

Dripwater organic matter and trace element geochemistry in a semi-arid karst environment

Rutledge, Helen; Baker, Andy; Marjo, Christopher E.; Andersen, Martin S.; Graham, Peter W.; Cuthbert, Mark O.; Rau, Gabriel C.; Roshan, Hamid; Markowska, Monika; Mariethoz, Gregoire; Jex, Catherine N.

DOI:

[10.1016/j.gca.2014.03.036](https://doi.org/10.1016/j.gca.2014.03.036)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Rutledge, H, Baker, A, Marjo, CE, Andersen, MS, Graham, PW, Cuthbert, MO, Rau, GC, Roshan, H, Markowska, M, Mariethoz, G & Jex, CN 2014, 'Dripwater organic matter and trace element geochemistry in a semi-arid karst environment: Implications for speleothem paleoclimatology', *Geochimica et Cosmochimica Acta*, vol. 135, pp. 217-230. <https://doi.org/10.1016/j.gca.2014.03.036>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Checked October 2015

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

1 **Dripwater organic matter and trace element geochemistry in a semi-arid karst**
2 **environment: implications for speleothem paleoclimatology**

3

4 Helen Rutledge,^{a,b,g*} Andy Baker,^{b,g} Christopher E. Marjo,^a Martin S. Andersen,^{c,g} Peter
5 Graham,^b Mark O. Cuthbert,^{c,d} Gabriel C. Rau,^{c,g} Hamid Roshan,^{c,g} Monika Markowska,^{b,e,g}
6 Gregoire Mariethoz,^{b,g} Catherine Jex^{b,f,g}

7

8 ^a Solid State and Elemental Analysis Unit, Mark Wainwright Analytical Centre, The
9 University of New South Wales, Kensington, NSW, Australia 2052

10 ^b Connected Waters Initiative Research Centre, The University of New South Wales,
11 Kensington, NSW, Australia 2052

12 ^c Connected Waters Initiative Research Centre, The University of New South Wales, 110
13 King Street, Manly Vale, NSW 2093, Australia

14 ^d School of Geography, Earth and Environmental Sciences, University of Birmingham,
15 Edgbaston, Birmingham, B15 2TT, UK

16 ^e Australian Nuclear Science and Technology Organisation, Lucas Heights NSW 2234,
17 Australia

18 ^f Water Research Centre, The University of New South Wales, Kensington, NSW, Australia
19 2052

20 ^g Affiliated to the National Centre for Groundwater Research and Training, Australia

21

22 * Corresponding author. Tel.: +612 9385 9327; fax: +612 9385 3327.

23 E-mail address: a.baker@unsw.edu.au

24

25 **Abstract**

26 A series of four short-term infiltration experiments which revealed hydrochemical responses
27 relevant to semi-arid karst environments were carried out above Cathedral Cave, Wellington,
28 New South Wales (NSW), Australia. Dripwater samples were collected at two sites for trace
29 element and organic matter analysis. Organic matter was characterised using fluorescence
30 and interpreted using a PARAFAC model. Three components were isolated that represented
31 unprocessed, soil-derived humic-like and fulvic-like material, processed humic/fulvic-like
32 material and tryptophan-like fluorescence. Principal Component Analysis (PCA) performed
33 on the entire dataset comprising trace element concentrations and PARAFAC scores revealed

34 two dominant components that were identified as soil and limestone bedrock. The soil
35 component was assigned based on significant contributions from the PARAFAC scores and
36 additionally included Ba, Cu, Ni and Mg. The bedrock component included the expected
37 elements of Ca, Mg and Sr as well as Si. The same elemental behaviour was observed in
38 recent stalagmite growth collected from the site. Our experiments demonstrate that existing
39 paleoclimate interpretations of speleothem Mg and Sr, developed in regions of positive water
40 balance, are not readily applicable to water limited environments. We provide a new
41 interpretation of trace element signatures unique to speleothems from water limited karst
42 environments.

43

44 **1. Introduction**

45 Trace elements are preserved in speleothem calcite and are increasingly used either in
46 chronology (where trace elements vary rhythmically; Smith et al., 2009) or as a paleoclimate
47 proxy (Sundqvist et al., 2013; Wassenburg et al., 2013). Trace elements can derive directly
48 from precipitation; from biogeochemical reactions between recharge and trace elements
49 associated with organic matter, colloids, clays and bedrock clasts within the overlying soil;
50 and from biogeochemical reactions between infiltration water and trace elements associated
51 primarily with the limestone bedrock overlying the cave (Fairchild et al., 2000; Fairchild and
52 Treble, 2009; Tremaine and Froelich, 2013). Therefore trace element composition of waters
53 infiltrating into a cave can be a product of many processes which include metal-organic
54 matter binding (Borsato et al., 2007; Hartland et al., 2012), soil cation exchange, incongruent
55 and congruent dissolution of bedrock and soil clasts (Hansen and Postma, 1995), and the
56 amount of prior calcite precipitation (PCP). Variable soil water residence times (related to
57 climatic conditions) and degrees of mixing between recently infiltrated precipitation, existing
58 older soil water, and vadose zone water may lead to variable elemental compositions for
59 elements that are released by kinetically controlled reactions, such as weathering of primary
60 silicate minerals (Appelo and Postma, 2005). Regardless, the trace element distribution in
61 speleothem deposits will be related to the infiltration water geochemistry and further
62 modified during calcite precipitation. For full reviews, we refer the reader to Fairchild and
63 Treble (2009), Fairchild and Baker (2012) and Tremaine and Froelich (2013).

64

65 Trace elements have been widely investigated in speleothem paleoclimatology because they
66 can give insights in the multitude of processes that determine infiltration. However they have
67 yielded quantifiable paleoclimate proxies in only a limited number of cases. The majority of

68 research has focussed on Mediterranean, temperate and alpine climatic regions, where mean
69 annual precipitation (P) is typically greater than mean annual evapotranspiration (ET).
70 Pioneering initial research by Roberts et al. (1998) demonstrated annual variability in Sr/Ca,
71 Mg/Ca and Ba/Ca in a temperate climate Scottish speleothem. Fairchild et al. (2000)
72 demonstrated that variations in water availability, which control the extent of prior calcite
73 precipitation (PCP) and incongruent dissolution of bedrock could be the primary controls on
74 speleothem Sr/Ca and Mg/Ca, and this has been recently demonstrated through the
75 investigation of many diverse sites by Tremaine and Froelich (2013). In drier conditions,
76 there is longer water residence time in the epikarst leading to decreased drip rates and
77 enhanced CO_2 degassing. This system results in higher Mg/Ca and Sr/Ca ratios than those
78 found in congruent dissolution of limestone due to preferential removal of Ca (Tremaine and
79 Froelich 2013). Organic matter associated trace elements have also been recognised which
80 include, P, Cu, Pb, Zn and Y (Borsato et al., 2007), and have been associated with infiltration
81 events that mobilise soil organic matter and colloids (Hartland et al., 2012). Where trace
82 element variations occur regularly, such as in climate regions with strong seasonality, high
83 resolution (sub-annual) analysis of these trace elements in speleothems provides an annual
84 chronology (Smith et al., 2009), which has been successfully used to provide high precision
85 records of past climate (for example, Sundqvist et al., 2013).

86
87 Although karst infiltration water trace element geochemistry increasingly is well understood,
88 the majority of research has been undertaken in temperate to alpine environments, where on
89 average mean annual $P > ET$. In these environments, soil organic matter is relatively abundant,
90 soil geochemistry is primarily controlled by weathering of the underlying bedrock, and
91 infiltration and associated speleothem deposition can be considered to be relatively
92 continuous (Fairchild and Baker 2012). These conditions contrast those in more arid
93 environments: where $P < ET$, soil organic matter may be limited and the soil is poor in
94 nutrients such as phosphorus. In these regions evaporation processes dominate over
95 infiltration, leading to salt accumulation within the soil profile (McDonald et al., 2007). With
96 increasing aridity, aeolian processes and dust deposition becomes an increasingly important
97 contributor to the soil geochemical profile (Greene et al., 2009). Soil trace element
98 geochemistry therefore depends on the interplay between the extent of soil salinisation
99 (controlled by ET), the proximity of potential dust sources, a site climatology that permits
100 dust transport and deposition, the soil organic matter content and character, and the bedrock
101 geochemistry. Infiltration events are irregular, often without an annual frequency.

102 Consequently speleothem deposition, and thus trace elemental composition, can be
103 considered to be episodic rather than seasonal. In a pioneering study in SE Australia,
104 McDonald et al. (2007) presented 5-yrs of trace metal data from cave dripwater and noted a
105 more complex response of dripwater Mg/Ca, Sr/Ca and Ba/Ca to climate than observed in
106 temperate regions. More recently, Frisia et al. (2012) demonstrated that the P record
107 preserved in Australian speleothems could be both a function of within-cave microbial
108 processes as well as soil-derived infiltration. However, despite these two studies, review of
109 available literature indicate that karst infiltration processes in arid and semi-arid zones are
110 rarely investigated and thus require further research.

111

112 In this paper we present the results of an infiltration experiment performed at the Wellington
113 Caves, NSW, Australia. We undertook an artificial infiltration experiment to better
114 understand the trace element geochemistry of dripwaters in semi-arid climate regions where
115 $P < ET$. We believe that this is the first such experiment undertaken to understand karst
116 dripwater trace element composition. Furthermore, water sampling comprised both inorganic
117 elements (trace metals) and dissolved organic matter analysis by fluorescence, permitting the
118 investigation of the association of organic matter with trace elements. Our results are
119 relevant to the interpretation of speleothem trace element records from any arid or semi-arid
120 regions where infiltration events are infrequent and evaporation dominates the soil water
121 balance. This of course includes modern day semi-arid and arid climate regions, as well as
122 regions which have experienced past aridity in the Quaternary or older time periods. Our
123 results will therefore facilitate the interpretation of speleothem trace element records from
124 regions such as Israel (Bar Matthews et al., 1991), Yemen (Van Rempelbergh et al., 2013),
125 Turkey (Siklósy et al., 2009) and Morocco (Wasserburg et al., 2013), as well as from
126 Australia (McDonald et al., 2007).

127

128 **2. Study site**

129 The Cathedral Cave in Wellington, NSW, Australia is located at 32°37'S; 148°56'E, in a
130 temperate semi-arid climate (Figure 1c), with mean annual precipitation of 619 mm (1956-
131 2005) and evaporation of 1825 mm (1965-2005) recorded at the nearby Wellington Research
132 Centre (Australia Bureau of Meteorology). There is a significant seasonal temperature
133 variation with monthly mean maximum ranging from 15 °C in July and 32 °C in January
134 (1956-1990, Australia Bureau of Meteorology). The limestone bedrock geology has been
135 described previously as a mixture of massive and thinly-bedded Devonian limestone

136 (Johnson 1975). The site of this study is within the massive limestone, with a red-brown soil
137 comprising clays, iron oxides, fine quartz sands, and calcite nodules (Frank, 1971), with
138 aeolian contributions (Hesse and McTanish, 2003).

139

140 Wellington is situated within a region where dryland salinity occurs. Dryland salinity is often
141 due to deforestation over the last 200 years, which results in the saline groundwater entering
142 the soil by capillary action and subsequent evaporation resulting in the accumulation of salts.
143 Regional soils are ubiquitously affected by aeolian dust deposition, with current estimates
144 ranging from 13 – 50 t km⁻² a⁻¹ in southeast Australia (Green et al., 2009). Potential dust
145 sources are diverse, and include distal arid climate sources such as Lake Eyre, and proximal
146 sources from deflation of alluvial material in the Murray-Darling Basin (Hesse and
147 McTanish, 2003).

148

149 The geomorphology of Cathedral Cave has been extensively researched (Osborne, 2007) and
150 has abundant evidence of hypogene formation processes in addition to conventional meteoric
151 water features, arguably typical of many caves in SE Australia (Osborne, 2010). The cave has
152 been a focus of long-term hydrogeological monitoring (concurrent to this study) by the
153 investigators, commencing in 2010 and continuing, primarily using a network of in-situ
154 Stalagmate © drip loggers. Mariethoz et al. (2012) utilised near-surface infiltration to identify
155 non-linear and chaotic drip behaviour and its relationship to surface connectivity. Jex et al.
156 (2012) described infiltration patterns and processes within the cave, and identified that
157 infiltration only occurs after high magnitude and duration rainfall events, with a total
158 precipitation of over ~60mm within 24-48 hours, however the necessary amount of rainfall
159 needed can vary dependant on antecedent conditions. Such rainfall events occur very
160 infrequently, typically 0-2 times a year, and require slow-moving weather systems. In winter,
161 this is mostly likely associated with westerly frontal rainfall, where the associated low
162 pressure system is slow moving, deep, and relatively close to the site. In summer, instability
163 and associated convective rainfall caused by slow moving or stationary troughs and
164 associated upper level systems, draws moist, unstable air from the north of the region. These
165 previous investigations have identified a section of the cave that had numerous near-surface,
166 intermittent dripping sites (see Figure 1a). Our irrigation experiment was therefore located
167 above this section of the cave, and the two dripwater sites reported here were designated as
168 Sites 1 and 2 (Figure 1b).

169

170 **3. Methods**

171 3.1 The irrigation experiment

172 In this study, an area, of approximately 3×7 m, directly above the study area in Cathedral
173 Cave was irrigated with Wellington town supply water. The experiment was done in the
174 height of the Australian summer and the antecedent soil moisture was very low (soil moisture
175 was measured at the nearby Wellington Research Centre as 0.1 weight fraction at the time of
176 the study). Two Monsoon pumps were used to distribute the irrigation water from a 1600 L
177 tank. The irrigations were carried out over a period of two hours each morning, for four
178 consecutive days from the 8th January 2013. The volume and size of the irrigation area was
179 chosen to achieve equivalent of more than 60 mm of rainfall over the irrigation site.
180 Infiltration events were designated 1 to 4 with the following volumes: Event 1: 840 L (start
181 time 7:00 am Day 1), Event 2: 1500 L (start time 8:00 am, Day 2), Event 3: 840 L (start time
182 8:00 am, Day 3), Event 4: 1500 L (start time 6:00 am, Day 4). The irrigation on Day 1 was
183 spiked with 0.5 L of 99.8 % deuterium (D_2O) into 840 L of town water. The resulting
184 deuterium enrichment was 6100 ‰ (VSMOW) as measured by laser cavity ring down
185 analysis (see below). For reference the tank water was sampled at the beginning and end of
186 each irrigation (for chemical composition see Supporting data table S1).

187

188 3.2 Cave dripwater sampling

189 The onset and rate of inflow to the cave was monitored at three stalactites using Stalagmate ©
190 drip loggers located under drip sites on the cave floor. Water samples were collected below
191 the drip loggers in a plastic funnel which was mounted at ~30 cm height from the cave floor
192 using commercial drainpipe. The base of the funnel drained into 1L HDPE water sample
193 collection bottles (Supporting data Figure S2a). Two of these drip sites activated during the
194 irrigation, and cave dripwater samples were collected from Sites 1 and 2 for trace element;
195 fluorescent organic matter analysis; and electrical conductivity (EC) measurements. Three
196 other sites also activated in close proximity (within 0.2 m either side) of Sites 1 and 2, but
197 sampling was not possible due to either uneven floor surface or proximity to Sites 1 and 2.
198 Water samples were collected regularly from the 1 L sample containers during day time. A
199 subsample of ~20 ml was used for EC measurements on site using a HACH HQ40d
200 multimeter and EC probe. When drip rates were slow, samples from Site 1 and 2 were mixed
201 in equal proportions to permit enough sample volume for EC analysis. For this reason EC
202 was not included in the PCA analysis. Subsamples for trace element and fluorescence
203 analysis were collected in 30 mL PET containers. 30 mL water samples for water isotope

204 analysis were collected in glass McCartney bottles. Therefore, all were integrated samples:
205 initial sample collection was at 30 minute intervals, reducing to hourly intervals during the
206 recession phase of each event. When dripping continued overnight, the sampling interval was
207 increased. A ~5 mL aliquot from the 30 mL PET container was filtered (0.45 μm PSE filters)
208 and analysed for organic matter fluorescence at the nearby UNSW Wellington Field Station
209 within 24 hrs. The remainder of the sample was refrigerated for up to one week, transported
210 in a coolbox to the UNSW Analytical Centre, Sydney, and filtered (0.45 μm PSE filters),
211 acidified (100 μL of concentrated HNO_3 to 10 mL of sample) ready for trace element
212 analysis. Isotope samples were sealed, stored and kept in the dark at room temperature until
213 analysis.

214

215 3.3 Cave dripwater analysis

216 Trace-element analysis of the dripwater samples (without dilution) was carried out using a
217 Perkin Elmer NexION 300D ICP-MS and Perkin Elmer Optima 7300 ICP-OES. The
218 following elements were analysed by ICP-OES: Ca, Mg, Si and Sr, and by ICP-MS: Al, Ba,
219 Cu, Fe, Ni, P, Pb, U and Zn (Supporting data Table S2 and S3). For both techniques multi-
220 element standards in 2% nitric acid were prepared from 1000 mg l^{-1} single element stock
221 solutions (High-Purity StandardsTM). Standards were prepared at the following concentrations
222 for ICP-OES, 0.2, 1, 10, and 100 mg l^{-1} and at 0.2, 1, 10 and 100 $\mu\text{g l}^{-1}$ for ICP-MS analysis.
223 Of these, the following elements were considered reliable for interpretation Ca, Mg, Si, Sr,
224 Ba, Cu, and Ni. P and Pb were below the detection limit (10 $\mu\text{g l}^{-1}$ and 0.10 $\mu\text{g l}^{-1}$
225 respectively) of the ICP-MS and the other excluded elements exhibited a high proportion of
226 outliers that would skew the subsequent PCA. A single spike in the Cu results was removed
227 from the data on the basis that there was no corresponding spike observed in any other
228 elemental data.

229

230 Organic matter characterisation was undertaken using fluorescence spectroscopy. A Horiba
231 Aqualog fluorescence spectrometer was used, which measures both absorbance and
232 fluorescence within the same instrument, with the absorbance data used to correct for any
233 reabsorption (or inner-filter) effects. Fluorescence excitation-emission matrices (EEMs) were
234 collected using an excitation range of 240 to 400 nm, with a step-size of 3 nm, and emitted
235 fluorescence detected between 210 and 600 nm with a CCD detector, at a spectral resolution
236 of 1.64 nm and integration time of 1 s. All data was inner-filter corrected, scatter lines

237 masked, and Raman normalised (to a mean Raman intensity of water in a sealed water cell,
238 excited at 380 nm, of 200 intensity units), using proprietary Aqualog software. The resultant
239 dataset of 83 EEMs was analysed using parallel factor analysis (PARAFAC) using
240 Eigenvector Research Solo © software. The PARAFAC method models the resulting data
241 cube and extracts fluorescence components. Standard checks (split-half analysis, core
242 consistency analysis, the presence of physically meaningful components) were applied to the
243 resultant models to ensure model integrity (Stedmon and Bro, 2008). This resulted in a three
244 component PARAFAC model being adopted.

245

246 The trace element concentrations and the PARAFAC scores were analysed by PCA for each
247 individual site. PCA was performed in the PLS toolbox (Eigenvalue Research, Inc.) with the
248 data auto-scaled prior to the analysis.

249

250 Water isotopic composition of irrigation and dripwater samples was determined using an
251 LGR-24 d off-axis, integrated cavity output, cavity ringdown mass spectrometer (ICOS
252 CRMS, Lis et al., 2007, Wassenaar et al., 2008) at the University of New South Wales.
253 Analytical precision was 0.1 per mil (1σ ; calculated from within run internal references
254 materials).

255

256 3.4 Soil and rock analysis

257 A limited sampling of the soil and bedrock was performed at the site. A single limestone
258 sample from the bedrock at an accessible exposure at the edge of the irrigation area was
259 collected, and a single soil sample was obtained approximately 30 cm below the soil surface
260 from within the centre of the irrigated area (Figure 1a). The soil and rock samples were
261 analysed to determine their mineralogy and elemental composition. Cave rock samples were
262 crushed to a ca. 20 micron powder in a tungsten-carbide ring mill. Soil samples were
263 prepared by drying for 3 hours at 90 °C, followed by grinding to a ca. 20 micron powder in a
264 mortar and pestle. The powdered samples were used for XRD analysis. Analysis for major
265 and trace elements was performed by preparing a glass bead using 1:10 weight percent of the
266 powdered sample in a 12:22 lithium metaborate flux (Norrish and Hutton, 1969). The
267 resulting bead was analysed for the major elements using a Panalytical PW2400 wavelength
268 dispersive XRF Spectrometer fitted with a rhodium anode end window X-ray source and
269 calibrated using glass beads prepared from the Panalytical WROXI element set and processed
270 using the Panalytical SuperQ software. Semi-quantitative trace element analysis was

271 conducted on the prepared glass bead using laser ablation ICPMS on a New Wave NWR213
272 laser ablation unit coupled to a Perkin Elmer NexION 300D ICP-MS and calibrated using the
273 NIST 612 silicate glass standard.

274

275 X-ray diffraction of soil and rock samples was performed on a PANalytical MPD
276 diffractometer fitted with a Pixel array detector and a copper anode X-ray source.
277 Measurements were performed between 5° and 70° with a step size of 0.001 2 θ whilst
278 spinning the sample. All powders were side-loaded into stainless steel sample holder for
279 analysis. Diffraction data was processed using the PANalytical HighScore Plus software to
280 remove artefacts from copper K β radiation, baseline-corrected using a polynomial function,
281 then fitted to a series of pseudo-Voigt functions to obtain the peak areas. A single calcite
282 phase was identified in the cave rock sample. In the soil samples low angle peaks at 9.95 Å,
283 9.01 Å, 7.10 Å supported the presence of illite, smectite, and kaolinite clays, along with
284 strong diffraction from a quartz phase. A semi-quantitative analysis was performed using the
285 clay 090 reflection (62.1° 2 θ , 1.49 Å) and the neighbouring quartz 211 reflection (60.0° 2 θ ,
286 1.54 Å) based on reliability of the 090 peak for clay quantitation, and the absence of overlap
287 with other peaks (Środoń et al., 2001). Semi-quantitation of the diffracting mineral phases
288 was performed using a standard addition of quartz (20 wt%), and then the resulting mineral
289 phase composition adjusted to include an amorphous (non-diffracting) phase of iron
290 oxide/hydroxide identified in the XRF measurements.

291

292 3.5 Stalagmite collection and analysis

293 The cave area below the irrigation site is in a public section of the cave and hence stalagmite
294 collection was not possible. However sampling was possible away from the public section in
295 a hydrologically active area known as South Passage, which is approximately 30-40 m from
296 the infiltration site and approximately 20 m deeper (Figure 1a) and within the monitoring
297 network reported by Jex et al. (2012), where drip rates generally increase 10 – 20 days after
298 rainfall. We therefore conceptualize that stalagmites in this area are subject to the same
299 parent hydrochemistry as Sites 1 and 2. A stalagmite was collected from South Passage in
300 2011. The trace element record was measured along the growth axis on one half of the cut
301 stalagmite by a New Wave NWR213 laser ablation unit coupled to a Perkin Elmer NexION
302 300D ICP-MS. Elemental data was collected continuously with a 25 μm spot size and a scan
303 speed of 25 $\mu\text{m s}^{-1}$. The following elements were analysed Ba, Cu, Mg, Ni, P, Si and Sr and
304 reported relative to Ca and converted to semi-quantitative data using NIST612 silicate glass

305 standard. PCA was performed on the stalagmite data using PLS toolbox (Eigenvalue
306 Research, Inc.) after the data were auto-scaled.

307

308 **4. Results**

309 4.1 Soil and rock mineralogy and elemental composition

310 A subset of relevant results for the XRF and LA ICPMS elemental analysis of the soil and
311 rock samples are given in Table 1, and the complete analysis is given in the Supporting data
312 Table S4. From these results it appears that Mg is present at similar levels in the soil and in
313 the bedrock, and Ba is only detectable in the soil sample. The soil sample contains a high
314 level of Si. P is only detected in the soil, presumably associated with organic matter. The
315 majority of the limestone bedrock sample comprised of calcite, with trace quantities of other
316 minerals, including quartz. The soil was found to be a mixture of kaolinite, illite, and smectite
317 (bentonite) clays (56%) that have been reported at this site (Frank, 1971, Gingele et al.,
318 2005), quartz (15%), and iron oxides (7%), with 20-22% volatiles.

319

320 4.2 Drip rates and dripwater stable isotope time series

321 The time series of drip rate and stable isotopes of the cave dripwater during the four days of
322 the short-term irrigation experiment above Cathedral Cave are plotted in Figure 2. On Day 1,
323 no dripwater was observed at any of our drip samplers, including Sites 1 and 2. Therefore, we
324 hypothesise that the irrigation water was primarily held in the overlying soil. On Day 2, three
325 hours after the start of irrigation Event 2, dripping was observed at Sites 1 and 2 for a period
326 of two hours and peaking at rates of 8.25 mL min⁻¹ for Site 1 and 2.95 mL min⁻¹ for Site 2.
327 On Day 3, following irrigation Event 3, dripping restarted at Sites 1 and 2 2.5 hours after
328 irrigation commenced and peaked at rates of 12.10 mL min⁻¹ for Site 1 and 10.20 mL min⁻¹
329 for Site 2. Site 1 then dripped continuously while Site 2 dripping ceased after 17.5 hours. On
330 Day 4, after irrigation Event 4, Site 1 continued to drip and dripping restarted at Site 2 one
331 hour after the start of the irrigation. Rates peaked at 11.55 mL min⁻¹ for Site 1 and 6.15 mL
332 min⁻¹ for Site 2. Both sites were monitored for a further 24 hours, during which time both
333 sites continued to drip.

334

335 The irrigation water on Day 1 was spiked with deuterium and used as an artificial tracer of
336 water movement and to permit a calculation of the dilution of cave dripwater with respect to
337 the irrigation water. Isotope analysis of the dripwater samples (Figure 2) demonstrated that an
338 increase above the background natural variability of deuterium (−9.2‰ vs −15.8‰) was not

339 observed until the end of dripping on Day 2 with the maximum value of +11.5‰ reached on
340 Day 3 and then steadily decreasing until the end of monitoring on Day 4 to values of about
341 -4‰, still above the natural background level.

342

343

344 4.3 Trace element analysis

345 Figure 2 shows the dripwater EC and selected elemental concentration changes over time for
346 Site 1 and 2. Every elemental plot is characterised by certain features. The dripwater EC data
347 generally started out high for each event with EC ranging from 430-493 $\mu\text{S cm}^{-1}$ for Site 1
348 and 430-488 $\mu\text{S cm}^{-1}$ for Site 2, depending on the day. As drip rates decreased the EC
349 decreased to between 406-430 $\mu\text{S cm}^{-1}$ for Site 1 and 406-466 $\mu\text{S cm}^{-1}$ for Site 2, depending
350 on the day. For most elements (Figure 2) the initial dripwater sample, collected on Day 2, had
351 high relative concentrations suggestive of initial flushing of ions during the first flow.
352 Subsequent samples on Day 2 showed a rapid decrease in concentrations, with the exception
353 of Si. Elemental concentrations on Day 3 showed an initial high concentration similar to that
354 observed initially on Day 2. This initial peak was smaller for Ba and Mg compared to the
355 initial peak on Day 2. Day 3 behaviour was repeated on Day 4 though on a smaller scale.
356 When the rate of dripping reduced, all trace element concentrations increased with the
357 exception of Ca (and EC), which decreased. Over the period of the experiment, Si and Sr
358 show an upward trend at both sites. Within each site Cu and Ni show very similar behaviour
359 over the period of the experiment. However, when comparing these elements between sites a
360 notable difference is the lack of a concentration spike on Day 4 for Site 1. Ba also shows a
361 difference between the two sites, with a concentration spike present on Day 3 at Site 2 and
362 Day 4 at Site 1.

363

364 4.4 Organic matter analysis

365 For the organic matter analysis, PARAFAC indicated that a three factor model provided
366 realistic excitation and emission spectral profiles and appropriately modelled the data. The
367 three factors were identical to those widely reported as the most common factors in
368 fluorescence EEMs from a wide range of aquatic environments (Stedmon et al., 2003;
369 Dainard and Guéguen, 2013). These three factors are characterised following Ishii and Boyer
370 (2012). Factor 1 fluoresces at relatively long emission wavelengths (peak centred at 460 nm)
371 and is commonly identified as unprocessed, soil-derived humic-like and fulvic-like material
372 that has a high aromaticity and/or molecular weight. Factor 2 fluoresced at a shorter emission

373 wavelength (peak centred at 400 nm) and is commonly identified as biogeochemically
374 processed humic/fulvic-like material, where aromatic structures have been bio- or photo-
375 degraded, with a resulting structure that is less aromatic and/or has lower molecular weight.
376 Factor 3 fluoresced in the short UV (peak centred at 340 nm) that is associated with living or
377 dead microbial matter (tryptophan-like fluorescence) and is therefore indicative of
378 microbiological activity (Hudson et al 2008). We hypothesise that all of the factors are soil-
379 derived given the 0-0.3 m thickness of soil overlying the infiltration site and a bedrock
380 thickness of 1.7-3 m limiting the likelihood of other sources of organic matter between the
381 soil surface and the drip sites.

382

383 The PARAFAC score for each factor (which provides a quantitative measure of fluorescent
384 dissolved organic matter (fDOM) for each component) is shown in Figure 3. Similar to the
385 trace element data on Day 2, each factor had an initial high amount of fDOM followed by a
386 rapid decrease suggestive of initial flushing. On the subsequent days the amount of fDOM
387 levelled out, peaking in the middle of Day 3 and 4 for Factors 1 and 2, potentially related to
388 time of maximum soil moisture.

389

390 4.5 Trace element and DOM PCA

391 For each site an individual PCA was performed on the entire dataset, comprising the trace
392 element concentrations and PARAFAC scores (representing the organic matter). For both
393 sites, the first two components account for approximately 70% of the variance in the dataset.
394 The contribution of each variable in the analysis is given in Table 2. The most notable
395 observation about component 1 in both sites is the contribution of the PARAFAC scores with
396 the concentrations of Ba, Cu, Mg, and Ni. The presence of the PARAFAC scores in
397 component 1 (but not component 2) suggests that component 1 represents soil-derived
398 material. Component 2 has significant contributions from Ca, Mg, and Sr for both sites,
399 cations that are typically derived from limestone bedrock, and in addition Si. These
400 elemental assignments are supported by the soil and bedrock elemental results, as Mg was
401 present at similar levels in the soil and bedrock component and Ba only detected in the soil
402 sample. However, despite PCA suggesting that the dissolved Si is a bedrock-derived element,
403 it was present at a high level in the soil sample. Further discussion of the Si results is found in
404 section 5.

405

406 The score plot for the soil and bedrock component is given in Figure 4 for Site 1 and 2. Both
407 components show evidence of an initial flushing on Day 2, however the soil component is
408 significantly higher indicating a higher proportion of elements and organics in that fraction.
409 On the subsequent days the level of the soil component remains relatively consistent,
410 however the daily average bedrock component increases. The reasons for this behaviour are
411 unclear but might be attributed to longer residence time or to contributions from zones not
412 activated on the previous days.

413

414 **5. Discussion**

415 Prior to the experiment the soil surface above the cave was dry and there were no active drip
416 sites, which is generally the case for the site. Dripping only activates after major rain events
417 of more than about 60 mm, although this depends on antecedent conditions of the soil
418 (Jex et al., 2012). In this area of the cave, dripping will only last for a maximum of two
419 weeks in accordance with the semi-arid conditions of the site. The residual soil moisture is
420 immobile for long periods of time between events and able to equilibrate with minerals and
421 organic material in the soil. The flow path on the cave wall below the exfiltration point is
422 observed to dry up between rain events to presumably leave traces of dissolved salts and
423 organic matter. Evidence of organic matter deposition can be seen by the discolouration along
424 the flow paths (see Figure S2b). This could explain the high concentrations of both trace
425 element and organic components during the first flush on the second day of the experiment.
426 Also, it was seen albeit to a smaller degree on the subsequent days, indicating that the system
427 was continually wetting up during the entire experiment. A conclusion supported by the more
428 sustained dripping on subsequent days.

429

430 During this study, the drip rates for Site 1 were consistently higher than for Site 2 and had a
431 longer recession on Day 3 (Figure 2) and at the end of dripping after Event 4 (not shown).
432 However, the longer recessions at Site 1 only corresponded to a small additional volume, for
433 example on Day 3 there was an additional 96 ml at Site 1 after dripping stopped at Site 2. We
434 believe the small differences in the hydrology of the two sites are due to the flow paths for
435 Site 1 and 2 only diverging within the cave (see Figure S2b). During periods of high drip
436 rates all sites are activated (additional dripping was observed at three adjacent sites). As the
437 drip rate slowed the outer flow paths dry up and dripping ceased at these sites, with Site 1
438 having a longer recession as it appears to be supplied by the central flow path.

439

440 The hypothesis that the irrigation water was initially held in the overlying soil is supported by
441 the morphology of the site and the deuterium results. The area irrigated was 3 x 7 m with a
442 continuous thin surface soil layer that we estimate to generally vary between 0-0.3 m.
443 However, additional soil is present at deeper levels in fractures in the underlying bedrock.
444 From these figures the estimated the soil volume is 2.1 – 6.3 m³ equivalent to 3.8 – 11.3
445 tonne of soil (assuming bulk density of 1.8 g ml⁻¹). The soil moisture records (November
446 2011 to May 2013) from the nearby Wellington Research Station indicate a soil moisture
447 capacity of up to 0.6 wfw, and the existing soil moisture was 0.1 wfw. Hence a conservative
448 estimate of the soil's additional water storage capacity is approximately 1890 – 5670 l
449 supporting the hypothesis that the 840 l of water from Event 1 was stored initially in the soil.
450 In addition, the appearance of an increase above the background natural variability of
451 deuterium in the dripwater confirms that the water from Day 1 was initially stored in the
452 overlying soil. Since this increase was not observed until the end of dripping on Day 2 this
453 demonstrates that the initial cave dripwater on Day 2 was stored water from before the
454 irrigation experiment, pushed into the cave by the applied irrigation water, and that the
455 irrigated water did not start to appear until the end of dripping on Day 2, with the majority of
456 the irrigation water appearing on Day 3.

457

458 The deuterium data permits an estimation of dilution of the irrigation water (in the tank) with
459 pre-existing soil and vadose zone water. The deuterium value measured for the irrigation
460 water on Day 1 was 6100‰ and the maximum deviation from the background of the
461 collected dripwater samples was ~27‰ at Site 1 and ~25‰ at Site 2. Using these values the
462 minimum dilution of the irrigation water was 0.45%. When this dilution factor is applied to
463 the elemental concentrations of the irrigation water, the measured elemental cave dripwater
464 concentrations are several orders of magnitude higher for all elements and organic component
465 scores (values are given Supporting data table S1). This is an important observation as it
466 demonstrates that the organic or elemental signature of the water used for the irrigation does
467 not need to be considered further and validates the use of the artificial irrigation to investigate
468 contributions of soil and bedrock to the chemistry of cave dripwaters.

469

470 In absolute terms the collected dripwater cation inorganic chemistry is dominated by the
471 dissolved Ca with concentrations ranging between 73 and 94 mg l⁻¹, as would be expected in
472 this system. When comparing to the EC values using the condition that the sum of cations (on
473 a milli-equivalent basis) should equal EC/100 (in $\mu\text{S cm}^{-1}$), Ca explains between 90-100% of

474 the dissolved cation load. Interestingly, both EC and Ca are observed to decrease when drip
475 rates are decreasing towards the end of each day (Figure 2). We hypothesise that this due to
476 slower flow on the cave features which allows more time for dissolved CO₂ to equilibrate and
477 degas to the cave atmosphere. This process could be driving PCP and explain the decrease in
478 Ca and consequently EC. Unfortunately, this hypothesis could not be tested by calcite
479 saturation calculations since the experimental setup and collected sample volumes did not
480 allow for alkalinity analysis and reliable pH measurements.

481

482 It was somewhat surprising that the PCA grouped dissolved Si with the limestone bedrock
483 trace elements since the total element analysis demonstrated that Si was of significantly
484 greater abundance in the soil than found in the bedrock (Table 2). This can be explained by
485 the generally dry nature of the site, and hence the relatively long water residence times in the
486 soil between infiltration events that allow weathering reactions in the soil to reach conditions
487 where Si concentrations are controlled by the equilibrium of precipitating secondary
488 minerals. Si concentrations therefore are controlled by equilibrium conditions rather than by
489 kinetically controlled weathering of primary silicate minerals (Appelo and Postma, 2005).
490 This is supported by the concentrations of Si and dissolved aluminium (Table S2 and S3),
491 which are consistent with equilibrium conditions for kaolinite (observed in the soil) at a
492 reasonable soil pH ca 4.8. Likewise Si concentrations are observed in a very tight range 5.4-
493 6.1 which is in the concentration range observed for equilibrium with a SiO₂(s) solid
494 somewhere in the range between quartz and amorphous SiO₂(s) (Appelo and Postma, 2005).
495 We hypothesise that the narrow observed range of Si is due to equilibrium control in the soil.
496 We further hypothesise that the PCA grouping of Si with the limestone bedrock trace
497 elements could be due to the frequent precipitation and re-dissolution of Si on the cave
498 features along the flow path related to the drying and wetting events.

499

500 5.1 Sr and Mg in dripwater

501 In a review of dripwater Sr and Mg trace element concentrations from diverse cave research
502 monitoring campaigns, Tremain and Froelich (2013) concluded that Sr/Ca and Mg/Ca in
503 dripwaters and stalagmites are likely to be useful indications of groundwater residence time
504 at sites where there was a single source of Sr and Mg (e.g. bedrock). Where this was stable
505 over time, Sr/Ca and Mg/Ca could be used as paleoclimate proxies, and the stability could be
506 tested through the analysis of the Sr/Mg ratio in stalagmites over time. Following the work of
507 Fairchild et al. (2000) Tremain and Froelich (2013) clearly demonstrated that for sites where

508 precipitation dominates over evaporation, PCP is the dominant process that controls
509 dripwater and stalagmite Sr and Mg.

510

511 Figure 5 presents Sr/Ca vs Ca and Mg/Ca vs Ca for the three days of the infiltration
512 experiment. Due to the short duration of the experiments, we expect PCP would be limited
513 during the initial stages of infiltration, but would increase as drip rates slow and residence
514 time increases. Overall, we would hypothesise that the evolution of Ca, Sr/Ca and Mg/Ca
515 over time would be dominated the interplay between rapid dissolution of carbonate minerals,
516 and any subsequent prior calcite precipitation, assuming a single bedrock source of Mg and
517 Sr. Figure 5a and b demonstrates that this is the case, with increasing Ca concentration
518 between Days 2, 3 and 4, a strong correlation between Ca and Sr/Ca during each drip event,
519 and with no significant change in Sr/Ca ratio between the drip events. However, Figure 5c
520 and d demonstrates a complex response, both within individual irrigation events and between
521 events. The complex behaviour of Mg results in extensive scatter in the Sr/Ca versus Mg/Ca
522 plot (Supporting data Figure S4) that precludes the use of this type of plot to identify PCP by
523 divergence from the mixing radial as demonstrated by Tremaine and Froelich 2013. The
524 difference in dripwater Sr and Mg responses during the irrigation events reflects the relative
525 geochemistry and mineral solubility of the soil and bedrock at our site (Table 2). Whereby,
526 soil geochemistry dominated by silicates and bedrock chemistry by carbonates, and a similar
527 abundance of magnesium in both the soil and bedrock when analysed as total elemental
528 composition.

529

530 At our site, in a region where loess contributes to the soil and salt accumulation within the
531 soil profile is expected to occur (Hesse and McTainsh, 2003), Mg fails the ‘single source’ test
532 of Tremaine and Froelich (2013). Instead, Mg accumulation occurs in the soil due to
533 evaporation, the relatively low proportion of Mg in the Devonian Limestone limits its
534 signature from the bedrock, and there is a relatively low contribution of regolith derived Mg
535 to the soil geochemistry at a site where dust deposition is frequent. Our observations are
536 made at an event scale, and the extent to which they apply at seasonal inter-annual timescales
537 needs further investigation. It is possible, that over long-time periods, PCP may become a
538 more dominant, and the Mg signature might be dominated by this process. We consider this
539 further in section 5.3.

540

541 5.2 Soil and bedrock trace element signatures in dripwater

542 Potentially, Sr is identified as a useful trace element signature of bedrock contact time over
543 the scale of individual irrigation events, typical of the occasional high rainfall amount events
544 that generate groundwater recharge at our research site. At the timescale of individual
545 recharge events, dripwater Sr concentration is dominated by dissolution. The Sr appeared in
546 the PCA as component 2, along with Si and Ca (Table 2, Figure 4), and component 2 had a
547 negative correlation with fDOM, indicating that this was a grouping of bedrock-derived trace
548 elements.

549

550 Dripwater PCA analysis demonstrates that trace elements which can be uniquely attributed to
551 being soil-derived are Ba, Ni, and less conclusively Cu. Both Ni and Cu have been previously
552 recognised as organo-colloid associated trace elements (Borsato et al., 2007; Hartland et al.,
553 2012) and their association with fDOM is expected. Ba has been previously interpreted as a
554 bedrock-derived trace element due to its ability to replace calcium in octahedrally-
555 coordinated lattice positions within CaCO_3 (Fairchild et al., 2010). However, Ba was
556 undetectable in the Devonian limestone sample, but found in the soil. Given the high
557 solubility of barium in water and acids, and its strong absorption by clay minerals, we
558 hypothesise our clay-rich soils provide the dominant source of Ba and it is therefore a soil
559 signature. McDonald et al. (2007), sampling dripwaters at Wombeyan Caves, 250 km to the
560 SE, found that Ba concentrations did not represent water residence times in the bedrock.

561

562 Therefore we hypothesise that Ba and organo-colloid associated trace elements such as Ni
563 and Cu provide trace element signatures of soil and only Sr provides a signature of the
564 bedrock, at least over event timescales. At our temperate semi-arid site, long term and
565 frequent aeolian deposition to the land surface has formed a silicate and clay rich soil which
566 can strongly bind Ba (Eylem et al., 1990), and provides a source of Si. Soil-derived dripwater
567 contains high concentrations of fDOM and associated metals with a high binding affinity.
568 The concentrations of Si, also a soil-derived element at this site, is controlled by the
569 equilibrium of the precipitation of secondary silica minerals. Where water is in contact with
570 the bedrock, Sr should be increasing with time. Over longer than event timescales, dripwater
571 Sr concentration will also be controlled by PCP. This suggests that Mg in the environment of
572 this study is a poor tracer as it has potential sources from soil salt accumulation due to the
573 high *ET*, a potential source in high Mg clays weathered from aeolian deposition, and a
574 limestone dissolution source. In addition, Mg will vary with the degree of PCP within the
575 bedrock above the cave. This suggests it may be necessary to investigate and interpret the

576 trace element response to recharge on a site-by-site basis to calibrate these proxies in
577 stalagmites. To test these hypotheses, we consider the recent stalagmite trace element record
578 from the cave.

579

580 5.3. Recent stalagmite trace element profile.

581 An actively-forming stalagmite from South Passage was sampled in 2011 and the top 2.6 mm
582 analysed using LA-ICPMS. Although the exact growth rate for this sample is not known,
583 speleothems in this part of the cave have deposited over infrastructure installed in 1926 when
584 it was the show cave. A total speleothem accumulation of 22 mm is indicative of a minimum
585 growth rate of 0.26 mm yr^{-1} . This is in agreement with that expected for the observed
586 dripwater Ca concentrations of 70-90 mg l^{-1} (Figure 2) (Dreybrodt, 1999). Therefore we
587 hypothesise that the top 2.6 mm represents the last 10 years of deposition. The stalagmite is
588 situated around 20 m below the site affected by the irrigation experiment. Jex et al. (2012)
589 demonstrated that drip rates in this part of the cave increases 10 to 20 days after long-
590 duration, high volume rainfall events, and dripping is maintained for several weeks to years,
591 depending on the flow path. We hypothesise that the dripwater from this section of the cave
592 has the same parent hydrochemistry as dripwater from the irrigation events and it has likely
593 to have undergone PCP.

594

595 Figure 6 presents the LA-ICPMS data for Mg, Si, Sr, Cu, P and Ba, normalised to Ca for the
596 stalagmite and Figure 7 shows the loading plot for component 1 versus component 2 from the
597 PCA performed on the stalagmite data. Although P was below detection in the dripwater data
598 concentrations were significantly above the detection limit in the stalagmites, and also
599 detectable in the total elemental analysis for the soil (Table 2). Whilst a bedrock or a soil
600 component could not be identified there appears to be a clustering of the soil-derived
601 dripwater elements in Ba and Cu with P (and additionally Si). This confirms the Ba
602 concentration being a signature for soil-derived water in the dripwater samples. We
603 hypothesised that the Mg/Sr ratio would not be constant over time and this is confirmed by
604 the separation of these elements in PCA loadings plot (Figure 7). In the stalagmite, Sr
605 contains little high-frequency variability compared to Mg, suggesting that the Sr does
606 comprise a smoothed, bedrock-derived signal. The elements Ba and Mg are also separated
607 confirming the complexity of the Mg signature. The source of the variability of Mg requires
608 further investigation.

609

610 **6. Conclusions**

611 Through a series of short-term infiltration experiments the trace element geochemistry of
612 dripwater was characterised in a semi-arid environment at Wellington Caves, Australia. Use
613 of PCA on the combined trace element concentrations and PARAFAC scores (representing
614 different fDOM pools) revealed two dominant components in the dripwater samples, a
615 bedrock component and a soil component. The soil component, identified based on the
616 contribution of the PARAFAC scores, also contained Ba, Cu, Mg, and Ni. The limestone
617 bedrock component comprised Ca, Mg and Sr that are typical bedrock-derived elements and
618 in addition Si, an element not normally associated with bedrock.

619

620 In contrast to temperate and alpine environments it is demonstrated that Mg can have
621 contribution from the soil in addition to being solely bedrock-derived. It is notable that Ba, a
622 typical bedrock-derived element was found to be soil-derived. These results were supported
623 by soil and rock analysis with similar levels of Mg present in the soil and limestone samples,
624 and Ba only detectable in the soil. Analysis of a stalagmite collected from this site supports
625 these conclusions.

626

627 Our results demonstrate that infiltration water trace element composition at a particular semi-
628 arid to arid site is likely to be site specific, and highly dependent on the existence of aeolian
629 soil and salt deposits in the soil profile, and the soil salinity as a function of climate. Results
630 from this study suggest that calibration of stalagmite trace element records should be on a site
631 by site basis in these regions thus further research is needed from other sites. We show that
632 Mg/Ca is highly unlikely to provide a unique or stationary paleoclimate proxy in these
633 environments, and that the test of a constant ratio of Mg/Sr in stalagmites as proposed by
634 Tremaine and Frolich (2013) is expected to fail.

635

636 In semi-arid to arid regions, recharge events are infrequent. Yet, the high rainfall amount
637 required to overcome soil moisture deficit and evaporation can lead to recharge, and storage
638 within the soil and the limestone bedrock which in turn can lead to episodes of both
639 continuous and discontinuous dripping and subsequent speleothem formation. This was
640 observed at our site. We have identified suites of trace elements that are indicative of soil and
641 bedrock contact time and dripwater evolution. The observed behaviour of these trace element
642 proxies in relation to speleothem paleoclimate reconstructions will form the basis of future
643 work by the investigators.

644

645 Our conclusions have implications for the interpretation of speleothem trace element records
646 in semi-arid to arid regions where $P < ET$. Typically, such sites are desert marginal and prone
647 to aeolian deposition, and our results are relevant to any site where aeolian contributions to
648 the soil might be significant. Overall, trace elements identified in this study in a semi-arid
649 environment, cannot be assumed to follow the conventional interpretations that are more
650 generally applicable in temperature climate zones. At these sites, models of Sr and Mg
651 dripwater concentration as a single source, bedrock residence time signal, are unlikely to
652 apply. Speleothem trace element records interpreted in this manner should be treated with
653 caution.

654

655 **7. Acknowledgements**

656 We thank the staff at Wellington Caves for their support. Funding for this research was
657 provided by the National Centre for Groundwater Research and Training, an Australian
658 Government initiative, supported by the Australian Research Council and the National Water
659 Commission. Thanks to Bruce Welsh and Philip Maynard from Sydney University
660 Speleological Society for providing the survey map. Darrel Tremaine and two anonymous
661 reviewers are thanked for their review comments.

662

663 **8. References**

- 664 Appelo, C.A.J., Postma, D., 2005. *Geochemistry, Groundwater, and Pollution*, second ed.
665 A.A. Balkema, Rotterdam, 649 pp.
- 666 Bar-Matthews, M., Matthews, A., Ayalon, A., 1991. Environmental Controls of Speleothem
667 Mineralogy in a Karstic Dolomitic Terrain (Soreq Cave, Israel). *The Journal of Geology*
668 **99**, 189-207.
- 669 Borsato, A., Frisia, S., Fairchild, I.J., Somogyi, A., Susini, J., 2007. Trace element
670 distribution in annual stalagmite laminae mapped by micrometer-resolution X-ray
671 fluorescence: Implications for incorporation of environmentally significant species.
672 *Geochimica et Cosmochimica Acta* **71**, 1494-1512.
- 673 Bowler, J.M., 1976. Aridity in Australia: age, origins and expressions in aeolian landforms
674 and sediments. *Earth Science Reviews* **12**, 279-310.
- 675 Dainard, P.G., Guéguen, C., 2013. Distribution of PARAFAC modeled CDOM components
676 in the North Pacific Ocean, Bering, Chukchi and Beaufort Seas. *Marine Chemistry* **157**,
677 216-223.

678 Dreybrodt, W., 1999. Chemical kinetics, speleothem growth and climate. *Boreas* **28**, 347-
679 356.

680 Eylem, C., Erten, H.N., Göktürk, H., 1990. Sorption-desorption behaviour of barium on
681 clays. *Journal of Environmental Radioactivity* **11**, 183-200.

682 Fairchild, I.J., Baker, A., 2012. *Speleothem Science*. Wiley-Blackwell 432pp.

683 Fairchild, I.J., Borsato, A., Tooth, A.F., Frisia, S., Hawkesworth, C.J., Huang, Y.,
684 McDermott, F., Spiro, B., 2000. Controls on trace element (Sr–Mg) compositions of
685 carbonate cave waters: implications for speleothem climatic records. *Chemical Geology*
686 **166**, 255-269.

687 Fairchild, I.J., Spotl, C., Frisia, S., Borsato, A., Susini, J., Wynn, P.W., Cauzid, J., 2010.
688 Petrology and geochemistry of annually laminated stalagmites from an Alpine cave (Obir,
689 Austria): seasonal cave physiology. *Geological Society, London, Special Publications* **336**,
690 295-321.

691 Fairchild, I.J., Treble, P.C., 2009. Trace elements in speleothems as recorders of
692 environmental change. *Quaternary Science Reviews* **28**, 449-468.

693 Frank, R., 1971. The clastic sediments of the Wellington Caves, New South Wales. *Helictite*
694 **9**, 3-26.

695 Frisia, S., Borsato, A., Drysdale, R.N., Paul, B., Greig, A., Cotte, M., 2012. A re-evaluation
696 of the palaeoclimatic significance of phosphorus variability in speleothems revealed by
697 high-resolution synchrotron micro XRF mapping. *Climate of the Past* **8**, 2039-2051.

698 Gingle, F.X., de Deckker, P., 2005. Clay mineral, geochemical and Sr-Nd isotopic
699 fingerprinting of sediments in the Murray-Darling fluvial system, southeast Australia,
700 *Australia Journal of Earth Sciences* **523**, 965-974.

701 Greene, R.S.B., Cattle, S.R., Mcpherson, A.A., 2009. Role of eolian dust deposits in
702 landscape development and soil degradation in southeastern Australia. *Australian Journal*
703 *of Earth Sciences* **56**, S55-65.

704 Hansen B.K., Postma D., 1995. Acidification, buffering, salt effects in the unsaturated zone
705 of a sandy aquifer, Klosterhede, Denmark. *Water Resources Research* **31**, 2795-2809.

706 Hartland, A., Fairchild, I.J., Lead, J.R., Borsato, A., Baker, A., Frisia, S., Baalousha, M.,
707 2012. From soil to cave: Transport of trace metals by natural organic matter in karst
708 dripwaters. *Chemical Geology* **304–305**, 68-82.

709 Hesse P.P., McTanish, G.H., 2003. Australian dust deposits: modern processes and the
710 Quaternary record. *Quaternary Sciences Reviews* **22**, 2007-2035.

711 Ishii, S.K., Boyer, T.H., 2012. Behavior of reoccurring PARAFAC components in fluorescent
712 dissolved organic matter in natural and engineered systems: a critical review.
713 *Environmental Science & Technology* **46**, 2006-2017.

714 Jex, C.N., Mariethoz, G., Baker, A., Graham, P., Andersen, M.S., Acworth, I., Edwards, N.,
715 Azcurra, C., 2012. Spatially dense drip hydrological monitoring and infiltration behaviour
716 at the Wellington Caves, South East Australia. *International Journal of Speleology* **41**,
717 285-298.

718 Johnson, B.D., 1975. The Garra Formation (early Devonian) at Wellington, N.S.W. *Journal*
719 *and Proceedings of The Royal Society of New South Wales* **108**, 111-118.

720 Lis, G., Wassenaar, I.L., Hendry, M.J., 2007. High-precision laser spectroscopy D/H and
721 18O/16O measurements of microliter natural water samples. *Analytical Chemistry* **80**,
722 287-293.

723 Mariethoz, G., Baker, A., Sivakumar, B., Hartland, A., Graham, P., 2012. Chaos and
724 irregularity in karst percolation. *Geophysical Research Letters* **39**, L23305.

725 McDonald, J., Drysdale, R., Hill, D., Chisari, R., Wong, H., 2007. The hydrochemical
726 response of cave drip waters to sub-annual and inter-annual climate variability,
727 Wombeyan Caves, SE Australia. *Chemical Geology* **244**, 605-623.

728 Norrish, K., Hutton, J.T., 1969. An accurate X-ray spectrographic method for the analysis of
729 a wide range of geological samples. *Geochimica et Cosmochimica Acta* **33**, 431-453.

730 Osborne, R.A.L., 2007. Cathedral Cave, Wellington Caves, New South Wales, Australia. A
731 multiphase, non-fluvial cave. *Earth Surface Processes and Landforms* **32**, 2075-2103.

732 Osborne, R.A.L., 2010. Rethinking eastern Australian caves. Geological Society, London,
733 Special Publications **346**, 289-308.

734 Roberts, M.S., Smart, P.L., Baker, A., 1998. Annual trace element variations in a Holocene
735 speleothem. *Earth and Planetary Science Letters* **154**, 237-246.

736 Siklósy, Z., Demény, A., Vennemann, T.W., Pilet, S., Kramers, J., Leél-Össy, S., Bondár, M.,
737 Shen, C.-C., Hegner, E., 2009. Bronze Age volcanic event recorded in stalagmites by
738 combined isotope and trace element studies. *Rapid Communications in Mass Spectrometry*
739 **23**, 801-808.

740 Smith, C.L., Fairchild, I.J., Spötl, C., Frisia, S., Borsato, A., Moreton, S.G., Wynn, P.M.,
741 2009. Chronology building using objective identification of annual signals in trace
742 element profiles of stalagmites. *Quaternary Geochronology* **4**, 11-21.

743 Środoń, J., Drits, V.A., McCarty, D.K., Hsieh, J.C.C., Eberl, D.D., 2001. Quantitative X-ray
744 diffraction analysis of clay-bearing rocks from random preparations. *Clays and Clay*
745 *Minerals* **49**, 514-528.

746 Stedmon, C.A., Bro, R., 2008. Characterizing dissolved organic matter fluorescence with
747 parallel factor analysis: a tutorial. *Limnology and Oceanography: Methods* **6**, 572-579.

748 Stedmon, C.A., Markager, S., Bro, R., 2003. Tracing dissolved organic matter in aquatic
749 environments using a new approach to fluorescence spectroscopy. *Marine Chemistry* **82**,
750 239-254.

751 Sundqvist, H.S., Holmgren, K., Fohlmeister, J., Zhang, Q., Matthews, M.B., Spotl, C.,
752 Kornich, H., 2013. Evidence of a large cooling between 1690 and 1740 AD in southern
753 Africa. *Nature Scientific Reports* **3**, 1767.

754 Tremaine, D.M., Froelich, P.N., 2013. Speleothem trace element signatures: A hydrological
755 geochemical study of modern cave dripwaters and farmed calcite. *Geochimica et*
756 *Cosmochimica Acta* DOI:10.1016/j.gca.2013.07.026.

757 Van Rangelbergh M., Fleitmann, D., Verheyden, S., Cheng, H., Edwards, L., De Geest, P.,
758 De Vleeschouwer, D., Burns, S.J., Matter, A., Claeys, P. and Keppens, E., 2013. Mid- to
759 late Holocene Indian Ocean Monsoon variability recorded in four speleothems from
760 Socotra Island, Yemen. *Quaternary Science Reviews* **65**, 129-142.

761 Wassenaar, L.I., Hendry, M.J., Chostner, V.L. and Lis G.P. 2008 High Resolution Pore Water
762 $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Measurements by $\text{H}_2\text{O}(\text{liquid})\text{-H}_2\text{O}(\text{vapor})$ Equilibration, *Environmental*
763 *Science and Technology* **42**, 9262–9267.

764 Wassenburg, J.A., A. Immenhauser, D.K. Richter, A. Niedermayr, S. Riechelmann, J.
765 Fietzke, D. Scholz, K.P. Jochum, J. Fohlmeister, A. Schröder-Ritzrau, A. Sabaoui, D.F.C.
766 Riechelmann, L. Schneider, J. Esper, 2013. Moroccan speleothem and tree ring records
767 suggest a variable positive state of the North Atlantic Oscillation during the Medieval
768 Warm Period. *Earth and Planetary Science Letters* **375**, 291-302.

769

770 Figure 1: (a) Plan view of Wellington Caves, New South Wales, with a boxed area indicating
771 where the surface irrigation was performed (Adapted from Sydney University Speleology
772 Society survey map 2006 – 2007). (b) Cross section from site survey indicating soil surface,
773 bedrock profile and dripwater sites. (c) Location of study site in the Murray-Darling Basin of
774 NSW showing possible dust sources indicated by arrows and climate zones, adapted from
775 Bowler, 1976.

776

777 Figure 2: Time series of drip rates, deuterium, EC and concentrations of a selection of metal
778 elements in response to infiltration events at Site 1 (red) and Site 2 (black).

779

780 Figure 3: PARAFAC scores over the course of the experiment for each factor at both sites.
781 Factor 1 (F1: unprocessed soil-derived humic and fulvic like material); Factor 2 (F2:
782 biogeochemically processed humic and fulvic like material; Factor 3 (F3: microbially-derived
783 material). (N.B. no calibration was performed hence relative difference between factor scores
784 do not necessarily represent the same relative differences in concentrations.)

785

786 Figure 4: Score plots of the principal component analysis of elemental and PARAFAC data
787 over time at Site 1 and Site 2.

788

789 Figure 5: Ca versus Sr/Ca and Mg/Ca molar ratio for Site 1 and Site 2.

790

791 Figure 6: Trace element record from the top 2.6 mm of stalagmite C collected from
792 Wellington Caves in 2011 A.D.

793

794 Figure 7: PCA loadings plot for components 1 and 2 of the Wellington stalagmite.

795

796 Table 1: Selected total elemental analysis results on dried soil and bedrock samples at the
797 site. (BLD: below limit of detection)

798

799 Table 2: Elemental and PARAFAC scores contributions to PC1 (bedrock component) and
800 PC2 (soil component).

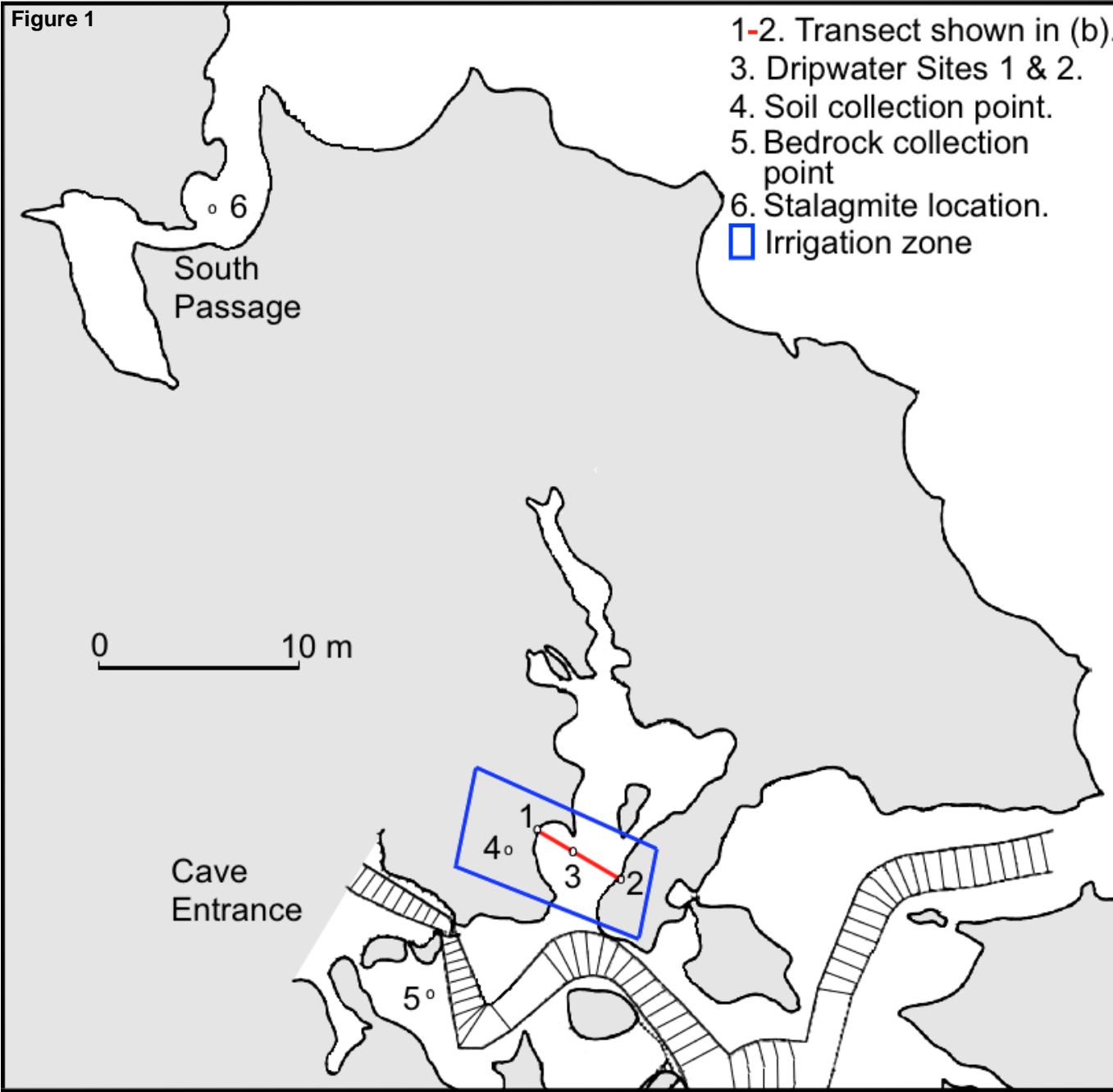
801

Table1

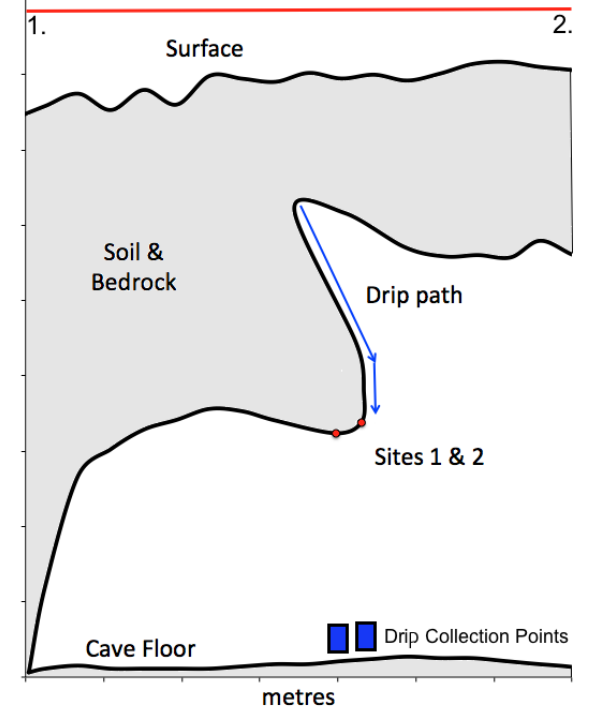
	Soil	Bedrock
XRF analysis	wt%	wt%
Na ₂ O	0.20	0.01
MgO	0.57	0.33
Al ₂ O ₃	13.33	0.07
SiO ₂	52.84	0.11
P ₂ O ₅	0.26	BLD
K ₂ O	1.73	BLD
CaO	2.19	57.49
Fe ₂ O ₃	7.02	0.13
Loss on ignition	20.63	43.16
LA ICPMS analysis	µg/g	µg/g
Ba	165.5	0
Sr	70	118.2

Table2

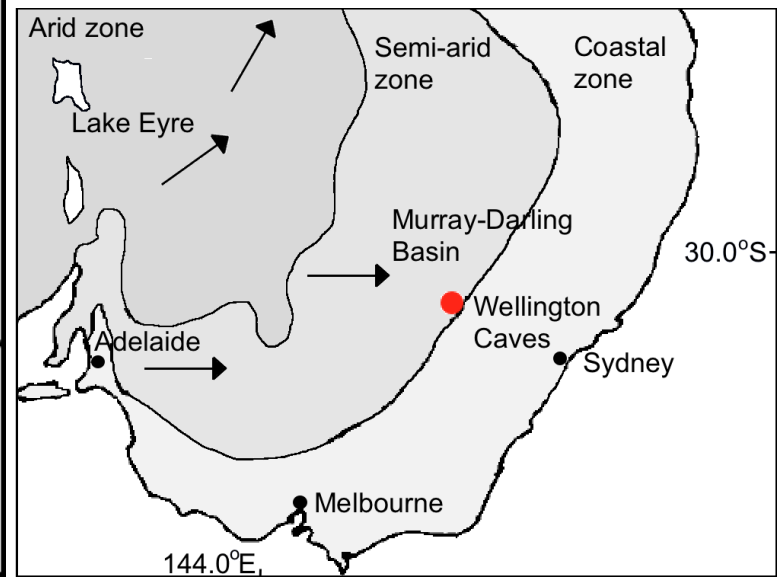
	Site 1		Site 2	
	PC 1	PC 2	PC 1	PC 2
% explained variance	47.08	27.25	55.16	25.22
Ba	0.41	0.12	0.40	0.06
Ca	-0.003	0.49	0.01	0.24
Cu	0.17	-0.06	0.35	0.16
Mg	0.35	0.34	0.34	0.32
Ni	0.32	0.05	0.39	0.15
Si	-0.18	0.51	-0.15	0.54
Sr	0.02	0.58	0.14	0.58
PARAFAC1	0.41	-0.08	0.36	-0.26
PARAFAC2	0.42	-0.12	0.39	-0.20
PARAFAC3	0.43	-0.02	0.37	-0.22



(a)



(b)



(c)

Figure 2
[Click here to download high resolution image](#)

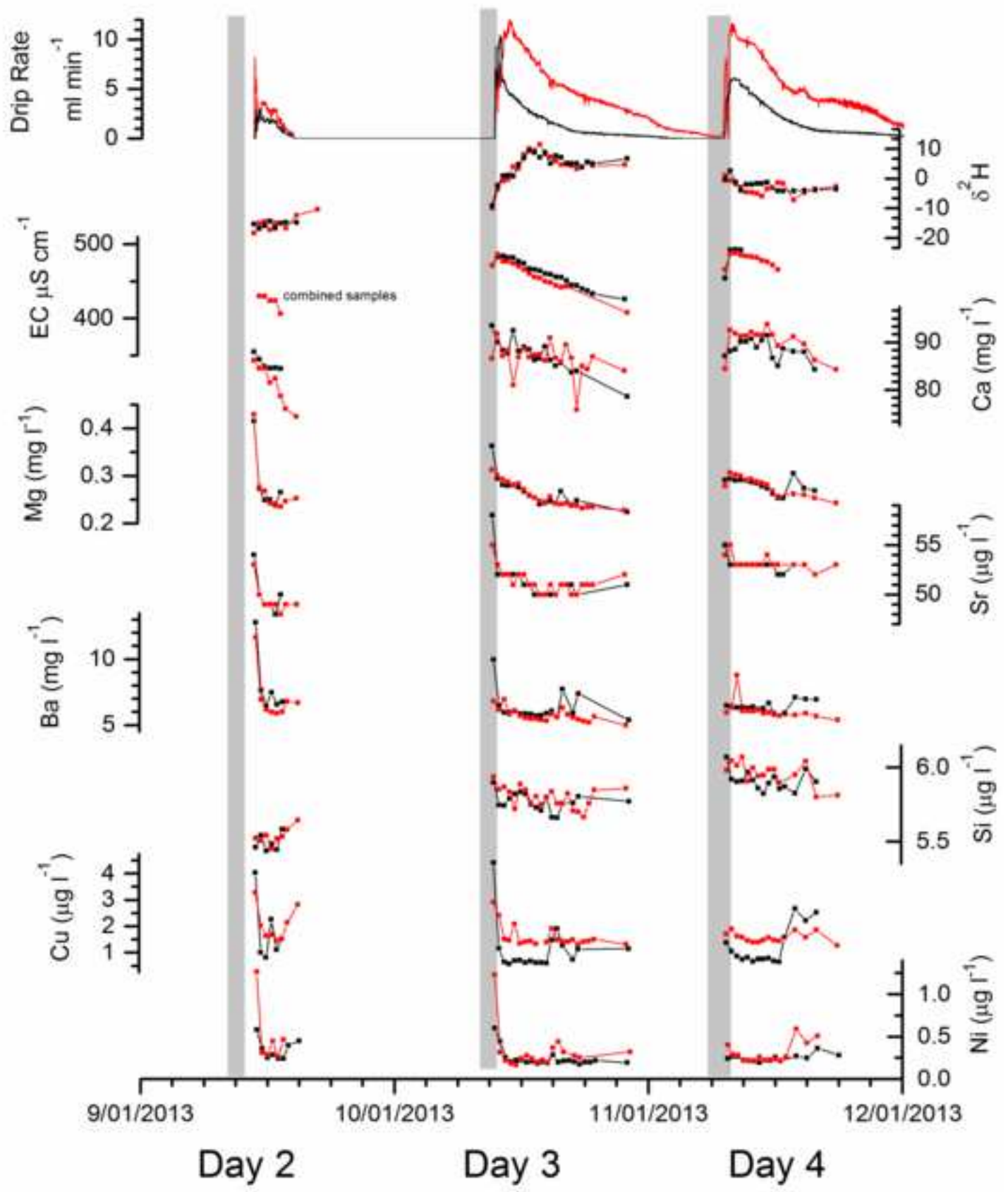


Figure 3
[Click here to download high resolution image](#)

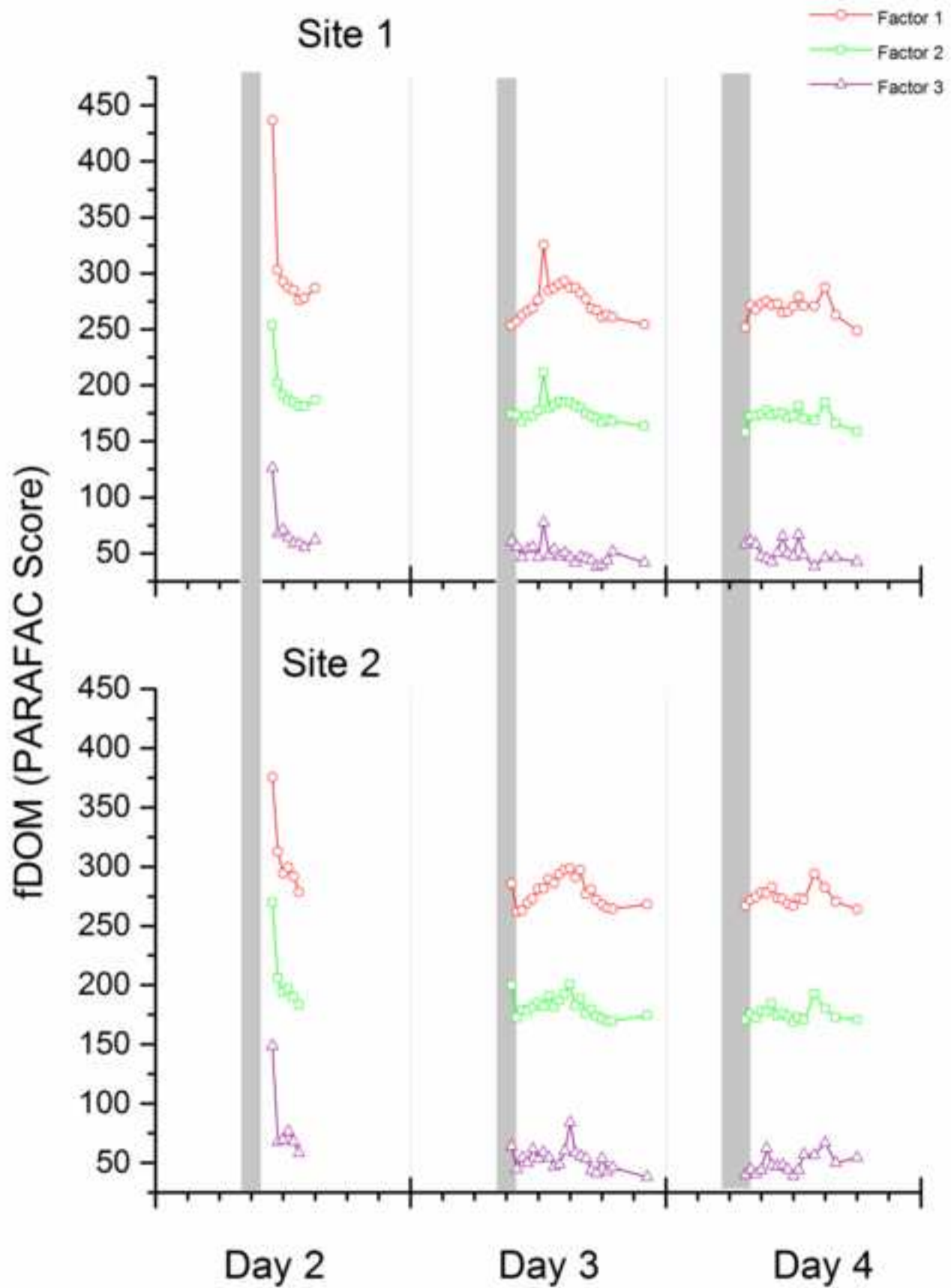


Figure 4

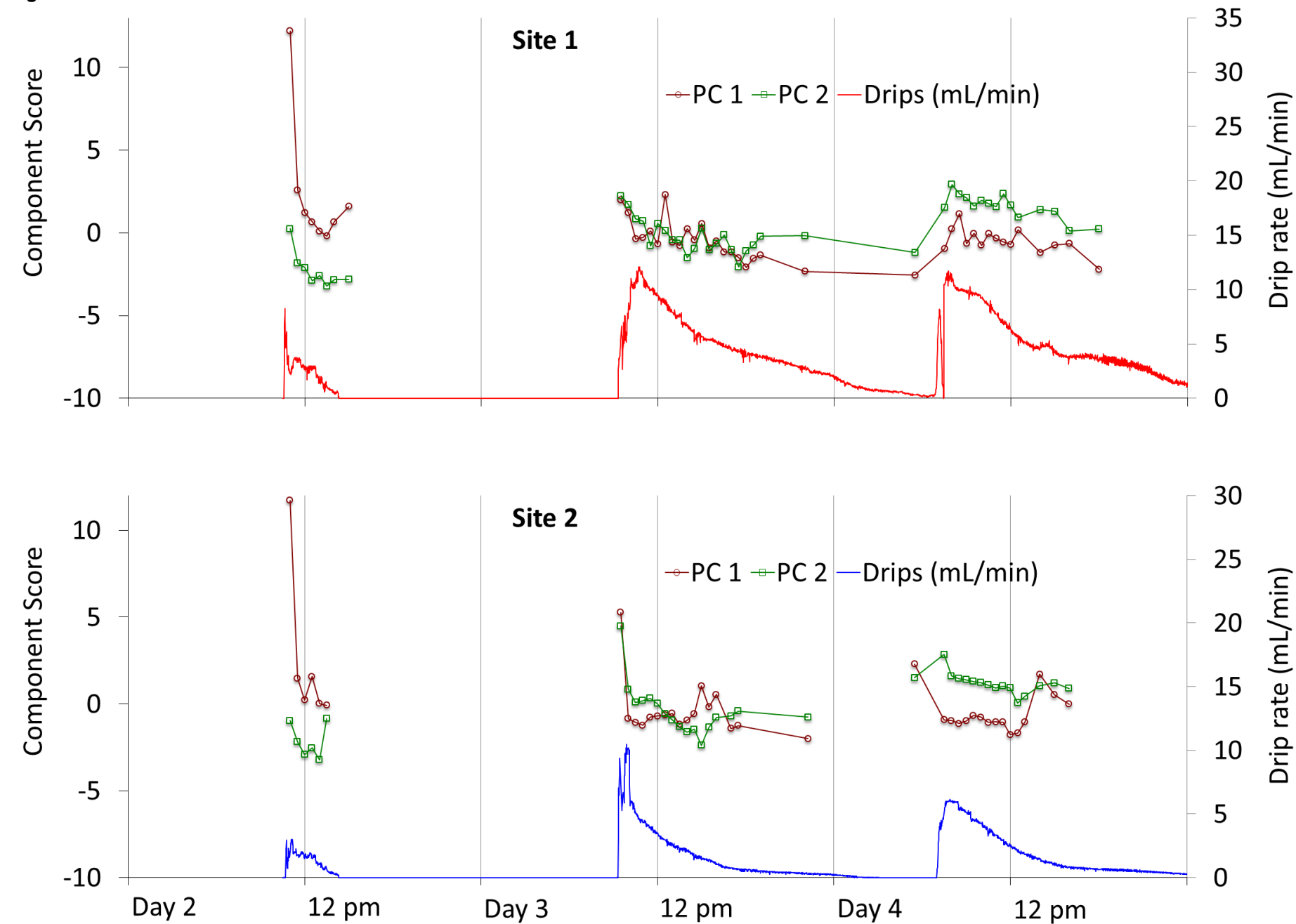


Figure 5

[Click here to download high resolution image](#)

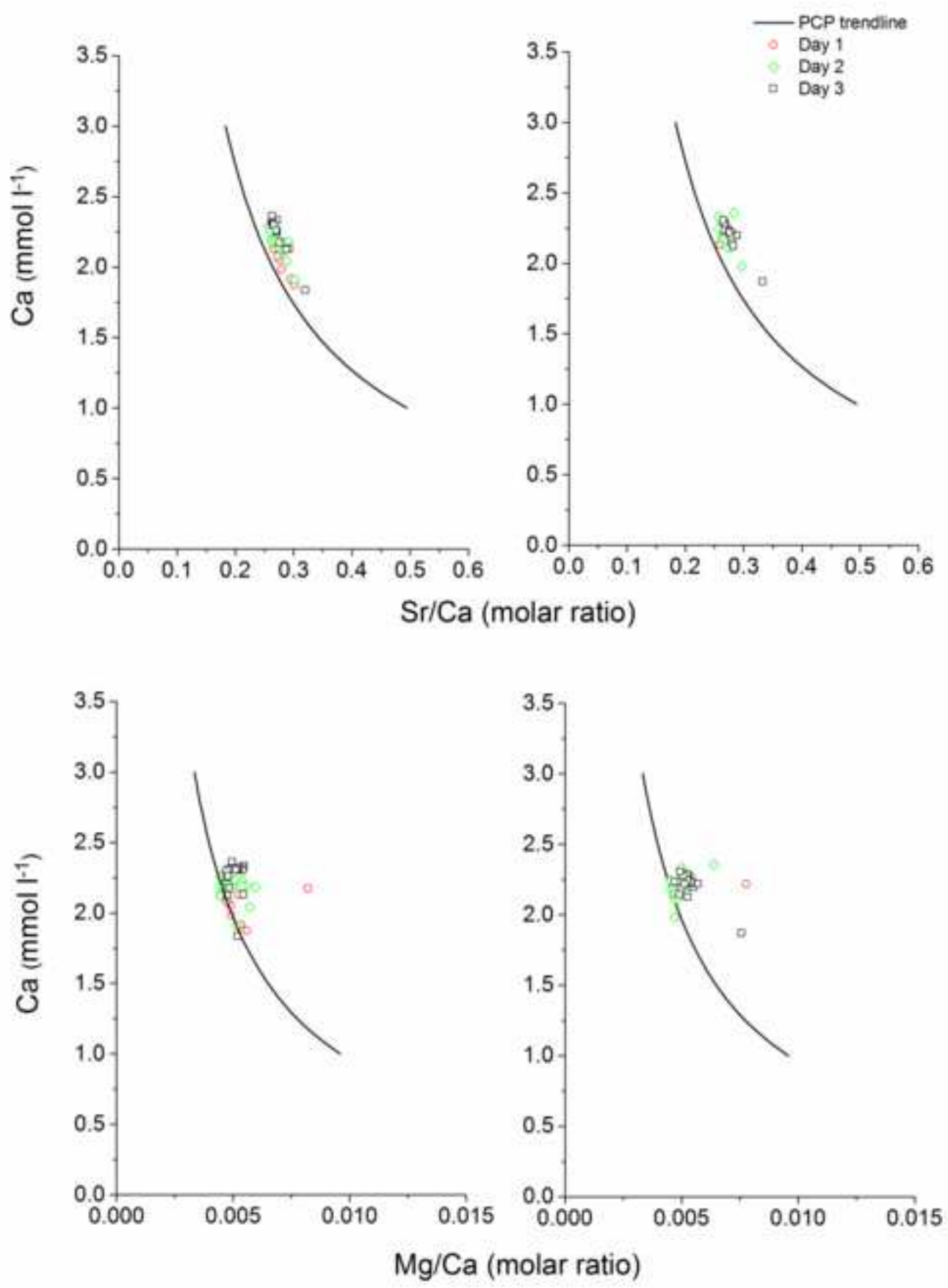


Figure 6

[Click here to download high resolution image](#)

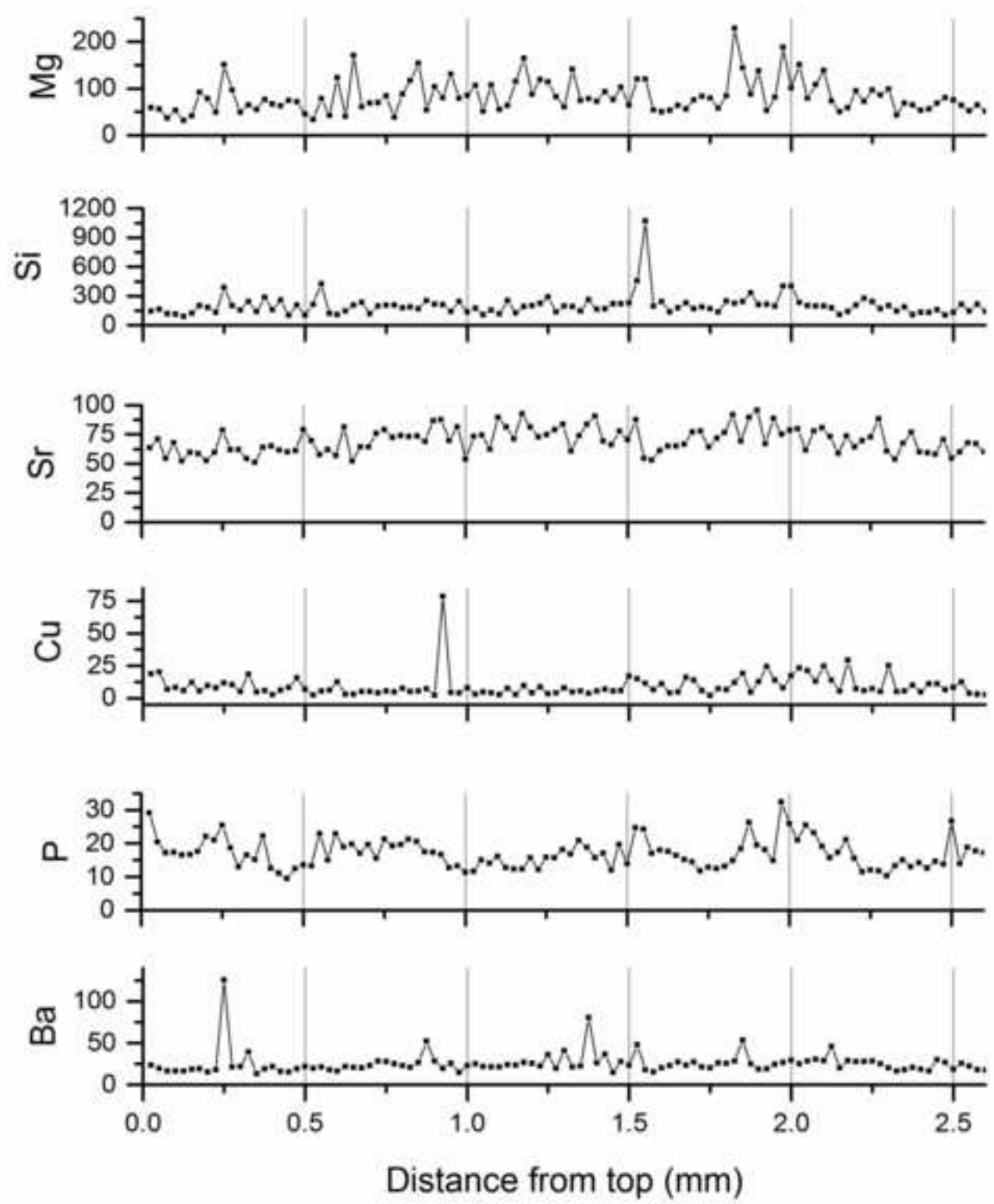
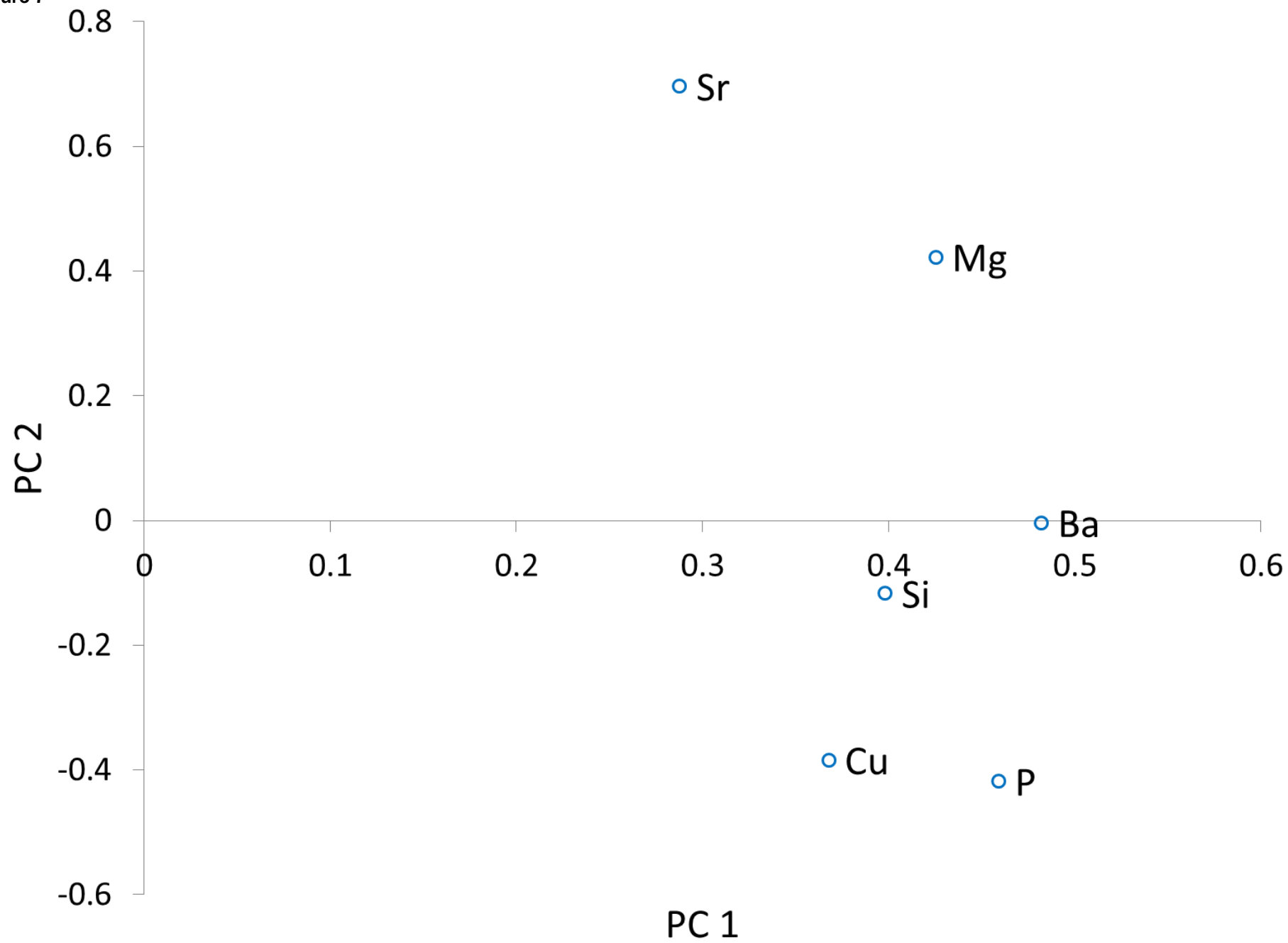


Figure 7



Supplementary Data

[Click here to download Electronic Annex: Wello Manuscript \(supporting\).docx](#)