerosols). Other elements display varying degrees of  
161 enrichment above their seawater ratios, with dissolved Sr concentrations being  
162 enriched by up to a factor of 30 (Table 1). Similar Sr enrichments and elevated Sr/Na  
163 ratios have been observed in the rainwater samples from the Azores, China and Congo  
164 (Fig. 1b; Pearce *et al.*, 2015) as well as in other regions (Chabaux *et al.*, 2005; Derry  
165 and Chadwick, 2007; Grosbois *et al.*, 2000; Négrel and Roy, 1998; Négrel *et al.*,  
166 2007), and imply significant atmospheric Sr contributions from non-marine aerosols.  
167 The extent of Sr enrichment in the Parisian rainwaters is generally correlated to  
168 enrichments in Mg, Ca and  $\text{SO}_4$ , but does not appear to show a strong seasonality  
169 (Table 1).

170

#### 171 *3.2 $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ composition*

172 The rainwater  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured in this study vary between 0.70796 and  
173 0.71093, although most samples fall between 0.70836 and 0.70915 (Table 1; Fig. 2).

174 These values are similar to the Parisian rainwater  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios previously reported  
175 by Seimbille *et al.* (1989) and Négrel *et al.* (2007) (0.70846 to 0.70895), and define  
176 almost identical non-weighted mean compositions of 0.70879 (this study) and 0.7087  
177 (Négrel *et al.*, 2007). Generally lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were observed in the autumn  
178 and winter (September to March) with higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values recorded in the spring  
179 and summer (April to August), although there was a slight decrease in  $^{87}\text{Sr}/^{86}\text{Sr}$  in  
180 early June (Fig. 2). Only one anomalous sample collected on 24/10/2002 falls  
181 significantly outside of these general trends; this is also the only sample that has a  
182  $^{87}\text{Sr}/^{86}\text{Sr}$  composition greater than seawater, thus most likely reflects a significant Sr  
183 contribution from a source not observed in the other samples.

184

185 The  $\delta^{88/86}\text{Sr}$  composition of rainwater varied significantly throughout the year (Fig. 2),  
186 with the range of 0.13 ‰ to 0.32 ‰ consistent with the composition of other  
187 rainwater samples measured to date (Pearce *et al.*, 2015). Unlike  $^{87}\text{Sr}/^{86}\text{Sr}$ , no clear  
188  $\delta^{88/86}\text{Sr}$  variations were resolvable between seasons, although the annual record was  
189 characterised by a progressive shift to lighter values in May/June and subsequent  
190 recovery in July/August (Table 1; Fig. 2). Interestingly, the sample collected on  
191 24/10/2002 has an almost identical  $\delta^{88/86}\text{Sr}$  composition to the following sample  
192 collected on 06/11/2002 (0.30 ‰ and 0.31 ‰ respectively), implying that the inferred  
193 change in atmospheric Sr source(s) on the 24/10/2002 only affected the  $^{87}\text{Sr}/^{86}\text{Sr}$   
194 isotopic composition. Finally, all of the rainwater samples analysed to date have  
195  $\delta^{88/86}\text{Sr}$  compositions that are significantly below seawater; even the sample collected  
196 on 08-09/08/2002 that has a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio very close to seawater (0.70915) only has a  
197  $\delta^{88/86}\text{Sr}$  composition of 0.32 ‰ (Fig. 2).

198



199 **4. Discussion**

200 *4.1 Contribution from sea-salt aerosols*

201 Although the Cl/Na ratio of the Parisian rainwaters is consistent with a predominantly  
202 marine origin for these elements, the large variation in their absolute concentrations  
203 demonstrates that the total amount of dissolved sea-salt varies between samples (Fig.  
204 1a). Similar variations in ionic abundances have been observed in other rainwaters  
205 over France as both a function of their distance from the ocean and the time of  
206 sampling (e.g. Négrel *et al.*, 2007; Meybeck, 1986). Therefore in order to assess what  
207 factors affect the composition of rainwater, separation of the sea-salt (SS) and non  
208 sea-salt (NSS) aerosols is required. The fraction of each element derived from sea-salt  
209 dissolution can be determined using the relationship in Equation 1,

210

211 
$$[X]_{SS} = [Cl]_{RW} \times ([X]/[Cl])_{SW} \quad \text{Eq. 1}$$

212

213 where  $[X]_{SS}$  represents the concentration of the sea-salt component,  $[Cl]_{RW}$  represents  
214 the measured concentration of Cl in rainwater and  $([X]/[Cl])_{SW}$  indicates the  
215 element/Cl ratio of seawater (here taken from Millero *et al.*, 2008). Chlorine is used  
216 as the reference element when determining the sea-salt component because unlike Na  
217 there is negligible Cl contribution from silicate weathering. Variations in the  
218 proportion of dissolved sea-salt in each sample can subsequently be expressed as the  
219 total fraction of major ions derived from sea-salts ( $F_{\text{sea-salt}}$ ), assuming that  $\text{NO}_3$  and  
220  $\text{NH}_4$  are only derived from anthropogenic sources (c.f. Chetelat *et al.*, 2009).

221

222 The samples analysed in this study have  $F_{\text{sea-salt}}$  contributions that vary from 0.06 to  
223 0.85 (Table 2). These values are similar to those obtained from the monthly-integrated

224 results of Chetelat *et al.* (2009), and support significant variations in the amount of  
225 seawater-derived material in these samples. A slight correlation between the measured  
226  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of rainwater and  $F_{\text{sea-salt}}$  ( $r^2 = 0.36$ ) is observed if the outliers on  
227 20/06/02, 24/10/02 and 06/11/02 are excluded (Fig. 3). This trend is consistent with  
228 varying Sr contributions from pure seawater (SS;  $F_{\text{sea-salt}} = 1.0$ ) and pure terrestrial  
229 (NSS;  $F_{\text{sea-salt}} = 0.0$ ) components with  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions of  $\sim 0.7090$  and  $\sim 0.7081$   
230 respectively (Fig. 3). These end-member compositions are similar to the seawater and  
231 carbonate weathering values of 0.70918 and  $\sim 0.7080$  determined by Pearce *et al.*  
232 (2015), suggesting that they may be the dominant controls on the  $^{87}\text{Sr}/^{86}\text{Sr}$   
233 composition of Parisian rainwater. A more significant correlation ( $r^2 = 0.72$ ) is  
234 observed between  $\delta^{88/86}\text{Sr}$  and  $F_{\text{sea-salt}}$  if the same outlier samples are excluded (Fig.  
235 3), suggesting that the  $\delta^{88/86}\text{Sr}$  composition of rainwater is more dependent on the  
236 extent of Sr contribution from sea-salt aerosols. The reason for the higher sensitivity  
237 of  $\delta^{88/86}\text{Sr}$  to  $F_{\text{sea-salt}}$  than  $^{87}\text{Sr}/^{86}\text{Sr}$  is currently unresolved, but may reflect a generally  
238 narrower range of  $\delta^{88/86}\text{Sr}_{\text{NSS}}$  compositions relative to  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{NSS}}$  (i.e. the  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{SS}}$   
239 contributions may have been masked by more variable  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{NSS}}$  ratios). Unlike  
240  $^{87}\text{Sr}/^{86}\text{Sr}$ , the sea-salt and non sea-salt end-member  $\delta^{88/86}\text{Sr}$  compositions implied by  
241 the trend shown in Fig. 3 ( $\sim 0.32$  ‰ and  $\sim 0.10$  ‰) are lower than the equivalent  
242 seawater and carbonate weathering compositions determined by Pearce *et al.* (2015)  
243 (0.39 ‰ and  $\sim 0.16$  ‰ respectively), suggesting that other Sr sources and/or processes  
244 may affect the net  $\delta^{88/86}\text{Sr}$  composition of rainwater.

245

#### 246 4.2 Contribution from non sea-salt sources

247 The non sea-salt (NSS) elemental contribution reflects the concentration difference  
248 between the measured rainwater and sea-salt components ( $[\text{X}]_{\text{RW}} - [\text{X}]_{\text{SS}}$ ). Most

249 samples display >70% non sea-salt contributions of Sr, Ca, K and SO<sub>4</sub>, with only the  
 250 sample collected on 14/05/2002 (~40% NSS) indicating a more significant Sr  
 251 contribution from sea-salt dissolution. The Sr isotopic composition of the non sea-salt  
 252 contribution in each sample can be determined via Equations 2 and 3, where  $F$   
 253 represents the fraction of Sr derived from sea-salt dissolution ( $[\text{Sr}]_{\text{SS}}/([\text{Sr}]_{\text{NSS}} + [\text{Sr}]_{\text{SS}})$ .

254

$$255 \quad \delta^{88/86}\text{Sr}_{\text{NSS}} = (\delta^{88/86}\text{Sr}_{\text{RW}} - F \delta^{88/86}\text{Sr}_{\text{SW}})/(1 - F) \quad \text{Eq. 2}$$

$$256 \quad {}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{NSS}} = ({}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{RW}} - F {}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{SW}})/(1 - F) \quad \text{Eq. 3}$$

257

258 The non sea-salt rainwater isotopic compositions determined in this manner are  
 259 generally similar to the measured compositions, with  $\delta^{88/86}\text{Sr}_{\text{NSS}}$  ranging from 0.12 ‰  
 260 to 0.30 ‰ and  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{NSS}}$  varying from 0.70792 to 0.71105 (Table 2). Because the  
 261 non sea-salt fraction of atmospheric Sr in rainwater includes contributions from both  
 262 natural (dust and vegetation) and anthropogenic (fertiliser, automobile exhaust and  
 263 urban heating) aerosols (e.g. Négre and Roy, 1998; Négre *et al.*, 2007), the  
 264 variations  $\delta^{88/86}\text{Sr}_{\text{NSS}}$  and  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{NSS}}$  compositions most likely reflect differences in  
 265 the extent of mixing between these sources (Fig. 4).

266

267 A significant Sr contribution from the dissolution of silicate-derived dust in these  
 268 samples is unlikely given the dominance of Mesozoic-Cenozoic sediments in the Paris  
 269 basin (Roy *et al.*, 1999). This is supported by the generally low  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{NSS}}$  ratios and  
 270 the fact that none of the samples plot close to the silicate weathering end-member  
 271 (Fig. 4; Gaillardet *et al.*, 1999; Pearce *et al.*, 2015); only the sample collected on  
 272 24/10/2002 has a slightly higher  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{NSS}}$  ratio of 0.711051 and  $\delta^{88/86}\text{Sr}_{\text{NSS}}$  value of  
 273 0.30 ‰ that may be consistent with some silicate-derived Sr (Fig. 4a). A strong

274 biotic/vegetation source of Sr is also unlikely in these samples as plant-released  
275 particles are unlikely to be significant within the urban area of Paris and there is no  
276 evidence for significant K/Sr enrichments in the analysed rainwaters (Artaxo *et al.*,  
277 1988). Consequently the dissolution of carbonate-derived dust and/or addition of  
278 anthropogenic aerosols are the most likely sources of non sea-salt Sr in these  
279 rainwaters.

280

281 A predominantly carbonate dust source of the terrestrial derived Sr in Parisian  
282 rainwater has previously been suggested by Négrel *et al.* (2007) and Seimille *et al.*  
283 (1989), and is consistent with the  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{NSS}}$  ratios determined in this study as most  
284 samples have  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions that fall within the range determined for the  
285 Jurassic to Tertiary limestones in France (0.7081 – 0.7094; Négrel and Roy, 1998;  
286 Négrel *et al.*, 2007). The  $\delta^{88/86}\text{Sr}_{\text{NSS}}$  values are also consistent with a carbonate dust Sr  
287 source, as several samples plot close to the inferred carbonate weathering end-  
288 member  $\delta^{88/86}\text{Sr}$  composition of  $\sim 0.16$  ‰ (Pearce *et al.*, 2015) (Fig. 4a). Although  
289 similarly light  $\delta^{88/86}\text{Sr}$  values of between 0.18 ‰ and 0.29 ‰ have been observed in a  
290 range of continental dust samples (including those derived from continental silicate  
291 terrains; Pearce *et al.*, 2015), a predominantly carbonate origin of the non sea-salt  
292 component in these Parisian rainwaters is supported by their generally elevated  
293 Ca/Sr<sub>NSS</sub> ratios (Figs. 4b and 4c).

294

295 Evidence for significant variations in Ca/Sr<sub>NSS</sub> ratios suggest, however, that there may  
296 also be a substantial non sea-salt Sr contribution from anthropogenic sources. Mixing  
297 lines between the inferred composition of carbonate dust and this anthropogenic end-  
298 member indicate that it is likely to have low Ca/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and a relatively

299 high  $\delta^{88/86}\text{Sr}$  value (Figs. 4b and 4c). The three agricultural fertiliser samples analysed  
300 in this study display Ca/Sr and Sr isotopic ratios that are broadly consistent with this  
301 trend, with two of the samples closely matching the inferred end-member composition  
302 (Table 1; Fig. 4). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of these fertilisers also agree with those  
303 previously reported by Négrel and Roy (1998) and Négrel *et al.* (2007) (0.7079-  
304 0.7087), and are consistent with the significant use of fertilisers in the surrounding  
305 agricultural regions of the Paris Basin (Roy *et al.*, 1999). An alternative potential  
306 source of anthropogenic contaminant in these samples is the burning of fossil-fuels  
307 (including vehicle exhaust, urban heating and coal-fired power plants), and this has  
308 previously been demonstrated to cause notable enrichments in Parisian rainwater  
309  $\text{NO}_3$ ,  $\text{SO}_4$  and  $\text{NH}_4$  concentrations as well as a decrease in  $\delta^{11/10}\text{B}$  compositions  
310 (Tables 1 and 2; Chetelat *et al.*, 2009). Although the  $\delta^{88/86}\text{Sr}$  compositions of these  
311 fossil-fuel related anthropogenic sources are currently unconstrained, a slight negative  
312 correlation between  $\delta^{88/86}\text{Sr}_{\text{NSS}}$  and  $\text{NO}_3/\text{Sr}$  (Table 2) suggests that such factors may  
313 affect the  $\delta^{88/86}\text{Sr}$  composition of rainwater, but that they are not significant in the  
314 samples analysed in this study. Similarly, although the  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{NSS}}$  ratios of our  
315 samples are consistent with the range reported for various urban pollutants including  
316 automobile exhaust and urban heating (Négrel *et al.*, 2007), no relationship is  
317 observed between  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{NSS}}$  and  $\text{NO}_3/\text{Sr}$ . This supports the inference that the  
318 primary source of anthropogenic contamination in these samples is likely to be  
319 agricultural fertiliser.

320

#### 321 *4.3 Implications for the $\delta^{88/86}\text{Sr}$ composition of the hydrological cycle*

322 The generally light  $\delta^{88/86}\text{Sr}$  compositions observed in Parisian rainwater agree with  
323 previous analyses of rainwater, dust and ice (Pearce *et al.*, 2015), and confirm that the

324  $\delta^{88/86}\text{Sr}$  composition of atmospheric Sr is not equivalent to seawater (Fig. 5).  
325 Although the low concentrations of Sr in rainwater mean that atmospheric deposition  
326 is unlikely to have a significant impact on marine  $\delta^{88/86}\text{Sr}$  budgets, it may be  
327 important in local hydrological settings and/or in regions significantly affected by  
328 anthropogenic contamination. For example; the  $\delta^{88/86}\text{Sr}$  composition of the River  
329 Seine decreases by 0.1 ‰, from 0.27 ‰ just before entering Paris to 0.17 ‰ near  
330 Rouen (Table 1; Fig. 5a). Major changes in the ionic content of the Seine have  
331 previously been attributed to agricultural inputs from the Paris Basin, which can  
332 actually exceed elemental contributions from carbonate and silicate weathering  
333 processes during high water stages (Roy *et al.*, 1999). Based on the fertilisers  
334 analysed in this study, this agricultural contamination would be expected to increase  
335 the  $\delta^{88/86}\text{Sr}$  composition of the Seine. However, the fact that  $\delta^{88/86}\text{Sr}$  decreases from  
336 Paris to Rouen (Fig. 5b) implies that fertiliser release is unlikely to be responsible for  
337 the observed changes. The absence of any tidal influence at the hydrological sampling  
338 site near Rouen means that natural contributions from seawater are also unlikely to  
339 account for the observed increases in element concentrations (an observation  
340 supported by the higher  $\delta^{88/86}\text{Sr}_{\text{seawater}}$  composition of 0.39 ‰). Consequently the  
341 decrease in  $\delta^{88/86}\text{Sr}$  most likely reflects anthropogenic contamination from the  
342 Achères water treatment plant and/or the release of domestic waters rich in dishwater  
343 salts etc. Further characterisation of the range of  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions in  
344 agricultural fertilisers and other anthropogenic sources may therefore provide a useful  
345 method for distinguishing between water contaminants in other regions.  
346  
347 In addition to being sensitive to anthropogenic contamination, the dependency of  
348 rainwater  $\delta^{88/86}\text{Sr}$  to mixing between non sea-salt aerosols means that precipitation is

349 expected to show significant temporal and spatial variations in  $\delta^{88/86}\text{Sr}$ . Although a  
350 strong  $\delta^{88/86}\text{Sr}$  seasonality was not observed in this study, changes in atmospheric Sr  
351 sources in response to varying weather patterns and/or distance from the ocean may  
352 affect the  $\delta^{88/86}\text{Sr}$  composition of atmospheric deposition in other regions. Such  
353 effects may be sufficient to drive changes in the composition of local hydrological  
354 catchments (for example in regions affected by seasonal monsoons), and may also  
355 significantly affect the  $\delta^{88/86}\text{Sr}$  composition of vegetation. Furthermore, by combining  
356  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements with other trace element data (e.g. Ca/Sr ratios), it  
357 may be possible to establish changes in the origin and/or relative contribution of  
358 continental dust in response to shifting climate patterns.

359

## 360 **5. Conclusions**

361 The stable ( $\delta^{88/86}\text{Sr}$ ) and radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotopic composition of strontium in  
362 Parisian rainwater shows significant variations over the course of a year, with  
363 measured  $\delta^{88/86}\text{Sr}$  compositions ranging from 0.13 ‰ to 0.32 ‰, and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios  
364 varying between 0.70796 and 0.71093. No seasonality was observed in  $\delta^{88/86}\text{Sr}$   
365 values, whereas  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were found to be generally more radiogenic in the  
366 summer and less radiogenic in the winter. Evidence for Sr enrichment factors  
367 significantly above the seawater contribution imply a predominantly terrestrial (non  
368 sea-salt) origin of Sr in most samples, which is attributed to a mixture of carbonate  
369 dust and anthropogenic sources. Although the anthropogenic end-member cannot be  
370 fully identified, both  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions are consistent with Sr  
371 derived from agricultural fertilisers. Evidence for a 0.1 ‰ decrease in the  $\delta^{88/86}\text{Sr}$   
372 composition of the River Seine suggests that, together with variations in continental  
373 dust supply, contamination from anthropogenic pollutants may contribute to

374 significant regional variations in the composition of Sr within the hydrological cycle.  
375 The potential for both temporal and spatial variations in the  $\delta^{88/86}\text{Sr}$  (and  $^{87}\text{Sr}/^{86}\text{Sr}$ )  
376 composition of rainwater should therefore be taken into consideration when  
377 considering the possible causes of  $\delta^{88/86}\text{Sr}$  variations in localised catchments and  
378 vegetation.

379

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387

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477

#### 478 **Table Captions**

479 Table 1: Sample information, measured  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions and major  
480 element concentrations for all samples analysed in this study. \* Indicates anion and pH  
481 measurements on the same samples from Chetelat *et al.* (2009). Where this  
482 information was not available for the same sample the monthly average value was  
483 used. n.d. = not determined.

484

485 Table 2: Calculated  $\delta^{88/86}\text{Sr}_{\text{NSS}}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{NSS}}$  and elemental concentrations of the  
486 terrestrial (non sea-salt) component in the analysed rainwaters. The total fraction of  
487 ions derived from sea-salt dissolution ( $F_{\text{sea-salt}}$ ) is also indicated. The sample collected  
488 on 08-09/08/2002 is not shown because Cl abundance data was not available for  
489 determining the relative SS and NSS contributions. \* Represents the anion  
490 measurements taken from Chetelat *et al.* (2009). n.d. = not determined.

491

#### 492 **Figure Captions**

493 Figure 1: Relationship between Cl and Na (A) and Sr and Na (B) concentrations in the  
494 analysed rainwaters. The strong correlation between Cl and Na implies a

495 predominantly marine origin of both elements in the Parisian rainwaters, and is  
496 supported by an average Cl/Na ratio of 1.14 that is similar to the seawater value of  
497 1.16 (Millero *et al.*, 2008). The strong Sr enrichment of Parisian rainwater matches  
498 similar enrichments seen in rainwater from the Azores, Congo and China (Pearce *et*  
499 *al.*, 2015) and in other regions, and demonstrates significant Sr contributions from  
500 terrestrial (non sea-salt) derived aerosols.

501

502 Figure 2: Variations in the  $\delta^{88/86}\text{Sr}$  (open circles) and  $^{87}\text{Sr}/^{86}\text{Sr}$  (solid squares)  
503 composition of Parisian rainwater between January and November 2002. Error bars  
504 indicate the internal precision (2 s.e.) of each measurement when larger than the  
505 symbol size (long-term  $\delta^{88/86}\text{Sr}$  reproducibility = 0.025 ‰ and  $^{87}\text{Sr}/^{86}\text{Sr}$  = 14 ppm).  
506 With the exception of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measured on 24/10/2002, all samples have  
507  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions that are less than seawater (0.39 ‰ and 0.70918  
508 respectively; Pearce *et al.*, 2015).

509

510 Figure 3: Variation in the measured  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of rainwater as  
511 a function of the total fraction of ions derived from sea-salt dissolution ( $F_{\text{sea-salt}}$ ).  $F_{\text{sea-}}$   
512  $_{\text{salt}}$  values were determined from major ion abundances, assuming that  $\text{NO}_3$  and  $\text{NH}_4$   
513 are only derived from anthropogenic sources (see Chetelat *et al.*, 2009 for details).  
514 The  $\delta^{88/86}\text{Sr}$  composition of rainwater (open circles) shows a positive relationship with  
515 the extent of sea-salt dissolution ( $r^2 = 0.72$ ), and there is evidence for a slight  
516 correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$  (solid squares) and  $F_{\text{sea-salt}}$  ( $r^2 = 0.36$ ). These trendlines  
517 and correlations were calculated without the outlier samples analysed on 20/06/02,  
518 24/10/02 and 06/11/02. Samples with an  $F_{\text{sea-salt}}$  value of 1.0 represent the composition  
519 of pure seawater.

520

521 Figure 4: Comparison between the  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  (A), Ca/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  (B),  
522 and Ca/Sr and  $\delta^{88/86}\text{Sr}$  (C) compositions of the non sea-salt (NSS) components in  
523 rainwater. Also shown are the riverine silicate and carbonate weathering end-member  
524 compositions determined by Pearce *et al.* (2015) as well as the three agricultural  
525 fertiliser samples analysed in this study. Arrows denote the mixing lines between the  
526 inferred silicate dust, carbonate dust and anthropogenic end-member compositions  
527 indicated by the shaded boxes.

528

529 Figure 5: Relationships between  $\delta^{88/86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  (A),  $\delta^{88/86}\text{Sr}$  and [Sr] (B), and  
530  $^{87}\text{Sr}/^{86}\text{Sr}$  and [Sr] (C) for all samples analysed in this study. The  $\delta^{88/86}\text{Sr}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and  
531 [Sr] compositions of seawater, glacial ice and global rainwater samples are taken from  
532 Pearce *et al.* (2015). The arrow between the two samples of the River Seine indicates  
533 the direction of flow, demonstrating a downstream decrease in  $\delta^{88/86}\text{Sr}$  and increase in  
534 [Sr] but negligible change in  $^{87}\text{Sr}/^{86}\text{Sr}$ .

535

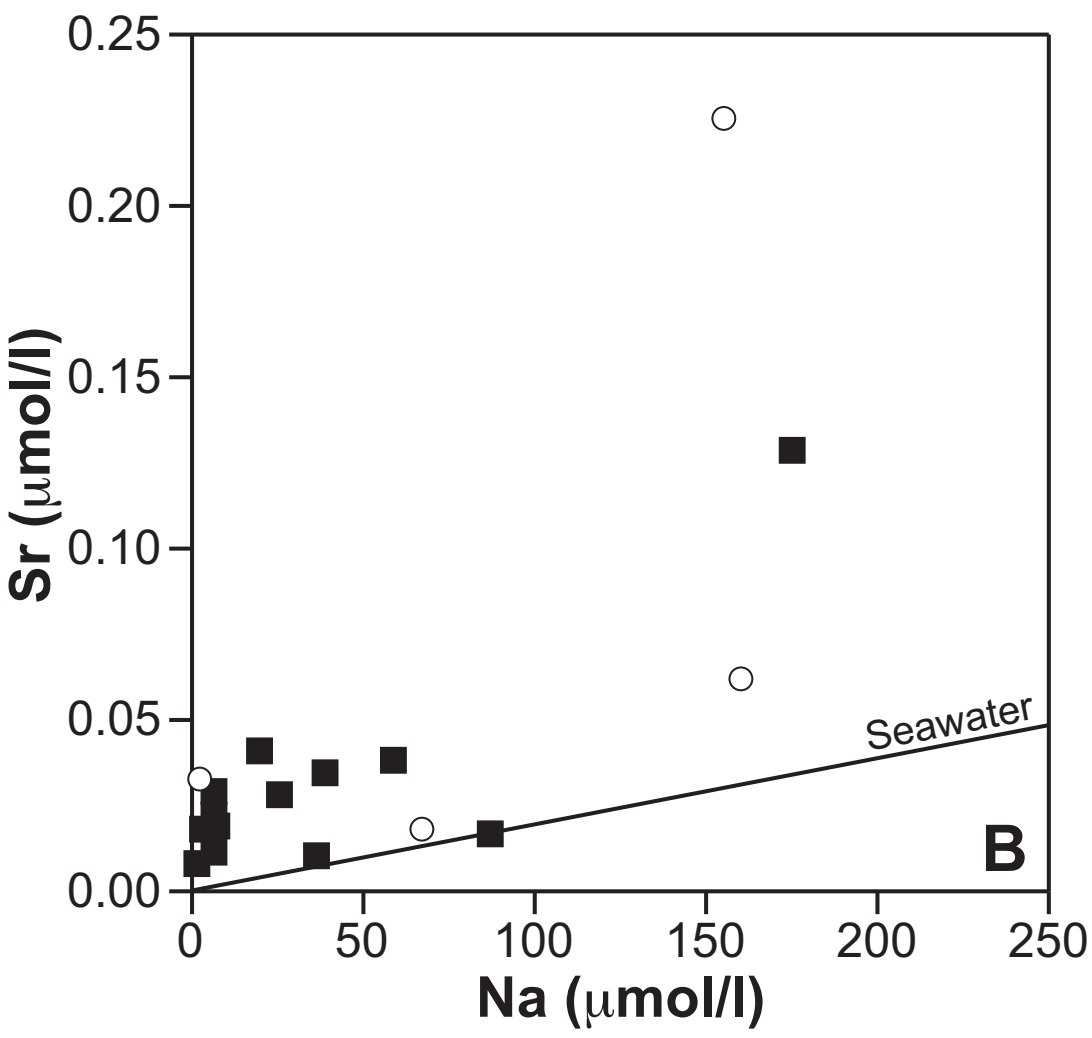
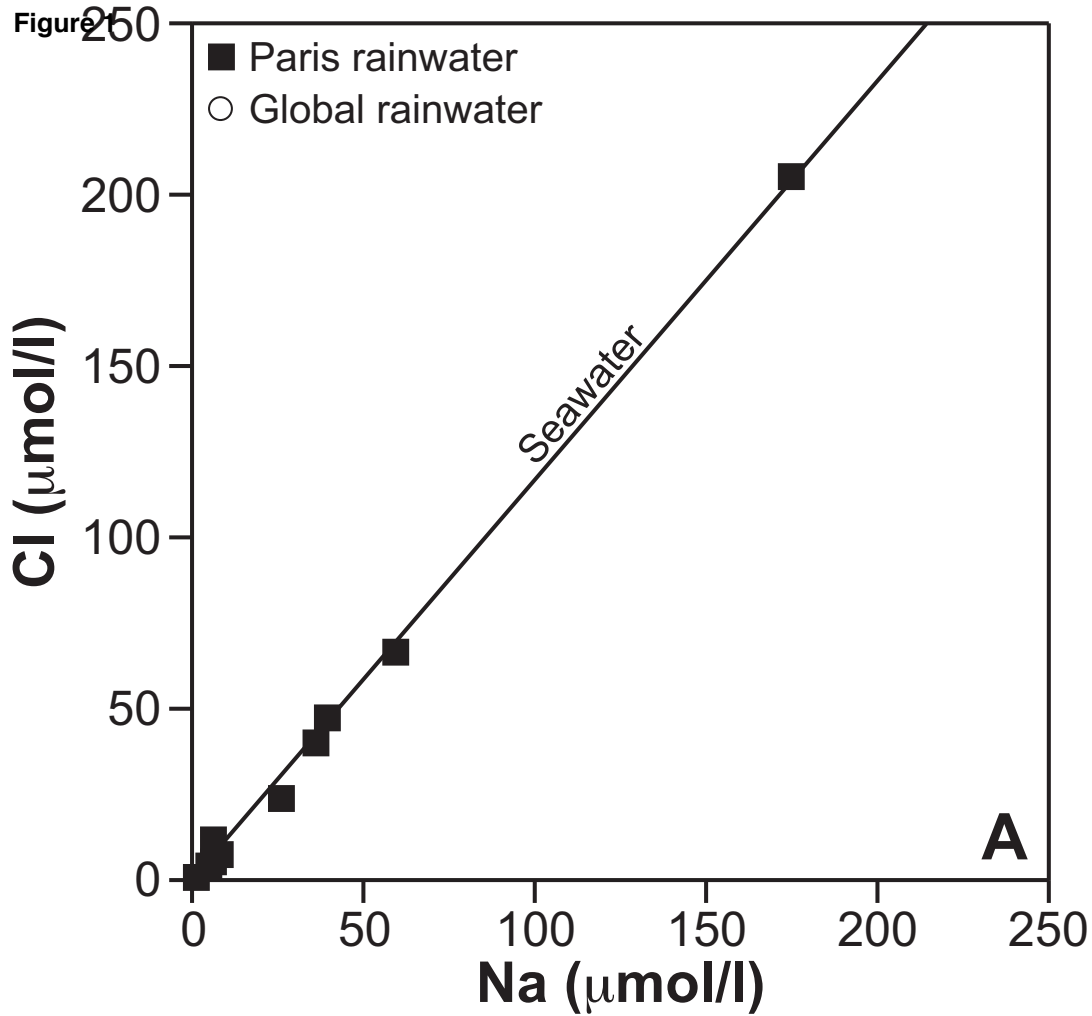


Figure 2

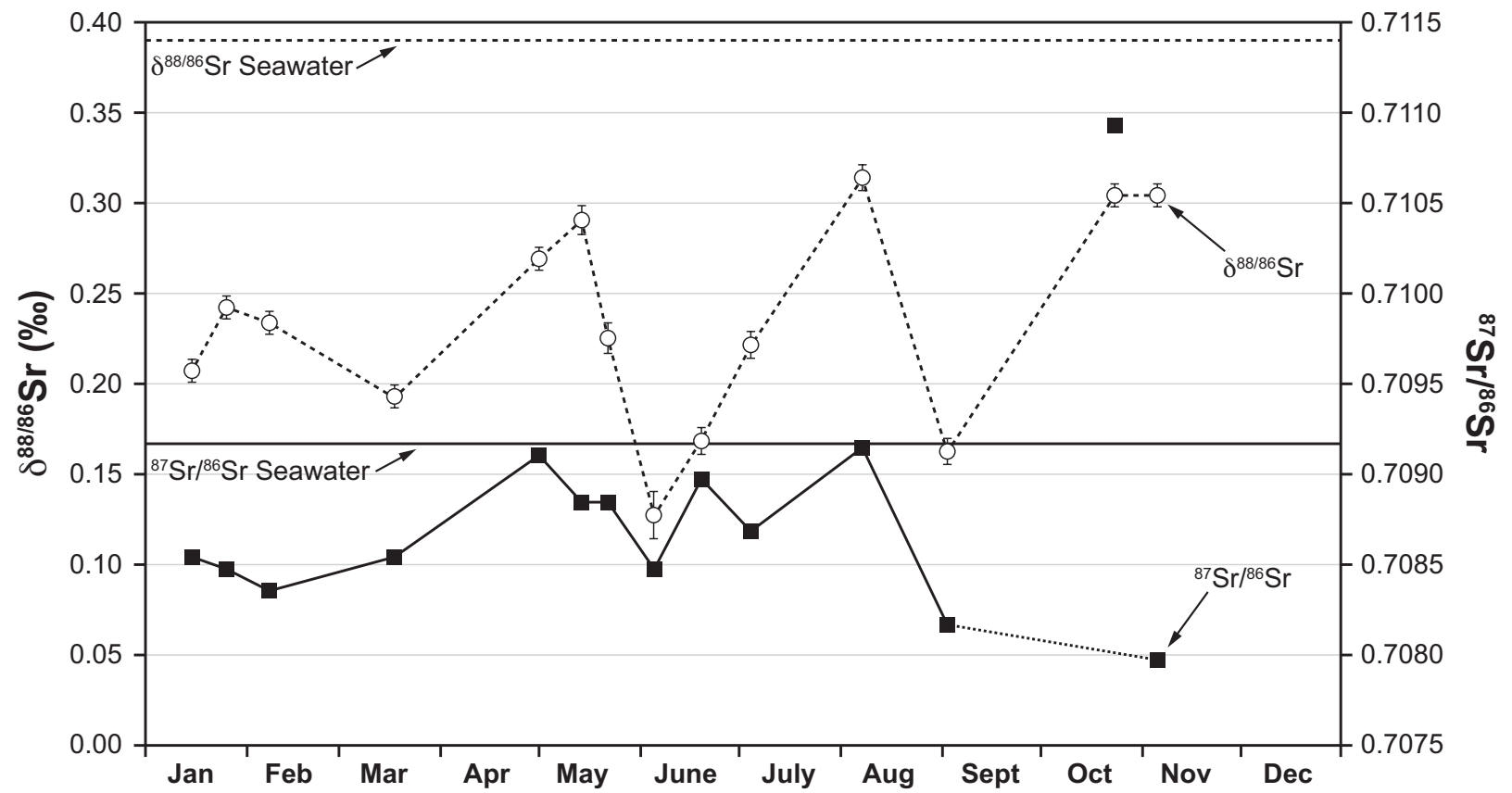
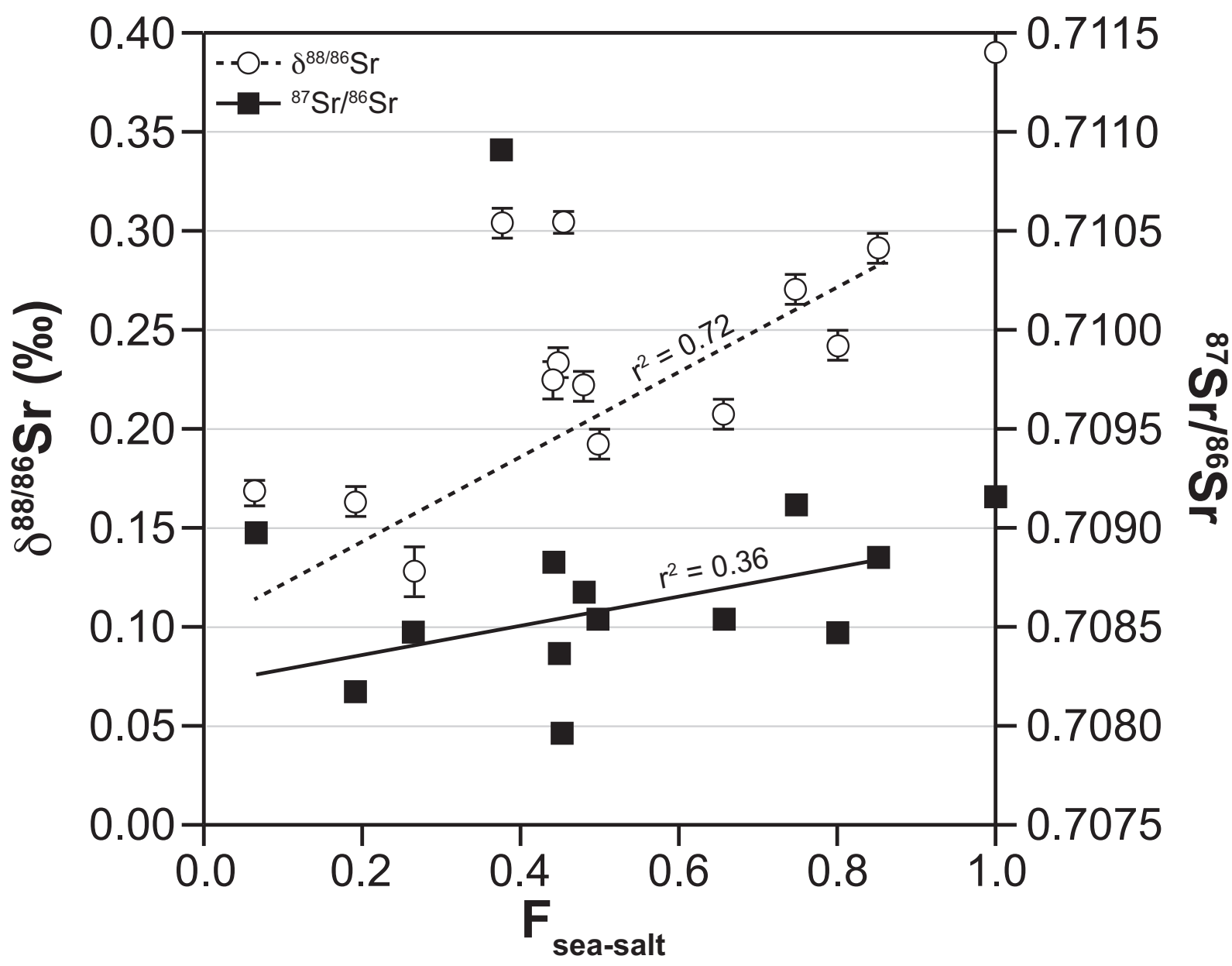
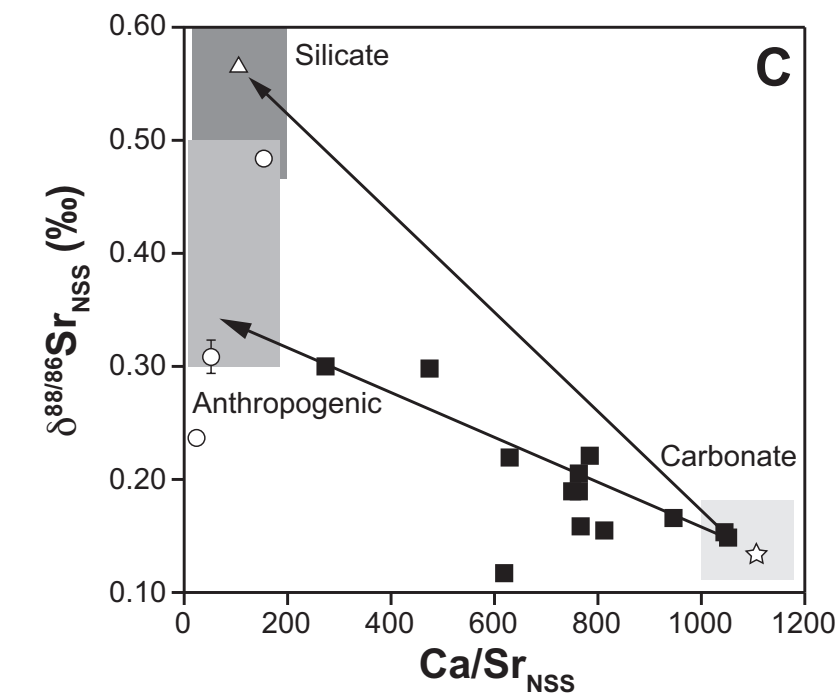
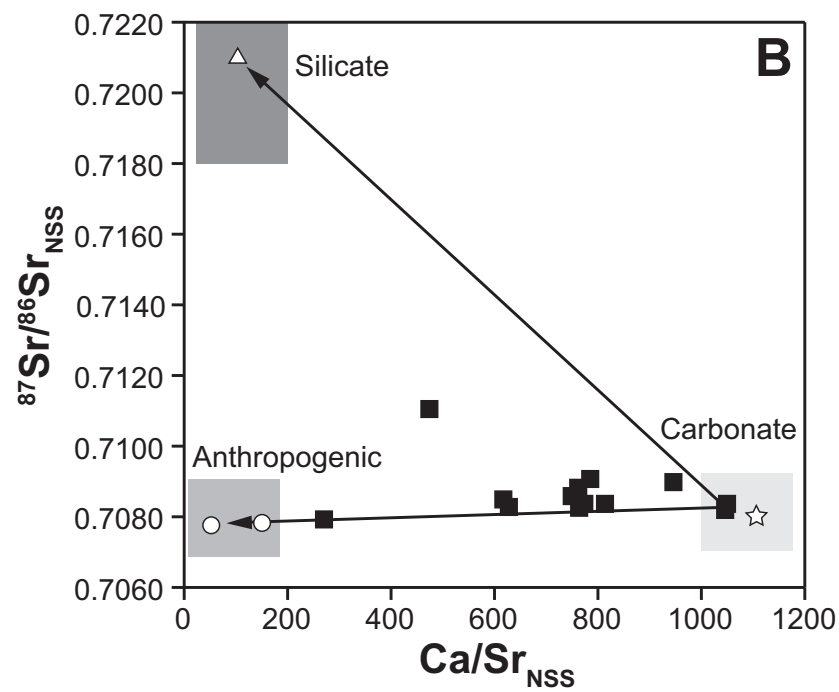
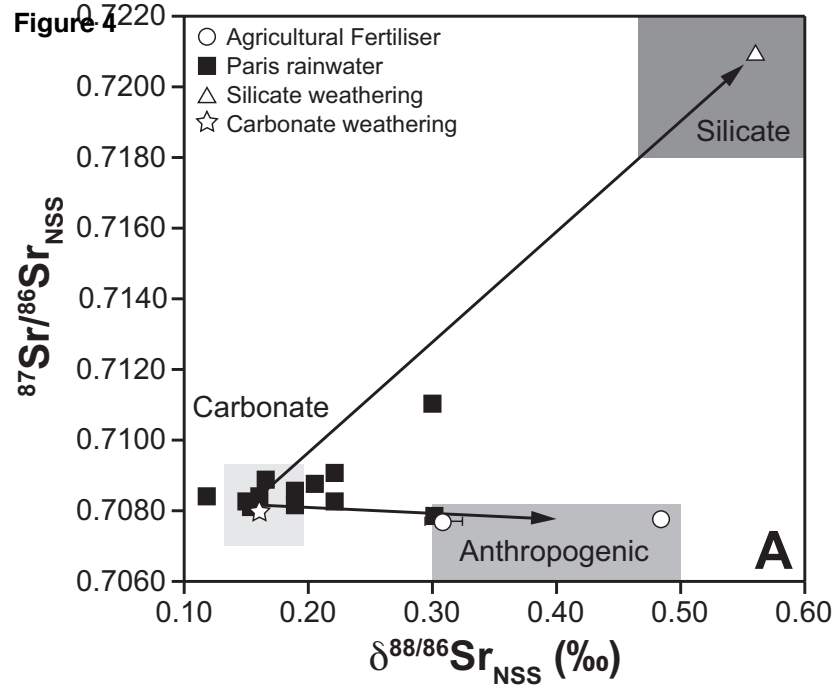




Figure 3





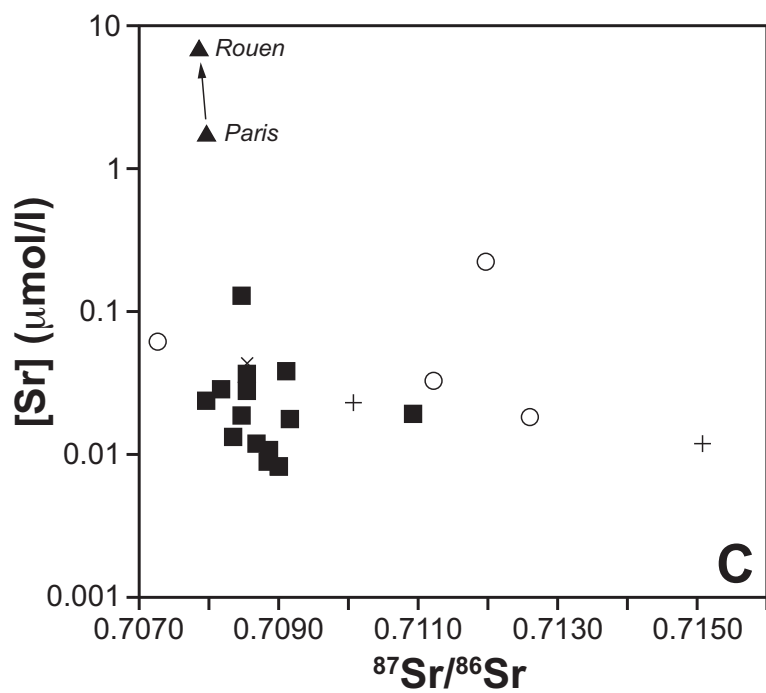
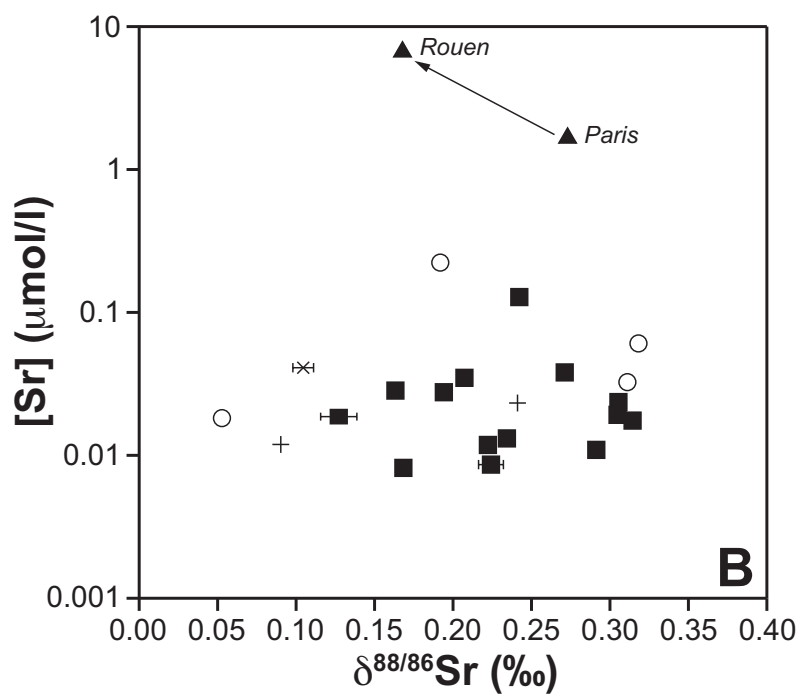
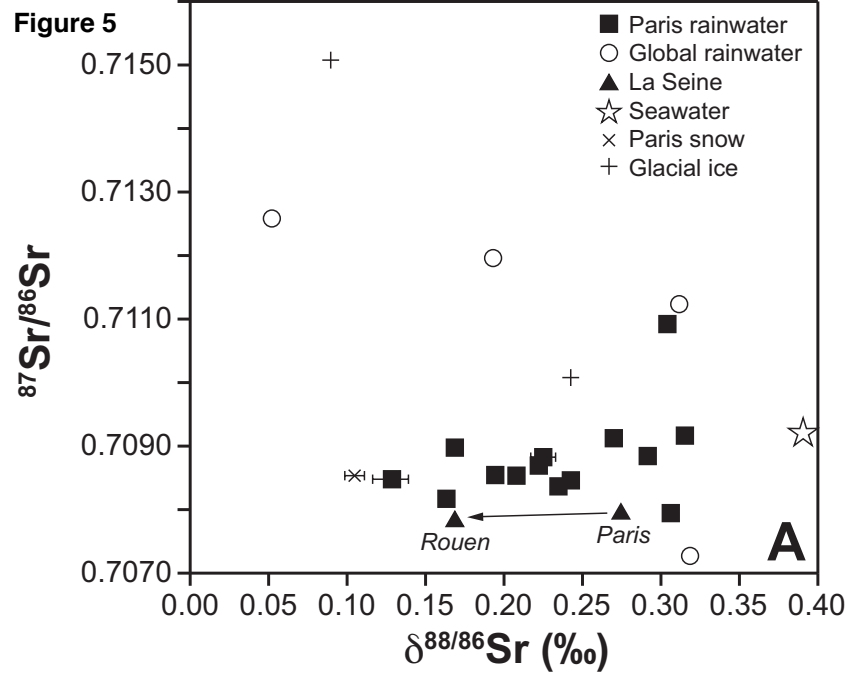


Table 1  
[Click here to download Table: Table 1.xls](#)

Sample Type	Sample Name/Date	<sup>88/86</sup> Sr (‰)	2 s.e.	<sup>87</sup> Sr/ <sup>86</sup> Sr	2 s.e.	Na (mol/l)	Cl (mol/l)*	Mg (mol/l)	K (mol/l)	Ca (mol/l)	Sr (mol/l)	NO <sub>3</sub> (mol/l)*	SO <sub>4</sub> (mol/l)*	NH <sub>4</sub> (mol/l)*	pH*
<b>Snow</b>	Naisy	0.104	0.007	0.70854	2.89E-06	19.91	n.d.	1.61	2.19	24.66	0.041	n.d.	n.d.	n.d.	n.d.
<b>Rain water</b>	15-17/01/2002	0.207	0.007	0.70853	2.33E-06	39.27	47.04	3.97	7.21	22.73	0.035	39.17	26.36	34.51	4.76
	26-27/01/2002	0.242	0.006	0.70847	2.12E-06	175.12	205.17	20.03	10.47	76.07	0.129	27.2	37.64	26.27	6.76
	08/02/2002	0.234	0.006	0.70836	2.64E-06	6.57	6.77	1.06	0.70	7.73	0.013	8.06	8.13	32.22	5.33
	18/03/2002	0.193	0.007	0.70854	2.48E-06	25.72	24.26	2.41	7.97	18.49	0.028	24.68	20.83	76.67	5.88
	01-02/05/2002	0.270	0.006	0.70911	2.41E-06	59.16	66.48	7.72	2.31	22.21	0.038	26.91	23.93	59.59	5.74
	14/05/2002	0.291	0.007	0.70885	2.60E-06	36.26	39.45	4.15	0.63	5.48	0.011	13.08	8.8	29.89	5.35
	22/05/2002	0.224	0.009	0.70883	3.45E-06	2.83	5.57	0.75	0.66	6.07	0.009	15.60	9.91	27.63	5.63
	05/06/2002	0.127	0.013	0.70847	2.67E-06	3.43	4.34	0.77	0.77	11.00	0.018	17.99	13.15	25.21	5.08
	20/06/2002	0.168	0.006	0.70898	2.54E-06	1.45	0.65	1.35	-0.58	7.76	0.008	12.24	9.83	21.76	4.59
	05-06/07/2002	0.222	0.007	0.70868	3.09E-06	6.38	11.33	1.18	1.56	7.75	0.012	21.26	19.91	49.39	n.d.
	08-09/08/2002	0.315	0.007	0.70915	2.54E-06	87.52	n.d.	9.56	3.58	5.62	0.017	n.d.	n.d.	n.d.	n.d.
	03-04/09/2002	0.163	0.007	0.70817	2.53E-06	6.75	6.82	2.28	1.37	28.37	0.028	83.38	27.45	90.23	4.59
	24/10/2002	0.304	0.007	0.71093	2.69E-06	8.11	7.60	1.37	0.86	8.71	0.019	8.81	14.78	12.29	5.70
	06/11/2002	0.305	0.006	0.70796	2.56E-06	6.48	5.38	1.01	0.69	6.21	0.023	3.7	4.55	0.22	4.95
<b>La Seine River</b>	Paris SP30	0.273	0.007	0.70797	2.47E-06	145	n.d.	118.91	29.41	2293	1.738	n.d.	n.d.	n.d.	n.d.
	Rouen	0.168	0.007	0.70787	2.38E-06	978	n.d.	306.48	136.63	2125	6.843	n.d.	n.d.	n.d.	n.d.
<b>Fertiliser</b>	Magni	0.237	0.008	0.703340	2.69E-06	65	n.d.	965	n.d.	72966	3105	n.d.	n.d.	n.d.	n.d.
	K <sub>2</sub> O	0.308	0.015	0.707745	5.57E-06	5534	n.d.	531	n.d.	159	3.02	n.d.	n.d.	n.d.	n.d.
	P <sub>2</sub> O <sub>5</sub>	0.484	0.007	0.707791	2.87E-06	2365	n.d.	2308	n.d.	145899	951	n.d.	n.d.	n.d.	n.d.

Table 2

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Sample Name/Date	$^{88/86}\text{Sr}_{\text{NSS}}$ (‰)	2 s.e.	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{NSS}}$	2 s.e.	$\text{Na}_{\text{NSS}}$ ( mol/l)	$\text{Mg}_{\text{NSS}}$ ( mol/l)	$\text{K}_{\text{NSS}}$ ( mol/l)	$\text{Ca}_{\text{NSS}}$ ( mol/l)	$\text{Sr}_{\text{NSS}}$ ( mol/l)	$\text{NO}_3_{\text{NSS}}$ ( mol/l)*	$\text{SO}_4_{\text{NSS}}$ ( mol/l)*	$\text{NH}_4_{\text{NSS}}$ ( mol/l)*	$F_{\text{sea-salt}}$
15-17/01/2002	0.154	0.007	0.708347	2.33E-06	0.00	0.00	6.33	21.85	0.027	39.17	23.93	34.51	0.66
26-27/01/2002	0.189	0.006	0.708218	2.12E-06	0.00	0.18	6.63	72.21	0.095	27.20	27.03	26.27	0.80
08/02/2002	0.220	0.006	0.708287	2.64E-06	0.76	0.40	0.57	7.60	0.012	8.06	7.78	32.22	0.45
18/03/2002	0.159	0.007	0.708436	2.48E-06	4.87	0.06	7.52	18.03	0.024	24.68	19.58	76.67	0.50
01-02/05/2002	0.220	0.006	0.709084	2.41E-06	2.04	1.29	1.07	20.96	0.027	26.91	20.49	59.59	0.75
14/05/2002	0.148	0.007	0.708374	2.60E-06	2.37	0.33	0.00	4.74	0.005	13.08	6.76	29.89	0.85
22/05/2002	0.205	0.009	0.708792	3.45E-06	0.00	0.21	0.56	5.96	0.008	15.60	9.62	27.63	0.44
05/06/2002	0.117	0.013	0.708445	2.67E-06	0.00	0.35	0.69	10.91	0.018	17.99	12.93	25.21	0.27
20/06/2002	0.165	0.006	0.708979	2.54E-06	0.89	1.29	0.00	7.75	0.008	12.24	9.80	21.76	0.06
05-06/07/2002	0.190	0.007	0.708591	3.09E-06	0.00	0.09	1.35	7.54	0.010	21.26	19.32	49.39	0.48
03-04/09/2002	0.153	0.007	0.708127	2.53E-06	0.89	1.62	1.25	28.24	0.027	83.38	27.10	90.23	0.19
24/10/2002	0.298	0.007	0.711051	2.69E-06	1.58	0.64	0.72	8.56	0.018	8.81	14.39	12.29	0.38
06/11/2002	0.301	0.006	0.707916	2.56E-06	1.85	0.49	0.59	6.11	0.022	3.70	4.27	0.22	0.45