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Biogeochemistry of selenium compounds in the water column of warm monomictic Lake Kinneret

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Biogeochemistry

Biogeochemistry of Selenium compounds in the water column of warm monomictic Lake Kinneret --Manuscript Draft--

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Funding Information:	<table border="1"> <tr> <td>israeli water authority (4500963096)</td> <td>Dr. Yaron Be'eri-Shlevin</td> </tr> <tr> <td>Agence nationale de la Recherche (ANR-11-RSNR-0002)</td> <td>Dr. Maite Bueno</td> </tr> </table>	israeli water authority (4500963096)	Dr. Yaron Be'eri-Shlevin	Agence nationale de la Recherche (ANR-11-RSNR-0002)	Dr. Maite Bueno
israeli water authority (4500963096)	Dr. Yaron Be'eri-Shlevin				
Agence nationale de la Recherche (ANR-11-RSNR-0002)	Dr. Maite Bueno				
Abstract:	<p>The biogeochemistry of dissolved selenium (Se) was investigated over three years (2015-2017) in the subtropical, warm monomictic and meso-eutrophic Lake Kinneret (Sea of Galilee , Israel). We monitored seasonal variation and vertical distribution of dissolved total Se (T.Se), inorganic oxyanions (Se(IV) & Se(VI)), reduced Se fraction (Red.Se), organic (Org.Se) and volatile Se compounds. Detected Org.Se form was probably Se metabolite(s) released by phytoplankton, and the most probable precursor of volatile selenium.</p> <p>Measured concentrations ranged between undetected (<2) and: 84 ng L⁻¹ for Se(IV), 90 ng L⁻¹ for Se(VI), 84 ng L⁻¹ for Org.Se. Depth profiles of Se species were uniform during winter-holomixis whereas vertical gradients became evident during summer-fall stratification. Total Se decreased during stratification, especially in the hypolimnion, due to anoxic conditions and reduction of soluble oxyanions to insoluble Se forms. In the hypolimnion, production of Red.Se seemed to be associated with organic matter degradation and Se(VI) and Se(IV) depletion. Org.Se was detected mainly at epilimnion during spring-summer representing large proportion of reduced Se fraction. Strong correlation was found between Org.Se and Chl- a during the spring algal bloom. Organic Se produced in the photic zone during the spring bloom was degraded during late summer/fall, producing volatile Se species close to the</p>				

	<p>chemocline. Se distribution in stratified productive Mediterranean lakes such as Lake Kinneret, was highly dependent on seasonal dynamics, exhibiting significant biotic transformations, under oxic and anoxic conditions, to form organic and inorganic reduced Se compounds playing determining role in Se removal and cycling in the water column.</p>
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Pau, 14th february 2021

Object: Submission of manuscript entitled “Biogeochemistry of Selenium compounds in the water column of warm monomictic Lake Kinneret”.

Dear Editor,

We would like you to consider for possible publication in *Biogeochemistry* the enclosed manuscript entitled “Biogeochemistry of Selenium compounds in the water column of warm monomictic Lake Kinneret”.

Selenium is an essential micronutrient in both oceanic and fresh water bodies, with a key role as growth limiting factor for phytoplankton. In the present study we report a 3-years survey conducted in Lake Kinneret, Israel, consisting of simultaneous depth profile monitoring of dissolved total selenium and its species including volatile and non-volatile compounds. This warm monomictic lake is characterized by high biological activity and strong seasonal stratification, with anoxic sulfide-rich hypolimnion in late summer. Selenium distribution exhibited large seasonal variations concomitant with the lake stratification dynamics. During holomixis, depth profiles of Se species were uniform whereas vertical gradients became evident during summer-fall stratification. Total selenium concentration decreased during stratification, especially in the hypolimnion, due to anoxic conditions and reduction of soluble oxyanions to insoluble reduced Se forms. Se-containing chromatographic peak, probably organic Se metabolite(s) released by phytoplankton, was detected ubiquitously, mainly at epilimnion during spring and summer representing a large fraction of operationally defined reduced Se in this lake layer. Organic Se was produced in the photic zone during the spring bloom as indicated by correlation with chlorophyll-a, and further degraded during late summer/fall, producing volatile Se species close to the chemocline.

We believe that the topic of this publication and the quality of the database are suitable for publication in *Biogeochemistry*. We declare that this research work is not submitted in other journal.

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Please feel free to contact us for any query.

On behalf of authors,

Sincerely yours,
Maïté Bueno

1 **Biogeochemistry of Selenium compounds in the water column of warm monomictic Lake Kinneret**

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9

10 **Abstract**

11 The biogeochemistry of dissolved selenium (Se) was investigated over three years (2015-2017) in the subtropical,
12 warm monomictic and meso-eutrophic Lake Kinneret (*Sea of Galilee*, Israel). We monitored seasonal variation
13 and vertical distribution of dissolved total Se (T.Se), inorganic oxyanions (Se(IV) & Se(VI)), reduced Se fraction
14 (Red.Se), organic (Org.Se) and volatile Se compounds. Detected Org.Se form was probably Se metabolite(s)
15 released by phytoplankton, and the most probable precursor of volatile selenium.

16 Measured concentrations ranged between undetected (<2) and: 84 ng L⁻¹ for Se(IV), 90 ng L⁻¹ for Se(VI), 84 ng
17 L⁻¹ for Org.Se. Depth profiles of Se species were uniform during winter-holomixis whereas vertical gradients
18 became evident during summer-fall stratification. Total Se decreased during stratification, especially in the
19 hypolimnion, due to anoxic conditions and reduction of soluble oxyanions to insoluble Se forms. In the
20 hypolimnion, production of Red.Se seemed to be associated with organic matter degradation and Se(VI) and
21 Se(IV) depletion. Org.Se was detected mainly at epilimnion during spring-summer representing large proportion
22 of reduced Se fraction. Strong correlation was found between Org.Se and Chl-*a* during the spring algal bloom.
23 Organic Se produced in the photic zone during the spring bloom was degraded during late summer/fall, producing
24 volatile Se species close to the chemocline.

25 Se distribution in stratified productive Mediterranean lakes such as Lake Kinneret, was highly dependent on
26 seasonal dynamics, exhibiting significant biotic transformations, under oxic and anoxic conditions, to form organic
27 and inorganic reduced Se compounds playing determining role in Se removal and cycling in the water column.

28 **Keywords:**

29 Selenium; Dissolved species; Volatile species; Lakes; Depth profile; Seasonal distribution

30

31 **Declarations:**

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40 The authors have no conflict or competing interest to declare.

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42 Data collected and used in this manuscript are available in supplementary information file.

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44 *Author contributions:*

45 **A. Romero-Rama:** Conceptualization, Formal analysis, Writing-original draft, Writing-review & editing

46 **M. Bueno:** Conceptualization, Investigation, Validation, Writing-original draft, Writing-review & editing,
47 Funding acquisition

48 **E. Tessier:** Conceptualization, Investigation, Validation, Writing-review & editing

49 **Y. Be'eri-Shlevin:** Conceptualization, Investigation, Resources, Writing-original draft, Writing-review &
50 editing, Funding acquisition

51 **A. Sukenik:** Conceptualization, Investigation, Resources, Writing-review & editing, Funding acquisition

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53 **D. Amouroux:** Conceptualization, Writing-original draft, Writing-review & editing, Funding acquisition

54

55 1. Introduction

56 Selenium (Se) can be found in water bodies in different oxidation states ((-II), (0), (IV) and (VI)). Selenite (IV)
57 and selenate (VI) occur in aquatic systems together with reduced and probably organically bounded Se species
58 (Conde and Sanz Alaejos 1997; Cooke and Bruland 1987; Cutter and Bruland 1984; Nakaguchi and Hiraki 1993;
59 Nishri et al. 1999). Transformations between different Se forms can be caused by the physicochemical
60 characteristics of the water (mainly E_h , pH and dissolved oxygen) or mediated by microorganisms, including the
61 formation of elemental Se (0) and reduced Se (-II) species. Reduced Se species include: inorganic, organically
62 bounded, and volatile Se compounds such as: dimethylselenide (DMSe), dimethyl diselenide (DMDS₂) and
63 dimethyl selenide sulphide (DMS₂SeS) (Amouroux and Donard 1997; Amouroux et al. 2001). Elemental Se is
64 present as non-soluble colloids and considered as non-bioavailable (Guo et al. 1999; Velinsky and Cutter 1990;
65 Winkel et al. 2012; Zhang et al. 2004).

66 It is well established that selenium is an essential micronutrient in both oceanic and fresh water bodies (Measures
67 and Burton 1980; Lindstrom et al. 1983), with a key role as growth limiting factor for phytoplankton (Harrison et
68 al. 1988, Duan et al. 2010). However, there is no consensus if a specific chemical form of Se is preferentially
69 uptaken by microorganisms in natural aquatic systems. Selenium compounds bioavailability can be driven by the
70 potential energy required for the reductive uptake of the more oxidized form (e.g. Se(VI)) or by competition with
71 other aquatic constituents such as sulphur analogues (Amouroux et al. 2001; Ivanenko 2018). In the Bohai Bay,
72 Duan et al. (2010) showed a correlation between the decrease of Se(IV) and the presence of dinoflagellates. In
73 contrast, selenate was associated with the biological oxidation of Se(IV) to Se(VI) carried out by diatoms.
74 Laboratory experiments suggest that planktonic green algae assimilate preferentially Se(VI) over Se(IV)
75 (Neumann et al. 2003; Simmons and Wallschläger 2011). In contrast, Nishri et al. (1999) reported important
76 removal of dissolved Se in Lake Kinneret that can be explained by the preferential uptake of Se(IV) by
77 phytoplankton, as it was demonstrated in previous experimental studies (Hu et al. 1997; Wrench and Measures
78 1982). Recent studies carried out using the chlorophyte (*Chlamydomonas reinhardtii*) showed that the uptake of
79 selenite was five times higher at pH 9 than at pH 7 (Ponton et al. 2018). In contrast, 15-50% decrease of Se(IV)
80 uptake was observed with increasing phosphate concentration from 100 to 450 μM (Vriens et al. 2016). The same
81 species showed a decrease by half of selenate uptake in the presence of 1 μM of sulfate (Ponton et al. 2018).
82 Several authors agree on the faster uptake of organic Se over inorganic species (Ponton et al. 2018; Vriens et al.
83 2016; Winkel et al. 2015). Therefore, Se uptake highly depends on the bioavailability of each species, the type of
84 microorganisms present in the water, and the concentration of different anions in the case of Se oxyanions.

85 The current knowledge on Se biotransformations has been reviewed by Chasteen and Bentley (2003) and, Lenz
86 and Lens (2009) but the mechanisms of the processes underlying Se biotransformations remain unclear. Since
87 aquatic microorganisms mediate several oxidation/reduction and alkylation/dealkylation processes that release
88 Se(0) species to the water and reduce Se, Se cycling is affected by phytoplankton and bacteria.

89 The most important potential removal pathways proposed for dissolved Se are: sorption of selenite into Fe, Mn
90 and Al oxy-hydroxides (Balistreri and Chao 1987; Nakamaru and Altansuvd 2014), scavenging and deposition of
91 Se-enriched organic matter (Weres et al. 1989,1990), reduction of Se oxyanions to either insoluble Se(0)
92 (Nancharaiyah and Lens 2015) and/or to Se(-II), including volatile compounds (Amouroux and Donard 1996, 1997;
93 Amouroux et al. 2001; Chau et al. 1976; Cooke and Bruland 1987). The chemical analogy between sulfur (S) and
94 Se are well known (Fernández-Martínez and Charlet 2009) and similar biogeochemical pathways for both elements
95 have been reported in marine, estuarine and wetland environments (Mehdi et al. 2013; Winkel et al. 2015).
96 Nevertheless, while many studies focused on volatile S, only few have been carried out to study volatile Se
97 speciation in lake waters (Cooke and Bruland 1987; Diaz et al. 2009; Lanceleur et al. 2019). In aquatic
98 environments, the production of volatile S and Se compounds has been strongly linked to microbial processes
99 suggesting biological mediated processes to be an important removal pathway for dissolved Se (Amouroux et al.
100 2001; Mason et al. 2018; Wen and Carignan 2007). Therefore, the study and characterization of the volatile Se
101 fraction in lake water is necessary to complete our understanding of the Se biogeochemical cycling in such
102 ecosystems (Diaz et al. 2009).

103 Lake Kinneret is suitable for studying Se aquatic biogeochemistry due to (i) the current understanding of its sulfur
104 biogeochemistry (Ginzburg et al. 1999; Knossow et al. 2015; Sela-Adler et al. 2016); (ii) the typical seasonal
105 alternation between oxic (winter) and anoxic (summer-fall) conditions in its hypolimnion and; (iii) because its
106 physical, chemical and biological features are well described and monitored routinely (Zohary et al. 2014a).
107 Oxygen depletion in the hypolimnion together with H₂S production are linked to the activity of sulfate reducing
108 bacteria (SRB) (Hadas and Pinkas 1995). Oremland et al. (1989) described the potential reduction of Se oxyanions
109 by SRB, whereas Nishri et al. (1999) suggested that the removal of Se(IV) was due to chemical reactivity with
110 H₂S. The present study is based on a 3-years survey conducted in Lake Kinneret, Israel, consisting of simultaneous
111 depth profile monitoring of volatile and non-volatile dissolved Se species. This warm monomictic lake is
112 characterized by high biological activity and strong seasonal stratification, with anoxic sulfide-rich hypolimnion
113 in late summer (Zohary et al. 2014a). Our main goal was to investigate the speciation and fate of dissolved selenium
114 in the water column of Lake Kinneret at seasonal and interannual time scales. A comparison with past data reported

115 by Nishri et al. (1999) is achieved to determine the main changes in terms of Se concentration and speciation over
116 the last decades.

117 **2. Materials and methods**

118 **2.1. Site description**

119 Lake Kinneret (Fig. 1) is a warm, monomictic, meso-eutrophic freshwater lake located at the northeast of Israel
120 (32°50'N; 35°35'E). The lake has an area of 170 km², mean depth of 25 m and maximum depth of 42 m (Berman
121 et al. 2014a). Lake Kinneret is stratified 8-9 months per year, from March-April until November-December, and
122 is homothermal during the remaining months. The stratified period is characterized by a strong separation and low
123 exchange of water between the warmer top (epilimnion) and cooler bottom (hypolimnion) layers, with resulting
124 strong vertical gradients of physicochemical and biological parameters along the water column. Primary
125 production is limited to the illuminated, well-oxygenated and warm epilimnion (18-31 °C). The cooler, dark
126 hypolimnion becomes anoxic within a few weeks after the onset of thermal stratification and maintains a constant
127 temperature (~15-16 °C) (Berman et al. 2014a). The interphase layer (metalimnion) is located at 15-20 m during
128 the summer. Nitrate (NO₃⁻) accumulates in the well-mixed water column in winter due to riverine inflows and
129 nitrification of ammonium (NH₄⁺) previously accumulated in the hypolimnion. Once stratification begins, the
130 NO₃⁻ concentration decreases in both the epilimnion and hypolimnion as a consequence of biological uptake and
131 denitrification, respectively (Berman et al. 2014a; Hadas 2014). Sulfate presents a conservative behavior in the
132 epilimnion, meanwhile reducing conditions at the hypolimnion lead to the production of hydrogen sulfide (HS⁻)
133 during stratification (Berman et al. 2014a; Ginzburg et al. 1999). Hypolimnetic reducing conditions are associated
134 with organic matter degradation by anaerobic microorganisms, in particular, with methanogenesis in sediments,
135 and with sulphate reduction both in sediments and water column leading to the accumulation of CH₄ and H₂S in
136 the hypolimnion (Eckert and Conrad 2007).

137 The Jordan river (annual inflow ~ 350 10⁶ m³ (Rom et al. 2014)), is the largest source of freshwater flowing into
138 Lake Kinneret, supplying ~65% of the incoming water, while direct precipitation contributes only ~10% of the
139 total water input to the lake (Rimmer and Gal 2003). Notably, during the three years of this study (2015-2017),
140 the annual minimum lake water level dropped by 1.34 m as a result of continuous drought, with below average
141 annual rainfall. Evaporation (~230 × 10⁶ m³ year⁻¹) and water withdrawal (~375 × 10⁶ m³ year⁻¹) for agricultural
142 and human consumption are usually the main water outflows (Ostrovsky et al. 2013; Rimmer and Givati 2014),
143 although during the years of this study, water pumping out of the lake was reduced drastically due to sever draught

144 conditions. The Jordan River is also the main external source of Se loading into the lake, mainly as inorganic Se
145 (selenite and selenate) originating from the Hula Valley (Nishri et al. 1999).

146 Lake Kinneret has been subjected to major man-made hydrological and other changes during the last decades
147 (Berman et al. 2014a). One dramatic hydrological change was the draining in the 1950s of Lake Hula and its
148 associated wetlands. Lake Hula, a natural shallow lake in the Hula basin, to the north of Lake Kinneret through
149 which the Jordan River used to flow before reaching Lake Kinneret, acted as a natural filter to Lake Kinneret
150 (Hambright and Zohary 1998) (Fig. 1). In an attempt to alleviate some of the ecological damages to the Hula
151 Valley caused by the drainage, a small shallow water body, Lake Agmon, was created in 1994 on part of the
152 historical site of Lake Hula (Hambright and Zohary 1998). With its creation, most water from the Hula Valley is
153 being diverted for agricultural use and no longer reaches Lake Kinneret (Berman et al. 2014a). In addition to the
154 water required for agriculture, municipal and domestic demands for water in the Lake Kinneret catchment have
155 increased during the last decades resulting in lower annual inflows compared to previous decades (Rimmer and
156 Givati 2014). The effects of these changes on Lake Kinneret microbiota and thus, on Se cycling are still not well
157 understood. The stress over Lake Kinneret ecosystem has been shown to affect the phytoplankton dynamics
158 (Zohary 2004; Zohary et al. 2014b). For example, the previously typical spring bloom of the dinoflagellate
159 *Peridinium gatunense* has gradually vanished and replaced by winter-spring bloom of cyanobacteria, mainly
160 *Microcystis*. A loss of species diversity in summer, together with the appearance and establishment of N₂-fixing
161 cyanobacteria has also been observed since the mid 90's, especially *Chrysochloris* (formerly *Aphanizomenon*)
162 *ovalisporum* and *Cylindrospermopsis raciborskii* (Sukenic et al. 2014). Cyanobacteria not only represent a major
163 concern for water quality, it also have the ability to uptake and transform Se, and may impact the Se cycle (Bender
164 et al. 1991; Chouhan and Banerjee 2010).

165 **2.2. Sampling, transport and samples storage**

166 Sampling was carried out four times a year during 2015-2017, at Station A (Fig. 1), using a 5 L vertical point water
167 sampler (Aquatic Research Instruments, Hope, ID, USA). For dissolved Se (total Se and species), water samples
168 were collected during January (winter holomixis), April (early spring when stratification commences at 10-12 m),
169 September (summer with thermocline around 15 m), and November (late fall, when the thermocline deepens to
170 ~25-30 m). For each sampling campaign at Station A, water samples were collected from discrete depths,
171 representing the epilimnion (samples from 1, 3, 5 and 10 m), hypolimnion (25, 30 and 35 m samples) and
172 metalimnion (intermediate-depth samples) in correlation with depths sampled for the routine weekly monitoring
173 of the lake. Samples were stored in cool conditions until arrival at the lab where they were filtered (cellulose

174 acetate 0.45 µm filter, Sartorius) and sealed with no headspace in 120 mL glass vials, precleaned with nitric acid
175 and deionized water. For volatile Se, sampling was concurrent to dissolved Se sampling. Pre-cleaned 1-L glass
176 bottles were filled directly from the water sampler on board without filtering, ensuring via overflow minimum
177 contact with atmosphere and sealing the bottles without any air bubbles. The samples for Se analysis were stored
178 at 4° C, under dark conditions up to two weeks until shipping to France (IPREM, Pau, France). More details about
179 Se compounds stability during storage are given in Supplementary Information (SI).

180 Accompanying physical, geo-chemical and biological parameters used in this study were obtained from the Lake
181 Kinneret Database (LKDB) of the Kinneret Limnological Laboratory, Israel Oceanographic and Limnological
182 Research, and based on the long-term monitoring program on the lake (Sukenik et al. 2014). In general, these
183 include sampling of the water column at station A and other stations at weekly (physical and geo-chemical) or
184 biweekly/monthly intervals (biological parameters). Sampling for Se in this study was usually made concurrently
185 with the sampling for the routine monitoring, from the same times, depths and sampling bottles at Station A.

186 **2.3. Reagents**

187 Ultrapure water (18.2 Ωcm) was obtained from a Milli-Q System (Millipore Co., Bedford, MA, USA). Commercial
188 chemicals of analytical reagent grade were used without further purification. DL-selenomethionine (Sigma),
189 sodium selenite and sodium selenate (Merck) were used. Stock standards solution of 1000 mg (Se) L⁻¹ were
190 prepared in ultrapure water and stored at 4°C in the dark. Working standard solutions were prepared daily by
191 dilution in ultrapure water.

192 **2.4. Total selenium analysis**

193 Total Se was determined with Agilent 7500ce or 7900 ICP-MS instruments (Agilent Technologies, Tokyo, Japan)
194 both equipped with octopole collision/reaction cell (CRC), concentric nebulizer and a Scott double pass spray
195 chamber cooled to 2°C. Argon-based polyatomic interferences were reduced by using H₂ as cell gas at a flow rate
196 of 5 ml min⁻¹. Acquisition parameters were: integration time, 200 ms per isotope; 10 (7900) or 15 (7500ce)
197 replicates; monitored *m/z* 77 and 78. External calibration (single element Se standard 1000 mg L⁻¹ SCP Science)
198 was performed. The instrumental detection limits of Se (based on ⁷⁸Se) were in the range 1.6-13 ng L⁻¹ depending
199 on the instrument. Typical analytical precision was <5% (relative standard deviation, 10 to 15 replicates)
200 (Darrouzès et al. 2008; Pokrovsky et al. 2018).

201 **2.5. Selenium speciation analysis**

202 **2.5.1. Non-volatile dissolved Se analysis**

203 The chromatographic system consisted of an Agilent 1100 or 1200 series HPLC pump, equipped with autosampler
204 and variable volume sample loop. The HPLC-ICPMS interface was made up of a polyetheretherketone (PEEK)
205 tube. Chromatographic separation was carried out on porous graphitic carbon stationary phase (Hypercarb, Thermo
206 Fisher Scientific, 100 × 4.6 mm i.d, part. size 5 µm) with formic acid mobile phase (240 mmol L⁻¹, 1% methanol
207 and pH 2.4 adjusted with ammonia) delivered at 1 mL min⁻¹ flow rate (Dauthieu et al. 2006). The injection volume
208 varied from 100 to 300 µL. Species quantification was achieved by standard addition with limit of detection (LoQ)
209 around 2 ng L⁻¹ for Se(IV) and Se(VI).

210 The chromatographic conditions used allowed the simultaneous separation of inorganic (selenite and selenate) and
211 organic (trimethylselenonium ion, methane seleninic acid, selenomethione and selenocystine) species. Some
212 selenium-containing compounds (up to 3) were detected in the samples. However, their retention times did not
213 match any of the organic Se standards available. A particular compound eluting between Se(VI) and
214 selenomethionine (SeMet) was detected in most samples. This uncharacterized Se containing compound is referred
215 here as Organic Se (Org.Se) (see Fig. SI 1). Its concentration was estimated using the standard addition slope of
216 Se(VI) as its retention time was between those of Se(VI) and SeMet and, corresponding slopes were similar (12%
217 difference). This compound was part of a reduced Se pool that was defined as the difference between total Se
218 (T.Se) and inorganic Se (Se(IV)+Se(VI)) concentrations and calculated as follow: Red.Se = T.Se - Se(IV) - Se(VI).

219 **2.5.2. Volatile Se analysis**

220 Volatile Se analysis was carried out by a cryo-trapping system coupled to a GC-ICP/MS. The low concentration
221 of the volatile species required the use of a preconcentration procedure based on purge and trap system as
222 previously described (Lanceleur et al. 2019; Tessier et al. 2002). Briefly, carbon traps were pre-cleaned by heating
223 three times at 250°C for 2 min, under argon flow (100 mL min⁻¹). After cooling in a laminar flow hood, they were
224 closed with caps until purge of 1 L sample applying a constant He flow (between 400 to 500 mL min⁻¹) for 90
225 minutes. A moisture trap, consisting of an acid-washed silanized glass kept at -20°C with an acetone/ice bath, was
226 used to dry the purged vapor. The carbon trap was then desorbed for 2 min at 250 °C and analytes were cryofocused
227 in the head of a U-shaped glass trap filled with acid-cleaned silanized glass wool (Chromosorb SP2100) and
228 immersed in liquid nitrogen (-196 °C). This procedure concentrates and stabilizes the analytes for their further
229 sequential desorption by heating the column for 6 min up to 300 °C. Thermodesorption efficiency was controlled
230 by carrying out two consecutive analyses of the activated charcoal trap. Volatile species quantification was
231 performed by external calibration. Analyses of purge blanks were done to estimate the efficiency of the sample
232 treatment procedure. Three selenium species (dimethylselenide (DMSe), dimethylselenide sulphide (DMSeS) and

233 dimethyldiselenide (DMDS_e) were detected with limit of detection of 0.1-0.5 pg Se L⁻¹. Total dissolved volatile
234 Se (TVSe) was calculated as the sum of detected species.

235 **2.5.3. Volatilization fluxes estimation**

236 The volatile emission fluxes across the air-water interface were calculated using an adapted version of the lake gas
237 exchange equation from Cole and Caraco (1998) using the total volatile Se data (TVSe; Table SI 5) from
238 sub-surface samples (1m depth). The model was originally used to estimate the gas transfer velocity of CO₂ as
239 function of wind speed. In our case the adaptation consisted in using the atmospheric data of DMSe and
240 calculations were carried out using weak wind speed (3 m s⁻¹) and strong wind speed (10 m s⁻¹). The same model
241 adaptation has been used previously for the same purpose (Lanceleur et al. 2019; Tessier et al. 2002).

242 **2.6. Stock and calculation of depth integrated Se concentration**

243 The stock of total Se or Se compounds per unit area of lake surface was calculated by weighting the measured
244 concentration at each depth by the respective part of the water column it represented, following Eq(1) :

$$245 \quad (1) \quad Se_{\text{stock}} \text{ (ng or } \mu\text{g Se m}^{-2}\text{)} = \sum \frac{C_i + C_{i+1}}{2} \times (h_{i+1} - h_i)$$

246 where $i = 1, \dots, 12$ the number of the depth level; h_i = depth in meters of the i -th level; C_i = selenium concentration
247 of the i -th level (pg L⁻¹ for volatile Se; ng L⁻¹ for non-volatile Se).

248 Depth-integrated average Se concentration ([Se]_{dia}) was then calculated by dividing Se_{stock} for a considered vertical
249 layer depth by the corresponding integration depth (Eq(2)). Depth-integrated average value gives a representative
250 value of average Se concentration considering entire or given water column depth allowing to take into account
251 interseasonal depth variability which is necessary for interseasonal comparisons.

$$252 \quad (2) \quad [\text{Se}]_{\text{dia}} \text{ (pg or ng Se L}^{-1}\text{)} = \frac{Se_{\text{stock}}}{h}$$

253 Depth-integrated average values were also calculated for the physico-chemical (T, pH, turbidity, dissolved oxygen
254 and conductivity) and biological parameters (chlorophyll a, primary production, phytoplankton taxa).

255 Stocks and depth-integrated average concentrations were calculated considering either the entire depth of the water
256 column (0-35 m) or epilimnion (0-10 m) or hypolimnion (25-35 m) except for primary production (PP) and
257 chlorophyll (Chl-a) data obtained from LKDB that were integrated from the surface to 15 m depth regardless of
258 thermocline depth.

259 Oxygen saturation ratio (% Ox. Sat.) was calculated by dividing the measured dissolved oxygen concentration
260 (DO) by the theoretical concentration at 100% saturation for the corresponding temperature (Mortimer 1981).

261

262 2.7. Statistical analysis

263 Statistical analyses were performed to compare seasonal and interannual selenium concentration variations.
264 Shapiro–Wilk normality test was applied to average concentrations. Results show that non-volatile dissolved Se
265 concentrations were normally distributed while volatile Se and biological data were not. A Student’s t-test was
266 then used to compare non-volatile Se species concentrations and, Mann-Whitney (MW) test was performed to
267 compare non-volatile Se values with other data sets, i.e. volatile Se and biological parameters. Pearson’s
268 correlation was used for linear regression analysis. All tests were conducted at a confidence level of 95% using
269 Origin8 (OriginLab Corporation).

270 3. Results and discussion

271 3.1. Seasonal and annual variabilities of hydrobiological characteristics in the water column

272 The seasonal variations of Se are inherent to the water column characteristics and changes during the year. Here
273 we describe the main dynamics of the lake in stratified (late spring – fall) and non-stratified periods (winter – early
274 spring) with special focus on Chlorophyll *a* (Chl-*a*) and primary productivity (PP), conductivity, temperature, pH,
275 turbidity and oxygen saturation.

276 *Physicochemical parameters (T, conductivity, pH & dissolved oxygen)*

277 Epilimnetic temperature gradually increased from around 15 – 16 °C in winter to ~30 °C in September each year
278 (Fig. SI 2, Tables SI 1 and SI 3). Hypolimnetic temperatures remained relatively stable for the three years studied
279 (~16 °C). At spring periods, lake surface water had higher pH and was oxygen-supersaturated due to the increase
280 of PP and weak winds that limit water-air gas exchange (Fig. 2, Fig. 3, Fig. SI 3 and Table SI 3). After the spring,
281 epilimnetic dissolved oxygen levels remained around 100% saturation (Fig. 3). Oxygen level decreased
282 progressively as stratification developed in the hypolimnion that became anoxic by June. This situation was
283 maintained until December or January as previously reported (Berman et al. 2014a). Conductivity values increased
284 during the period monitored (Table 1) from 1235 in April 2015 to 1376 $\mu\text{S cm}^{-1}$ in November 2017, representing
285 an increase in salinity, as a result of declining inflows but continued inflow of saline springs during those draught
286 years.

287 *Chlorophyll a and Primary Productivity*

288 Chl-*a* maximum values were observed during January and February in 2015 (450 mg m^{-2}) and 2016 (378 mg m^{-2}),
289 with another peak in May of both years (Fig. 2a). In 2017 the early year peak was missing, a spring peak was
290 noticed, and an unusual peak, the highest value of the year, was observed in November (451 mg m^{-2}) (Fig. 2a).
291 Statistically, 1-tail Mann-Whitney test did not show interannual significant variations ($P < 0.05$). Previous studies

292 reported a typical annual pattern with maximum values of Chl-*a* in spring (Yacobi et al. 2014). This annual pattern
293 continues to be typical of high rainfall years with *Peridinium* blooms, but in drought years, different patterns were
294 reported (Zohary et al. 2012).

295 In contrast to Chl-*a*, primary productivity followed similar annual patterns for the 3 years studied (Fig. 2a). Annual
296 minimum values occurred around the time of overturn, late December or early January, followed by a sharp
297 increase in the following weeks. It then remained high (with fluctuations) until the end of summer, declining again
298 to the December minimum values. Despite interannual similarities, the annual average values increased from 1108
299 ± 340 mg C m⁻² day⁻¹ in 2015 to 1272 ± 526 and 1635 ± 530 mg C m⁻² day⁻¹ in 2016 and 2017 respectively.

300 In summary, the increase of major elements concentration in water due to evaporation increased the conductivity
301 as consequence of the dry period recorded during the 3 years studied. Under these conditions, Chl-*a* peaked earlier
302 than previously reported suggesting that the lake biological productivity was activated earlier. Figure 4 shows the
303 main phytoplankton species present in the water (0 – 15 m). Similar dynamics were observed for the three years.
304 At the beginning of stratification, dinophyta and chlorophyta increased and were predominant taxa. During late
305 summer and fall, bacillariophyta and cyanobacteria increased.

306 **3.2. Seasonal dynamics of selenium speciation in the entire water column (0–35 m)**

307 **3.2.1. Dissolved total Se and inorganic Se(IV) and Se(VI)**

308 During the three years studied, depth-integrated average total Se ($TSe_{\text{dia}(0-35\text{m})}$) concentration ranged from $103 \pm$
309 6 to 160 ± 18 ng Se L⁻¹ (Table 1) and showed an overall declining trend from April to the end of the year, each
310 year (Fig. 2b). An increase of T.Se for the entire depth-integrated concentration occurred between January and
311 April corresponding to the end of holomixis–beginning of stratification each year ($135 - 160$ ng Se L⁻¹), more
312 markedly in 2015 and 2017. From then and until the end of stratification these concentrations decreased by 18 to
313 27% to reach a minimum in September (2016) or November (2015, 2017) (Table 1).

314 Depth integrated average concentrations of Se(IV) in the water column ranged from 14 ± 3 to 42 ± 3 ng Se L⁻¹
315 during the 2015-2017 period with an exceptional low value of 6 ± 1 ng Se L⁻¹ in September 2017 (Fig. 2b, Table
316 1). The t-tests do not show significant differences among selenite seasonal concentrations integrating the entire
317 depth of the water column. Although no statistically significant differences were found, $[Se(IV)]_{\text{dia}(0-35\text{m})}$ increased
318 during stratification in 2015, by 80% from April to September (Fig. 2b), whereas in 2016-2017, during the same
319 period Se(IV) exhibited opposite trend with 67-84% decrease.

320 The seasonal pattern for Se(VI) was similar to the one of Se(IV) described above (Fig. 2b). Higher average
321 concentrations values were found in April, followed by 50-60% decrease in September and November. Statistically
322 significant differences were found, comparing seasonal $\text{Se(VI)}_{\text{dia (0-35m)}}$ ca. April > January (1-tail t-test: $t= 5.7$,
323 $P<0.003$) \approx November ($t=6.1$, $P<0.002$) \approx September ($t= 8.4$, $P<0.001$).

324 3.2.2. Dissolved reduced Se species

325 Reduced Se depth-integrated average (0 – 35 m) concentrations ranged from 57 ± 9 to 91 ± 14 ng L⁻¹ (Fig. 2b,
326 Table 1). No interannual significant differences were statistically found. Seasonal Red.Se concentration only
327 proved to be statistically higher in September than in November ($t=3.1$, $P<0.02$). However, a more detailed view
328 of $\text{Red.Se}_{\text{dia (0-35m)}}$ showed relatively stable concentrations of Red.Se in 2015 with a decrease in November
329 compared to other seasons. In 2016, January showed the highest annual Red.Se concentration (Table 1), it
330 decreased in April (57 ± 9 ng Se L⁻¹) and increased again in September (74 ± 6 ng Se L⁻¹). From November to
331 April of 2017, concentrations were between 62 – 68 ng Se L⁻¹ and increased in September to 87 ± 6 ng Se L⁻¹
332 with a subsequent decrease in November to 70 ± 6 ng Se L⁻¹. Additionally, depth profiles for Red.Se (Fig. 3 and
333 Fig. SI 4) show its predominance in the hypolimnion during anoxic periods.

334 A Se-containing compound whose retention time did not match any of the organic Se standards available was
335 detected ubiquitously during the three years studied except in January 2015. This compound that is referred to here
336 as Org.Se showed a repeated trend each year with lower values occurring in January and increased concentrations
337 in spring and fall. Concentrations of $\text{Org.Se}_{\text{dia (0-35m)}}$ were in the range of $<\text{LoD} - 21 \pm 5$ ng Se L⁻¹ in January
338 while the concentration of other seasons was between 12 ± 2 to 52 ± 4 ng Se L⁻¹ (Table 1). Despite the differences
339 were not statistically significant, the trend observed indicates an increase during (late) spring and summer that
340 occurred mainly at epilimnion. A strong correlation was observed between Chl-a and Org.Se concentrations in
341 spring for the three years studied (Fig. SI 5, R² values between 0.946 and 0.983 ($P<0.01$)). It is worth noting that
342 during spring, dinophyta and chlorophyta were dominant species. No evidence of correlation was found in other
343 seasons.

344 As suggested by Nishri et al. (1999) increase of total selenium during winter seems to be associated with the
345 oxidation of reduced Se species to Se(IV) and Se(VI). This seems to be a common process for water column and
346 for the sediments as the deepening of the thermocline reached oxygen depleted zones. In addition, Se(VI) or
347 Se(IV)+Se(VI) decrease coincided with an increase of Org.Se and/or Red.Se pool (Fig. 2b). The variation of
348 Org.Se seems to be associated in parallel with phytoplankton growth, increased concentrations being observed
349 during spring or summer when phytoplankton primary production rates are high. However, in 2016, lower Chl-a

350 concentrations (that may result from lower amount of dynophyta (Fig. 4)) compared to other years resulted in a
351 higher slope of the regression Org.Se vs Chl-a (Fig. SI 5). This could be caused by different assimilation,
352 production and release Se rates of the different species, and could indicate that dynophyta would not be the main
353 producer in the lake nowadays.

354 The behavior of Red.Se pool is somehow different; it accounted between 40-60% of total selenium during
355 holomixis period until April. From April to the end of stratification, as oxyanions concentration decreased, this
356 fraction became the main component of T.Se, representing about 80% under anoxic conditions at hypolimnion
357 (25-35 m depth). Selenate and selenite reduction in the hypolimnion is most probably due to oxygen deficient
358 conditions as long as stratification evolves. The trends observed indicates an inversely proportional relation
359 between Red.Se fraction and Se(IV) ($R = -0.497$, $P < 0.01$) during the three years of this study.

360 Comparing our results to those published for other lakes (Table 2), similar ranges of concentrations for T.Se,
361 Se(IV) and Se(VI) were obtained, as long as we exclude lakes impacted by mining activities. Notably, despite the
362 physical variations in the Hula Basin, in the drainage basin of Lake Kinneret (Fig. 1) and almost 20 years after the
363 study of Nishri et al. (1999) the T.Se concentration remained very similar. However, while total Se lake reservoir
364 remains the same, Se species distribution has changed. The range of total selenium and Se(IV) measured in our
365 study (2015-2017 period) was similar to that reported by Nishri et al. (1999) for the period 1993-1995. In those
366 years T.Se values oscillated in the range of 50 - 184 ng Se L⁻¹, Se (IV) between <5 to 78 ng Se L⁻¹ (Table 2) and
367 Se(VI) ranged between 31 - 103 ng Se L⁻¹, slightly higher than in the present work. Likewise, the concentration
368 range of the Red.Se oscillated between <5 - 50 ng Se L⁻¹ in the first half of the 90's, while it was three times
369 higher in the present work (Table 2).

370 3.2.3. Volatile dissolved selenium

371 Depth integrated total volatile Se concentrations ranged from 12 ± 1 to 755 ± 38 pg Se L⁻¹, and was higher in late
372 summer and fall (Table 3) than in winter-spring seasons, especially at epilimnetic depths close to thermocline (Fig.
373 3 and Fig. SI 4, Table SI 1). Concentrations of TVSe_{dia (0-35m)} oscillated between 12 ± 1 and 149 ± 7 pg Se L⁻¹
374 during winter-spring seasons; while in summer-fall the concentrations were between 88 ± 4 and 755 ± 38 pg L⁻¹
375 (Table 3). Three volatile Se compounds were identified in the water column: dimethyl diselenide (DMDS_{Se}) and
376 the mixed S-Se compound dimethyl selenide sulphide (DMSeS) as the dominant species and, DMSe in lower
377 concentration except in Sep 2016. In brief, during stable thermal stratification DMSe_{dia (0-35m)} ranged from 31 ± 2
378 to 198 ± 10 pg Se L⁻¹ (30% of TVSe in average), DMSeS_{dia (0-35m)} from 30 ± 2 to 343 ± 7 pg Se L⁻¹ (36% of
379 TVSe) and DMDS_{dia (0-35m)} from 16 ± 2 to 246 ± 6 pg Se L⁻¹ (32% of TVSe) (Table 3). In contrast, concentration

380 during holomixis was usually close or below the detection limit ($<0.5 \text{ pg Se L}^{-1}$). During winter and spring seasons
381 $\text{DMSe}_{\text{dia (0-35m)}}$ range was $10 \pm 1 - 45 \pm 2 \text{ pg Se L}^{-1}$, $\text{DMSeS}_{\text{dia (0-35m)}} < \text{LoD} - 77 \pm 2$ and $\text{DMDS}_{\text{dia (0-35m)}} < \text{LoD}$
382 $- 27 \pm 2 \text{ pg Se L}^{-1}$ (Table 3).

383 Only few studies reported volatile Se measurement values in similar environments (Table 2). Compiled data
384 include Se impacted lakes affected by mining activities or containing large geogenic sulfate and inorganic Se
385 enrichments (Diaz et al. 2009; Domagalski et al. 1989). To the best of our knowledge, only Lancelleur et al. (2019)
386 reported TVSe concentrations in non-polluted freshwater lakes, and these are one order of magnitude lower than
387 in the present study. For further comparison, measurements of volatile Se compounds in European estuaries surface
388 waters (Tessier et al. 2002; Amouroux and Donard 1997) are reported in Table 2. The production of volatile Se
389 compounds has been found to be inherent to the biodegradation of organic matter in estuarine environments
390 (Amouroux and Donard 1997; Tessier et al. 2002). Despite the differences between tidal estuaries and the
391 freshwater lake in our study, TVSe in Lake Kinneret is in the same range of concentrations measured in 3 estuaries
392 (Gironde: $22 - 1350 \text{ pg Se L}^{-1}$, Rhine: $37 - 2423 \text{ pg Se L}^{-1}$, Scheldt $51 - 8067 \text{ pg Se L}^{-1}$) (Amouroux and Donard
393 1997; Tessier et al. 2002). There are however, some differences in the speciation of volatile Se compounds. In
394 estuaries, DMSe was the main compound while DMSeS and DMDS were frequently detected but were residual
395 in comparison to DMSe. We observed, in Lake Kinneret, the opposite with DMDS and DMSeS the dominant
396 species, whereas DMSe was usually detected in lower amounts. Vriens et al. (2016) observed that DMDS was
397 produced 3.5 and 10 times more than DMSe when exposing the chlorophyte *Chlamydomonas reinhardtii* to selenate
398 and selenite respectively. They suggested that under high Se concentration, DMDS containing two Se atoms
399 would be a more efficient detoxification product as it happens in hyperaccumulator plants (Pilon-Smits and Quinn
400 2010). In a more recent study, Luxem et al. (2017) showed that a mixed culture of algae and bacteria exposed to
401 Se(IV) produced greater concentration of volatile Se than the algae alone. In Lake Kinneret, both selenite and
402 selenate are present, therefore both could be assimilated by algae.

403 3.3. Selenium compounds biogeochemistry along with water column stratification

404 3.3.1. Epilimnetic selenium (0 – 10 m)

405 During winter-spring periods, relatively homogeneous profiles were observed in the water column compared to
406 stratified periods (Fig. 3, Fig. SI 4 and Table SI 1). Nishri et al. (1999) obtained similar vertical profiles in the 90's
407 when holomixis exposed sediments to oxidizing conditions. In September, T.Se concentration decreased with
408 respect to April with marked minimum (around minus 30-35% compared to 1 m depth) in the thermocline region.

409 Total dissolved Se regeneration occurred together with holomixis in January. Se(IV) and Se(VI) concentrations
410 also increased from fall to winter however in 2016, Se(IV) regeneration was observed later on.

411 Org.Se depth-integrated average (0 – 10m) concentrations in winter-spring were between <LoD and $27 \pm 2 \text{ ng L}^{-1}$
412 except in 2016 where they reached $55 \pm 1 \text{ ng L}^{-1}$, similar to the maximum values found in late summer (and fall
413 of 2017) that were between 62 ± 10 and $67 \pm 7 \text{ ng L}^{-1}$. Org.Se values in fall of 2015 and 2016 decreased to
414 approximately half of those observed in summer. The production of Org.Se increased after a Chl-a maximum at
415 late winter or early spring. Org.Se appeared together or just before the maximum PP of the corresponding year
416 (Fig. 2).

417 In general, the maximum accumulation of volatile Se was detected between 10-15 m matching with thermocline
418 depth. The maximum production of volatile Se in this region coincided with maximum turbidity values (Table SI
419 3). In estuarine systems high turbidity zones, associated with an intense heterotrophic activity leading to organic
420 matter degradation, consequently produced significant amounts of volatile Se compounds (Amouroux and Donard
421 1997; Lanceleur et al. 2019; Tessier et al. 2002). An estimation of the volatilization flux from Lake Kinneret was
422 made resulting in annual emissions of TVSe between 6.5 and 9.6 kg Se year⁻¹. Compared to the annual T.Se input,
423 ~110 kg Se yr⁻¹ in the 90's from Nishri et al. (1999), volatilization can account as a significant Se removal pathway
424 in lake Kinneret. This reasonable estimation only provides an order of magnitude of Se effluxes but is associated
425 to large uncertainties inherent to our limited dataset and water-air exchange modelling.

426 Luxem et al. (2017) observed that marine bacteria contributed significantly to the algal production of volatile Se.
427 The data presented here revealed a direct link between metalimnion biological turnover and the production of
428 volatile species. The decrease of Org.Se concentration may not only be due to dilution but partially caused by the
429 abiotic decomposition of the dissolved Org.Se. The mechanisms for these processes remains unclear. The lack of
430 data for Se forces the comparison with sulfur. Hu et al. (2007) observed in a monomictic lake that dimethyl sulfide
431 (DMS) showed its maximum at the interface between oxic/anoxic layers. In addition, previous studies on Lake
432 Kinneret reported the production of DMS in the metalimnion and suggested that *Peridinium gatunense* produced
433 DMDS and oligosulfides, in particular dimethylsulfopropionate (DMSP), the precursor of DMS in natural waters
434 (Ginzburg et al. 1998; Ginzburg et al. 1999; Knossow et al. 2015; Sela-Adler et al. 2016). We suggest that the
435 similarities between sulfur and selenium, allow assuming that phytoplankton and bacteria responsible for organic
436 matter degradation, produce not only DMSP but also selenium compounds during high productive seasons as
437 suggested previously (Cooke and Bruland 1987; Amouroux et al. 2000). Although further molecular identification
438 is required, such precursor of volatile Se compounds could presumably correspond to the Org.Se compound

439 detected in this study. Cyanobacteria (quantified as cyanophyta) and bacillariophyta are the main species present
440 between September and November (Fig. 3). In cyanophyte cultures in agricultural drainage waters, the production
441 of volatile Se from oxyanions has been demonstrated (Fan et al. 1998). The precursors ($\text{CH}_3\text{-Se-Met}$ and $\text{CH}_3\text{-Se-}$
442 Cys) were also characterized by Fan et al. (1998). Some of these precursors could be composing the Red.Se fraction
443 and potentially the Org.Se detected and could eventually be converted to the corresponding volatile Se compounds
444 detected in this study (Amouroux et al. 2000). Therefore, the key processes occurring in the epilimnion are the
445 production of organically bound Se as a function of plankton dynamics and its further depletion associated with
446 dilution and conversion into volatile species during late summer and fall. The presence of organic matter degrading
447 bacteria and the subsequent production of volatile species could be an important removal pathway of dissolved Se
448 to the atmosphere.

449 **3.3.2. Hypolimnetic selenium (25 – 35 m)**

450 During late stratification, hypolimnetic concentration of T.Se decreased compared to winter-spring period (Table
451 SI 2). In addition, a sharp depletion of oxyanions was observed in September, especially for Se(VI) but also for
452 Se(IV) in 2016 and 2017. According to Winkel et al. (2012), the reduction of dissolved Se oxyanions to Se(0) is
453 mediated by microbial reduction processes and represents an efficient removal pathway for dissolved Se in anoxic
454 waters. In Lake Kinneret, the sulfate reducing bacteria are, most probably, the Se(VI) reducing organisms
455 (Oremland et al. 1989). In fact, when oxygen and SO_4^{2-} are consumed in late summer (Fig. SI 2), there is a
456 depletion of total Se and selenate. As suggested by Nancharaiah and Lens (2015), Se-respiring bacteria can use
457 selenate and selenite as electron acceptors and reduce these species to insoluble elemental selenium via
458 dissimilatory reduction under anaerobic conditions.

459 In late summer, a maximum of Se(IV) is observed below the thermocline (25 m depth), which rapidly decreases
460 at a greater depth (Fig. 3 and Fig. SI 4). It is possible that selenite observed in this region is related to organic
461 matter degradation and that selenite disappearance at greater depths is a consequence of i) a potential complexation
462 with dissolved or particulate organic matter (McNeal and Balistrieri 1989) or ii) its reduction due to anoxic
463 conditions.

464 Organic Se concentrations were lower at hypolimnion compared to epilimnion during the study (1-tail t-test:
465 $t=2.95$, $P<0.01$). The difference of Org.Se concentration between epilimnion and hypolimnion was greater during
466 stratification, with average epilimnetic concentration of $64 \pm 2 \text{ ng Se L}^{-1}$ versus $16 \pm 7 \text{ Se L}^{-1}$ at hypolimnion in
467 September. At April and November hypolimnetic Org.Se_{dia (25 – 35m)} concentration was the half compared to the
468 same period for epilimnion. We suggest that the residual concentrations of Org.Se in the hypolimnion may have

469 their origin at epilimnion where Org.Se is produced. Red.Se concentration in the hypolimnion increased in summer
470 and subsequently decreased in fall because of the thermocline deepening and the dilution effect in the water
471 column. T.Se concentration decreased with time during this study. The presence of Fe, Al and Mn (Hadas and
472 Pinkas 1995; Shaked et al. 2004) among other metals in the waters and sediments, suggests the scavenging of
473 insoluble reduced Se into sediments as a key process for Se sink in Lake Kinneret, as it happens in Canadian
474 thermokarst ponds (Lanceleur et al. 2019) and Siberian lakes (Pokrovsky et al. 2018). In addition, the presence of
475 Red.Se during holomixis periods (around 40-60% of total selenium) suggests that reduced Se is not completely
476 recycled (i.e. oxidized) every year.

477 Hypolimnetic TVSe production is limited. Low production extent has been observed during spring at 35 m, in the
478 water-sediment interface (Fig. 3). In September 2016 and November 2017 some production or accumulation was
479 observed as well close to the water-sediment interface (Fig. 3 and Fig. SI 4), although, the maximum concentration
480 of volatile species was detected close to the thermocline as described previously. Volatile Se production near the
481 sediments may be due to microbial production at this location linked to organic matter degradation as observed in
482 heterotrophic and reducing waters of upper European estuaries (Tessier et al. 2002) or in permafrost lakes
483 (Lanceleur et al. 2019). In our study, the mixed Se-S compounds (DMS₂Se and DMDSe) were the dominant species.
484 In the literature, it is common to find DMSe as the dominant component of TVSe. Nevertheless, studies carried
485 out at Gironde estuary (France) and Mediterranean Sea showed a significant concentration of DMDSe (Amouroux
486 and Donard 1997; Amouroux et al. 2001). Laboratory experiments using synthetic sea water and selenoamino
487 acids as the main precursors over inorganic Se species, demonstrated that DMSe, DMS₂Se and DMDSe were
488 produced under light and dark conditions (Amouroux et al. 2000). The same study suggested that the production
489 of DMSe would have a specific precursor, most probably a dimethylselenonium compound. The authors suggested
490 that the production of DMS₂Se and DMDSe would be the result of abiotic reactions in the presence of seleno-
491 methionine in the extracellular medium. Thereby, the presence of DMS₂Se in Lake Kinneret seems to be the
492 consequence of having organically bounded Se species (i.e. precursors) and sub-millimolar concentrations of
493 sulfides in the water and H₂S accumulation at hypolimnion (Ginzburg et al. 1999; Knossow et al. 2015).

494 The thermocline zone presented the highest levels of turbidity (Table SI 3) of the water column, presumably due
495 to the presence of dead particulate organic matter (detritus) and the presence of bacteria, which is also enriched in
496 Se. Stability studies have shown that at depths close to thermocline (~20-25m) DMSe concentrations are higher
497 after stocking the samples more than 15 days, which may explain the predominance of DMSe of Sep 2016 samples.

498 In summary, hypolimnetic anoxia developed during stratification and caused mostly by microbial oxygen
499 respiration. Such anoxia affected considerably selenium distribution, causing the complete reduction of Se(VI) to
500 reduced Se species and, partial reduction of Se(IV) with end product as Se(0). Elemental Se can remain in
501 suspension in the colloidal form for a certain period of time (Buchs et al. 2013). However, due to organic matter
502 or other particulates, Se(0) colloids will form aggregates and settle to the sediments, a process that is an important
503 sink for Se. The higher concentration of Red.Se pool compared to previous studies (Nishri et al. 1999) may be due
504 to an extended period of reducing conditions at hypolimnion. The decrease of T.Se could be a consequence of the
505 partial but not total Se re-oxidation during holomixis periods as it happened in the lake two decades ago.

506 **4. Biogeochemical implication**

507 During the 3 years of this study, the lake dynamics were the main driver for Se speciation fluctuations. Figure 5
508 provides a schematic overview of observed Se biogeochemical cycle in Lake Kinneret. Considering the increase
509 of conductivity and decrease in total lake volume over the study period, an increase of T.Se would be expected.
510 However, the decrease of dissolved T.Se indicates either the loss of Se by sinking into the sediments or by high
511 rates of volatilization and emission to the atmosphere. The annual pattern for Se oxyanions is similar to the one
512 previously observed by Nishri et al. (1999). However, selenate concentration is not as high as reported by these
513 authors. Additionally, Red.Se concentration is tripled nowadays, suggesting either that natural conditions have
514 changed or that this is related to differences of method performance. Questions such as the potential instability of
515 some compounds was not investigated previously, therefore we cannot completely discard a difference between
516 both methods. However, if natural conditions are responsible for the change, we suggest that more reducing
517 conditions in the hypolimnion during stratified periods, especially in low water level drought years, are the main
518 mechanism responsible for higher levels of Red.Se.

519 For the first time, epilimnetic production of organic Se compound(s) (potentially an organoselenium metabolite
520 or methylated Se-amino acid form to be identified) could be statistically correlated with Chl-a (Fig. SI 5) and
521 related to specific phytoplankton taxa. Our *in situ* observations suggest that Org.Se is directly released to the water
522 by phytoplankton, probably by the main species: Dinophyta (*Peridinium gatunense*) and Cyanobacteria
523 (*Aphanizomenon ovalisporum* and *Cylindrospermopsis raciborskii*) (Zohary 2004; Zohary et al. 2014b); but also
524 with a lesser contribution of minor phytoplankton species in the lake. Once released, Org.Se may be either uptaken
525 by bacteria present close to metalimnion, or abiotically transformed into volatile compounds close to the surface
526 (Fig. 5). Photo-degradation may enhance Org.Se decomposition, but also volatile Se compounds degradation.
527 Org.Se could also undergo fast uptake by bacteria associated with the production of volatile Se that has been

528 observed with higher rates close to the metalimnion. Our calculated estimates indicate that the production of
529 volatile Se close to the surface and emission to the atmosphere can be a significant pathway for selenium removal
530 from the lake that was not considered in previous studies.

531 The increase of turbidity in September and November near the thermocline zone is an indicator of higher solid
532 particulate matter, which also includes, dead organic matter sinking through the water column. The maximum
533 production of TVSe close to metalimnion coincides each year with the end of summer and the increase of turbidity
534 at metalimnion; therefore, we suggest that volatile Se formation is strongly related to the microbial turnover in the
535 water column. In Lake Kinneret, the presence of sub-millimolar concentrations of sulfur explains the high extent
536 of DMSeS versus DMDSe and DMSe, in contrast with studies in other environments with lesser prevalence of
537 sulfur (Table 2).

538 Our data demonstrates that Org.Se production happens primarily in the epilimnion, while the reduction of selenate
539 to elemental Se or other reduced species is a key process in the anoxic hypolimnion. The intense activity of sulfate
540 reducing bacteria during anoxic hypolimnetic periods (Berman et al. 2014b) contributes to the reduction of Se
541 oxyanions. Therefore, reduced species predominantly insoluble, such as elemental Se(0), can be scavenged and
542 sink to sediments. This is probably the major process removing Se from the hypolimnion. The higher
543 concentrations of Red.Se pool compared with previous studies together with the T.Se concentration decrease
544 observed during this work probably indicate more reducing conditions in the hypolimnion of the lake during
545 drought years with low water levels. The deepening of the thermocline occurring in fall transports nutrients and
546 Se from hypolimnion to epilimnion. The sinking of Se into the sediments is then followed by incomplete
547 regeneration during holomixis.

548 In conclusion, after observing a decrease of total Se during this study, and the non-negligible increase of Red.Se
549 compared to the results of Nishri et al. (1999), such biogeochemical scenario may be of increasing importance
550 under dryer hydrological and warming climatic conditions in the near future. Lakes located in semi-arid regions
551 like Lake Kinneret will most probably suffer a decrease of water inflow and elevated impacts of human activities
552 nearby. Additionally, climate change will most probably affect not only algal blooms but also water temperature,
553 and could have an impact on stratification, nutrients availability and redox conditions, and phytoplankton
554 population. So, the evolution of total Se and Se speciation will potentially be subjected to changes in the next
555 years.

556

557 **5. Bibliography**

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770

771 **Figure captions**

772 **Figure 1.** Satellite images of Lake Kinneret (right) and its location in Israel (left). St. A indicates the sampling
773 point located at the centre of the lake. Additional samples were collected at two sites (yellow dots) along the Jordan
774 River, at Joseph Bridge and Huri Bridge, located north and south of the Hula Valley (respectively).

775 **Figure 2.** Temporal variations in various limnological parameters in Lake Kinneret during 2015-2017: a)
776 chlorophyll-a (Chl-a), and primary production (PP) stocks (0-15 m depth) ; b, c) stocks and depth-integrated
777 concentrations for total selenium and selenium species (0-35 m). Vertical red-shaded rectangles indicate holomixis
778 periods. Figure 2b includes: Total Se (T.Se), selenite (Se(IV)), selenate (Se(VI)), estimated organic (Org.Se) and
779 reduced Se (Red.Se). Figure 2c includes: total volatile Se (TVSe), dimethylselenide (DMSe), dimethylselenide
780 sulphide (DMSeS) and dimethyldiselenide (DMDS). For more detail: Se data in Tables SI 4 and SI 5.

781 **Figure 3.** Depth profiles in Lake Kinneret in 2016: A) conductivity ($\mu\text{S cm}^{-1}$), temperature ($^{\circ}\text{C}$), pH and turbidity
782 (NTU), B) Chl-a ($\mu\text{g L}^{-1}$), PP ($\mu\text{g C L}^{-1} \text{ day}^{-1}$) and oxygen saturation (%), C) T.Se, Se(IV), Se(VI), Org.Se and
783 Red.Se in ng L^{-1} , D) TVSe, DMSe, DMSeS and DMDS in pg L^{-1} .

784 **Figure 4.** Temporal dynamics of depth-integrated (0-15 m) wet-weight biomass, in g m^{-2} , of the major
785 Phytoplankton taxa, (Dinophyta, Cyanobacteria, Bacillariophyta, Chlorophyta and Cryptophyta), 2015-2017.
786 Vertical pink-shaded rectangles correspond to holomixis periods. Source of data: Tamar Zohary, Lake Kinneret
787 database, Kinneret Limnological Laboratory, Israel Oceanographic & Limnological Research.

788 **Figure 5.** Schematic overview of Se biogeochemical cycle in Lake Kinneret. Abbreviations: selenate (Se(VI)),
789 selenite (Se(IV)), organic Se (Org.Se), reduced Se pool (Red.Se), dimethylselenide (DMSe), dimethyl selenide
790 sulphide (DMSeS) and dimethyl diselenide (DMDS). [†]Phytoplankton species are detailed Fig. 4 [‡]Dissolution
791 occurred mainly during holomixis period.

Biogeochemistry of Selenium compounds in the water column of warm monomictic Lake Kinneret

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Figure 1.

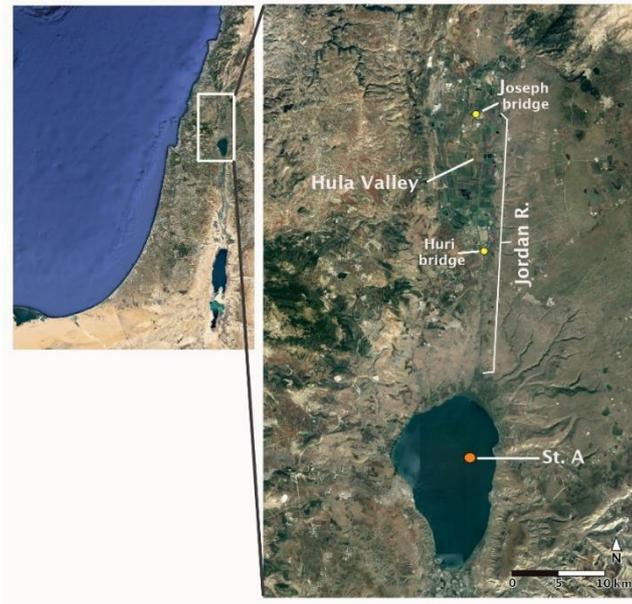


Figure 2.

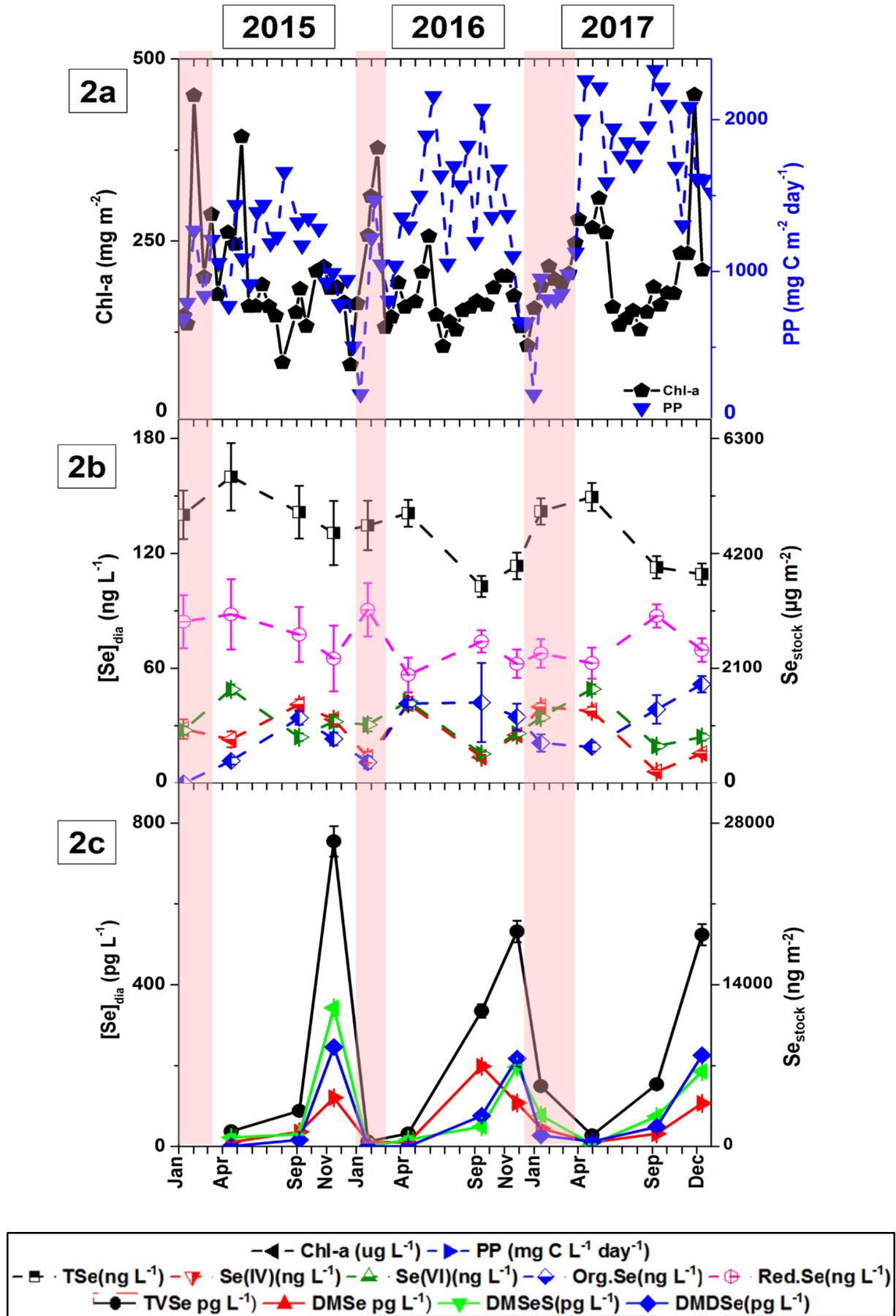


Figure 3.

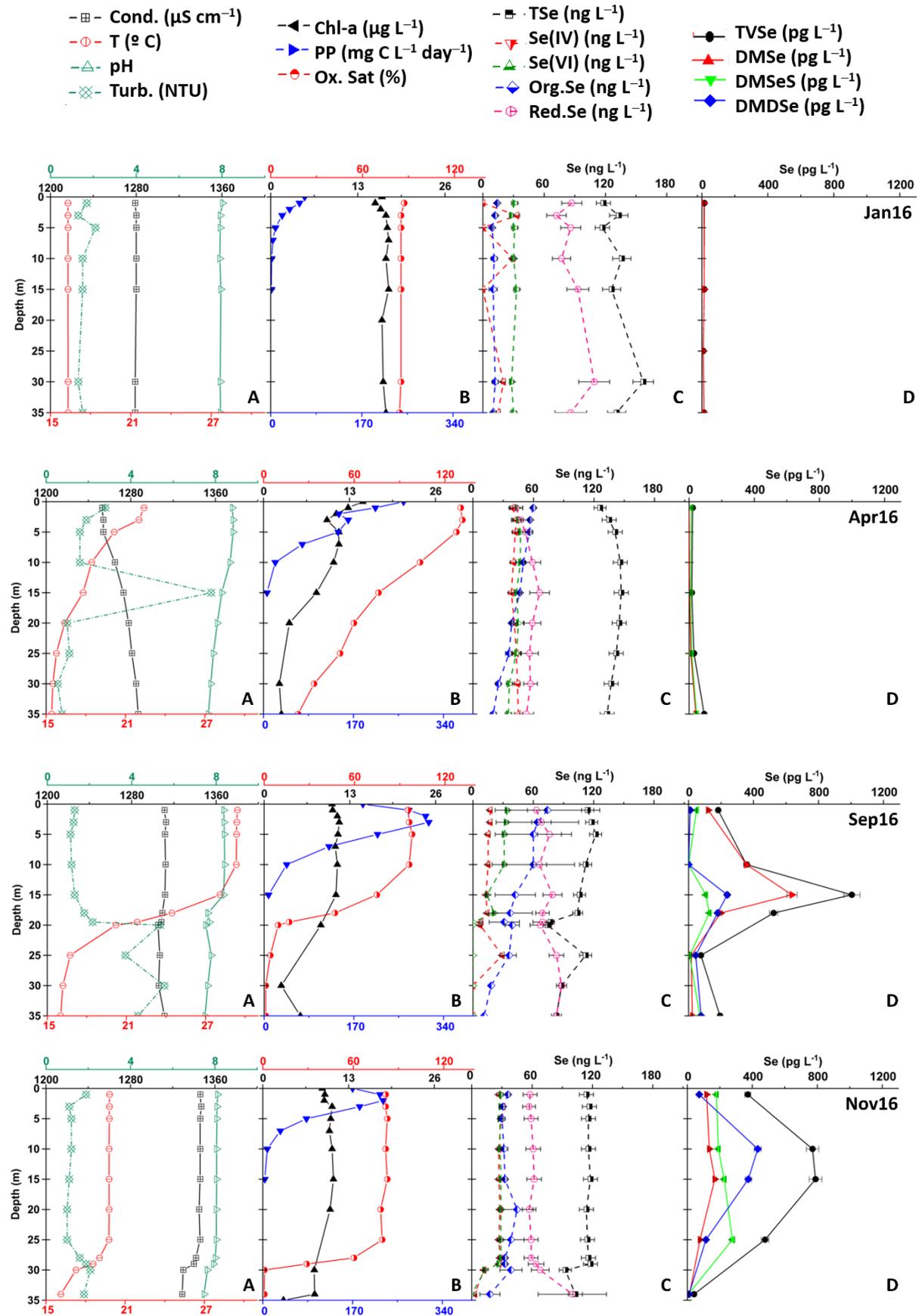


Figure 4.

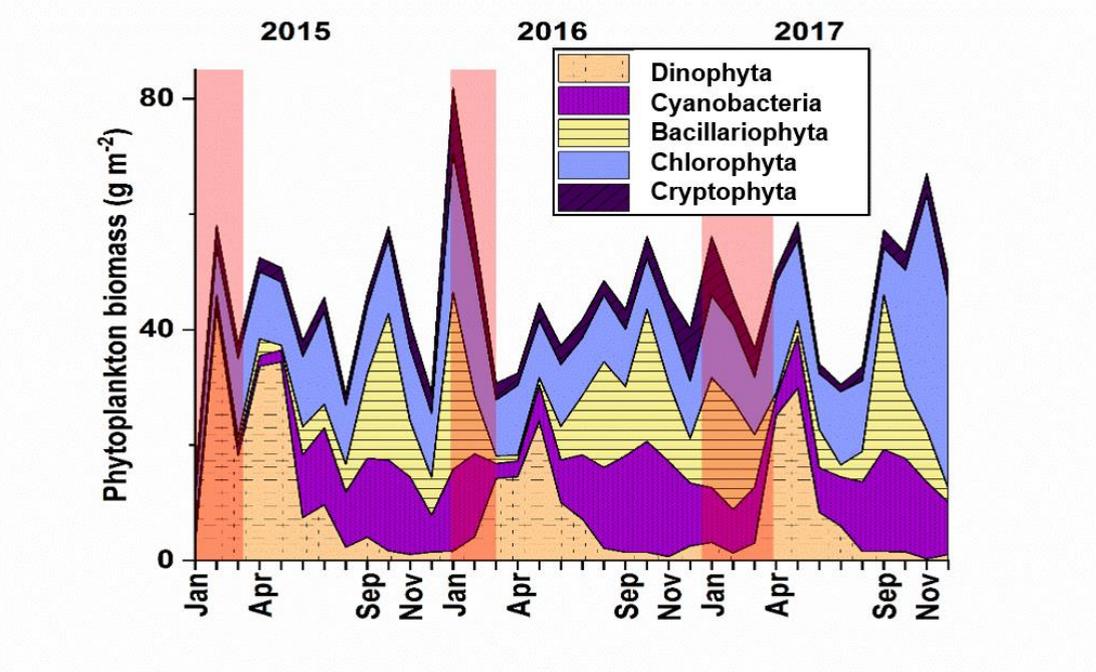
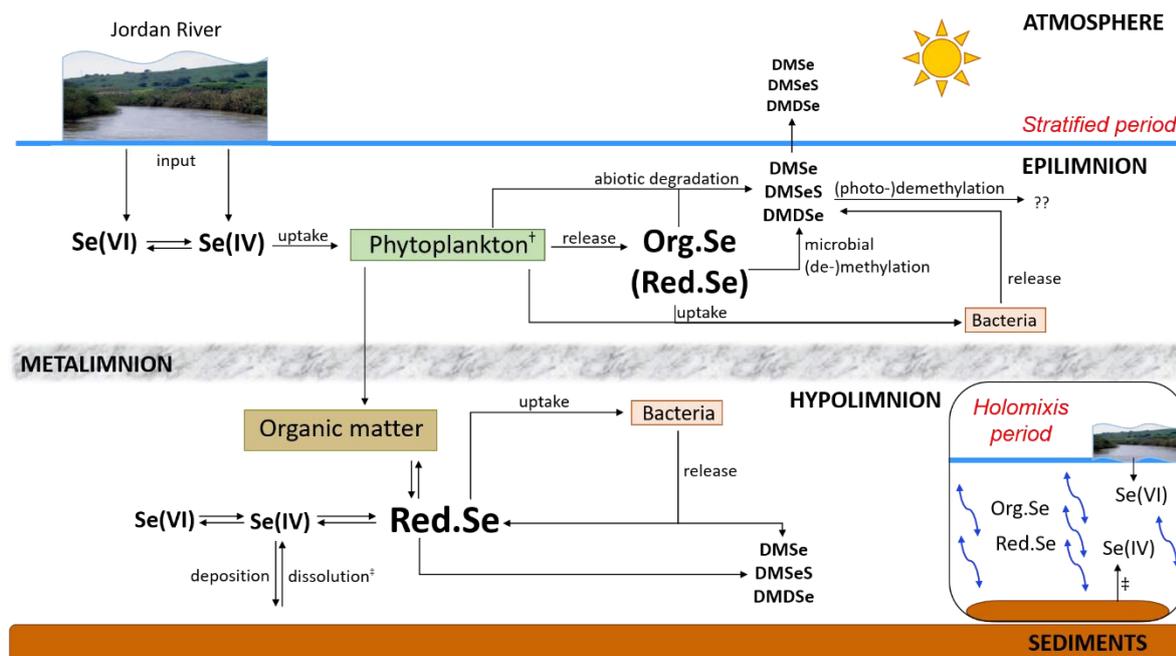


Figure 5.



Biogeochemistry of Selenium compounds in the water column of warm monomictic Lake Kinneret

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Table 1. Depth-integrated average concentrations (entire depth of the water column 0-35 m) for non-volatile and volatile dissolved Se (total dissolved Se (T.Se), Se(IV), Se(VI), organic Se (Org.Se) and reduced Se pool (Red.Se) in ng L⁻¹; total volatile Se (TVSe) in pg L⁻¹) and, for the main physicochemical parameters (monthly means if n>1): % of oxygen saturation (Ox. Sat), pH, temperature (T), conductivity (Cond.) and turbidity (Turb). For detailed data see Tables SI 3, SI 4 and SI 5. Confidence interval is indicated in brackets and in italics. Source of conductivity, temperature, pH, turbidity, oxygen saturation, Chl-a and PP data: Tamar Zohary and Yaron Be'ery-Shlevin, Lake Kinneret database, Kinneret Limnological Laboratory, Israel Oceanographic & Limnological Research. <LoD: below detection limit, n.d. means no data.

	Jan 15 11/01/15	Apr 15 19/04/15	Sep 15 06/09/15	Nov 15 16/11/15	Jan 16 25/01/16	Apr 16 17/04/16	Sep 16 15/09/16	Nov 16 27/11/16	Jan 17 15/01/17	Apr 17 30/04/17	Sep 17 10/09/17	Nov 17 12/12/17
T.Se (ng L ⁻¹)	140 (<i>13</i>)	160 (<i>18</i>)	141 (<i>14</i>)	131 (<i>17</i>)	135 (<i>13</i>)	141 (<i>7</i>)	103 (<i>6</i>)	113 (<i>7</i>)	142 (<i>7</i>)	149 (<i>7</i>)	113 (<i>6</i>)	109 (<i>6</i>)
Se(IV) (ng L ⁻¹)	28 (<i>5</i>)	23 (<i>4</i>)	41 (<i>3</i>)	33 (<i>2</i>)	14 (<i>3</i>)	42 (<i>3</i>)	14 (<i>1</i>)	25 (<i>2</i>)	40 (<i>2</i>)	38 (<i>2</i>)	6 (<i>1</i>)	16 (<i>1</i>)
Se(VI) (ng L ⁻¹)	28 (<i>2</i>)	49 (<i>3</i>)	24 (<i>2</i>)	32 (<i>3</i>)	31 (<i>3</i>)	43 (<i>4</i>)	15 (<i>1</i>)	26 (<i>2</i>)	34 (<i>2</i>)	49 (<i>2</i>)	19 (<i>1</i>)	24 (<i>2</i>)
Org.Se (ng L ⁻¹)	<LoD	12 (<i>2</i>)	34 (<i>4</i>)	23 (<i>3</i>)	11 (<i>3</i>)	42 (<i>2</i>)	42 (<i>21</i>)	35 (<i>7</i>)	21 (<i>5</i>)	19 (<i>2</i>)	39 (<i>7</i>)	52 (<i>4</i>)
Red.Se (ng L ⁻¹)	84 (<i>14</i>)	88 (<i>18</i>)	78 (<i>14</i>)	65 (<i>17</i>)	91 (<i>14</i>)	57 (<i>9</i>)	74 (<i>6</i>)	62 (<i>7</i>)	68 (<i>7</i>)	63 (<i>8</i>)	87 (<i>6</i>)	70 (<i>6</i>)
TVSe (pg L ⁻¹)	n.d.	37 (<i>2</i>)	88 (<i>4</i>)	755 (<i>38</i>)	12 (<i>1</i>)	32 (<i>2</i>)	335 (<i>17</i>)	532 (<i>27</i>)	149 (<i>7</i>)	28 (<i>1</i>)	154 (<i>8</i>)	524 (<i>26</i>)
O ₂ Sat (%)	85 (<i>9</i>)	63 (<i>5</i>)	43 (<i>6</i>)	57 (<i>4</i>)	76 (<i>9</i>)	63	47 (<i>4</i>)	59 (<i>7</i>)	88 (<i>5</i>)	87 (<i>1</i>)	37 (<i>5</i>)	53 (<i>9</i>)
pH	8.1 (<i>0.1</i>)	8.0 (<i>0.1</i>)	7.8 (<i>0.1</i>)	7.8 (<i>0.1</i>)	7.9 (<i>0.1</i>)	8.0 (<i>0.1</i>)	7.8 (<i>0.1</i>)	8.0 (<i>0.1</i>)	8.1 (<i>0.2</i>)	8.2 (<i>0.1</i>)	8.0 (<i>0.1</i>)	7.9 (<i>0.1</i>)
T (°C)	16.5 (<i>0.9</i>)	17.2 (<i>0.3</i>)	23.3 (<i>0.3</i>)	20.8 (<i>0.7</i>)	16.7 (<i>0.3</i>)	17.6	23.3 (<i>0.1</i>)	20.9 (<i>1.1</i>)	15.5 (<i>0.5</i>)	17.0 (<i>0.8</i>)	22.8 (<i>0.3</i>)	20.3 (<i>0.7</i>)
Cond (µS cm ⁻¹)	1259 (<i>5</i>)	1235 (<i>7</i>)	1248 (<i>5</i>)	1271 (<i>6</i>)	1280 (<i>3</i>)	1277 (<i>5</i>)	1310 (<i>3</i>)	1337 (<i>4</i>)	1335 (<i>6</i>)	1319 (<i>2</i>)	1357 (<i>3</i>)	1376 (<i>5</i>)
Turb (NTU)	2.0 (<i>1.7</i>)	1.3 (<i>0.2</i>)	1.9 (<i>1.1</i>)	1.4 (<i>0.3</i>)	1.6 (<i>0.6</i>)	1.5 (<i>0.6</i>)	2.5 (<i>0.7</i>)	1.9 (<i>0.6</i>)	1.7 (<i>0.4</i>)	2.4 (<i>0.3</i>)	3.7 (<i>1.7</i>)	3.8 (<i>2.1</i>)
Chl-a (µg L ⁻¹)	9.5 (<i>0.5</i>)	17 (<i>1</i>)	11 (<i>2</i>)	12.4 (<i>0.1</i>)	19 (<i>2</i>)	11	11.0 (<i>0.3</i>)	12 (<i>1</i>)	12 (<i>2</i>)	18.3 (<i>0.5</i>)	12 (<i>1</i>)	14
PP (µgC L ⁻¹ d ⁻¹)	49 (<i>5</i>)	74 (<i>31</i>)	84 (<i>8</i>)	59 (<i>10</i>)	64 (<i>45</i>)	86	114 (<i>34</i>)	59 (<i>20</i>)	57 (<i>5</i>)	149 (<i>2</i>)	144 (<i>5</i>)	74 (<i>39</i>)

Table 2. Bibliographic data for Se speciation in lake waters. Data for non-volatile Se speciation and T.Se are expressed in ng L⁻¹. TVSe is expressed in pg L⁻¹ and volatile speciation is given as a percentage of TVSe.

Site	T.Se ng Se L ⁻¹	Se(IV) ng Se L ⁻¹	Se(VI) ng Se L ⁻¹	Red. Se ng Se L ⁻¹	TVSe pg Se L ⁻¹	References
North America						
Great Salt Lake, USA	500				40-22,700	Diaz et al. (2009)
Mining area, Canada	35 - 3063	<21 - 1616	<21 - 918	<21 - 528		Ponton and Hare (2013)
Kuujuarapik, Canada	35 - 63				1 - 32	Lanceleur et al. (2019)
Europe						
Gola di Lago, Switzerland	500 - 1500				10,000	Vriens et al. (2014)
Belgium	<50 - 230	<40 - 150	<50 - 80			Cutter (1978)
Campus Lake, Belgium	230 ^a	150 ^a	80 ^a			Robberecht et al. (1983)
Artificial L., Germany	190	30	171			Tanzer and Heumann (1991)
Coal mining area, Germany	830	46	805			Tanzer and Heumann (1991)
Moorland L., Germany	210 - 240	27 - 141	35 - 47			Tanzer and Heumann (1991)
Valkea-Kotinenjärvi, Finland	58	4	5	37		Wang et al. (1994, 1995) Wang et al. (1994, 1995)
Iso-Hietajärvi L., Finland	34	4	4			Wang et al. (1995)
Pääjärvi L., Finland	143	10	17			Wang et al. (1995)
Pesosjärvi L., Finland	89	7	7			Wang et al. (1995)
Pyhäjärvi L., Finland	81	6	5			Wang et al. (1995)
Pszczewski Landscape, Poland	<150 - 740					Niedzielski et al. (2002)
Park Lakes, Poland						Niedzielski et al. (2002)
Erken L., Sweden	65 - 200 ^a	10 - 40 ^a	30 - 160 ^a			Lindström (1983)
Asia						
Kinneret Lake, Israel	50 - 184	<5 - 78	31 - 103	<5 - 50		Nishri et al. (1999)
	74 - 203	<1 - 84	<1 - 90	34 - 147	28 - 755	This study

Table 3. Dissolved volatile selenium depth-integrated average concentrations in the entire depth of the water column (0-35 m), epilimnion (0-10 m) and hypolimnion (25-35 m). Concentrations are reported in pg (Se) L⁻¹. Confidence interval is indicated in brackets and in italics. <LoD: below detection limit.

		Apr 15	Sep 15	Nov 15	Janv 16	Apr 16	Sep 16	Nov 16	Janv 17	Apr 17	Sep 17	Nov 17
		19/04/15	06/09/15	16/11/15	25/01/16	17/04/16	15/09/16	27/11/16	15/01/17	30/04/17	10/09/17	12/12/17
Water column (0 – 35 m)	TVSe	37 (2)	88 (4)	755 (38)	12 (1)	32 (2)	335 (17)	532 (27)	149 (7)	28 (1)	154 (8)	524 (26)
	DMSe	11 (1)	36 (2)	120 (6)	11 (1)	10 (0.5)	198 (10)	108 (5)	45 (2)	10 (1)	31 (2)	107 (5)
	DMSeS	22 (1)	30 (2)	343 (7)	< LoD	17 (0.5)	49 (10)	196 (5)	77 (2)	5 (1)	74 (2)	185 (5)
	DMDS _e	0.9 (0.6)	16 (2)	246 (6)	< LoD	< LoD	76 (10)	217 (5)	27 (2)	12 (0.5)	48 (2)	226 (5)
Epilimnion (0 – 10 m)	TVSe	15 (1)	122 (6)	965 (48)	14 (1)	19 (1)	260 (13)	551 (28)	134 (7)	14 (1)	198 (10)	455 (23)
	DMSe	< LoD	38 (2)	65 (3)	13 (1)	1 (0.1)	226 (11)	126 (6)	44 (2)	7 (0.4)	39 (2)	107 (5)
	DMSeS	12 (0.1)	60 (2)	674 (7)	< LoD	11 (0.1)	27 (11)	184 (7)	64 (2)	5 (0.4)	92 (2)	162 (5)
	DMDS _e	1 (0.003)	24 (2)	193 (4)	< LoD	< LoD	6 (11)	235 (6)	25 (2)	2 (0.3)	67 (2)	187 (5)
Hypolimnion (25 – 35 m)	TVSe	54 (3)	22 (1)	610 (30)	10 (1)	61 (3)	135 (7)	259 (13)	< LoD	49 (2)	21 (1)	583 (29)
	DMSe	19 (1)	8 (0.4)	140 (7)	10 (0.5)	25 (1)	20 (1)	45 (2)	< LoD	16 (1)	11 (1)	74 (4)
	DMSeS	30 (1)	3 (0.4)	147 (7)	< LoD	30 (1)	38 (1)	142 (2)	< LoD	4 (1)	3 (1)	238 (4)
	DMDS _e	1 (1)	5 (0.4)	278 (7)	< LoD	< LoD	60 (1)	62 (2)	< LoD	29 (1)	7 (1)	247 (4)



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