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

Y. Be'eri-Shlevin, Maïté Bueno, Emmanuel Tessier, A. Romero-Rama, A. Sukenik, T. Zohary, David Amouroux

Biogeochemistry

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--Manuscript Draft--

Manuscript Number:	
Full Title:	Biogeochemistry of Selenium compounds in the water column of warm monomictic Lake Kinneret
Article Type:	Manuscript
Keywords:	Selenium; Dissolved species; Volatile species; Lakes; Depth profile; Seasonal distribution
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Funding Information:	israeli water authority (4500963096) — Dr. Yaron Be'eri-Shlevin
	Agence nationale de la Recherche (ANR-11-RSNR-0002) — Dr. Maite Bueno
Abstract:	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. 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

	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.
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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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On behalf of authors,

Sincerely yours,
Maïté Bueno

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

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Abstract

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.

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 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.

Keywords:

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

Declarations:

Acknowledgements:

Y. Be'eri-Shlevin wishes to dedicate this paper to D. Solnik.

Funding:

The research leading to these results received funding from the Israeli Water Authority (grant #4500963096) and, Aquitaine Region (AQUITRACES project n° 20131206001-13010973) & ANR IA RSNR (AMORAD project n°ANR-11-RSNR-0002) for equipment funding. The financial support of A. Romero−Rama Doctoral fellowship was received from UPPA and IPREM.

Conflicts of interest/Competing interests:

The authors have no conflict or competing interest to declare.

Availability of data and material:

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

***Code availability*:** not applicable

Author contributions:

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

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1. Introduction

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

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

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

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

Lake Kinneret is suitable for studying Se aquatic biogeochemistry due to (i) the current understanding of its sulfur biogeochemistry (Ginzburg et al. 1999; Knossow et al. 2015; Sela-Adler et al. 2016); (ii) the typical seasonal alternation between oxic (winter) and anoxic (summer-fall) conditions in its hypolimnion and; (iii) because its physical, chemical and biological features are well described and monitored routinely (Zohary et al. 2014a). Oxygen depletion in the hypolimnion together with H_2S production are linked to the activity of sulfate reducing bacteria (SRB) (Hadas and Pinkas 1995). Oremland et al. (1989) described the potential reduction of Se oxyanions by SRB, whereas Nishri et al. (1999) suggested that the removal of Se(IV) was due to chemical reactivity with H_2S. The present study is based on a 3-years survey conducted in Lake Kinneret, Israel, consisting of simultaneous depth profile monitoring of volatile and non-volatile dissolved Se species. This warm monomictic lake is characterized by high biological activity and strong seasonal stratification, with anoxic sulfide-rich hypolimnion in late summer (Zohary et al. 2014a). Our main goal was to investigate the speciation and fate of dissolved selenium in the water column of Lake Kinneret at seasonal and interannual time scales. A comparison with past data reported

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

2. Materials and methods

2.1. Site description

Lake Kinneret (Fig. 1) is a warm, monomictic, meso-eutrophic freshwater lake located at the northeast of Israel (32º50'N; 35º35'E). The lake has an area of 170 km^2, mean depth of 25 m and maximum depth of 42 m (Berman et al. 2014a). Lake Kinneret is stratified 8-9 months per year, from March-April until November-December, and is homothermal during the remaining months. The stratified period is characterized by a strong separation and low exchange of water between the warmer top (epilimnion) and cooler bottom (hypolimnion) layers, with resulting strong vertical gradients of physicochemical and biological parameters along the water column. Primary production is limited to the illuminated, well-oxygenated and warm epilimnion (18-31 ºC). The cooler, dark hypolimnion becomes anoxic within a few weeks after the onset of thermal stratification and maintains a constant temperature (~15-16 ºC) (Berman et al. 2014a). The interphase layer (metalimnion) is located at 15-20 m during the summer. Nitrate (NO_3^-) accumulates in the well-mixed water column in winter due to riverine inflows and nitrification of ammonium (NH_4^+) previously accumulated in the hypolimnion. Once stratification begins, the NO_3^- concentration decreases in both the epilimnion and hypolimnion as a consequence of biological uptake and denitrification, respectively (Berman et al. 2014a; Hadas 2014). Sulfate presents a conservative behavior in the epilimnion, meanwhile reducing conditions at the hypolimnion lead to the production of hydrogen sulfide (HS^-) during stratification (Berman et al. 2014a; Ginzburg et al. 1999). Hypolimnetic reducing conditions are associated with organic matter degradation by anaerobic microorganisms, in particular, with methanogenesis in sediments, and with sulphate reduction both in sediments and water column leading to the accumulation of CH_4 and H_2S in the hypolimnion (Eckert and Conrad 2007).

The Jordan river (annual inflow ~ 350 10^6 m^3 (Rom et al. 2014)), is the largest source of freshwater flowing into Lake Kinneret, supplying ~65% of the incoming water, while direct precipitation contributes only ~10% of the total water input to the lake (Rimmer and Gal 2003). Notably, during the three years of this study (2015-2017), the annual minimum lake water level dropped by 1.34 m as a result of continuous drought, with below average annual rainfall. Evaporation (~230 × 10^6 m^3 $year^{-1}$) and water withdrawal (~375 × 10^6 m^3 $year^{-1}$) for agricultural and human consumption are usually the main water outflows (Ostrovsky et al. 2013; Rimmer and Givati 2014), although during the years of this study, water pumping out of the lake was reduced drastically due to sever draught

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

Lake Kinneret has been subjected to major man-made hydrological and other changes during the last decades (Berman et al. 2014a). One dramatic hydrological change was the draining in the 1950s of Lake Hula and its associated wetlands. Lake Hula, a natural shallow lake in the Hula basin, to the north of Lake Kinneret through which the Jordan River used to flow before reaching Lake Kinneret, acted as a natural filter to Lake Kinneret (Hambright and Zohary 1998) (Fig. 1). In an attempt to alleviate some of the ecological damages to the Hula Valley caused by the drainage, a small shallow water body, Lake Agmon, was created in 1994 on part of the historical site of Lake Hula (Hambright and Zohary 1998). With its creation, most water from the Hula Valley is being diverted for agricultural use and no longer reaches Lake Kinneret (Berman et al. 2014a). In addition to the water required for agriculture, municipal and domestic demands for water in the Lake Kinneret catchment have increased during the last decades resulting in lower annual inflows compared to previous decades (Rimmer and Givati 2014). The effects of these changes on Lake Kinneret microbiota and thus, on Se cycling are still not well understood. The stress over Lake Kinneret ecosystem has been shown to affect the phytoplankton dynamics (Zohary 2004; Zohary et al. 2014b). For example, the previously typical spring bloom of the dinoflagellate *Peridinium gatunense* has gradually vanished and replaced by winter-spring bloom of cyanobacteria, mainly *Microcystis*. A loss of species diversity in summer, together with the appearance and establishment of N_2-fixing cyanobacteria has also been observed since the mid 90's, especially *Chrysosporum (*formerly *Aphanizomenon) ovalisporum* and *Cylindrospermopsis raciborskii* (Sukenik et al. 2014). Cyanobacteria not only represent a major concern for water quality, it also have the ability to uptake and transform Se, and may impact the Se cycle (Bender et al. 1991; Chouhan and Banerjee 2010).

2.2. Sampling, transport and samples storage

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

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

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

2.3. Reagents

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

2.4. Total selenium analysis

Total Se was determined with Agilent 7500ce or 7900 ICP-MS instruments (Agilent Technologies, Tokyo, Japan) both equipped with octopole collision/reaction cell (CRC), concentric nebulizer and a Scott double pass spray chamber cooled to 2°C. Argon-based polyatomic interferences were reduced by using H_2 as cell gas at a flow rate of 5 ml min^{-1}. Acquisition parameters were: integration time, 200 ms per isotope; 10 (7900) or 15 (7500ce) replicates; monitored *m*/*z* 77 and 78. External calibration (single element Se standard 1000 mg L^{-1} SCP Science) was performed. The instrumental detection limits of Se (based on ^{78}Se) were in the range 1.6-13 ng L^{-1} depending on the instrument. Typical analytical precision was <5% (relative standard deviation, 10 to 15 replicates) (Darrouzès et al. 2008; Pokrovsky et al. 2018).

2.5. Selenium speciation analysis

2.5.1. Non-volatile dissolved Se analysis

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

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

2.5.2. Volatile Se analysis

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

dimethyldiselenide (DMDSe)) were detected with limit of detection of 0.1-0.5 pg Se L^{-1}. Total dissolved volatile Se (TVSe) was calculated as the sum of detected species.

2.5.3. Volatilization fluxes estimation

The volatile emission fluxes across the air-water interface were calculated using an adapted version of the lake gas exchange equation from Cole and Caraco (1998) using the total volatile Se data (TVSe; Table SI 5) from sub−surface samples (1m depth). The model was originally used to estimate the gas transfer velocity of CO_2 as function of wind speed. In our case the adaptation consisted in using the atmospheric data of DMSe and calculations were carried out using weak wind speed (3 m s^{-1}) and strong wind speed (10 m s^{-1}). The same model adaptation has been used previously for the same purpose (Lanceleur et al. 2019; Tessier et al. 2002).

2.6. Stock and calculation of depth integrated Se concentration

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

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

where i = 1,…,12 the number of the depth level; h_i = depth in meters of the i-th level; C_i = selenium concentration of the i-th level (pg L^{-1} for volatile Se; ng L^{-1} for non-volatile Se).

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

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

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

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

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

2.7. Statistical analysis

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

3. Results and discussion

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

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

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

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

Chlorophyll a and Primary Productivity

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

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

In contrast to Chl-a, primary productivity followed similar annual patterns for the 3 years studied (Fig. 2a). Annual minimum values occurred around the time of overturn, late December or early January, followed by a sharp increase in the following weeks. It then remained high (with fluctuations) until the end of summer, declining again to the December minimum values. Despite interannual similarities, the annual average values increased from 1108 ± 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.

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

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

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

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

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

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

3.2.2. Dissolved reduced Se species

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

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

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

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

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

Comparing our results to those published for other lakes (Table 2), similar ranges of concentrations for T.Se, Se(IV) and Se(VI) were obtained, as long as we exclude lakes impacted by mining activities. Notably, despite the physical variations in the Hula Basin, in the drainage basin of Lake Kinneret (Fig. 1) and almost 20 years after the study of Nishri et al. (1999) the T.Se concentration remained very similar. However, while total Se lake reservoir remains the same, Se species distribution has changed. The range of total selenium and Se(IV) measured in our study (2015-2017 period) was similar to that reported by Nishri et al. (1999) for the period 1993-1995. In those 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 Se(VI) ranged between 31 - 103 ng Se L^{-1}, slightly higher than in the present work. Likewise, the concentration 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 higher in the present work (Table 2).

3.2.3. Volatile dissolved selenium

Depth integrated total volatile Se concentrations ranged from 12 ± 1 to 755 ± 38 pg Se L^{-1}, and was higher in late summer and fall (Table 3) than in winter-spring seasons, especially at epilimnetic depths close to thermocline (Fig. 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} during winter-spring seasons; while in summer-fall the concentrations were between 88 ± 4 and 755 ± 38 pg L^{-1} (Table 3). Three volatile Se compounds were identified in the water column: dimethyl diselenide (DMDSe) and the mixed S-Se compound dimethyl selenide sulphide (DMSeS) as the dominant species and, DMSe in lower concentration except in Sep 2016. In brief, during stable thermal stratification $DMSe_{dia\ (0-35m)}$ ranged from 31 ± 2 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 TVSe) and $DMDSe_{dia\ (0-35m)}$ from 16 ± 2 to 246 ± 6 pg Se L^{-1} (32% of TVSe) (Table 3). In contrast, concentration

during holomixis was usually close or below the detection limit (<0.5 pg Se L^{-1}). During winter and spring seasons $DMSe_{dia\ (0-35m)}$ range was 10 ± 1 – 45 ± 2 pg Se L^{-1}, $DMSeS_{dia\ (0-35m)}$ <LoD – 77 ±2 and $DMDSe_{dia\ (0-35m)}$ <LoD – 27 ± 2 pg Se L^{-1} (Table 3).

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

3.3. Selenium compounds biogeochemistry along with water column stratification

3.3.1. Epilimnetic selenium (0 – 10 m)

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

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

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

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

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

detected in this study. Cyanobacteria (quantified as cyanophyta) and bacillariophyta are the main species present between September and November (Fig. 3). In cyanophyte cultures in agricultural drainage waters, the production of volatile Se from oxyanions has been demonstrated (Fan et al. 1998). The precursors (CH_3-Se-Met and CH_3-Se-Cys) were also characterized by Fan et al. (1998). Some of these precursors could be composing the Red.Se fraction and potentially the Org.Se detected and could eventually be converted to the corresponding volatile Se compounds detected in this study (Amouroux et al. 2000). Therefore, the key processes occurring in the epilimnion are the production of organically bound Se as a function of plankton dynamics and its further depletion associated with dilution and conversion into volatile species during late summer and fall. The presence of organic matter degrading bacteria and the subsequent production of volatile species could be an important removal pathway of dissolved Se to the atmosphere.

3.3.2. Hypolimnetic selenium (25 – 35 m)

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

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

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

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

Hypolimnetic TVSe production is limited. Low production extent has been observed during spring at 35 m, in the water-sediment interface (Fig. 3). In September 2016 and November 2017 some production or accumulation was observed as well close to the water-sediment interface (Fig. 3 and Fig. SI 4), although, the maximum concentration of volatile species was detected close to the thermocline as described previously. Volatile Se production near the sediments may be due to microbial production at this location linked to organic matter degradation as observed in heterotrophic and reducing waters of upper European estuaries (Tessier et al. 2002) or in permafrost lakes (Lanceleur et al. 2019). In our study, the mixed Se-S compounds (DMSeS and DMDSe) were the dominant species. In the literature, it is common to found DMSe as the dominant component of TVSe. Nevertheless, studies carried out at Gironde estuary (France) and Mediterranean Sea showed a significant concentration of DMDSe (Amouroux and Donard 1997; Amouroux et al. 2001). Laboratory experiments using synthetic sea water and selenoamino acids as the main precursors over inorganic Se species, demonstrated that DMSe, DMSeS and DMDSe were produced under light and dark conditions (Amouroux et al. 2000). The same study suggested that the production of DMSe would have a specific precursor, most probably a dimethylselenonium compound. The authors suggested that the production of DMSeS and DMDSe would be the result of abiotic reactions in the presence of seleno-methionine in the extracellular medium. Thereby, the presence of DMSeS in Lake Kinneret seems to be the consequence of having organically bounded Se species (i.e. precursors) and sub-millimolar concentrations of sulfides in the water and H_2S accumulation at hypolimnion (Ginzburg et al. 1999; Knossow et al. 2015).

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

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

4. Biogeochemical implication

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

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

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

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

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

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

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Figure captions

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

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

Figure 3. Depth profiles in Lake Kinneret in 2016: A) conductivity (µS cm^{-1}), temperature (ºC), pH and turbidity (NTU), B) Chl-a (µg L^{-1}), PP (µg C L^{-1} day^{-1}) and oxygen saturation (%), C) T.Se, Se(IV), Se(VI), Org.Se and Red.Se in ng L^{-1}, D) TVSe, DMSe, DMSeS and DMDSe in pg L^{-1}.

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

Figure 5. Schematic overview of Se biogeochemical cycle in Lake Kinneret. Abbreviations: selenate (Se(VI)), selenite (Se(IV)), organic Se (Org.Se), reduced Se pool (Red.Se), dimethylselenide (DMSe), dimethyl selenide sulphide (DMSeS) and dimethyl diselenide (DMDSe). †Phytoplankton species are detailed Fig. 4 ‡Dissolution 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.

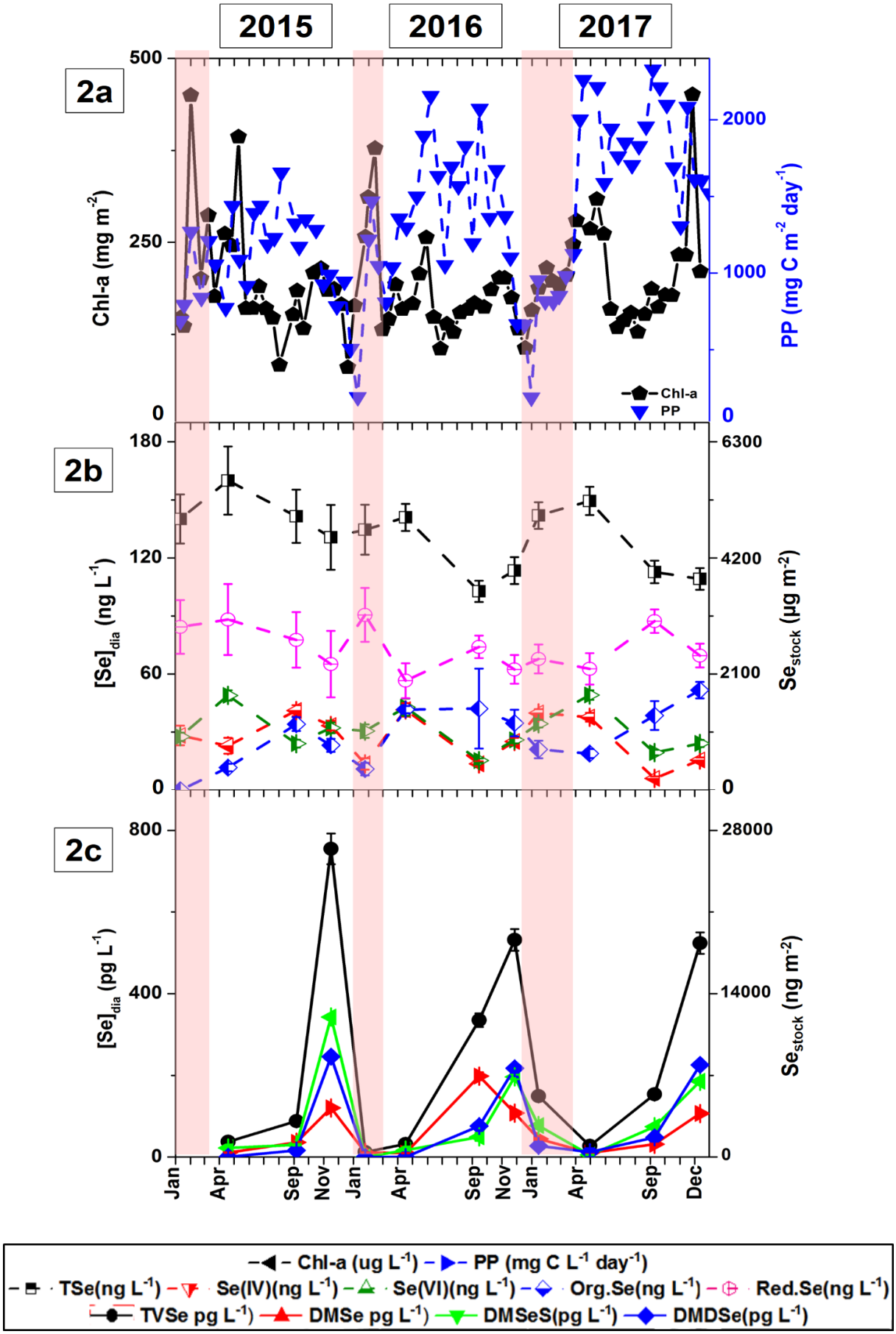

2015
2016
2017
2a
Chl-a (mg m-2)
PP (mg C m-2 day-1)
Chl-a
PP
2b
[Se]dia (ng L-1)
Sestock (µg m-2)
2c
[Se]dia (pg L-1)
Sestock (ng m-2)
Jan
Apr
Sep
Nov
Jan
Apr
Sep
Nov
Jan
Apr
Sep
Dec
Chl-a (ug L-1)
PP (mg C L-1 day-1)
TSe(ng L-1)
Se(IV)(ng L-1)
Se(VI)(ng L-1)
Org.Se(ng L-1)
Red.Se(ng L-1)
TVSe pg L-1)
DMSe pg L-1)
DMSeS(pg L-1)
DMDSe(pg L-1)

Figure 3.

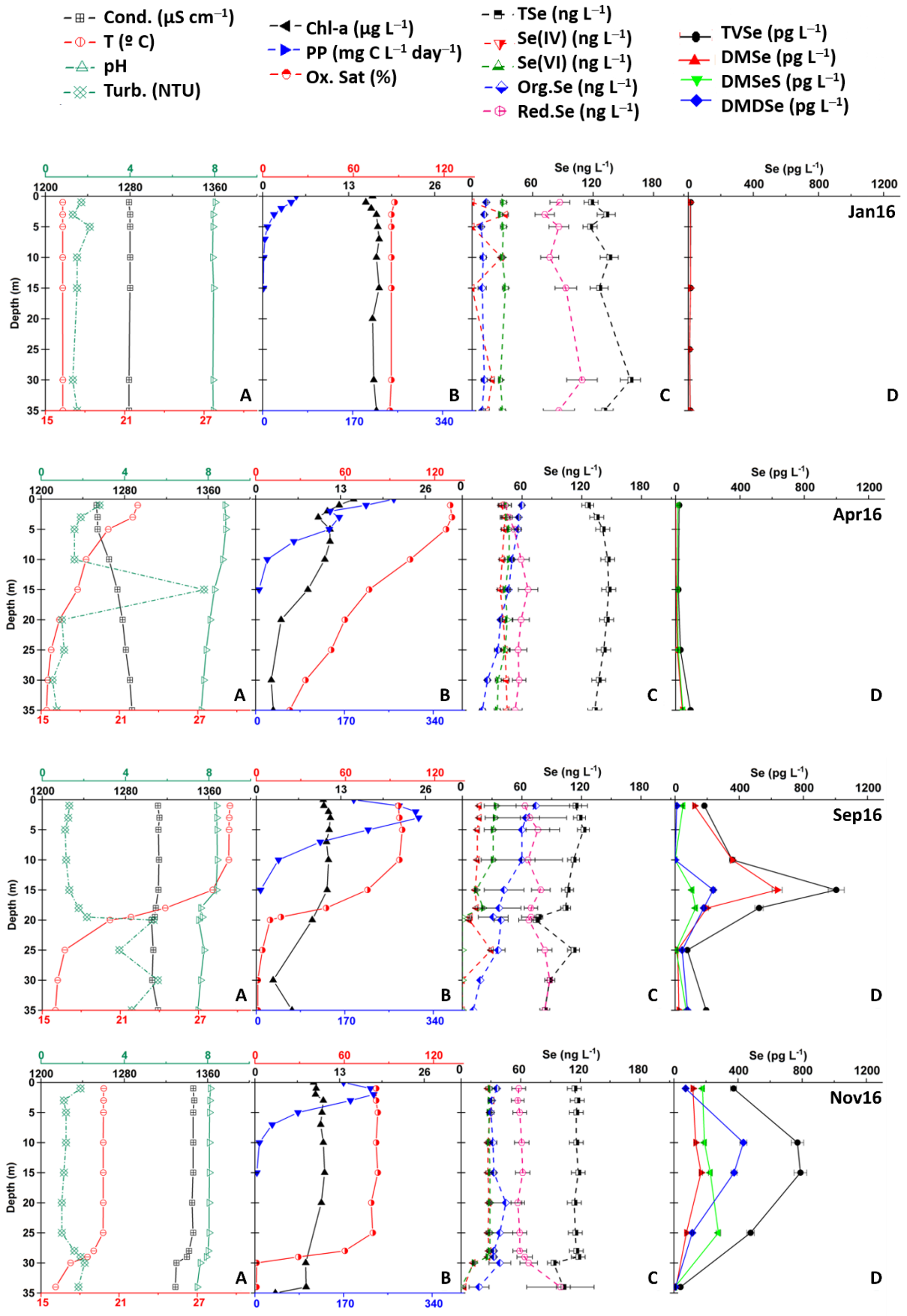

Cond. (µS cm⁻¹)
T (º C)
pH
Turb. (NTU)
Chl-a (µg L⁻¹)
PP (mg C L⁻¹ day⁻¹)
Ox. Sat (%)
TSe (ng L⁻¹)
Se(IV) (ng L⁻¹)
Se(VI) (ng L⁻¹)
Org.Se (ng L⁻¹)
Red.Se (ng L⁻¹)
TVSe (pg L⁻¹)
DMSe (pg L⁻¹)
DMSeS (pg L⁻¹)
DMDSe (pg L⁻¹)
Depth (m)
Se (ng L⁻¹)
Se (pg L⁻¹)
Jan16
Apr16
Sep16
Nov16
A
B
C
D

Figure 4.

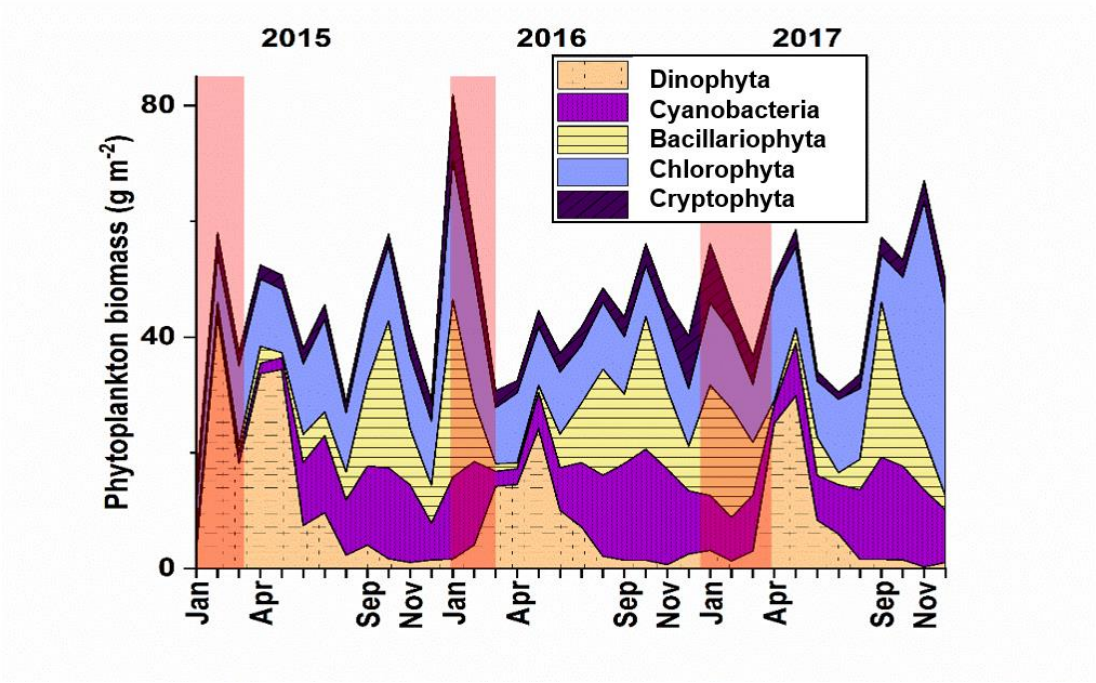
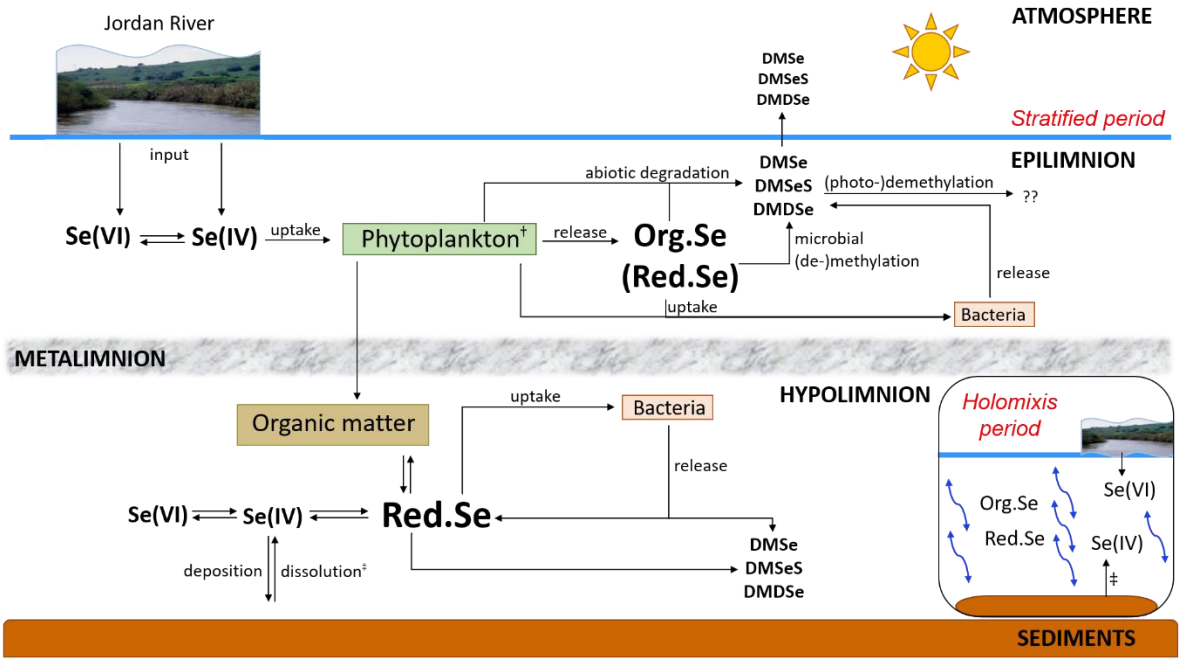

2015
2016
2017
Dinophyta
Cyanobacteria
Bacillariophyta
Chlorophyta
Cryptophyta
Phytoplankton biomass (g m-2)
80
40
0
Jan
Apr
Sep
Nov
Jan
Apr
Sep
Nov
Jan
Apr
Sep
Nov

Figure 5.


Jordan River
ATMOSPHERE
DMSe
DMSeS
DMDSe
Stratified period
input
EPILIMNION
abiotic degradation
DMSe
DMSeS
DMDSe
(photo-)demethylation
??
Se(VI) Se(IV)
uptake
Phytoplankton+
release
Org.Se
(Red.Se)
microbial
(de-)methylation
release
uptake
Bacteria
METALIMNION
HYPOLIMNION
Holomixis
period
Organic matter
uptake
Bacteria
release
Se(VI)
Org.Se
Red.Se
Se(IV)
Se(VI) Se(IV)
Red.Se
deposition
dissolution‡
DMSe
DMSeS
DMDSe
‡
SEDIMENTS

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 (*13*)	160 (*18*)	141 (*14*)	131 (*17*)	135 (*13*)	141 (*7*)	103 (*6*)	113 (*7*)	142 (*7*)	149 (*7*)	113 (*6*)	109 (*6*)
Se(IV) (ng L^{-1})	28 (*5*)	23 (*4*)	41 (*3*)	33 (*2*)	14 (*3*)	42 (*3*)	14 (*1*)	25 (*2*)	40 (*2*)	38 (*2*)	6 (*1*)	16 (*1*)
Se(VI) (ng L^{-1})	28 (*2*)	49 (*3*)	24 (*2*)	32 (*3*)	31 (*3*)	43 (*4*)	15 (*1*)	26 (*2*)	34 (*2*)	49 (*2*)	19 (*1*)	24 (*2*)
Org.Se (ng L^{-1})	<LoD	12 (*2*)	34 (*4*)	23 (*3*)	11 (*3*)	42 (*2*)	42 (*21*)	35 (*7*)	21 (*5*)	19 (*2*)	39 (*7*)	52 (*4*)
Red.Se (ng L^{-1})	84 (*14*)	88 (*18*)	78 (*14*)	65 (*17*)	91 (*14*)	57 (*9*)	74 (*6*)	62 (*7*)	68 (*7*)	63 (*8*)	87 (*6*)	70 (*6*)
TVSe (pg L^{-1})	n.d.	37 (*2*)	88 (*4*)	755 (*38*)	12 (*1*)	32 (*2*)	335 (*17*)	532 (*27*)	149 (*7*)	28 (*1*)	154 (*8*)	524 (*26*)
O_2 Sat (%)	85 (*9*)	63 (*5*)	43 (*6*)	57 (*4*)	76 (*9*)	63	47 (*4*)	59 (*7*)	88 (*5*)	87 (*1*)	37 (*5*)	53 (*9*)
pH	8.1 (*0.1*)	8.0 (*0.1*)	7.8 (*0.1*)	7.8 (*0.1*)	7.9 (*0.1*)	8.0 (*0.1*)	7.8 (*0.1*)	8.0 (*0.1*)	8.1 (*0.2*)	8.2 (*0.1*)	8.0 (*0.1*)	7.9 (*0.1*)
T (°C)	16.5 (*0.9*)	17.2 (*0.3*)	23.3 (*0.3*)	20.8 (*0.7*)	16.7 (*0.3*)	17.6	23.3 (*0.1*)	20.9 (*1.1*)	15.5 (*0.5*)	17.0 (*0.8*)	22.8 (*0.3*)	20.3 (*0.7*)
Cond (µS cm^{-1})	1259 (*5*)	1235 (*7*)	1248 (*5*)	1271 (*6*)	1280 (*3*)	1277 (*5*)	1310 (*3*)	1337 (*4*)	1335 (*6*)	1319 (*2*)	1357 (*3*)	1376 (*5*)
Turb (NTU)	2.0 (*1.7*)	1.3 (*0.2*)	1.9 (*1.1*)	1.4 (*0.3*)	1.6 (*0.6*)	1.5 (*0.6*)	2.5 (*0.7*)	1.9 (*0.6*)	1.7 (*0.4*)	2.4 (*0.3*)	3.7 (*1.7*)	3.8 (*2.1*)
Chl-a (µg L^{-1})	9.5 (*0.5*)	17 (*1*)	11 (*2*)	12.4 (*0.1*)	19 (*2*)	11	11.0 (*0.3*)	12 (*1*)	12 (*2*)	18.3 (*0.5*)	12 (*1*)	14
PP (µgC L^{-1} d^{-1})	49 (*5*)	74 (*31*)	84 (*8*)	59 (*10*)	64 (*45*)	86	114 (*34*)	59 (*20*)	57 (*5*)	149 (*2*)	144 (*5*)	74 (*39*)

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)
Kuujjuarapik, 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)
Iso-Hietajärvi L., Finland	34	4	4			Wang et al. (1994, 1995) 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 19/04/15	Sep 15 06/09/15	Nov 15 16/11/15	Janv 16 25/01/16	Apr 16 17/04/16	Sep 16 15/09/16	Nov 16 27/11/16	Janv 17 15/01/17	Apr 17 30/04/17	Sep 17 10/09/17	Nov 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*)
	DMDSe	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*)
	DMDSe	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*)
	DMDSe	1 (*1*)	5 (*0.4*)	278 (*7*)	< LoD	< LoD	60 (*1*)	62 (*2*)	< LoD	29 (*1*)	7 (*1*)	247 (*4*)