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Tracing the fate of atmospheric nitrate in a subalpine watershed using $\Delta^{17}\text{O}$

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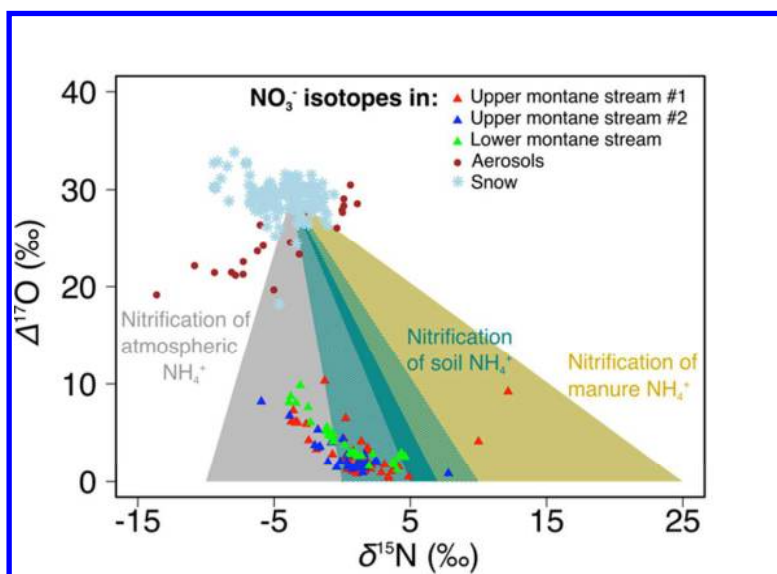
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25 **Abstract**

26 Nitrogen is an essential nutrient for life on Earth, but in excess, it can lead to
27 environmental issues (e.g., N saturation, loss of biodiversity, acidification of lakes,
28 etc.). Understanding the nitrogen budget (*i.e.*, inputs and outputs) is essential to
29 evaluate the prospective decay of the ecosystem services (e.g., freshwater quality,
30 erosion control, loss of high patrimonial-value plant species, etc.) that subalpine
31 headwater catchments provide, especially as these ecosystems experience high
32 atmospheric nitrogen deposition. Here, we use a multi-isotopic tracer ($\Delta^{17}\text{O}$, $\delta^{15}\text{N}$ and
33 $\delta^{18}\text{O}$) of nitrate in aerosols, snow and streams to assess the fate of atmospherically
34 deposited nitrate in the subalpine watershed of the Lautaret Pass (French Alps). We
35 show that atmospheric deposition contributes significantly to stream nitrate pool year-
36 round, either by direct inputs (up to 35 %) or by *in situ* nitrification of atmospheric
37 ammonium (up to 35 %). Snowmelt in particular leads to high exports of atmospheric
38 nitrate, most likely fast enough to impede assimilation by surrounding ecosystems.
39 Yet, in a context of climate change, with shorter snow seasons, and increasing
40 nitrogen emissions, our results hint at possibly stronger ecological consequences of
41 nitrogen atmospheric deposition in the close future.

42

43 **Keywords:** atmospheric deposition, nitrate isotopes, subalpine streams, Lautaret
44 Pass

TOC

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45 **1. Introduction**

46 Reactive Nitrogen (Nr) has long been known for its duality. At low to moderate
47 concentrations, it is an essential nutrient for natural ecosystems in general, and plant
48 nutrition in particular (¹). In excess, Nr becomes an environmental issue for endemic
49 terrestrial plant species and aquatic ecosystems (²⁻⁴), and may pose threats to
50 human health (⁵). Human activities have increased N input to the environment by
51 150% over the last century (⁶), with a rising contribution – among other distribution
52 processes – of atmospheric deposition (^{7,8}). Fossil-fuel combustion, agriculture and
53 food production are responsible for direct or indirect emissions of atmospheric N-
54 species with the capacity to reach remote ecosystems such as mountainous regions
55 (^{9,10}) where Nr equilibrium is very sensitive to small perturbations (^{11,12}). Alpine and
56 subalpine watersheds are particularly vulnerable to this increasing Nr-supply (^{13,14}),
57 as they are usually N-limited ecosystems (¹⁵). The critical load for these ecosystems
58 has been estimated to 1-4 kg-N.ha⁻¹.yr⁻¹, making alpine and subalpine grasslands the
59 most sensitive to N deposition among grasslands and tall forb habitats (¹⁶⁻¹⁸). In
60 some regions of the globe, such as in the Colorado Front Range, USA, shifts from N-
61 limitation to N-saturation state have been observed leading to regional and national
62 policies to regulate this phenomenon (¹⁹⁻²¹). As a consequence of increasing nitrogen
63 deposition, a slow but persistent change of alpine and subalpine landscape has been
64 noticed in several regions (^{22,23}). Species more competitive for nitrogen uptake tend
65 to develop in abundance at the expense of usually oligotrophic native plants, leading
66 to plant diversity loss and changes in ecosystem functioning and services.

67 Freshwater quality and erosion control are, per instance, threatened by this cascade
68 of changes (^{24,25}). Yet, and mainly because of the paucity of monitoring facilities in
69 isolated areas and of the logistical difficulties in accessing these regions, key
70 biogeochemical processes regulating N cycling in mountains are still not well
71 understood (²⁶).

72 More specifically, atmospheric nitrate (NO_3^-) and ammonium (NH_4^+), deriving
73 principally from anthropogenic NO_x (NO and NO_2) and agricultural NH_3 emissions,
74 are transferred to the land surface through wet and dry deposition. Dissolved
75 inorganic nitrogen (DIN) species (*i.e.*, NO_3^- and NH_4^+) are of capital importance in
76 ecological studies given their high solubility in water; the strong hydrological
77 connectivity and typical topography of alpine and subalpine watersheds can lead to a
78 fast transport and a potentially long reach of the above-mentioned nutrients in
79 surrounding ecosystems (^{27,28}). Traditionally, environmental studies on NO_3^- sources
80 partitioning are essentially based on $\delta^{15}\text{N}$ and $\delta^{18}\text{O}\text{-NO}_3^-$ values (²⁹⁻³¹), to constrain
81 the biogeochemical processes affecting the various N forms in mountains. Yet, the
82 wide range of observed values for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}\text{-NO}_3^-$ from atmospheric and other
83 sources limits accurate quantification of contributing sources (^{32,33}).

84 In this study we focus – for the first time (to the best of our knowledge) – on year-
85 round NO_3^- dynamics in a mountainous watershed in the French Alps, using a multi-
86 isotopic ($\Delta^{17}\text{O}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}$) tracer of NO_3^- in subalpine surface waters. This relatively
87 new method has been increasingly used, as it enables a more refined understanding
88 of atmospheric NO_3^- ($\text{NO}_3^-_{\text{atm}}$) contribution to ecosystems N pool (^{32,34,35}). With the
89 aim to clearly delineate the fate of atmospheric Nr in a subalpine watershed, we first
90 characterized the triple isotopic composition of NO_3^- in aerosols and snow deposited
91 in high altitude catchments (> 1000m a.s.l.) of the central French Alps (*i.e.*, the input

92 flux). Second, we evaluated the fate of the deposited $\text{NO}_3^-_{atm}$ by monitoring NO_3^-
93 riverine exports from the watersheds (*i.e.*, the output flux).
94 We hypothesized that (i) the triple isotopes approach will enable a clear delineation
95 of NO_3^- sources and the quantification of their respective contribution to small and
96 medium-scale watersheds N budget and (ii) seasonal dynamics of $\text{NO}_3^-_{atm}$ exports in
97 stream will provide additional insights on N cycling controls in high altitude
98 catchments.

99

100

101 **2. Material and Methods**

102 **2.1 Study Site**

103 The studied catchments are located in the upper Romanche valley, near the Lautaret
104 Pass (central French Alps, SI Figure S1). The experimental site is part of the national
105 research infrastructure for the study of continental ecosystems and their biodiversity
106 (AnaEE – France, <https://www.anaee-france.fr>), and of the Long Term Ecological
107 Research network (LTER, <https://lternet.edu>). The streams monitored throughout
108 2015 are located close to the research facilities of the Alpine Research Station
109 (Station Alpine Joseph Fourier (SAJF), CNRS-UGA, UMS 3370,
110 <https://www.jardinalpindulautaret.fr>), where atmospheric and climatic parameters
111 were monitored (Figure S2).

112 The climate is subalpine with a strong continental influence. The annual precipitation
113 in 2015 (year of study) was 537 mm, significantly drier than the mean annual
114 precipitation of 956 mm observed between 2004 and 2013 (³⁶). In 2015, *ca.* 45 % of
115 the precipitation occurred during the growing season from snowmelt (in April) to late
116 September. Winters are cold and snowy. The mean temperature was $-7.5\text{ }^\circ\text{C}$ in

117 February 2015 and 13.9 °C in July 2015. More detailed information about the
118 sampling site can be found elsewhere (^{36,37}).

119 The first studied sub-watershed (hereafter called Lautaret) is mainly constituted of
120 calcareous substrate and extends over 3.4 km². At the outlet of this sub-watershed
121 runs a stream called Tufiere. Samples were collected at an altitude of *ca.* 2015 m
122 a.s.l, just before the stream merges with the outlet of the second sampled watershed
123 (Figure S1). Altitude on this watershed spans from 1665 to 2725 m a.s.l. Mean slope
124 is 25%, and the vegetation cover Normalized Difference Vegetation Index (NDVI) is
125 0.38.

126 The second sub-watershed (hereafter called Laurichard) is constituted of granitic
127 rocks on an ancient volcanic layer and extends over 5.3 km². It is part of the North
128 exposed side of the Combeynot mountain range, which highest peak culminates at
129 3155 m. The Laurichard stream, fed in part by glacier melt, runs down this
130 mountainous area and is sampled downhill, just before it joins the Tufiere stream.
131 Altitude on this watershed ranges from 1665 to 3155 m a.s.l. Mean slope is 30%, and
132 the vegetation cover NDVI is 0.33.

133 The last river is Romanche, which integrates the response of the whole Romanche
134 Valley, and is fueled by smaller tributaries such as Tufiere and Laurichard from the
135 Lautaret Pass and the Ecrins National Park down to the artificial Chambon Lake. Our
136 sampling point for this river is about 1000 m lower in altitude and approximately 12
137 km away from the first two tributaries (contributing area \approx 220 km²).

138

139 **2.2 Field sampling**

140 Aerosols were collected on the Lautaret watershed from November 2014 to
141 September 2015 using a homemade apparatus (similar to a Digitel[®] DA77) equipped

142 with a Digitel[®] PM2.5 cutting head. We used QMA Whatman quartz filters for
143 aerosols collection, burnt at 800 °C for 1 h to lower the blank signal (³⁸). Filters were
144 changed on a weekly basis, thus accumulating enough material for isotopic analysis.
145 Airflow was fixed at 0.5 m³ per hour.

146 From December 2014 to April 2015 a snow pit (SP) was dug every month on the
147 Lautaret watershed to provide profiles of NO₃⁻_{atm} concentration and isotopic values in
148 the snowpack. For each pit, snow was dug until the soil was reached, then after
149 cleaning the vertical profile, samples were collected every 3 cm starting from surface
150 snow.

151 Water samples were collected in the three streams (SI Figure S1, in red) from
152 November 2014 to December 2015 to obtain a full one-year hydrological cycle and
153 stream N chemistry. The samples were taken according to the Niwot Ridge LTER
154 protocol (³⁹). Samples were taken on a weekly basis when possible, and at most 2
155 weeks separated two consecutive samples.

156 More details regarding aerosols, snow and water sampling can be found in the SI,
157 Appendix 1. Unfortunately, neither rivers discharge measurements nor wet deposition
158 collection could be done at the time of the study because of the lack of equipment.
159 Appreciation of snowmelt timeframe, peak and length was based on visual
160 observation of snow cover and rivers flow. The Laurichard stream could not be
161 sampled from mid-January to mid-April as the riverbed was completely covered by
162 the snowpack.

163

164 **2.3 Samples pre-treatment and NO₃⁻ concentration analysis**

165 Aerosols samples were analyzed by extracting NO₃⁻ from filters, immersed in 40 mL
166 of ultrapure water in a centrifugal ultrafiltration unit (Milipore Centricon plus-70, 100

167 000 Daltons), shaken a few times, and then centrifuged at 4500 RPM for 20 minutes.
168 The extract was then collected in a 50 mL Corning[®] centrifuge tube and kept frozen
169 until further analysis.
170 Water and snow samples underwent the same pre-treatment for isotopic analysis.
171 Frozen samples were melted at room temperature overnight before being filtered
172 using 0.45 µm Whatman GD/X syringe filters linked to a peristaltic pump.
173 Ultimately, aerosols, snow and stream samples were concentrated using an anionic
174 resin (0.6 mL AG 1-X8 resin, Cl⁻-form, Bio-Rad) with recovery efficiency over 98.5%
175 (⁴⁰) and eluted with 10 mL of a 1 M NaCl solution for isotopic analysis (⁴¹). Sample
176 aliquots were taken before the resin concentration step for [NO₃⁻] determination using
177 a Continuous Flow Analysis spectrophotometer (SEAL Analyzer QuAAtro) based on
178 cadmium-reduction of NO₃⁻ to nitrite (⁴²). [NO₃⁻] values are given with an uncertainty
179 of 0.02 mg.L⁻¹, calculated as the mean standard deviation of ten successive
180 measurements of the calibrating standards.

181

182 **2.4 Isotopic analysis**

183 Aerosols, snow and river samples were analyzed for $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of NO₃⁻
184 using the bacterial denitrifier technique in combination with the N₂O gold
185 decomposition method (⁴³⁻⁴⁵). More details about the analytical procedure can be
186 found elsewhere (⁴⁶) and in the SI, Appendix 1.

187 All samples isotopic values were corrected for any isotopic effect possibly occurring
188 during the procedure by processing simultaneously international reference materials
189 (International Atomic Energy Agency USGS 32, USGS 34 and USGS 35) through the
190 same analytical batch. The isotopic standards were prepared in the same
191 background matrix as samples (*i.e.*, 1M NaCl). Standard deviation of the residuals

192 from the linear regression between the measured reference standards ($n = 20$) and
 193 their expected values served as indicator of the accuracy of the method. In our study,
 194 the $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of aerosols, snow and streams NO_3^- are given, with
 195 respect to atmospheric N_2 (AIR) and Vienna Standard Mean Ocean Water (VSMOW)
 196 standards, with a mean uncertainty of 0.2, 1.4 and 0.4 ‰ respectively.

197

198 2.5 End-member mixing analysis

199 The triple stable isotope approach using $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ enables exclusive
 200 quantification of unprocessed $\text{NO}_3^-_{atm}$. Because chemical pathways leading to the
 201 production of atmospheric NO_3^- involve NO_x oxidation by ozone, which is the bearer
 202 of ^{17}O -excess in the first place, it shows a significant positive deviation from the
 203 terrestrial fractionation line (TFL: $\delta^{17}\text{O} \approx 0.52 * \delta^{18}\text{O}$)^(47,48). $\Delta^{17}\text{O}$ is a quantification of
 204 this deviation from the TFL, calculated as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 * \delta^{18}\text{O}$ in the present
 205 work. $\Delta^{17}\text{O}$ value of atmospheric NO_3^- generally ranges between 20 and 35 ‰ in
 206 temperate latitudes^(46,49) whereas $\Delta^{17}\text{O}$ value of NO_3^- from all other sources
 207 (industrial fertilizers, nitrification) or biologically processed $\text{NO}_3^-_{atm}$, is 0^(32,50). In this
 208 study, we used these two distinct $\Delta^{17}\text{O}$ values as end-members in a simple mixing
 209 model to quantify unprocessed $\text{NO}_3^-_{atm}$ proportion in streams. Calculation of
 210 atmospheric contribution, noted f_{atm} , was derived from the following equation:

211

$$212 \text{ (Eq.1) } \quad \Delta^{17}\text{O-NO}_3^-_{sample} = f_{atm} * \Delta^{17}\text{O-NO}_3^-_{atm} + (1 - f_{atm}) * \Delta^{17}\text{O-NO}_3^-_{bio}$$

213 With f_{atm} (= % $\text{NO}_3^-_{atm}$), the mole fraction of the atmospheric contribution⁽³²⁾, $\Delta^{17}\text{O-}$
 214 $\text{NO}_3^-_{sample}$ the measured value of $\Delta^{17}\text{O-NO}_3^-$ in a sample and $\Delta^{17}\text{O-NO}_3^-_{bio}$ the value
 215 of ^{17}O -excess of biologically-derived NO_3^- ($\text{NO}_3^-_{bio}$).

216

217 As $\Delta^{17}\text{O-NO}_3^-_{bio} = 0 \text{ ‰}$ (³²), Eq.1 simplifies to

218

219 (Eq. 2)
$$f_{atm} = (\Delta^{17}\text{O-NO}_3^-_{sample} / \Delta^{17}\text{O-NO}_3^-_{atm}) * 100$$

220

221 Choice for the atmospheric end-member values of $\Delta^{17}\text{O-NO}_3^-_{atm}$ is further discussed
222 in section 4.1.

223 Post-deposition processes such as denitrification or assimilation should enrich $\delta^{18}\text{O}$
224 and $\delta^{15}\text{N}$ along a 2:1 to 1:1 line (^{51,52}), but co-occurring soil production of NO_3^- by
225 nitrification can lead to lower enrichment proportions (⁵³). The $\Delta^{17}\text{O}$ value of residual
226 NO_3^- are unaffected by post-deposition processes leading to NO_3^- loss because it is
227 independent of the absolute $\delta^{18}\text{O}$ values (³²). It therefore provides a robust
228 quantification of unprocessed $\text{NO}_3^-_{atm}$, and subsequently, of $\text{NO}_3^-_{bio}$ as described in
229 Eq. 2.

230

231 **2.6 Statistical Analysis**

232 We used two non-parametric statistical tests in our study. The choice for non-
233 parametric tests lies in the small population size of the aerosols (n=26), snow (n=30,
234 22, 29, 36 and 26 for December, January, February, March and April SP,
235 respectively), and stream water samples (n=42, 29 and 28 for Tufiere, Laurichard
236 and Romanche, respectively).

237 A Mann-Whitney test was applied on river samples to determine whether mean
238 concentrations and isotopic values were significantly different between streams. A
239 Spearman test was applied to evaluate the correlation between stream water
240 parameters (typically $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}$ and $[\text{NO}_3^-]$). Differences and correlations were
241 held significant when the *p* value reached a 0.01 credible interval.

242 All statistical analyses were conducted using R software (v3.2.3).

243

244

245 **3. Results**

246 **3.1 Nitrate input to ecosystems: $\text{NO}_3^-_{atm}$**

247 Evolution of mean concentration, $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of NO_3^- in snow pits
248 throughout the winter and in aerosols throughout year 2015 can be found in Table 1
249 and Figure S3. First snow falls occurred mid-November 2014 with several freeze-
250 thaw events before it started to accumulate. On days of snow pits sample collection,
251 snowpack depths were 66, 64, 139, 142 and 101 cm in December 2014, January,
252 February, March and April 2015, respectively. Maximum snow accumulation (ca. 1.6
253 m) occurred early March 2015 (SI, Appendix 1). By the end of April 2015, the
254 snowpack had completely melted. In December and January, low $[\text{NO}_3^-]$ were
255 measured in all snow pits layers (SI, Figure S3a). In February and March, a peak of
256 $[\text{NO}_3^-]$ up to 5 mg.L^{-1} between 70 and 90 cm of snow accumulation was recorded.
257 This peak was also measured in April (orange line in Figure S3), but at a lower depth
258 (40-60 cm) and to a lesser extent (2.7 mg.L^{-1}), due to elution of the snowpack NO_3^-
259 by snowmelt water. $\Delta^{17}\text{O}-\text{NO}_3^-$ in snow varied between 20 and 35 ‰ (SI, Figure
260 S3b), well within the atmospheric range of NO_3^- isotopic values reported in the
261 literature (^{46,54}). $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values were between 60 and 90 ‰ and -10 and 0 ‰,
262 respectively (SI, Figure S3c and d), consistent with a reservoir exclusively made of
263 $\text{NO}_3^-_{atm}$ (⁵¹). Mean (\pm standard deviation) isotopic values of snow NO_3^- were $29.3 \pm$
264 1.6 , 77.0 ± 5.6 and -3.6 ± 1.6 ‰ for $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$, respectively.
265 Mean isotopic values of NO_3^- in aerosols were also consistent with other
266 measurements of particulate NO_3^- (⁵⁵), featuring significantly lower mean $\Delta^{17}\text{O}-\text{NO}_3^-$

267 and $\delta^{15}\text{N-NO}_3^-$ in summer (23.1 ± 2.4 and -6.5 ± 3.4 ‰, respectively) than in winter
268 (28.9 ± 1.7 and -1.0 ± 1.7 ‰, respectively), a temporal pattern discussed in the SI,
269 Appendix 3. Winter aerosols NO_3^- isotopic values were in the range of the snowpack
270 NO_3^- values.

271

272 **3.2 Nitrate output in rivers**

273 All streams [NO_3^-] data can be found in the SI, Table S1. Laurichard showed
274 significantly higher year-round [NO_3^-] compared to the other streams, with a mean
275 value of 2.6 ± 1.3 mg.L^{-1} . Mean annual [NO_3^-] was 0.09 ± 0.06 mg.L^{-1} and 1.02 ± 0.48
276 mg.L^{-1} in Tufiere and Romanche, respectively. Seasonal variations were similar in all
277 streams, featuring higher [NO_3^-] in late spring and lower [NO_3^-] in summer (Figure
278 1a).

279 Tufiere had the widest range in $\Delta^{17}\text{O-NO}_3^-$ values, varying from 0.5 to 10.3 ‰, with a
280 mean value of 3.2 ± 2.4 ‰. $\Delta^{17}\text{O-NO}_3^-$ values in Laurichard ranged from 0.8 to 8.2
281 ‰, with a mean value of 2.8 ± 1.7 ‰. In Romanche, $\Delta^{17}\text{O-NO}_3^-$ values remained
282 above 3 ‰ for a period spanning several months, with a mean value of 4.3 ± 2.3 ‰
283 (Figure 1b). Mean $\Delta^{17}\text{O-NO}_3^-$ was significantly higher in Romanche than in Tufiere
284 and Laurichard, whereas there was no significant difference between Tufiere and
285 Laurichard mean $\Delta^{17}\text{O-NO}_3^-$ (p-value = 0.5).

286 All streams showed similar range for $\delta^{18}\text{O-NO}_3^-$ and $\delta^{15}\text{N-NO}_3^-$, between -5 and 25 ‰
287 for $\delta^{18}\text{O-NO}_3^-$ and between -6 and 13 ‰ for $\delta^{15}\text{N-NO}_3^-$. Our findings were in the same
288 range of previously measured NO_3^- isotopic values in alpine streams (^{31,56,57}).

289

290 **4. Discussion**

291 **4.1 $\text{NO}_3^-_{atm}$ end-member**

292 Our choice to use snow-NO₃⁻ as the atmospheric end-member laid on simple but
293 robust assumptions. First, snow is a good conservator of atmospheric nitrate in high
294 accumulation sites (> 30 cm of snow accumulation) and preserves its isotopic
295 composition (^{49,59}). Second, the snowpack is representative of winter bulk deposition,
296 as it aggregates both wet and dry deposition (^{60,61}). Third, most of NO₃⁻_{atm} measured
297 in streams was assumed to come from snowmelt, as previously observed in other
298 seasonally snow-covered catchments (^{60,62}). Little temporal variation of NO₃⁻
299 concentration and isotopic values in snow pits profiles, along with no isotopic
300 evidence of post-deposition processes further supported this assumption (SI,
301 Appendix 2, Figures S3 and S4).

302 By inputting mean snow Δ¹⁷O-NO₃⁻ in Eq.2, we obtained:

303

304 (Eq.3)
$$f_{atm} = (\Delta^{17}\text{O-NO}_3^- \text{ sample} / 29.3) * 100$$

305

306 The error range on f_{atm} was inferred from snow Δ¹⁷O-NO₃⁻ standard deviation, and
307 calculated as 2 %.

308 It must be underlined that snow as atmospheric end-member might not account
309 correctly for wet or dry deposition of NO₃⁻ in summer. Wet N deposition has *de facto*
310 been shown to contribute significantly to freshwaters NO₃⁻ contents, either through
311 direct inputs due to flashy hydrology (^{34,56}) or through indirect contribution *via*
312 enhanced nitrification of atmospheric NH₄⁺ (⁶³). We show that summer deposition of
313 NO₃⁻ (wet or dry) as atmospheric end-member results in higher calculated NO₃⁻_{atm}
314 fraction in streams, up to 6% in this study (SI, Appendix 3). For that reason, all
315 calculated f_{atm} values in the following sections must be considered as a lower
316 estimate of NO₃⁻_{atm} inputs in this system.

317

318 **4.2 Identification of $\text{NO}_3^-_{bio}$ sources**

319 No correlation was found between $\Delta^{17}\text{O}-\text{NO}_3^-$ and $[\text{NO}_3^-]$ in Tufiere, Laurichard and
320 Romanche (Figure 2a, b and c), indicating that $\text{NO}_3^-_{atm}$ is not the main contributor to
321 streams nitrate load on a yearly basis. For all streams, $\Delta^{17}\text{O}-\text{NO}_3^-$ was significantly
322 correlated to $\delta^{18}\text{O}-\text{NO}_3^-$ (Figure 2d, e and f) with the best correlation found in
323 Romanche. Deviations from linear regressions are attributed to occasionally intense
324 biological processes affecting $\delta^{18}\text{O}$ signal but leaving $\Delta^{17}\text{O}$ intact. Otherwise, the
325 strong linear correlations observed here suggest that mixing of sources more than
326 biological processes could explain the observed seasonal variations of NO_3^- isotopic
327 values. As a consequence, by extrapolating this linear relationship to $\Delta^{17}\text{O}-\text{NO}_3^- = 0$
328 (*i.e.*, 100 % biologically derived NO_3^-), we can determine the mean $\delta^{18}\text{O}$ value of
329 $\text{NO}_3^-_{bio}$ produced in the three watersheds: -6.0, -4.6 and -6.6 ‰ in Tufiere, Laurichard
330 and Romanche, respectively. These results for $\text{NO}_3^-_{bio}$ were consistent with other
331 studies estimation of $\delta^{18}\text{O}-\text{NO}_3^-_{bio}$ in streams, either calculated *via* the same method
332 (^{32,64}) or deduced from measured $\delta^{18}\text{O}$ values of soil-water and O_2 , assuming they
333 respectively contributed to NO_3^- -O accordingly to $\delta^{18}\text{O}-\text{NO}_3^- = 1/3 (\delta^{18}\text{O}-\text{O}_2) + 2/3$
334 $(\delta^{18}\text{O}-\text{H}_2\text{O})$ (^{51,58}). Note that our approach (*i.e.*, $\Delta^{17}\text{O}$ vs $\delta^{18}\text{O}$) might yield lower
335 uncertainty compared to the traditional one (*i.e.*, $\delta^{18}\text{O}$ calculation) which comes with
336 a number of assumptions and caveats that are thoroughly dissected elsewhere (^{58,65}).
337 Conversely, we found a significant negative correlation between $\Delta^{17}\text{O}-\text{NO}_3^-$ and $\delta^{15}\text{N}-$
338 NO_3^- (Figure 2g, h and i) in the three streams, with once again the best fit for
339 Romanche. With the same method as cited above, we can infer the mean $\delta^{15}\text{N}-\text{NO}_3^-_{bio}$
340 $\text{NO}_3^-_{bio}$: 4.4, 5.0 and 6.1 ‰ in Tufiere, Laurichard and Romanche, respectively. These
341 values characterizing the $\text{NO}_3^-_{bio}$ end-member are typical of NO_3^- produced from soil

342 NH_4^+ nitrification (⁵¹). On the other hand, extrapolating this correlation to $\Delta^{17}\text{O}-\text{NO}_3^- =$
343 29.3 ‰ (*i.e.*, 100% $\text{NO}_3^-_{atm}$) should give $\delta^{15}\text{N}-\text{NO}_3^-_{atm}$ and $\delta^{18}\text{O}-\text{NO}_3^-_{atm}$ consistent
344 with otherwise measured snow NO_3^- isotopic values. We found values of 77.7, 79.0
345 and 74.7 ‰ for $\delta^{18}\text{O}-\text{NO}_3^-_{atm}$ in Tufiere, Laurichard and Romanche, respectively,
346 consistent with the mean $\delta^{18}\text{O}$ value of 77.0 ‰ measured for snow NO_3^- (Table 1).
347 Surprisingly, $\delta^{15}\text{N}-\text{NO}_3^-_{atm}$ values of *ca.* -30 ‰ were inferred in all streams, far from
348 measured $\delta^{15}\text{N}-\text{NO}_3^-$ in snow and aerosols (Table 1) and from existing literature data
349 showing a range of $\delta^{15}\text{N}$ values for NO_3^- between -15 and 15 ‰ (^{51,66–68}). This
350 suggested that a two end-members mixing model cannot account for the different
351 sources of N that might have served as substrate for nitrification in subalpine
352 meadows, and the subsequent large distribution of $\delta^{15}\text{N}-\text{NO}_3^-_{bio}$. Such pattern can
353 only be explained by an additional source of $\text{NO}_3^-_{bio}$, with low $\delta^{15}\text{N}$ values, leading to
354 the observed weak slopes in Figures 2g, h and i. By lowering the slopes of the
355 correlations, this additional source was responsible for the low extrapolated $\delta^{15}\text{N}-$
356 NO_3^- values, which in this case (*i.e.*, three sources) do not correspond to any source
357 end-member.

358 Similar work in alpine watersheds in the Colorado Front Range suggested that
359 possible sources of NO_3^- in streams, apart from snow $\text{NO}_3^-_{atm}$, could be nitrification of
360 snow NH_4^+ in the snowpack and in soils during snowmelt, or flushing of soil NO_3^-
361 produced under the snowpack during winter (²⁹). Nitrification in the snowpack is
362 highly unlikely; indeed, such a process would have overprinted snow $\Delta^{17}\text{O}-\text{NO}_3^-$
363 values, which is not the case here (SI, Figure S3 and Appendix 2). However, the dual
364 isotopes plot presented in Figure 3 hints at a stronger contribution of atmospheric N
365 deposition – either as snow or rain – than previously assessed in subalpine
366 watersheds. Deposition of $\text{NH}_4^+_{atm}$ in particular was likely to enrich soils N pool, and

367 could account for part of $\text{NO}_3^-_{bio}$ exported in streams. Snow at the Lautaret Pass has
368 been shown to hold a non-negligible pool of NH_4^+ – equivalent to NO_3^- pool ⁽³⁷⁾ –
369 whereas undetectable $[\text{NH}_4^+]$ was monitored in all streams (data not shown)
370 suggesting that NH_4^+ released from snow is either adsorbed on clay minerals or
371 biologically processed. If the entire snow- NH_4^+ pool (if considered about roughly the
372 same size as snow- NO_3^- pool) was nitrified in soils and exported as NO_3^- into
373 streams during snowmelt, it would account for as much as 54 and 18 % of $\text{NO}_3^-_{bio}$
374 production in Tufiere and Laurichard, respectively (Figure 1b). The additional $\text{NO}_3^-_{bio}$
375 exported in streams can only be explained by soil leaching at snowmelt. Strong
376 microbial activity under the snowpack is not uncommon in cold mountainous regions
377 ^(36,62,69,70) and could justify the observed pattern. At snowmelt, cold adapted microbial
378 communities massively turn over when confronted to warmer air temperatures ⁽⁷¹⁾,
379 releasing nitrified N from lysed cells into the soils where it leaches towards
380 groundwater and streams ⁽⁷²⁾. Sources of nitrified N under the snowpack may be
381 related to soil organic matter and litter decomposition ⁽⁷³⁾ or soil NH_4^+ pool resulting
382 from previous year's N deposits ^(29,72). At this point we cannot conclude which source
383 contributed the most to $\text{NO}_3^-_{bio}$ yield, but overwinter isotopic monitoring of N pools
384 under the snowpack might bring clarification.

385

386 **4.3 Seasonal variations of $\text{NO}_3^-_{atm}$ exports**

387 All stream water samples in this study had positive $\Delta^{17}\text{O}-\text{NO}_3^-$ values, showing
388 unquestionable inputs of $\text{NO}_3^-_{atm}$ in all streams year-round (Figure 1b). However,
389 Tufiere and Laurichard, although sampled at the same altitude, showed different
390 NO_3^- export patterns, certainly due to different hydrological behaviors and respective
391 basins characteristics ⁽⁵⁸⁾.

392 NO_3^- dynamic in Tufiere were most likely governed by snowmelt. Brief but high peaks
393 of ^{17}O -excess of NO_3^- in March 2015, coincident with higher $[\text{NO}_3^-]$, were attributed to
394 direct runoff of snowmelt water to the stream (^{56,64}). Rapid melting of the lower
395 watershed snowpack washed away labile $\text{NO}_3^-_{atm}$ deposits and contributed up to 35
396 % of the total stream NO_3^- pool. Leached $\text{NO}_3^-_{bio}$ from snow-free soils by subsurface
397 melt or rain water accounted for both higher $[\text{NO}_3^-]$ and lower $\Delta^{17}\text{O}-\text{NO}_3^-$ in the
398 stream later in spring (⁷⁴). Gentle hillslopes and the calcareous substrate of the
399 Lautaret sub-watershed were also likely to facilitate snowmelt water infiltration and
400 mixing with groundwater, a common feature in subalpine catchments (⁷⁵). Starting
401 early May, a slow but persistent increase in $\Delta^{17}\text{O}-\text{NO}_3^-$ suggested a resurgence of
402 $\text{NO}_3^-_{atm}$ loaded water entering the stream, increasing $\text{NO}_3^-_{atm}$ proportion up to 25 %
403 again at the end of August. Significantly higher precipitation in May and in August,
404 compared to the previous months (SI, Figure S2a) could have triggered this
405 resurgence by filling the aquifer with rain water, thus flushing stored water. The wide
406 temporal range of this $\Delta^{17}\text{O}$ increase, encompassing six months from May to
407 October, is in line with a temporally spread transit time of infiltrated melt water along
408 an altitude gradient. Direct contribution of rain $\text{NO}_3^-_{atm}$ was unlikely to explain such
409 pattern, given the low response of Tufiere $[\text{NO}_3^-]$ and $\Delta^{17}\text{O}-\text{NO}_3^-$ to the storm in June
410 (Figure 1a and b). Considering the basin topography and geology (*i.e.*, gentler slopes
411 and higher vegetation cover), most rain N inputs were certainly retained in soils or
412 assimilated before either infiltration or direct runoff of rainwater in Tufiere (⁶³).

413 Oppositely, $\text{NO}_3^-_{atm}$ contributed only between 4 and 15 % of total NO_3^- in Laurichard
414 stream from April to May (Figure 1b), coincident with the snowmelt period for this
415 northern exposed watershed. Laurichard rock glacier is an actively monitored

416 permafrost-related landform, which increased surface velocities over the past twenty
417 years hint at increased permafrost temperatures, possibly to the point of thawing (⁷⁶).
418 Considerably higher year-round [NO₃⁻] in Laurichard compared to snow-fed Tufiere –
419 by 1-2 orders of magnitude – suggested that Laurichard NO₃⁻ exports were mainly
420 driven by increasing soil exposure (⁷⁷) more than any other geomorphic or
421 biogeographic feature (⁷⁸). Sources of such elevated levels of NO₃⁻, while still
422 debated (^{79,80}), were likely linked to glaciers retreat and permafrost thawing leading to
423 enhanced stream solutes fluxes (^{81,82}), increased nitrification and/or mobilization of
424 stored N from disturbed soils (⁸³). Steeper slopes (SI, Figure S1), and potentially
425 increased deposition loading because of increased orographic precipitations (²¹) –
426 relative to the Lautaret watershed – were certainly responsible for the occasional
427 higher $\Delta^{17}\text{O-NO}_3^-$ peaks, concomitant with rain events (Figure 1b). Lower vegetation
428 cover – and therefore reduced plant NO_{3⁻ atm} uptake– and the poor buffering capacity
429 of Laurichard watershed granitic bedrock are additional factors that could have
430 fostered punctually enhanced exports of NO_{3⁻ atm} from wet deposition (^{77,58}). The
431 storm in June 2015 (Figure S2) led to the strongest input of NO_{3⁻ atm} in this stream,
432 accounting for 29 % of Laurichard NO_{3⁻ pool} (Figure 1b). Simultaneous $\Delta^{17}\text{O-NO}_3^-$
433 peaks and [NO₃⁻] minima in July and September were further evidence of this flashy
434 hydrology and illustrated stream glacial melt water dilution by rain.
435 Conversely, we did not observe an early snowmelt runoff-linked peak in Romanche
436 stream water $\Delta^{17}\text{O-NO}_3^-$ in spring. Instead, NO_{3⁻ atm} contribution increased steadily
437 from April to July (34 % of NO_{3⁻ atm} on July 9th) then declined until reaching a baseflow
438 value of about 5 % of NO_{3⁻ atm} during the dormant season. Romanche is the main
439 stream of the valley, fueled by myriad smaller tributaries like Tufiere and Laurichard.
440 Lower altitude catchments contributed most in spring, but as air temperature and

441 solar radiation increased in summer, melting snowpack from higher watersheds of
442 the Ecrins National Park may have led to enhanced $\text{NO}_3^-_{atm}$ export in Romanche
443 stream leading to the wide $\Delta^{17}\text{O}-\text{NO}_3^-$ temporal pattern observed in this stream.
444 Why $[\text{NO}_3^-]$ decreased from Laurichard to Romanche is uncertain, but dilution by
445 snow-fed streams like Tufiere between sampling locations is a possibility. Other
446 possible sinks include denitrification, in-stream algal and phytoplankton assimilation
447 or uptake by the riparian vegetation (⁸⁵). Denitrification and assimilation should
448 discriminate $\delta^{18}\text{O}$ against $\delta^{15}\text{N}$ of residual NO_3^- following a line with a positive slope
449 (*i.e.*, enrich the residual nitrate with heavier isotopes), which was not observed in our
450 study (SI, Figure S5). However, frequent recharge of NO_3^- by smaller tributaries such
451 as Laurichard may have overprinted any biological isotopic signature (⁵³).
452 On all basins, the strong controls seemingly exerted either by snowmelt (Tufiere and
453 Romanche) or by glacier melt water (Laurichard) on stream $\text{NO}_3^-_{atm}$ exports
454 precluded the quantification of the direct $\text{NO}_3^-_{atm}$ summer deposition contribution.
455 Summer deposition loads of $\text{NO}_3^-_{atm}$ to streams were either buffered by vegetation
456 uptake and/or soil immobilization on Lautaret watershed, subdued by high $\text{NO}_3^-_{bio}$
457 except on intense rain events on Laurichard watershed, or combined with the wide
458 temporal response of the Romanche to snowmelt from uplands. Nevertheless,
459 summer deposition of $\text{NH}_4^+_{atm}$ contributed significantly to subalpine soils N pool and
460 was partly responsible for the $\text{NO}_3^-_{bio}$ exports in streams.
461 Simultaneous monitoring of $\Delta^{17}\text{O}-\text{NO}_3^-$, streams discharge, water isotopes and
462 chemical tracers of hydrological paths remain needed to further constrain water
463 sources and their respective contribution to NO_3^- exports in subalpine streams.
464 Longer monitoring of streams exports is also warranted to better evaluate annual
465 variability in this subalpine watershed, as year 2015 was significantly drier than

466 previous years at the Lautaret Pass. Hydrological responses to rain events, and
467 resulting NO_3^- export dynamics under different precipitation conditions, need to be
468 assessed.

469

470 **4.4 Nitrogen saturation and ecological implication**

471 Despite presenting different N export dynamics, all streams shared uninterrupted
472 presence of NO_3^- year-round, with a significant contribution from atmospheric
473 deposition. In a supposedly N-limited ecosystem, such a pattern was unexpected as
474 demand for dissolved inorganic nitrogen (DIN) from plants and microbial communities
475 in spring and summer should have exceeded mobile NO_3^- reservoir in soils,
476 precluding leaching to the streams.

477 Nitrogen saturation has first been evaluated in an ecosystem subjected to increasing
478 N deposition (²). Several stages of saturation have been distinguished, ranging from
479 0 (N-limited ecosystem) to 3 (fully saturated ecosystem characterized by N-leaching
480 and higher streams [NO_3^-]). [NO_3^-] in Tufiere and Romanche was within the range of
481 reported alpine and mountain stream [NO_3^-] (⁸⁴), but [NO_3^-] in Laurichard was higher
482 than in streams pinned as indicators of stage 2 or 3 (³⁴). However, similar seasonal
483 variations of [NO_3^-] in Tufiere, Laurichard and Romanche – high in spring after
484 snowmelt, decreasing in summer, then increasing again as air temperature starts
485 falling down (Figure 1) – were symptomatic of plants and microbial biomasses
486 working as N sinks during the growing season. Evaluation of N saturation according
487 to the conceptual model of biological demand exceeded by N supply does not take
488 into account other drivers of N exports (⁵⁸), and may not be adapted to describe the N
489 saturation state of subalpine watersheds. Another approach to N saturation has been
490 described as kinetic N saturation, where the rate of N inputs exceeds the rate of N

491 assimilation in an ecosystem and its remediation capacity, and can lead to intensive
492 exports of N in streams (⁸⁶). Given the highest percentage of unprocessed $\text{NO}_3^-_{atm}$
493 during hydrological events, our results provided additional evidence that catchment
494 hydrology is certainly responsible for the kinetic N saturation in subalpine
495 watersheds. Anyhow, assessment of N deposition load could help us estimate
496 whether the critical threshold has been crossed, as evidenced in other alpine
497 environments (^{17,18,87}), and will be the object of future studies.

498 N inputs at the watershed scale, through $\text{NO}_3^-_{atm}$ direct contribution or $\text{NH}_4^+_{atm}$
499 nitrification, are likely to substantially impact surrounding ecosystems, especially
500 during the growing season following snowmelt. For instance, the lake Chambon, a
501 freshwater reservoir fueled by the Romanche stream, which supplies downhill
502 villages and cities – including Grenoble (163 000 inhabitants) – with drinking water,
503 showed high $\text{NO}_3^-_{atm}$ contribution from May to November (up to 25 %, Table S2).
504 While $[\text{NO}_3^-]$ in the lake averaged $2.0 \pm 0.8 \text{ mg.L}^{-1}$ during the growing season, far
505 below the limit of 50 mg.L^{-1} (guideline value from The World Health Organization
506 translated in the EU Water Framework Directive 2000/60/EC), the presence of $\text{NO}_3^-_{atm}$
507 $_{atm}$ in this elevated freshwater reservoir is yet another warning signal of potential
508 threats due to atmospherically deposited pollutants. Evidence of lakes fertilization by
509 atmospheric deposition in high altitude watersheds has been demonstrated before
510 (⁸⁸). Fast cycling dynamics of high atmospheric N_r in lakes (⁸⁹) can lead to well-
511 documented ecological consequences such as acidification (¹⁷), shift of algal and
512 phytoplankton communities (^{90,91}) and disturbance of lakes food web (⁹²), and
513 highlight the necessity to protect critical water resources. In winter, limited
514 hydrological connectivity between soils and streams cannot explain the year-round
515 export presence of unprocessed $\text{NO}_3^-_{atm}$ in subalpine streams, highlighting the

516 potential contribution of groundwater contamination to streams exports. Previous
517 studies also showed that most alpine and subalpine plants acquire N during
518 snowmelt (⁹³). In traditionally N-poor subalpine ecosystems, increasing inputs of NO_3^-
519 *atm* together with climate change could accelerate diversity and composition losses of
520 plant communities.

521 In a 21st century with a shorter snow season, a higher fraction of the yearly deposited
522 NO_3^- will be brought to subalpine ecosystems at a slower rate, during the growth
523 season, instead of abruptly at snowmelt. If NO_3^- saturation is indeed kinetic – as our
524 study suggested – then this climate driven change in NO_3^- influx timing could result in
525 higher NO_3^- absorption in the environment, and lead to capacity saturation. This
526 would come with a wide number of changes in the ecosystem, which have been
527 extensively detailed elsewhere at a global scale (^{2,3,8}), and more specifically in high
528 altitude catchments (^{11,18,92}).

529 These findings emphasize the need for more joint monitoring of subalpine soils and
530 plant communities, with the objective being a better understanding of atmospheric N
531 deposition consequences on biogeochemical cycling in these semi-isolated
532 ecosystems. In particular, prospective studies should continue focusing on potential
533 synergetic effects of land use management coupled with atmospheric deposition on
534 ecosystems alteration, to better orient policy makers in N emissions mitigation and
535 adaptation efforts.

536

537

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549

550

551 **Supporting Information**

552 Appendix 1 includes complementary information on sampling and analytic protocols.
553 Appendix 2 and 3 provide explanation on the choice of snow nitrate as atmospheric
554 end-member. Figures show the study site (S1), the meteorological conditions at the
555 Lautaret Pass in 2015 (S2), the concentration and isotopic values of NO_3^- in snow
556 during winter 2014-2015 (S3), correlation plots of snow NO_3^- isotopic values (S4) and
557 a correlation plot of rivers $\delta^{18}\text{O}$ vs $\delta^{15}\text{N-NO}_3^-$ (S5). Tables give $[\text{NO}_3^-]$ for each
558 sampling date in Tufiere, Laurichard and Romanche (S1) and in the Chambon Lake
559 (S2). This information is available free of charge via the Internet at
560 <http://pubs.acs.org>.

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840 **List of Figures**

841

842 **Table 1** Mean volume-weighted concentration and concentration-weighted isotopic
843 values for NO_3^- in snow pits (SP) and aerosols at the Lautaret Pass. Snow pits mean
844 values are always calculated over the entire depth of the snow pack. Dates for SP
845 are given in a dd/mm/yy format. SD is the standard deviation.

846

847 **Figure 1** Seasonal variations of a) $\log([\text{NO}_3^-]$ in $\mu\text{g}\cdot\text{L}^{-1}$) (for an easier comparison of
848 streams $[\text{NO}_3^-]$); b) $\Delta^{17}\text{O}$ (‰) and corresponding f_{atm} (%), the relative amount of
849 atmospheric nitrate in streams); c) $\delta^{18}\text{O}$ (‰) and d) $\delta^{15}\text{N}$ (‰) of NO_3^- in streams
850 Red, blue and green colors stand for Tufiere, Laurichard and Romanche,
851 respectively. Highlighted in yellow is a two-days rainstorm that occurred mid-June.
852 The grey frames highlight the dormant season while the green one highlights the
853 growing season. Transitions between both seasons are snowmelt period in spring,
854 and plant senescence in autumn.

855

856 **Figure 2** Correlation between nitrate $\Delta^{17}\text{O}$ (‰) and a), b), c) $\log([\text{NO}_3^-])$; d), e), f)
857 $\delta^{18}\text{O}$ (‰); g), h), i) $\delta^{15}\text{N}$ (‰).

858 Red, blue and green colors stand for Tufiere, Laurichard and Romanche,
859 respectively. Outliers (surrounded by stars) were not considered in the linear
860 regression model, as we assume they result from biological processes (e.g.,
861 denitrification) and would blur determination of NO_3^- sources.

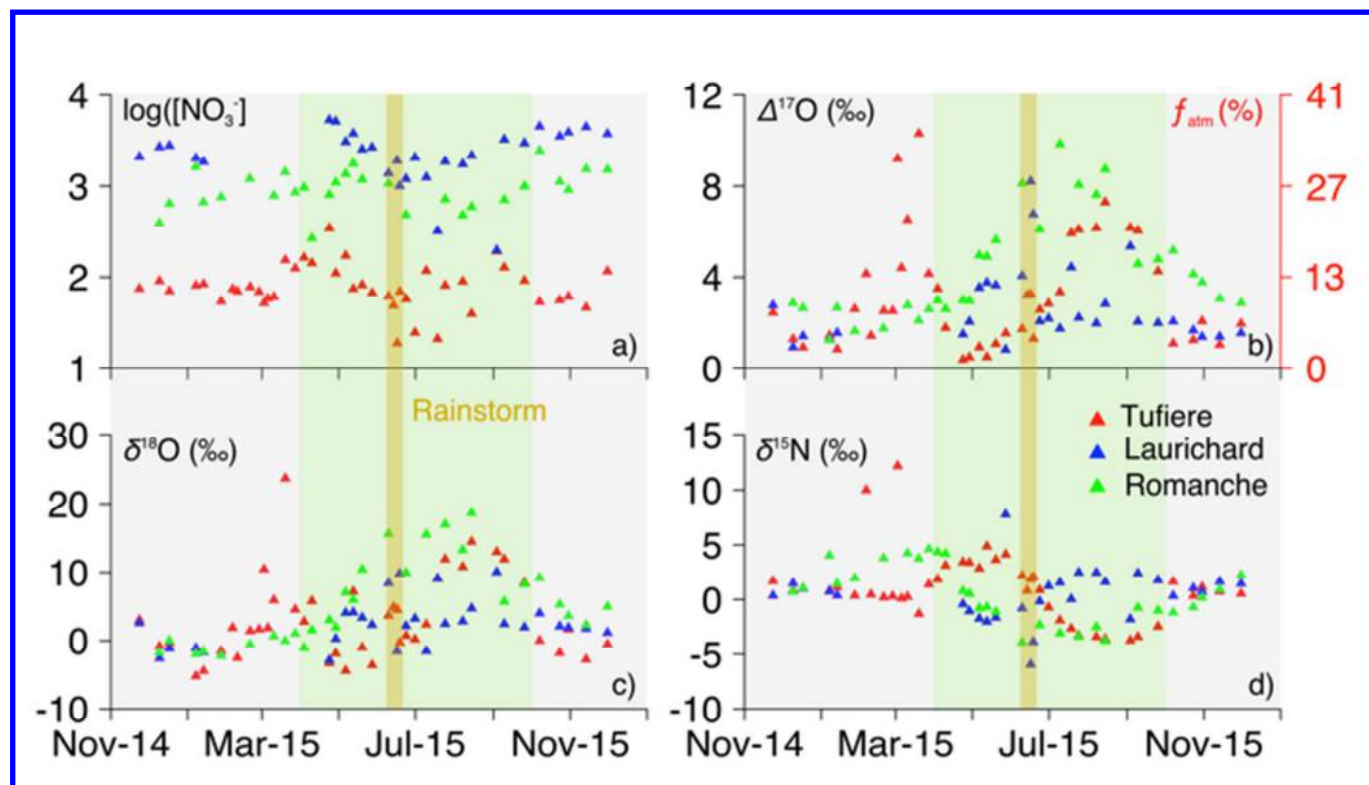
862

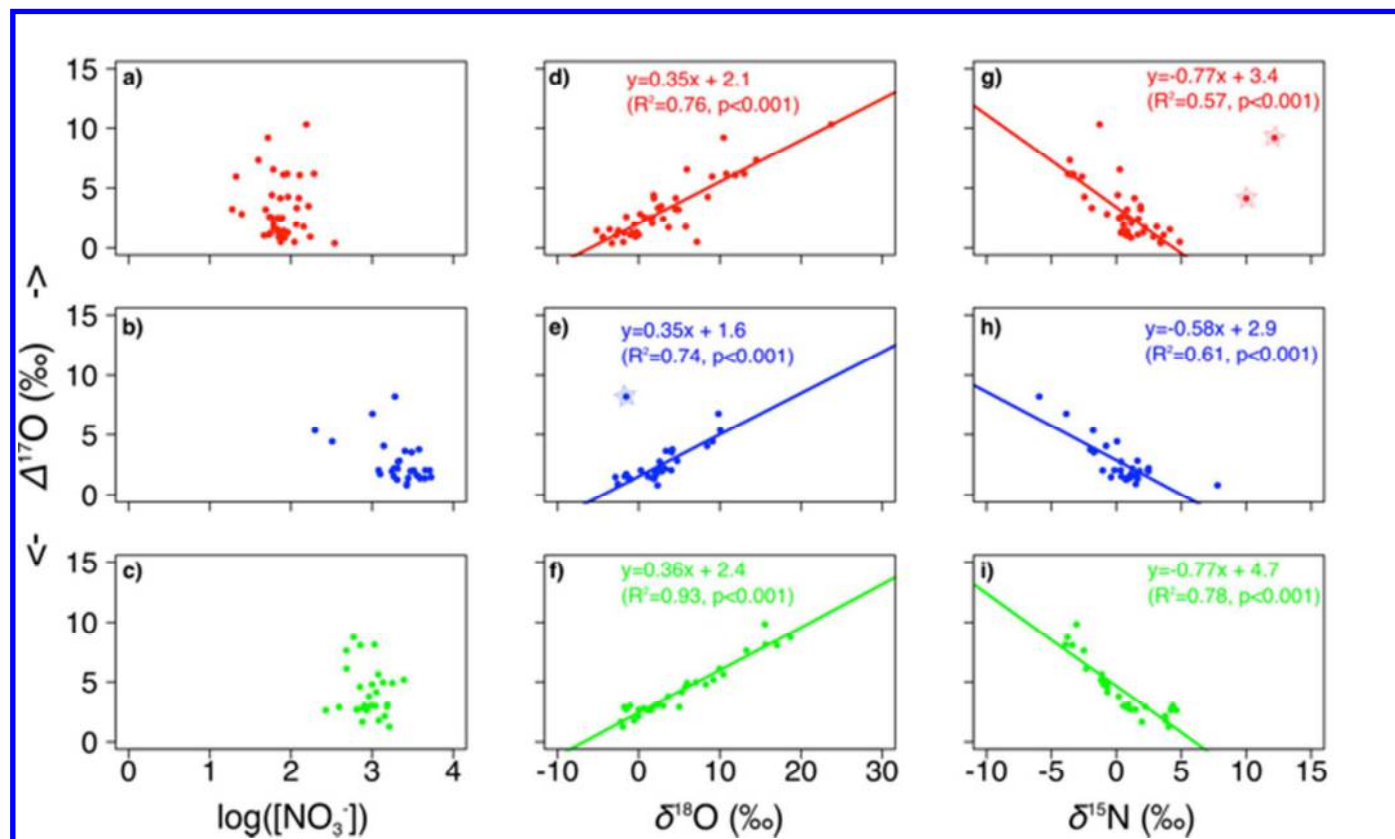
863 **Figure 3** Dual isotopes plot ($\Delta^{17}\text{O}$ vs. $\delta^{15}\text{N}$) illustrating the mixing between three
864 sources of NO_3^- in our study sites. The plain triangles feature the mixing range
865 between snow $\text{NO}_3^-_{atm}$ and NO_3^- from nitrified $\text{NH}_4^+_{atm}$ in grey, NO_3^- from nitrified
866 $\text{NH}_4^+_{bio}$ in turquoise and NO_3^- from manure or sewage in beige. The dashed triangles
867 of similar colors (i.e., grey-turquoise and turquoise-beige) illustrate the overlapping of
868 sources $\delta^{15}\text{N}$ - NO_3^- values. The dashed purple triangle illustrates the mixing range
869 between $\text{NO}_3^-_{atm}$ and NO_3^- from nitrified $\text{NH}_4^+_{bio}$ if summer deposition was the
870 atmospheric end-member.

871 When $\Delta^{17}\text{O}$ - NO_3^- values are high, $\delta^{15}\text{N}$ - NO_3^- is characteristic of nitrified $\text{NH}_4^+_{atm}$,
872 delineating the coupled contribution of atmospheric N deposition *via* direct inputs
873 ($\text{NO}_3^-_{atm}$) and indirect inputs (nitrified $\text{NH}_4^+_{atm}$). Decreased contribution of atmospheric
874 N sources (low $\Delta^{17}\text{O}$ - NO_3^- values) results in a higher proportion of $\text{NO}_3^-_{bio}$.

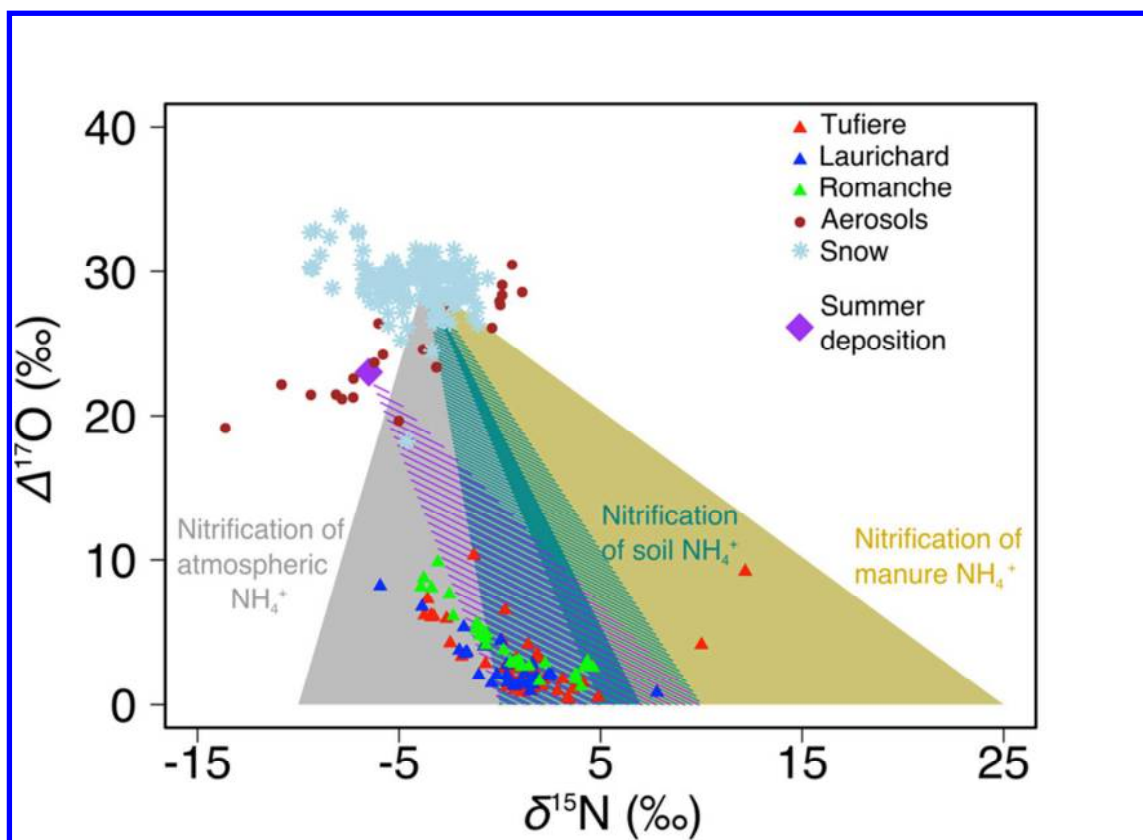
	Snow depth (cm)	$\delta^{15}\text{N}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	$[\text{NO}_3^-]$ (mg.L ⁻¹)
		Mean (SD)	Mean (SD)	Mean (SD)	Mean (SD)
SP 09/12/14	66	-5.5 (2.7)	77.0 (5.0)	29.8 (1.9)	0.1 (0.4)
SP 13/01/15	64	-3.6 (1.7)	76.6 (7.2)	28.6 (2.5)	0.1 (0.9)
SP 19/02/15	139	-2.4 (1.2)	77.7 (4.5)	29.3 (1.2)	1.2 (1.3)
SP 19/03/15	142	-2.3 (1.6)	76.3 (4.6)	28.5 (1.3)	0.9 (1.0)
SP 09/04/15	104	-4.1 (1.1)	77.2 (6.8)	30.1 (1.0)	0.6 (0.6)
Aerosols (summer)	-	-6.5 (3.6)	62.9 (6.5)	23.1 (2.4)	0.1 (0.1) mg.m ⁻³
Aerosols (winter)	-	-1.0 (1.7)	74.7 (4.4)	28.9 (1.0)	0.1 (0.2) mg.m ⁻³

Table 1

**Figure 1**



Comment citing this document: **Figure 2**

**Figure 3**