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► **To cite this version:**

Maïté Bueno, Bastien Duval, Emmanuel Tessier, Andrea Romero-Rama, Leire Kortazar, et al.. Selenium distribution and speciation in waters of pristine alpine lakes from central-western Pyrenees (France–Spain). *Environmental Science: Processes & Impacts*, 2022, 24 (9), pp.1430-1442. 10.1039/D1EM00430A . hal-03807710

**HAL Id: hal-03807710**

**<https://univ-pau.hal.science/hal-03807710>**

Submitted on 21 Nov 2022

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1 **Selenium distribution and speciation in waters of pristine alpine lakes from central-western**  
2 **Pyrenees (France-Spain)**

3

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15

16 **Abstract**

17 The speciation of both redox reactive and volatile selenium (Se) compounds, barely reported in  
18 pristine aquatic environments, has never been investigated in remote alpine lakes, considered as  
19 sensitive ecosystems to detect the effect of global change. This work presents an integrated  
20 investigation on Se distribution and speciation conducted in 20 high altitude pristine lakes from the  
21 central-western Pyrenees. Five seasonal sampling campaigns were carried out after snowmelt  
22 (June/July) and in early fall (October) for the period 2017–2019. Concentrations of total dissolved  
23 Se (TDSe) ranged from 7 to 78 ng L<sup>-1</sup>, being selenate ubiquitously observed in most cases (median  
24 of 61% of TDSe). Selenite was only occasionally detected up to 4 ng L<sup>-1</sup>, therefore a fraction of  
25 TDSe was presumably in the forms of elemental Se(0) and/or selenides. Depth profiles carried out  
26 in different lakes showed the occurrence of such Se(-II, 0) pool in bottom hypoxic to anoxic waters.  
27 The production of volatile Se compounds presented a low median total concentration (TVSe) of 33  
28 pg L<sup>-1</sup> (range 3–120 pg L<sup>-1</sup>), mainly in the form of dimethylselenide in sub-surface samples (median  
29 of 82% of TVSe). Se concentration in lake waters was significantly correlated with sulphate  
30 concentration ( $\rho=0.93$ ,  $p<0.0001$ ), demonstrating that it is influenced by erosion and dissolution of  
31 Se and S-enriched parent bedrocks. In addition, for Se depleted alpine lake-bedrock systems, long-  
32 range transport and wet atmospheric depositions represent a major source of Se for lake waters.

33

34

## 35 **1. Introduction**

36 High-mountain lakes are pristine ecosystems characterized by extreme environmental conditions.  
37 No data on selenium behaviour have been reported in these aquatic environments. The existing data  
38 about Se biogeochemistry in lakes are mainly provided by research in low altitude temperate and  
39 tropical lakes and have been reviewed elsewhere (Conde & Sanz Alaejos, 1997; Simmons &  
40 Wallschläger, 2005; Ponton et al., 2020). In unpolluted waters, total Se concentrations are typically  
41 below 200 ng L<sup>-1</sup> (Ponton et al., 2020). In more extreme environments, reported total Se  
42 concentrations in western Siberian lakes range from 12 to 311 ng L<sup>-1</sup> (Pokrovsky et al., 2018). In  
43 Canadian subarctic thermokarst ponds, total dissolved Se ranged from 18 to 67 ng L<sup>-1</sup> (Lanceleur et  
44 al., 2019), similarly to values from 20 to 60 ng L<sup>-1</sup> reported in Norwegian (Økelsrud et al., 2016) or  
45 Finish (Wang et al., 1994; 1995) lakes. In North Carolina, Se concentrations in lakes impacted by  
46 coal combustion effluents were between 0.3 and 2 µg L<sup>-1</sup> while Se was not detected (< 0.22 µg L<sup>-1</sup>)  
47 in reference lakes (Brandt et al., 2017). Among its four oxidation states (-II, 0, IV and VI), Se  
48 oxyanions, particularly selenate, are expected to be the major species in well-aerated surface waters  
49 and oligotrophic environments (Sharma et al., 2014). Aqueous selenium speciation measurements  
50 in lake waters indicated the predominance of selenite (Robberecht et al., 1983; Ponton & Hare,  
51 2013; Tanzer & Heumann, 1991) or selenate (Lindström, 1980; Nishri et al., 1999; Ponton & Hare,  
52 2013). Despite the lack of analytical procedures to identify and quantify elemental selenium and  
53 selenide forms, several authors have reported the presence of such Se pool in lake waters. For  
54 example in Finish lakes, the sum of selenite and selenate represented less than 20% of total Se  
55 (Wang et al., 1994; 1995). In Lake Kinneret up to 40% of total Se was associated with colloidal  
56 elemental Se and selenide forms (Nishri et al., 1999). In Canadian lakes, organo-Se proportion could  
57 attain 95% of total Se (Ponton & Hare, 2013).

58 Reduced Se include also volatile selenides seldom tested and reported in lake waters. Reported total  
59 volatile Se concentrations varied in a wide range (1 pg L<sup>-1</sup> to 109·ng L<sup>-1</sup>), being dimethylselenide

60 (DMSe) the major species ( $\geq 49\%$ ), followed by dimethyl selenide sulphide (DMSeS) (4–41%) and  
61 dimethyl diselenide (DMDS<sub>2</sub>) ( $\leq 7\%$ ) (Lanceleur et al., 2019 and references therein). In a mountain  
62 minerotrophic peatland (elevation 972 m a.s.l.) a DMSe concentration of 10 ng L<sup>-1</sup> was reported in  
63 surface water samples (Vriens et al., 2014). In Canadian thermokarst ponds, Lanceleur et al. (2019)  
64 found DMSe to be the main volatile species with concentrations between <0.17 to 31 pg Se L<sup>-1</sup>,  
65 while in European estuaries, volatile Se ranged from 22–8067 pg L<sup>-1</sup>, being DMSe the main species  
66 found (Amouroux & Donard, 1997; Tessier et al., 2002).

67 Ninety two per cent of Pyrenean lakes are classified as ultraoligotrophic or oligotrophic (Catalan et  
68 al., 2006). Bedrock composition associated with slow weathering and limited soil development  
69 determine waters with low mineralization (Catalan et al., 2006). In high altitude mountain lakes, Se  
70 can originate either from local (geogenic) or remote sources (atmospheric transport). In the  
71 Pyrenees, the main groups of rocks are granites, sedimentary limestones, metamorphic slates and  
72 schists, detrital sandstones (Catalan et al., 2006). These rocks generally contain low selenium  
73 concentrations (0.01 – 0.08 mg kg<sup>-1</sup>) although shales can show variable concentrations worldwide  
74 (0.1 – 675 mg kg<sup>-1</sup>) (Plant et al., 2014; Fernández-Martínez & Charlet, 2009). Previous studies have  
75 estimated that Se wet deposition (7.4–20.0 Gg Se yr<sup>-1</sup>) was responsible for 80% of its global  
76 atmospheric deposition and was thus dominant over its dry deposition (1.1–5.0 Gg Se yr<sup>-1</sup>) (Blazina  
77 et al., 2017; Pan & Wang, 2015). Suess et al. (2019) reported Se concentration values in rain samples  
78 from Pic du Midi (central Pyrenees) between 13–184 ng L<sup>-1</sup>. The authors determined that the  
79 dominant source of Se in rain at the Pic du Midi was the North Atlantic Ocean (54%) with a  
80 contribution of terrestrial emissions of 40% with seasonal fluctuation.

81 Pyrenean lakes are also characterized by surface frost periods comprised generally between  
82 November and May (Gascoin et al., 2015; López-Moreno & Vicente-Serrano, 2007). During these  
83 ice-covered periods, high mountain lakes have shown oxygen depletion leading to anoxic conditions  
84 in bottom waters (Catalan et al., 2002). These winter conditions, when oxygen is consumed, may

85 promote conditions favourable to microbial (and possibly sequential) reduction of Se oxyanions to  
86 elemental Se, process which has been shown to be environmentally significant (Nancharaiah &  
87 Lens, 2015) and may lead to selenium settle out of water column. Although situated in different  
88 climatic conditions, depletion of total dissolved selenium and selenate concentrations were  
89 previously observed in Lake Kinneret bottom waters when O<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> were consumed (Nishri et  
90 al., 1999; Be'eri-Shlevin et al., 2021).

91 In this study, we surveyed during three years the seasonal concentrations of total Se and its species  
92 (including non-volatile and volatile dissolved species) in twenty alpine lakes of the central-western  
93 Pyrenees. To this end, sub-surface water samples were collected in June/July 2017–2019 (late  
94 spring–early summer) and October 2017–2018 (early fall). Additionally, depth-profiles and  
95 temporal monitoring were conducted at some lakes in 2018 and 2019 to investigate the effects of  
96 water stratification and day-time sampling on Se distribution. To our knowledge, nos studies or data  
97 are available about Se in such aquatic systems. Our aim was thus both to contribute to  
98 comprehensive data set of selenium occurrence and speciation in such pristine ecosystems and to  
99 provide a unique “baseline” (Se background level) that allows to evaluate respective contribution  
100 of headwaters and atmospheric inputs versus the impact of land uses in a specific watershed (Adour  
101 river watershed on the French slope).

102

## 103 **2. Materials and Methods**

### 104 **2.1. Study site**

105 All the lakes considered in this study are located along a north-south transect of the Pyrenees (Fig.  
106 1). Lakes can be divided into three sectors according to their location: Caunterets, Panticosa, and  
107 Ossau/Ayous Valleys. Most of the studied lakes are located on granitic rocks (GR). The study area  
108 lays on three different geological periods: Devonian, Permo-Triassic and Cretaceous (Zaharescu et  
109 al., 2016; Gleizes et al., 1998; Zwart & De Sitter, 1979) which may impact Se bedrock  
110 concentration. The geology of the Central Pyrenees has been described in detail elsewhere (Van

111 Lith, 1968; Catalan et al., 2006). In brief, granite (pDe-GR) originated during mountain formation  
112 in the pre-Devonian geological age are found ubiquitously. Devonian sedimentary rocks (De-SR)  
113 consisted of limestone, marble, shale and sandstone; Permo-Triassic bedrock (PT-SR) contains  
114 sedimentary rocks in the form of conglomerates, sandstone and red or green shales; and, the most  
115 recent formations, Cretaceous sedimentary rocks (Cr-SR) consist of limestone and sandstone.  
116 Studied lakes are ice-covered during 5-6 months per year (Santoloria et al., 2015). Late spring  
117 sampling (June/July) was thus scheduled to coincide with the thawing phase, to probe the effect of  
118 recent ice melting and early lake productivity. Late summer-early fall sampling preceded holomixis  
119 phase, to probe the effect of summer time stratification and whole biological production (both auto  
120 and heterotrophic).

121

## 122 **2.2. Sampling lake waters and in-situ sample treatments**

123 A total of 71 subsurface water samples (0.2 – 0.5 m) were collected in 20 lakes during June/July  
124 and October 2017–2019. Details of the sampling locations are summarized in Table 1. In brief, five  
125 sampling campaigns were carried out in June/July 2017, October 2017, June 2018, October 2018  
126 and June 2019. In the two first sampling campaigns of June and October 2017, three replicate  
127 subsurface samples were collected in the upstream, central and downstream sectors of each lake to  
128 examine intra-lake variabilities. Diurnal and depth profiles from lakes Gentau and Sabocos were  
129 sampled in June 2018, October 2018 and June 2019. Azules diurnal and depth profiles were sampled  
130 in June and October 2018, while Arratille profiles were sampled only in June 2018. The diurnal  
131 cycle consisted in the acquisition of subsurface samples carried out every few hours from dawn to  
132 sunset mainly to evaluate the effect of light in Se speciation.

133 For the Bachimaña reservoir and other lakes of difficult access, water samples were collected from  
134 the shore, below the surface, using nitrile gloves to avoid contamination. For all other lakes, samples  
135 were collected onboard an inflatable rubber boat using a non-metallic and PTFE coated sampler (5  
136 L Go-Flo; General Oceanic). The sampler was operated with gloves for subsurface waters and fixed

137 on a Kevlar cable (scaled every meter from 0 to 40 m) for samples collected at depth. One litre of  
138 the sample was immediately transferred into two 500 mL Teflon bottles with a pre-cleaned silicone  
139 tubing, avoiding bubbles and head-space as for dissolved oxygen sampling, and stored in the dark  
140 as fresh as possible for its subsequent purge and trap of the gaseous species.

141 Two aliquots either unfiltered, for bulk, or filtered, for dissolved, total Se analyses were collected  
142 in 15 mL polypropylene tubes and acidified to 1% v/v HNO<sub>3</sub> (69%, trace metal grade). For total  
143 dissolved Se (TDSe), samples were filtered (PVDF Sterivex filter units, 0.22µm, Millipore) prior to  
144 their acidification. To study Se speciation, filtered water samples were stored without headspace in  
145 50 mL Falcon tubes, as fresh as possible (4–10 °C) in the field in the dark. Once in the lab, all  
146 samples were stored at ca. 4 °C in the dark until the analysis (less than two weeks). Additional  
147 samples were collected and analyzed at the University of the Basque Country (Bilbao) for the main  
148 anions, non-purgeable organic carbon (NPOC), and dissolved inorganic carbon (DIC) as previously  
149 described elsewhere (Kortazar et al., 2020). Samples of depth profiles ( $3 \leq n \leq 6$ ) and temporal  
150 monitoring were treated following the same protocols detailed here and all procedures were  
151 conducted trying to minimize their exposition to daylight.

152 The physicochemical parameters in water lakes were measured simultaneously to the sampling  
153 using a multiparametric probe YSI EXO2 (temperature, conductivity, oxidation-reduction potential,  
154 dissolved oxygen, turbidity). The pH was calculated according to Kortazar et al. (2020) with the  
155 help of the CO2SYS software, this methodology providing a better precision and accuracy in  
156 comparison with the pH measured by the probe.

157

## 158 **2.2. Total Se analysis**

159 Bulk total Se (TSe Bulk) was determined in unfiltered bulk samples (15 mL) after digestion with  
160 300 µL HNO<sub>3</sub> (69%, tracepure grade) and 150 µL HCl (37%, tracepur grade) in sealed tubes and  
161 incubated for 3 h at 90 °C in a hot block (DIGIPREP, SCP Science). The dilution factor was  
162 corrected by weighting samples before and after the digestion.

163 Total Se concentrations were measured in bulk (TSe Bulk) and filtered (TDS<sub>Se</sub>) samples with an  
164 Agilent 7900x Series inductively coupled plasma mass spectrometer (ICP-MS) system (Agilent  
165 Technologies, Tokyo, Japan) equipped with an octopole reaction cell, concentric nebulizer and a  
166 Scott double pass spray chamber cooled to 2 °C. Argon-based polyatomic interferences were  
167 reduced by using H<sub>2</sub> as cell gas at a flow rate of 5 mL min<sup>-1</sup> as previously optimised and validated  
168 (Darrouzes et al., 2005). The parameters settings were as follow: Ar plasma gas flow, 15 L min<sup>-1</sup>;  
169 Ar auxiliary gas flow, 0.86 L min<sup>-1</sup>; Ar nebulizer gas flow, 1–1.1 L min<sup>-1</sup>; radio frequency (RF)  
170 forward power, 1550 W. Acquisition parameters consisted of 10 replicates with 50 sweeps/replicate  
171 and integration time of 2s per isotope; m/z monitored ratios were 77 and 78. External calibration  
172 (range 5 – 100 ng L<sup>-1</sup> from single element Se standard 1000 mg L<sup>-1</sup> SCP Science) was performed.  
173 Quality control used for quantification methodology was based on several repetitions (3 to 4 times)  
174 of standard measurements during the day of analysis that led to calibration line slope relative  
175 standard deviation <10%. Limits of quantification (based on <sup>78</sup>Se and according to IUPAC  
176 recommandations) were between 0.7–2.1 ng L<sup>-1</sup>. Typical analytical precision was <12% in the range  
177 of measured concentrations of dozen ng Se L<sup>-1</sup> (relative standard deviation of the 10 replicates).

178

### 179 **2.3. Dissolved non-volatile Se speciation analysis**

180 Chromatographic separation was carried out with an Agilent 1200 HPLC pump hyphenated to ICP-  
181 MS. Most samples were analyzed using a porous graphitic carbon stationary phase (Thermo  
182 Hypercarb column 10 cm × 4.6 mm i.d) with a formic acid mobile phase (240 mmol L<sup>-1</sup>, 1%  
183 methanol and pH 2.4 adjusted with ammonia) delivered at 1 mL min<sup>-1</sup> flow rate (Dauthieu et al.,  
184 2006). Chromatographic conditions allowed the separation of inorganic selenite and selenate and,  
185 organic species (trimethylselenonium ion, methane seleninic acid, selenomethionine and  
186 selenocystine) (Lanceleur et al., 2019; Be-eri-Shlevin et al., 2021). Standard addition was used for  
187 quantification using daily diluted certified aqueous standards of 1 g L<sup>-1</sup> Se as selenite and 0.1 g L<sup>-1</sup>

188 Se as selenate (Spectracer) (see example chromatogram Fig. SI 1). Quantification limits (LoQ) were  
189 3.6 and 2.2 ng Se L<sup>-1</sup> for selenite (Se(IV)) and selenate (Se(VI)) respectively for 200 µl injected  
190 volumes. Exceptionally, samples of October 2017 and part of those of October 2018 were analyzed  
191 using the mixed-mode column OmniPac PAX-500 (Thermo, 25 cm x 4 mm i.d.) with a 20 mmol  
192 L<sup>-1</sup> ammonium nitrate mobile phase containing 2% methanol at pH 8.0 (adjusted with ammonia),  
193 delivered at 1 ml min<sup>-1</sup> flow rate. In this case, LoQ were 12 and 10 ng Se L<sup>-1</sup> for Se(IV) and Se(VI),  
194 respectively, for 100 µl injected volumes. Duplicates of all samples were injected obtaining a  
195 relative standard deviation below 10%, except for some samples close to the LoQ for which relative  
196 standard deviation was up to 15%. Only selenate and eventually selenite were detected. The  
197 operationally defined Se (-II, 0) fraction was then calculated by subtraction of species concentrations  
198 from the total dissolved Se concentration.

199

#### 200 **2.4. Dissolved gaseous Se speciation analysis**

201 Dissolved gaseous Se species were purged and trapped within the day of sampling in the field lab  
202 set in a mountain hut. This allowed the pre-concentration of dissolved gaseous Se compounds and  
203 the preservation of their speciation as described by Lanceleur et al. (2019). Samples (2x500 mL)  
204 were purged with pure N<sub>2</sub> (500 mL min<sup>-1</sup>) for 45 min. The resulting water vapour during the purge  
205 was removed from the gas stream in a moisture trap maintained at -20 °C. The gas stream was then  
206 carried through a volatile Se compounds trap (glass tube packed with Carbotrap sorbent). After the  
207 purge, the glass columns were tightly closed with Teflon lined plugs and stored in the dark at 4 °C  
208 in a sealed double PE bags until analysis. In the laboratory, samples were analyzed within a week  
209 after sampling using a cryogenic GC-ICP/MS set-up. Samples were thermo-desorbed from  
210 carbotraps at 250 °C for 2 minutes under He flow (100 mL min<sup>-1</sup>). Samples were flushed and trapped  
211 on the head of a Cryo GC column submerged in liquid N<sub>2</sub>, prior to GC elution on Chromosorb  
212 SP2100 (Amouroux et al., 1998). Quantification was obtained by external calibration. The limits of

213 quantification were between 1.3–3.8 pg Se L<sup>-1</sup> for DMSe and DMS<sub>2</sub>Se and between 1.3–5.4 pg Se  
214 L<sup>-1</sup> for DMDS<sub>2</sub>Se. Thermodesorption efficiency was controlled by carrying out two consecutive  
215 analyses of the same carbotrap column. TVSe content was determined as the sum of DMSe, DMS<sub>2</sub>Se  
216 and DMDS<sub>2</sub>Se concentrations.

217

## 218 **2.5. Data processing and statistics**

219 In samples that did not contain quantifiable selenite and/or selenate (<LoQ), a value of one half their  
220 quantification limit (with associated error of 100%) was used for Se (-II, 0) fraction calculation. The  
221 limit of quantification of Se (-II, 0) fraction was calculated as the square root of the sum of the  
222 squares of TDSe, Se(IV) and Se(VI) limits of quantification and, was in the range 4.5–15 ng Se L<sup>-1</sup>.  
223 For the statistical treatment, a value of one half the quantification limit (with associated error of  
224 100%) was also assigned to the species (selenate, volatile species) and the Se (-II, 0) fraction  
225 concentrations in samples that did not contain quantifiable levels.

226 All data sets were tested for normality using the Shapiro-Wilk test. The non-parametric pairwise  
227 Wilcoxon test or Kruskal-Wallis followed by Conover-Iman tests for multiple, two-tailed,  
228 comparisons were performed. Spearman coefficients were used for correlation analysis. These  
229 analyses were carried out using using R Commander package (R Core Team, 2021, version 4.0.5)  
230 and XLSTAT software (version 2021.2.1).

231

## 232 **3. Results and Discussion**

### 233 **3.1. Subsurface lake waters**

234 Detailed data for physicochemical characteristics and selenium concentrations are available in  
235 Supporting information Tables SI 1 and SI 2. In June and October 2017 sampling campaigns, the  
236 triplicate samples, collected in each lake to check intra-lake variabilities, exhibited no remarkable  
237 differences between replicates (relative standard error of the mean was ≤13, 11 and, 9 %, respectively,  
238 for bulk and dissolved total Se and Se(VI), data not shown). The diurnal cycle

239 measurements (June 2018, October 2018, and June 2019) also did not show significant variability  
240 along the day for total Se, nor for speciation (data not shown). These results indicated primarily a  
241 slow reactivity of Se compounds and Se turnover in the surface waters. We can thus assume that no  
242 apparent bias was due to the sampling time of the day and that our measurements were representative  
243 of sampled lakes in a given seasonal period.

### 244 *3.1.1 Physicochemical characteristics and selenium total concentrations*

245 Lake waters presented temperatures ranging from 2 to 19 °C (Table SI 1) and subsurface samples  
246 were always oxygenated (>62% of oxygen saturation, data not shown). Conductivity ranged  
247 between 4.5 and 130  $\mu\text{S cm}^{-1}$ . The pH varied from slightly alkaline (7.91) to acidic values (4.87).  
248 Oxidation-reduction potential ( $E_{\text{H}}$ ) ranged from slightly reducing (36 mV) to oxidising (285 mV)  
249 conditions. No significant differences were observed for conductivity, pH and  $E_{\text{H}}$  values between  
250 June and October (Wilcoxon test,  $p>0.05$ ). Some of the anions measured, such as fluoride ( $\text{F}^-$ ),  
251 bromide ( $\text{Br}^-$ ), nitrites ( $\text{NO}_2^-$ ) or phosphates ( $\text{PO}_4^{3-}$ ), were frequently not detected (<LoQ, Table SI  
252 1). Sulphate ( $\leq 7.56 \text{ mg L}^{-1}$ ) was the main anion found in waters with a median value of  $1.6 \text{ mg L}^{-1}$   
253 ( $n=71$ ). The highest sulphate concentrations were observed in Azul Superior (from 4.84 to  $7.56 \text{ mg}$   
254  $\text{L}^{-1}$ ) and Badète (from 2.96 to  $5.43 \text{ mg L}^{-1}$ ) (Table SI 1). The median value found in October ( $1.89$   
255  $\text{mg L}^{-1}$ ,  $n=27$ ) was slightly higher than in June ( $1.36 \text{ mg L}^{-1}$ ,  $n=44$ ) but statistically not significantly  
256 different (Wilcoxon test,  $p=0.48$ ). Nitrate concentration was  $\leq 1.16 \text{ mg L}^{-1}$  at all sites with highest  
257 values found at Azul Superior (June 2019,  $1.16 \text{ mg L}^{-1}$ ), Badète (June 2018,  $1.13 \text{ mg L}^{-1}$ ) and  
258 Bachimaña (June 2019,  $1.08 \text{ mg L}^{-1}$ ) (Table SI 1). Nitrate median concentration of sub-surface  
259 samples was  $0.46 \text{ mg L}^{-1}$  ( $n=71$ ). The median value in June samples ( $0.56 \text{ mg L}^{-1}$ ,  $n=44$ ) was almost  
260 double that in October ( $0.29 \text{ mg L}^{-1}$ ,  $n=27$ ) and significantly different (Wilcoxon test,  $p=0.004$ ).  
261 Dissolved organic matter ranged from 0.63 to  $5.3 \text{ mg L}^{-1}$  and median values were significantly  
262 different between June ( $1.03 \text{ mg L}^{-1}$ ,  $n=43$ ) and October ( $1.72 \text{ mg L}^{-1}$ ,  $n=26$ ) (Wilcoxon test,  
263  $p=0.0006$ ).

264 Total Se bulk concentrations ranged from  $9 \pm 1$  to  $82 \pm 5$  ng L<sup>-1</sup> while dissolved Se ranged between  
265  $7 \pm 1$  and  $78 \pm 7$  ng L<sup>-1</sup> (Table SI 2). No significant differences were found for both concentrations  
266 between June and October sampling campaigns (Wilcoxon test,  $p > 0.05$ ) but bulk and filtered Se  
267 concentrations were significantly different (Wilcoxon test,  $p < 0.0001$ ). However most of the Se was  
268 in the dissolved or colloidal phase in these lakes (Fig. SI 2). Measured dissolved Se concentrations  
269 in Pyrenean lakes were similar to those reported in Norwegian lakes located on granitic gneisses  
270 ( $16\text{--}75$  ng L<sup>-1</sup>) (Økelsrud et al., 2016). The highest total Se concentrations were found at Badète  
271 ( $59.3$  ng L<sup>-1</sup> on average) and Azul Superior lakes ( $57.8$  ng L<sup>-1</sup> on average). Grouping lakes  
272 according to underlying bedrock, the average dissolved Se concentration was  $19 \pm 6$  ng L<sup>-1</sup> for lakes  
273 located at the granitic core (pDe-GR) ( $n=31$ ),  $48 \pm 18$  ng L<sup>-1</sup> for Devonian sedimentary bedrocks  
274 (De-SR) lakes ( $n=21$ ),  $12 \pm 1$  ng L<sup>-1</sup> at lakes located over Permo-Triassic sedimentary bedrock (PT-  
275 SR) ( $n=9$ ) and  $14 \pm 2$  ng L<sup>-1</sup> for lake Sabocos ( $n=3$ ) (Cretaceous prevailing bedrock, Cr-SR).  
276 Selenium concentrations (bulk and dissolved) were thus significantly higher in De-SR lakes  
277 compared to other bedrock lakes (Kruskall-Wallis and Conover-Iman tests,  $p < 0.0001$ ) (Fig. 2A,  
278 Table SI 2).

279 No relationship was found between total Se concentration and lake or catchment surface area. Lake  
280 surface area demonstrating a linear relationship with water residence time (personal communication,  
281 Lluís Camarero, CSIC, Spain), the lack of correlation between Se concentration and surface area  
282 indicated that Se contents in lake waters were not drastically affected by water residence times.  
283 Correlation analysis showed that total dissolved selenium concentrations were positively correlated  
284 with those of sulphate, dissolved inorganic carbon and nitrates (Table SI 3, Fig. SI 3). Among them,  
285 sulphate and dissolved inorganic carbon concentrations were also correlated (Table SI 3). The strong  
286 link between total dissolved selenium concentrations and those of sulphate has been previously  
287 reported in freshwaters with higher Se concentrations ( $> 100$  ng L<sup>-1</sup>, Ponton et al., 2020) and will  
288 be further discussed in Paragraph 3.3. TDSe did not correlate with NPOC, meaning that Se was

289 weakly incorporated or bound to organic matter in such oligotrophic lakes. Very weak or no  
290 correlation of TDSe with dissolved organic matter was previously reported in Siberian thaw lake  
291 waters in spring time corresponding to frozen underlying peat preventing leaching of dissolved  
292 organic matter and Se from peat layers (Pokrovsky et al., 2018).

### 293 *3.1.2 Selenium speciation*

294 Among non-volatile dissolved species, selenate was most often the only species detected with no  
295 significant difference between June and October (Wilcoxon test,  $p > 0.05$ ). The average values within  
296 each lake group followed the same trend as for total dissolved Se (Fig. 2A), and were:  $12 \pm 7$  (n=21),  
297  $42 \pm 25$  (n=15),  $8 \pm 2$  (n=6) and  $10.3 \pm 0.4$  (mean deviation, n=2) ng Se L<sup>-1</sup> for pDe-GR, De-SR,  
298 PT-SR and Cr-SR groups, respectively for June sampling campaigns. After summer, selenate  
299 concentration values were slightly lower:  $10 \pm 5$  (n=14),  $37 \pm 17$  (n=9),  $<10$  (n=3) and 6 (n=1) ng  
300 Se L<sup>-1</sup>, respectively. Spring to late summer selenate concentrations decrease in meso-eutrophic  
301 freshwater lake has been related to phytoplankton uptake, and was associated also to selenite  
302 concentration decrease (Be'eri-Shlevin et al., 2021). Selenate, which is the stable form of Se in  
303 oxic waters (Belzile et al., 2000), accounted for  $64 \pm 28$  % of total dissolved Se, and both  
304 concentrations were thus significantly different (Wilcoxon test,  $p < 0.0001$ ). This was particularly  
305 the case for pDe-GR, PT-SR and Cr-SR lake groups (Fig. SI 4) where other species may thus coexist  
306 at extremely low concentration. This may be the case of selenite, which was typically undetected  
307 ( $<$ limit of quantification, in the range 3.6–12 ng Se L<sup>-1</sup>) and the Se(-II, 0) fraction (LoQ in the range  
308 4.5–15 ng Se L<sup>-1</sup>). Pyrenean lakes are usually oligotrophic due to low contents of nutrient and  
309 organic matter (Catalan et al., 2006), the presence of organic selenide was thus not expected as main  
310 component of Se(-II, 0) fraction and no unknown selenium-containing compound could be  
311 chromatographically detected (see example chromatogram Fig. SI 1). Considering  $E_H$  and pH values  
312 observed in lake waters, elemental Se should be thermodynamically stable in most lakes (Seby et  
313 al., 2001). Estimation of Se(-II, 0) fraction (Table SI 2) indicated the presence of such fraction in  
314 both seasons in the range 4.7–17 ng L<sup>-1</sup> in subsurface waters at some lakes (Bachimaña Bajo,

315 Coanga and Baños de Panticosa pDe-GR lakes and, Ordicuso De-SR lake). Bibliographic data for  
316 Se speciation in lakes is scarce, especially in remote lakes. Existing publications report selenate  
317 concentrations in the range of 4–17 ng Se L<sup>-1</sup> in Finish lakes representing 6–12% of total Se, while  
318 most of Se present was linked to organic matter (Wang et al., 1994; 1995). In Canadian lakes,  
319 selenate was predominant (≥60%) in lakes where Se inputs occur principally in this form (Ponton  
320 et al., 2013).

321 Total volatile Se ranged from 2.6 to 118 pg L<sup>-1</sup> with an exceptionally high value observed in June  
322 2017 at Ordicuso (484 pg L<sup>-1</sup>) without significant seasonal variation in each lake group (Fig. 2B  
323 and Table SI 2). Concentrations showed similar wider range of values for pDe-GR and De-SR lakes  
324 (4 to 118 pg L<sup>-1</sup> excluding Ordicuso in June 2017) compared to PT-SR and Cr-SR lakes (3 to 36 pg  
325 L<sup>-1</sup>). In pDe-GR lake groups, although not statistically different, average TVSe concentration in  
326 June samples (66 ± 34 pg L<sup>-1</sup>), just after the ice-cover melting, was higher compared to October  
327 samples (41 ± 24 pg L<sup>-1</sup>), which may indicate volatile species accumulation during ice capping  
328 period. The main species found in all lakes was DMSe, representing in average 76 % of the TVSe  
329 detected. Previous studies in remote arctic thermokarst ponds reported total volatile Se in the range  
330 1–32 pg L<sup>-1</sup> including 96% of DMSe (Lanceleur et al., 2019). The low concentrations of TDSe and  
331 sulphate in Pyrenean lakes seem to limit the production of dimethyldiselenide (DMDS<sub>2</sub>) or dimethyl  
332 selenyl sulfide (DMSeS) observed in other environments, such as meso-eutrophic lakes,  
333 minerotrophic peatlands or estuarine and marine systems (Amouroux & Donard, 1997; Tessier et  
334 al., 2002; Vriens et al., 2014; Be'eri-Shlevin et al., 2021). For TVSe, no clear trend was observed  
335 with any of the measured parameters in water samples (Spearman coefficient  $|\rho| < 0.3$ ), most  
336 probably because of the extremely low concentration of gaseous Se species in most lakes. The  
337 limited nutrient supplement and further biological activity of Pyrenean lakes seem to be the main  
338 limit for volatile Se production. In addition, the short lifetime and rapid degradation of volatile Se

339 compounds in the photic zone could make it difficult to establish correlation trends (Mason et al.,  
340 2018).

341

### 342 **3.2. Profiles of selenium and dissolved species in lake waters**

343 During the sampling campaigns of 2018 and 2019, depth profiles were carried out in four lakes:  
344 Arratille and Azul Superior (De-SR lakes), Gentau (PT-SR lake) and Sabocos (Cr-SR lake).  
345 Detailed data are available in Table SI 4.

#### 346 *3.2.1 Shallow lakes (maximum depth < 15 m)*

347 Arratille and Azul Superior lakes belong respectively to Cauteret and Panticosa areas of similar  
348 geological structure (mostly granitic and, limestone, marble, shale and sandstone sedimentary rocks)  
349 but respectively located in the northern and southern slope. Oxygen and temperature depth profiles  
350 demonstrate that Arratille exhibited a small oxygen depletion only at the bottom water sample in  
351 June, while Azul Superior, with a maximum depth of around 8 m, had a well-mixed water column  
352 (Fig. SI 5). In both lakes, total Se concentration did not vary significantly and the main species was  
353 selenate with less than 6 and 7% variation, respectively, along the water column. Selenite and Se(-  
354 II, 0) fraction were both below the LoQ. The profile of volatile species was different from those of  
355 non-volatile selenium species. In June, the concentration of DMSe was increased at half-depth in  
356 both lakes. This concentration peak was more visible in Aratille lake where DMSe concentration  
357 stayed constant to the bottom. In Azul Superior lake, DMSe profile appeared to be similar to the  
358 one of nitrate in June while it was opposite in October where DMSe concentrations were clearly  
359 lower. The formation of DMSe has been shown to occur with similar production rates from selenate  
360 or selenite in bottom pond waters (i.e oxygen depleted) (Lanceleur et al., 2019). Although, DMSe  
361 production in the photic zone could not be excluded, it should be of lesser extent in such oligotrophic  
362 lakes if compared to deeper microbial processes in bottom waters and sediments (Amouroux &  
363 Donard, 1997; Lanceleur et al., 2019). Minor volatile algal production was also previously observed

364 comparing marine algae, bacteria and mixed bacteria-algae culture experiments (Luxem et al.,  
365 2017). Observed difference between sub-surface and bottom volatile Se concentrations could thus  
366 be indicative of its formation and accumulation at depth during winter-early spring (i.e ice-covered  
367 period promoting reducing conditions), upward diffusion and volatilization and/or photodegradation  
368 in the surface layer during summer period.

### 369 *3.2.2 Deep lakes*

370 Gentau and Sabocos lakes are located at lower elevation and belong respectively to Ayous and  
371 Panticosa areas where agropastoralism activities can represent a source of organic matter and  
372 nutrients (Kortazar et al., 2020). Both lakes are affected by thermal and oxygen stratification and  
373 during 2018 samplings, the deepening of thermocline and oxycline was observed in both lakes from  
374 late spring to autumn (Fig. 3). Hypoxic conditions ( $\text{DO} < 4 \text{ mg L}^{-1}$ ) were maintained in the deepest  
375 5 m. Nitrate and sulphate concentrations in Sabocos were a little lower than the mean values ( $\approx 1$   
376 and  $4 \text{ mg L}^{-1}$ , respectively) measured in 2012 (Santoloria et al., 2015) and, higher compared to  
377 Gentau. This was particularly the case for sulphate concentration that was extremely low ( $\leq 0.7 \text{ mg}$   
378  $\text{L}^{-1}$ ) in Gentau. After summer, a nitrate depletion was observed in the photic zone (4–8 m depth in  
379 Sabocos, up to 12 m depth in Gentau). Conductivity values were also higher in Sabocos due to its  
380 calcareous basin (Santoloria et al., 2015; Kortazar et al., 2020). An increase of conductivity values  
381 from the surface to the bottom was observed in Gentau. With the exception of two deviant values  
382 observed in Gentau (abnormally high values for TDS<sub>Se</sub> at 0.5 m depth in June 18 and, TSe bulk at 18  
383 m depth in June 19), total Se concentrations did not vary significantly along the water column ( $<$   
384 14% variation) as previously observed in shallower lakes.

385 Selenite concentration was in both lake profiles below the LoQ and, selenate demonstrated opposite  
386 profiles. Selenate was not detected in October profile of Gentau lake which may be related to the  
387 high LoQ of  $10 \text{ ng L}^{-1}$  of the chromatographic conditions used. However, reproducible profiles were  
388 observed in June where selenate concentration decreased with increasing depth, resulting in

389 quantifiable Se(-II, 0) fraction in hypoxic deepest 5 m. These data suggested either abiotic and/or  
390 microbial reduction of selenate or its slower re-oxidation in bottom waters of Gentau lake as  
391 observed in other lentic systems (Lanceleur et al., 2019; Be'eri-Shlevin et al., 2021). In Sabocos,  
392 however, selenate proportion in June profiles did not vary significantly along the water column ( $67$   
393  $\pm 7$  and  $90 \pm 9$  % of total dissolved Se in 2018 and 2019, respectively). The lower proportion of  
394 selenate in June 2018 resulted in occasional quantifiable Se(-II, 0) fraction at values marginally  
395 above the LoQ. In October, despite an oxygen saturation above 70%, Se(VI) depletion was observed  
396 in the photic zone as was the case for nitrate. These data could indicate biological uptake of selenate  
397 as previously suggested elsewhere (Harrison et al., 1988; Duan et al., 2010; Be'eri-Shlevin et al.,  
398 2021). Observed differences between selenate proportion in oxygen-depleted bottom waters of both  
399 lakes may be related to the fact that Gentau lake receives mineral inputs, mainly iron (Kortazar et  
400 al., 2020), which may promote the existence of Fe-selenides or colloidal elemental selenium at the  
401 sediment-water interface (Fernández-Martínez & Charlet, 2009).

402 The total volatile Se concentration sharply peaked in both bottom waters in June 2018 at values that  
403 were not measured afterward. This increase mainly resulted from DMDSe contribution (43 to 76%  
404 of TVSe). In comparison with shallower lakes, DMSeS contribution to total volatile selenium was  
405 non negligible in the photic zone of Gentau and Sabocos lakes. In addition to enhanced production  
406 of DMSe, Lanceleur et al. (2019) have reported that DMDSe was formed in bottom pond waters  
407 enriched with local biofilm with a production rate approximately 100 times lower compared to the  
408 one of DMSe. The significant proportion of DMDSe with respect to DMSe observed in-depth of  
409 these oligotrophic aquatic systems may thus be related to their respective volatility (Karlson et al.,  
410 1994) and dark conditions favourable to formation and stability of diselenide bond (Amouroux et  
411 al., 2000). The presence of DMSeS in shallower waters suggested its possible formation from  
412 DMDSe and sulphur-containing volatile compounds (Chasteen, 1993; Swearingen et al., 2006).  
413 Likewise previous observations in shallow lakes, enhanced concentration levels of TVSe were

414 observed in springtime after the ice coverage period preserving such compounds from volatilization  
415 and photodegradation that seem to control TVSe in sub-surface waters.

416  
417 **3.3. Sources of Selenium in alpine lake waters: bedrocks leaching/erosion versus wet**  
418 **depositions inputs**

419 Because most of the investigated lakes have a limited watershed size (Table 1), main Se inputs are  
420 suggested to be related to the elemental composition of the prevailing bedrocks through dissolution  
421 and erosion pathways, and direct atmospheric inputs. Among major anions and considering all lakes  
422 and sampling dates, correlation analysis showed a very strong positive relationship between total  
423 dissolved Se and sulphate (Fig. SI 3). Sulphate's concentration mainly depends on the geological  
424 substrate while the intensive study of Camarero et al. (2009) in European mountain lakes revealed  
425 that lakes having sulphate concentration  $< 2.3 \text{ mg L}^{-1}$  could be considered as mainly controlled by  
426 S atmospheric inputs. During our recent field sampling program, a similar threshold sulphate  
427 concentration value of  $0.7 \text{ mg L}^{-1}$  has been observed and proposed to distinguish between  
428 atmospheric or geological sources in lakes of studied zone (Duval, 2020). This value agrees with  
429 the annual sulphate concentration of  $0.67 \text{ mg L}^{-1}$  reported by Suess et al. (2019) at the Pic du Midi  
430 de Bigorre high altitude station. In the western Pyrenees region, shales formed during the Devonian  
431 geological period are the main source of  $\text{SO}_4^{2-}$  (Van Lith, 1968). Lakes presenting the highest  
432 sulphate and selenium concentrations are those located over sedimentary rocks containing shales  
433 (De-SR lakes group). Their  $\text{SO}_4^{2-}$  concentration is higher than concentrations found in rainwaters  
434 (Roulier et al., 2021; Suess et al., 2019) that may thus, similarly to S, indicate selenium geological  
435 supply as selenium concentrations are typically higher in shales than in granite, limestone or  
436 sandstone (Plant et al., 2014; Fernandez-Martinez & Charlet, 2009).

437 To evaluate the contribution of geogenic versus atmospheric Se sources, the molar ratio of Se/S  
438 measured in lake waters in this study was compared with Se/S ratios calculated for different rock  
439 types using a standard database (Reimann & De Caritat, 1998) as no data was available for local

440 bedrocks. Molar Se/S ratios measured in lake waters were also compared with Se/S ratios in wet  
441 deposition at the Pic du Midi de Bigorre (calculated from Suess et al., 2019) and Adour watershed  
442 (calculated from Roulier et al., 2021). The molar ratios Se/S in Pyrenean lakes were in the range  
443  $(0.7\text{--}6.8) \cdot 10^{-5}$  (average values per lake groups in Table 2) and do not allow to provide clear  
444 discrimination of potential major sources of Se in those lakes. However, considering the threshold  
445 value of sulphate concentration in rain waters ( $0.7 \text{ mg L}^{-1}=7.5 \text{ } \mu\text{mol L}^{-1}$ ) below which wet  
446 depositions is the main source of S (Duval, 2020; Camarero et al., 2009), a strong direct relationship  
447 was obtained between Se/S ratio and sulphate concentration for half of the studied lakes belonging  
448 to pDe-GR and PT-SR groups (Spearman coefficient  $\rho=-0.75$ ,  $p<0.0001$ , Fig. 4). For the other half  
449 of lakes, including all De-SR group lakes, for which sulphate concentration was higher than  $7.5$   
450  $\mu\text{mol L}^{-1}$  and controlled by geological substrate, only a weak correlation was obtained (Spearman  
451 coefficient  $\rho=-0.34$ ,  $p<0.05$ , Fig. 4).

452 An estimation of Se input from wet deposition was calculated using the average annual Se flux in  
453 Adour watershed located downstream the northern section of the west Pyrenees ( $50 \pm 20 \text{ } \mu\text{g Se m}^{-2}$   
454  $\text{yr}^{-1}$ , Roulier et al., 2021). The estimation considered the surface area and volume of each lake to  
455 compare the input of Se from wet deposition with the stock of Se at each lake. The lake volume and  
456 surface area data were taken from Duval (2020) and the results are presented in Table SI 5. We  
457 found that Se provided from annual wet deposition could account for 12 to 100% (median value of  
458 39%) of Se stored in lake water at a specific time of the year. Thus, wet depositions through rain or  
459 snow events and during the snowmelt period is a non-negligible source of selenium in such alpine  
460 Pyrenean lakes, which can be counterbalanced by a Se-enriched geological substrate.

461 The emission of volatile Se compounds could then contribute to lower the extent of Se in surface  
462 lake waters, mainly in the form of DMSe. We used our measurements to estimate Se gaseous output  
463 from lake water to the atmosphere, but as they corresponded only to two months of the year the  
464 variability of TVSe concentrations was not well constrained. However, due to the low TVSe

465 concentrations and low seasonal variability observed before and after summer, together with the  
466 low surface area of most lakes (Table 1), low volatilization fluxes are expected. A rough estimation  
467 of Se emission was carried out similarly to Lanceleur et al. (2019) using the model of Cole & Caraco  
468 (1998) developed for small lakes considering  $3 \text{ m s}^{-1}$  as maximum average wind speed, as recorded  
469 in those sheltered lake systems (ca.  $1\text{--}3 \text{ m s}^{-1}$ , from Duval et al., in preparation). We assumed that  
470 atmospheric exchange occurred for approximately 6 months, while during late fall to late spring the  
471 ice cover prevented volatilization. The annual Se emission (Table SI 5) was compared with the  
472 estimated total Se stock in the corresponding lake. These values ( $3.8\text{--}31 \text{ ng Se day}^{-1} \text{ m}^{-2}$ ) were  
473 similar to the daily emission reported at thermokarst ponds ( $1\text{--}97 \text{ ng Se day}^{-1} \text{ m}^{-2}$ ) (Lanceleur et  
474 al., 2019). The results indicated that annual Se emission from lakes to the atmosphere  
475 approximately represents 0.2 to 6.4% of the Se stock in lakes at a specific time of the year (median  
476 value of 3%), remaining thus a minor pathway for Se removal from lake waters.

477

#### 478 **4. Conclusions**

479 Pyrenean lakes showed similar bulk and dissolved total Se concentrations, in the low range of a  
480 dozen to a few dozen of  $\text{ng Se L}^{-1}$ . Total dissolved Se varied between  $7\text{--}78 \text{ ng L}^{-1}$  and, on average,  
481 64% was in the form of selenate in subsurface samples. The extremely low Se concentration in  
482 alpine lakes limited the detection of other Se species such as selenite. Volatile Se speciation was  
483 mainly limited to the production of DMSe and volatilization appeared to not represent an important  
484 removal pathway for Se in Pyrenean lakes.

485 Since no significant seasonal variations (June versus October) was observed neither for total Se  
486 concentrations nor its species in subsurface waters, it is suggested that Se concentrations in lake  
487 waters are regulated by downstream export and possible scavenging. The proportion of Se (-II, 0)  
488 fraction was for example increased in-depth of deep lakes, such as Gentau lake, together with  
489 oxygen depletion probably because of microbial reduction. Further studies are required to ascertain

490 how this process promotes Se scavenging, precipitation and further sedimentation in those lakes, as  
491 shown in thermokarst artic ponds (Lanceleur et al., 2019).

492 The values of molar ratios Se/S in Pyrenean lakes overlap those for comparable bedrock types and  
493 wet depositions. Our interpretation suggests that atmospheric inputs represent an important source  
494 of Se to remote lakes when bedrock geochemistry is depleted with Se and sulphate. This study  
495 provides a unique set of data that allows to better assess Se biogeochemistry in lakes and watershed  
496 mainly affected by global emissions and long-range transport and atmospheric depositions.

497

#### 498 **Conflicts of interest**

499 There are no conflicts of interests to declare.

500

#### 501 **Acknowledgements**

502 This work is a contribution to the REPLIM-OPCC project and has been partially supported (65%)  
503 by the FEDER funds through the INTERREG V-A Spain-France-Andorra (POCTEFA 2014-2020)  
504 (REPLIM project, ref. EFA056/15). A. Romero–Rama thanks the UPPA and IPREM for her PhD  
505 grant (Sciences Doctoral School, UPPA). The contributions of the Aquitaine Region  
506 (AQUITRACES project n° 20131206001-13010973) and ANR IA RSNR (AMORAD project  
507 n°ANR-11-RSNR-0002) for equipment funding are also acknowledged. Ainara Gredilla and Olaia  
508 Liñero Campo (University of the Basque Country) are acknowledged for the analysis of anions.

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