



HAL
open science

PCB mass budget in a perialpine lake undergoing natural decontamination in a context of global change

Thibault Masset, Nathalie Cottin, Christine Piot, Phillippe Fanget,
Emmanuel Naffrechoux

► To cite this version:

Thibault Masset, Nathalie Cottin, Christine Piot, Phillippe Fanget, Emmanuel Naffrechoux. PCB mass budget in a perialpine lake undergoing natural decontamination in a context of global change. *Science of the Total Environment*, 2019, 693, pp.133590. 10.1016/j.scitotenv.2019.133590. hal-02520704

HAL Id: hal-02520704

<https://univ-smb.hal.science/hal-02520704v1>

Submitted on 20 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 PCB mass budget in a perialpine lake undergoing natural decontamination in 2 a context of global change.

3 **Thibault MASSET**^{a,*}, **Nathalie COTTIN**^a, **Christine PIOT**^a, **Phillippe FANGET**^a, **Emmanuel NAFFRECHOUX**^a

4 ^a Univ. Savoie Mont-Blanc, LCME, 73000 Chambéry, France

5

6 **1. Introduction:**

7 Lake PCB (polychlorobiphenyl) contamination has been extensively studied worldwide, and the mass
8 budget was evaluated to highlight the main fluxes driving the PCB dynamics in lakes. Many studies
9 have investigated the American Great Lakes, which have been undergoing important PCB
10 contamination since the 1970s. The PCB mass budget for Lake Michigan shows that the most
11 important flux responsible for decontamination was volatilization followed by sedimentation^{1,2}. The
12 same pattern was observed in 1994 for Lake Superior³. In Europe, small rural Lake Cumbria (England)
13 showed important PCB contamination resulting from surface water runoff. The mass budget
14 indicated that a large part of the decontamination was due to outflow and volatilization⁴. The same
15 conclusion was drawn for several high-altitude lakes⁵⁻⁸. PCB mass budgets are based on a
16 compilation of the measured and estimated fluxes to which uncertainties are inherently associated.
17 Indeed, several fluxes (i.e., sediment resuspension and molecular diffusion at the air/water and
18 sediment/water interfaces) are often modeled considering important uncertainties^{9,10}. These
19 uncertainties are related to the approximations of PCB quantification methods, analysis and
20 partitioning constants (i.e., Henry's law constant and the octanol-water partition coefficient). The
21 impacts of these uncertainties on the calculated fluxes should be identified and considered to build
22 accurate PCB mass budgets.

23

24 PCB mass budgets are lake-dependent given that a lake's trophic and physical or chemical
25 characteristics influence its contaminant flux. Although the American Great Lakes have been
26 extensively studied and a few studies have focused on the particular case of high-altitude mountain
27 lakes, information concerning medium-sized perialpine lakes remains scarce. A few studies have
28 investigated Lake Geneva (France/Switzerland)¹¹⁻¹³ and Lake Maggiore, as well as Lake Lugano in
29 Italy^{14,15}, but PCB mass budgets were not obtained. These perialpine lakes are often used as
30 resources for many activities (fishing, leisure sports, drinking water supply). In this context, it is of
31 critical importance to identify the main fluxes driving PCB dynamics in such lakes. Lake Bourget
32 (France) has similar physical and chemical characteristics to many other perialpine lakes
33 contaminated with PCBs in Europe but greatly differs from the American Great Lakes. With a
34 catchment area/lake surface area ratio of 13, a surface area/volume ratio of 12.3 and a residence
35 time of 11 years, Lake Bourget is a medium-sized (44.5 km²) perialpine lake. It is currently considered
36 meso-oligotrophic¹⁶ (i.e., chlorophyll α concentration = 3.3 $\mu\text{g}\cdot\text{L}^{-1}$, total phosphorus concentration =
37 10 $\mu\text{g}\cdot\text{L}^{-1}$ and total organic carbon concentration = 1.7 $\text{mg}\cdot\text{L}^{-1}$). However, lake Bourget remains heavily
38 contaminated with PCBs, and the water still exceeds the US-EPA recommended maximum
39 concentration of 170 $\text{pg}\cdot\text{L}^{-1}$ for the sum of the 7 indicator PCBs ($\Sigma 7\text{PCB}_i$) for the protection of aquatic
40 wildlife.

41 To fill the knowledge gap regarding PCB dynamics in perialpine lakes, this study aimed to (i) establish
42 a PCB mass budget to identify the main fluxes involved in the decontamination process and (ii)

43 identify and accurately quantify the uncertainties associated with both measured and modeled PCB
44 fluxes in Lake Bourget for the period of 2013-2017.

45 Our hypothesis was that volatilization and sediment burial were the main fluxes ruling the PCB
46 decontamination process in Lake Bourget. Both flux intensities are susceptible to environmental
47 factors. Indeed, as in many other perialpine lakes¹⁷⁻¹⁹, Lake Bourget underwent a period of
48 eutrophication and is currently facing reoligotrophication. Consequently, the diminution of primary
49 production could impact the sedimentation flux of PCBs in Lake Bourget through the modification of
50 the process of “biological pumping”^{20,21}. Therefore, the oligotrophication of the lake could reduce the
51 intensity of the flux of PCBs escaping the water column through settling and sediment burial. Alpine
52 regions could be particularly affected by climate change with an exacerbated increase in temperature
53 expected compared to the moderate increase in the northern hemisphere²². Hence, relatively small
54 water bodies, such as perialpine lakes, could specifically experience increased water temperatures,
55 as is already the case in Lake Bourget¹⁶. This phenomenon will be amplified in the near future with
56 perialpine lakes first affected by climate change. Since the volatilization flux of PCBs is dependent on
57 the water temperature, an increase in the water temperature could have an impact on the intensity
58 of the volatilization flux. Therefore, in regards to the singular situation of perialpine lakes, this study
59 considered (i) the impact of oligotrophication on the intensity of the settling and burial fluxes of PCBs
60 and (ii) the impact of an increase in water temperature on the intensity of the volatilization flux of
61 PCBs.

62

63

64

65

66 **2. Materials and methods**

67

68 **2.1 Study site:**

69 Lake Bourget is the largest natural lake in France, with a surface area of 44 km², a length of 18 km, a
70 width between 1.6 km and 3.5 km and a mean depth of 85 m (maximum: 145 m) (Fig. S1). Its main
71 PCB source is the Tillet River running through the city of Aix les Bains. Lake Bourget was
72 contaminated from 1930 to 1987 by an electrical transformer factory using Pyralène® (French
73 equivalent for Aroclor®). Ever since, the PCBs contained in sediment have been slowly released into
74 the lake and have spread throughout the whole water body. The PCB concentration could increase
75 substantially to 250 ng·L⁻¹ during rain events, with up to 1500 g·yr⁻¹ reaching the lake in that period²³.
76 Remediation measures have resulted in a decline in PCB input, but contamination still remains
77 elevated today. The Terre-nue Canal and the Lysse River run through urbanized and industrialized
78 areas and have been considered potential sources of PCBs for the lake (Fig. S1). As a direct
79 consequence of climate change, an elevation of the water temperature in Lake Bourget has been
80 highlighted since the first records. The average water temperature at 2 m depth was 13.0°C in 1984
81 and rose constantly to 15.5°C in 2017¹⁶. Following a period of eutrophication (1950-1990), Lake
82 Bourget is currently on the way to oligotrophication (characterized by an increasing transparency: 3
83 m in 1981 and 6 m in 2017)¹⁶

84 **2.2 Sampling**

85 2.2.1 Water sampling

86 Water from Lake Bourget was regularly sampled 5 times between May 2013 and March 2016 at an
87 average depth of 5 m in the middle of the lake (point B, Fig. S3). Each time, 30 L was pumped and
88 stored for 2 h at room temperature in a steel barrel until processing. Water from the Tillet River was
89 sampled with a surface water automatic sampler (Portable sampler ISCO 3700, Ijinus®) for two and
90 five weeks (in March-April 2014 and in October-November 2014, respectively) and enabled
91 continuous suspended particulate matter (SPM) concentration determination for rainy (n = 4) and
92 dry (n = 5) periods. A sediment trap was deployed alongside the automatic sampler to collect
93 sufficient amounts of settling particles for integrative PCB concentration measurements. To ensure
94 an exhaustive budget of PCB inputs through the Tillet River, three measurements of dissolved PCBs at
95 the outlet were performed in 2017. A total of 60 L of water was pumped through precleaned glass
96 fiber filters (GFF) (porosity 0.7 µm, Whatman®) followed by precleaned polyethylene foam plugs
97 (diameter = 20 mm, L = 100 mm, Ecomesure®) for the adsorption and determination of dissolved
98 PCBs. Water PCB concentrations from the Terre-Nue River and Leysse River were determined in 2014
99 and 2015 by the "Agence de l'eau RMC"²⁴. Water samples from Lake Bourget were brought back to
100 the laboratory and immediately pumped through precleaned (kiln-fired 2 h at 525°C) GFF and C18
101 (Empore®) filters for the retention of particulate PCBs and dissolved PCBs, respectively. Every sample
102 was wrapped in aluminum foil and stored at -16°C before analysis.

103 2.2.2 Settling particles and sediment sampling

104 To evaluate the PCB settling rate, three experimental setups were performed from July 2016 to July
105 2017. An automated sediment trap (TECHNICAP® PPS6) was set at a depth of 40 m, 200 meters from
106 the coast (see SI). Two additional sediment traps were set up at 20 m depth, one at the same site as
107 the automated trap and the other at the south portion of the lake (GPS coordinates: 45.656°, 5.886').
108 They both operated in July 2016 and in October 2016, each time for an integrative period of one
109 month. All settling particle samples (n = 6) were stored in clean glass bottles at -16°C before analysis.

110 Nine sediment cores were obtained using a gravity corer (UWITEC®) at five locations along a north-
111 south transect in the lake (n = 4 in May 2013 and n = 5 in May 2015) (Fig. S3 in SI). The first
112 centimeter of the core was collected and analyzed to determine the PCB concentration, as it
113 represented the sedimentation of the last 2.5 years because the sedimentation rate of 0.37 cm·yr⁻¹ in
114 Lake Bourget is considered constant²⁵. The PCB concentrations determined for these five locations
115 were used for resuspension, sediment/water diffusion and sediment burial calculations.

116 2.2.3 Air sampling

117 The atmospheric bulk deposition flux was measured on the bank of Lake Bourget (GPS coordinates:
118 45.693°, 5.890') positioned under the influence of the prevailing winds. Sampling was performed
119 using a lab-designed stainless steel Owen gauge (surface = 0.5 m²) equipped with a precleaned
120 polyurethane foam (PUF) plug (diameter = 20 mm, L = 100 mm, Ecomesure®). Sixteen samples were
121 collected, which enabled a follow-up period of 4 years from 2013 to 2016. The sampling of gaseous
122 PCBs was performed with a precleaned PUF disk (Ø= 140 mm, H = 13 mm, Ecomesure®) housed in
123 protective chambers as described by Harner et al.²⁶ and deployed alongside the Owen gauge. After
124 exposure, all PUFs were retrieved, wrapped in aluminum foil and stored at -16°C before analysis.
125 Samples (n = 9) were collected by continuous follow up for a period of 3 years (2014 – 2016).

126 2.2.4 Fish sampling

127 Fish sampling was performed by professional fishermen year-round from 2013 to 2017 and was
128 concerned with the two most emblematic fishes of Lake Bourget: the arctic char ($n = 138$) and
129 whitefish ($n = 110$) used for human consumption²⁷. Due to their high lipid content, these species are
130 susceptible to the bioaccumulation of large amounts of PCBs. Therefore, intensive fishing of these
131 two species could represent a nonnegligible loss of PCBs from Lake Bourget.

132 **2.3 Chemicals**

133 Heptane, acetone, dichloromethane and methanol were of HPLC quality and purchased from Carlo
134 Erba®. Anhydrous sodium sulfate was purchased from Fisher Chemical® (analytical reagent grade).
135 Silica gel 60 (70-230 mesh) for column chromatography was purchased from Merck®. Copper was
136 activated with 10 mL of 1 N sulfuric acid (Chimie Plus®) and then rinsed three times with Milli-Q®
137 water to a neutral pH followed by rinses with acetone for water removal. A standard mixture of
138 indicator PCB congeners (28, 52, 101, 118, 138, 153, 180) at $10 \mu\text{g}\cdot\text{mL}^{-1}$ in iso-octane and the internal
139 standard PCB116-d5 at $100 \mu\text{g}\cdot\text{mL}^{-1}$ in iso-octane were purchased from Cluzeau Info Lab® (France).

140

141 **2.4 PCB extraction and analysis**

142 Prior to extraction, sediments were dried with anhydrous sodium sulfate and ground into fine
143 powder. PCB 116-d5 was spiked before the extraction of all samples and used as an internal
144 standard. Sediments, glass fiber filters, PUF plugs and PUF disks were extracted by an Accelerated
145 Solvent Extractor (ASE 200 Dionex®) at 100°C and a pressure of 138 bar for 3 cycles with a mixture of
146 acetone/dichloromethane (50:50 v/v). C18 filters were eluted with 10 mL of
147 heptane/dichloromethane (80:20 v/v) followed by 10 mL of heptane/dichloromethane (98:2 v/v).
148 The extraction and clean-up of fish samples are described elsewhere²⁷.

149 Prior to cleanup, only the sediment samples were treated with an acid-activated copper powder to
150 remove sulfur. Then, all extracts were concentrated to 2 mL using a TurboVap® II and purified on an
151 SPE column loaded with 3 g of silica, eluted successively with 15 mL of a mixture of
152 heptane/dichloromethane (98:2 v/v) and 10 mL of heptane/dichloromethane (80:20 v/v). Eluates
153 were reconcentrated to 1 mL and passed through a $0.2 \mu\text{m}$ PTFE filter. They were evaporated near
154 dryness with nitrogen and resuspended in $100 \mu\text{L}$ of heptane for analysis. All PCB solutions were
155 analyzed using a Clarus 580 gas chromatograph from Perkin-Elmer® with an Optima® HP-5-MS accent
156 $30 \text{ m} \times 0.25 \text{ mm}$ nonpolar fused silica capillary column from Macherey-Nagel® coupled with a pulsed
157 discharge detector in photoionization mode (Vici®). The samples were injected in splitless mode at
158 300°C . Helium was used as the carrier gas ($1.0 \text{ mL}\cdot\text{min}^{-1}$). After injection, the oven temperature was
159 set to 60°C for 1 min and increased gradually at a rate of $10^\circ\text{C}/\text{min}$ to 240°C and then at a rate of
160 $5^\circ\text{C}/\text{min}$ to 320°C , and then remained steady for 5 min.

161 **2.5 Quality control**

162 Quantification was ensured for the 7 indicator PCB congeners ($\text{PCBi} = \text{PCB}_{28, 52, 101, 118, 153, 138, 180}$)
163 as they represent approximately 50% of the compounds found in Pyralene® mixtures²⁸.
164 Calibration curves were established with authentic standards (Fig. S2). Extraction yields were
165 determined from certified material (sediment) or from spiked material (water, air samples) (Tab. S1).
166 Extraction yields were not used for correction, and normalization to PCB116-d5 values spiked before
167 extraction accounted for extraction correction. Detection limits were determined as the mean
168 response plus three times the standard deviation of procedural blanks for each PCB (Tab. S2). When
169 appropriate, field blanks were subtracted from the sample concentrations to avoid false positives.
170 Unless specified, every PCB concentration, flux and mass budget mentioned hereafter refer to
171 $\Sigma 7\text{PCBi}$.

172 **2.6 Calculation**

173 *Air/water gaseous PCB exchange model:*

174 The net gas exchange of PCBs across the air–water interface, F_{aw} ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), is given by equation
175 (1):

$$176 \quad F_{aw} = K_{ol} \left(\frac{C_a}{H'} - C_w \right) \quad (1)$$

178 where K_{ol} is the overall mass transfer coefficient ($\text{m}\cdot\text{s}^{-1}$), H' is the temperature-corrected Henry's law
179 coefficient (dimensionless), and C_a and C_w are the dissolved PCB concentrations ($\text{mol}\cdot\text{m}^{-3}$) in air and
180 water, respectively. A positive F_{aw} represented a net input of PCBs from the air into water, and a
181 negative F_{aw} represents a net volatilization of PCBs. The Henry's law coefficient values (H) presented
182 in the literature can vary by two orders of magnitude. In this study, H values were collected from the
183 compilation of Sander et al.²⁹. The minimum and maximum values were disregarded and mean \pm
184 standard deviation values were obtained (Tab. S3) and used for air/water exchange calculations and
185 propagation analysis.

186 More details regarding input parameter calculations for air/water exchange modeling (i.e., K_{ol} , H' , C_a
187 and C_w) are described in the Supporting Information.

188 *Settling particle flow:*

189 The settling particle flow F_{sed} ($\text{g}\cdot\text{yr}^{-1}$) was calculated as follows in equation (2):

$$190 \quad F_{sed} = C_{sp} R_{sed_{85m}} A_b \quad (2)$$

191 where F_{sed} is the PCB settling rate ($\text{g}\cdot\text{yr}^{-1}$), C_{sp} is the mean PCB concentration of the settling particles
192 ($\text{g}\cdot\text{kg}^{-1}$), $R_{sed_{85m}}$ is the settling rate at the lake mean depth (85 m) ($\text{kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$), and A_b is the surficial
193 sediment surface of lake Bourget (m^2).

194 $R_{sed_{85m}}$ was calculated using equation (3) as recently proposed by Corcoran et al.³⁰, suggesting that
195 settling rates are related to depth, following a power-law relationship:

$$196 \quad R_{sed_x} = 1.91x^{-0.90} \quad (3)$$

197 $R_{sed_{40m}}$ calculated with equation (3) (i.e., $0.07 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$) was half of $R_{sed_{40m}}$ experimentally
198 determined from the sediment trap (i.e., $0.14 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$). This could be explained by (i) a much larger
199 catchment area/lake surface area ratio in Lake Bourget (i.e., 13) compared to that of the American
200 Great Lakes³⁰ (i.e., 1.8 – 3.37), which could result in higher suspended material loads to the lake³⁰ and
201 (ii) a higher primary production rate enhanced by the important precipitation of calcium carbonate in
202 summer³¹. Therefore, $R_{sed_{85m}}$ estimated from equation (3) was multiplied by a factor of 2 to offset
203 this gap.

204 *Tributary flows*

205 The inflow of PCBs into Lake Bourget were due to three main sources, identified as the Leysse River,
206 the Tillet River and Terre-Nue Canal.

207 PCBs entering the lake through the three tributaries could be estimated individually as follows in
208 equation (4):

$$209 \quad F_{in_{Trib}} = C_{w_{Trib}} * Q_{m_{Trib}} * 365 \quad (4)$$

210 where F_{in_Trib} is the annual PCB input through the tributary, C_{w_Trib} is the total PCB concentration in
211 the water at the tributary output ($ng \cdot L^{-1}$), Q_{m_Trib} is the water flow ($L \cdot d^{-1}$) and t_{Trib} is the time of the
212 experiment (d).

213 For the Tillet River, the fluxes were determined considering two distinct meteorological situations
214 (i.e., dry and rainy weather), as inputs could be impacted by a change of flow and a change of water
215 PCB concentration due to the remobilization of contaminated particles from the riverbed sediment.

216 *Atmospheric deposition*

217 PCB input by deposition onto the lake surface (F_{ad} in $ng \cdot yr^{-1}$) was calculated as follows in equation
218 (5):

$$219 \quad F_{ad} = F_a A_l \quad (5)$$

220 where F_a is the measured bulk deposition mean flux ($ng \cdot m^{-2} \cdot yr^{-1}$) deduced from the PUF collected in
221 the Owen Gauge and A_l is the Lake surface area (m^2).

222 *Outflow*

223 The Savières Canal was identified as the sole outlet for Lake Bourget water. PCB annually outflowing
224 the lake through the Savières Canal, F_{out} ($g \cdot yr^{-1}$), could be estimated using equation (6):

$$225 \quad F_{out} = C_w * Q_m * 365 \quad (6)$$

226 where C_w is the mean total (dissolved + particulate) PCB concentration of the lake water ($ng \cdot L^{-1}$),
227 Q_m is the mean river flow ($L \cdot d^{-1}$) and t (d) is the time of the experiment.

228 *Output through fishing activity*

229 The quantity of PCBs withdrawn from the lake via fishing (F_{fish} in $g \cdot yr^{-1}$) was estimated with equation
230 (7):

$$231 \quad F_{fish} = C_{fish} m_{fish} \quad (7)$$

232 where C_{fish} is the concentration in the fish filets ($ng \cdot gW \cdot W^{-1}$) and m_{fish} is the mass of fish captured
233 each year ($g \cdot yr^{-1}$).

234

235 *Sediment-water diffusion flux*

236 Sediment-water diffusion flux, F_{sw} ($g \cdot yr^{-1}$), was calculated using equation (8):

$$237 \quad F_{sw} = [-V_{diff} (C_w - C_{wp})] A_b \quad (8)$$

238 where A_b is the surficial sediment surface (m^2), C_w is the lake water-dissolved PCB concentration
239 ($g \cdot m^{-3}$), C_{wp} is the pore water PCB dissolved concentration ($g \cdot m^{-3}$), and V_{diff} is the estimated
240 sediment-water exchange velocity ($m \cdot yr^{-1}$). A positive F_{sw} value corresponds to a net flux of PCBs
241 from the sediment to the water column. The sediment surface A_b was divided into five zones (zones I
242 – V) of the same surface around the five sediment sampling locations along the north-south transect
243 to account for heterogeneous sediment contamination (Fig. S3). More information about the
244 calculation of V_{diff} and C_{wp} can be found in the SI.

245 *Resuspension:*

246 The resuspension of PCBs from the surficial sediment, F_{res} ($\text{g}\cdot\text{yr}^{-1}$), was calculated with equation (9):

$$247 \quad F_{res} = C_s R_{res} A_b \quad (9)$$

248 where C_s is the surficial sediment PCB concentration ($\text{g}\cdot\text{g}_{\text{DW}}^{-1}$), A_b is the lake sediment surface, and
249 R_{res} ($547 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) is the resuspension rate estimated by Eadie et al.³² for lake Michigan. This value
250 was used to calculate of F_{res} since the main parameters affecting resuspension rates (i.e., water
251 column depth, wind speed, bioturbation) were relatively similar for both Lake Michigan and Lake
252 Bourget.

253 *Sediment Burial flow:*

254 The sediment burial flow represents the quantity of PCBs being buried and no longer accessible for
255 resuspension or bioturbation, as they are supposed to be permanently removed from the water
256 column³³.

257 The sediment burial flow was calculated with equation (10):

$$258 \quad F_{sed} = C_s A_{acc} R_{sed(acc)}' \quad (10)$$

259 where C_s is the mean sediment PCB concentration ($\text{g}\cdot\text{kg}_{\text{DW}}^{-1}$), A_{acc} is the surface of the bottom of the
260 lake that allows sediment accumulation, calculated as described by Blais et al.³⁴ The A_{acc} for lake
261 Bourget was estimated to be 11 km^2 .

262 $R_{sed(Aacc)}'$ is the converted accumulation rate ($\text{kg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) calculated with equation (11):

$$263 \quad R_{sed(Aacc)}' = R_{sed(Aacc)} \rho_{sed} \quad (11)$$

264 where $R_{sed(Aacc)}$ is the accumulation rate ($\text{m}^3\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) previously measured at the deepest point of
265 Lake Bourget²⁵ and ρ_{sed} is the sediment density ($\text{kg}\cdot\text{m}^{-3}$).

266 *Net PCB mass balance:*

267 The net PCB mass balance, F_{net} ($\text{g}\cdot\text{yr}^{-1}$), was calculated with equation (12) by subtracting the outputs
268 from the inputs without accounting for internal processes:

$$269 \quad F_{net} = F_{trib} + F_{ad} - (F_{aw} + F_{sed} + F_{fish} + F_{out}) \quad (12)$$

270 A positive F_{net} means that the lake is accumulating PCBs, whereas a negative F_{net} shows a decrease
271 in PCB contamination.

272 An appropriate conversion factor was applied to all fluxes to express the results in ($\text{g}\Sigma 7\text{PCB}\cdot\text{yr}^{-1}$) to
273 facilitate intercomparison.

274 *Water inventory*

275 The total mass of the PCBs in water I_{water} (g) was calculated as follows using equation (13):

$$276 \quad I_{water} = C_w V_w \quad (13)$$

277 where C_w is the total (dissolved + particulate) PCB concentration in the lake water ($\text{g}\cdot\text{m}^{-3}$) and V_w is
278 the volume of the lake water ($3.6 \times 10^9 \text{ m}^3$).

279 *Sediment inventory*

280 The total mass of the PCBs in the surficial sediment, $I_{sediment}$ (kg) (0 – 4 cm), was estimated with
281 equation (14):

282
$$I_{sediment} = \sum_{i=1}^V 4(CS_i \rho S_i) \quad (14)$$

283 where CS_i is the PCB concentration in the sediment in the first centimeter of the five cores
 284 corresponding to zones I to V ($\text{kg}\cdot\text{g}^{-1}$) and ρS_i is the sediment density in zones I to V ($\text{g}\cdot\text{cm}^{-3}$). A factor
 285 of 4 is applied to expend the stock in the first centimeter of sediment to the 4 cm of the surficial
 286 sediment.

287 ***Residence time of PCBs***

288 The residence times in the water (τ_{water}) and in sediment (τ_{sed}) (in days) were calculated as follow
 289 in order to be consistent with the methodology applied for the Lake Michigan Mass Balance Project¹:

290
$$\tau_{water} = \frac{I_{water}}{F_{aw} + F_{out} + F_{set} + F_{sw}}$$

291 and

292
$$\tau_{sed} = \frac{I_{sediment}}{F_{sed} + F_{res}}$$

293

294 **2.7 Error propagation analysis:**

295 To estimate the impact of the uncertainty of the input parameters on the PCB fluxes, error
 296 propagation analysis was performed considering uncertainties in the input parameters (C_w , C_a , H , K_{ol} ,
 297 f_{OM} and C_s). Uncertainties in C_s , C_w and C_a were linked to year-to-year variability, measurement errors
 298 and random analysis errors (see Tab. 1), whereas the uncertainties in H , K_{ow} and the diffusive
 299 boundary layer thickness (δbl) values were discussed above and mentioned in Tab. S3. An
 300 uncertainty of 40% for K_{ol} (including the uncertainty in wind speed and water (K_w) and air (K_a) mass
 301 transfer coefficient estimates) was assumed as commonly accepted^{9,35-37}. Error propagation analysis
 302 was performed with R software using the package “propagate” ([https://cran.r-
 303 project.org/web/packages/propagate/propagate.pdf](https://cran.r-project.org/web/packages/propagate/propagate.pdf)). The software calculated the error propagation
 304 using first-order Taylor expansion accounting for a full covariance structure using a matrix-based
 305 approach.

306

307 **3. Results and discussion**

308 **3.1 Inputs**

309 ***Tributaries***

310 SPM-bound PCBs entering the lake for both the dry and rainy periods were estimated at $23 \pm 3 \text{ mg}\cdot\text{d}^{-1}$
 311 and $146 \pm 85 \text{ mg}\cdot\text{d}^{-1}$, respectively. A nonnegligible part of the PCB input could be attributed to freely
 312 dissolved PCBs with fluxes of $15 \pm 2 \text{ mg}\cdot\text{d}^{-1}$ and $61 \pm 8 \text{ mg}\cdot\text{d}^{-1}$ in the dry and rainy periods,
 313 respectively. Therefore, the total input into the lake (SPM-bind + dissolved PCBs) was estimated at 21
 314 $\pm 6 \text{ g}\cdot\text{yr}^{-1}$. Larger fluxes recorded for the rainy period were due to (i) riverbank erosion, (ii) a higher
 315 water flow due to precipitation and (iii) a substantial resuspension of the highly contaminated
 316 riverbed sediment.

317 The annual flow of the Terre-nue canal over the 2014-2015 period was $0.15 \text{ m}^3\cdot\text{s}^{-1}$ (CISALB, personal
 318 communication). The PCB (dissolved + particulate) concentrations in the river water were $6.5 \text{ ng}\cdot\text{L}^{-1}$

319 and 4.3 ng·L⁻¹ in 2014 and 2015, respectively (“Agence de l’eau RMC”). Therefore, the PCB fluxes
320 entering the lake through Terre-nue canal could be estimated at 24 ± 5 g·yr⁻¹.

321 The PCB (dissolved + particulate) concentrations were measured in the Leyse River by the “Agence
322 de l’eau RMC” in water from 2011 to 2014 (n = 27)²⁴. Unfortunately, water PCB concentration data
323 were not available for the period 2015-2017. PCB concentrations for 2015-2017 were estimated from
324 the mean value of the data from 2011 to 2014 since a steady contamination was observed for this
325 period. Nondetectable values in the “Agence de l’eau RMC” dataset were substituted by LQ/2, as
326 generally accepted³⁸, and were suitable for basic data processing³⁹. Therefore, the mean PCB
327 concentration was estimated at 3.5 ± 0.5 ng·L⁻¹ and was mainly represented by high-molecular-
328 weight PCBs. The mean water flow (2015-2016) of the Leyse River was 6.5 m³·s⁻¹ (CISALB, personal
329 communication). Hence, the annual flux of PCBs entering the lake through the Leyse River was
330 estimated at 724 ± 100 g·yr⁻¹.

331 PCB annual inflows through the three main tributaries can be estimated at 769 ± 100 g·yr⁻¹. The
332 major contributor to PCB inflow in the lake was identified as the Leyse River, mainly because of a
333 higher water flow since the PCB water concentration was on the same order as in the Tillet River and
334 Terre-Nue Canal.

335

336 *Atmospheric deposition*

337 Eighteen samples were analyzed and showed a mean deposition flux of 1.4 ± 0.7 ng·m⁻²·d⁻¹. A
338 seasonal variation was observed, with higher fluxes recorded in the winter than in the summer (i.e.,
339 1.6 ± 0.8 ng·m⁻²·d⁻¹ and 1.0 ± 0.5 ng·m⁻²·d⁻¹, respectively). The PCB profile was dominated by PCB153
340 (27%) but was evenly distributed between low- and high-molecular weight congeners. An increase in
341 the contributions of PCB101, 153, and 138 was observed in the winter compared to the summer. A
342 possible explanation is that heavy PCBs represent a lower proportion of the total gaseous PCBs in the
343 summer (data not shown). Consequently, the heavy PCBs are less exposed to dry and/or wet
344 deposition during this period. Altogether, the average PCB input to the lake through atmospheric
345 deposition for the period 2013-2016 was 23 ± 12 g·yr⁻¹.

346 Uncertainties related to the inputs from rivers and the atmosphere were rather restricted. Indeed,
347 every parameter necessary for the flux calculation was measured, and the need for modeling or
348 extrapolating data was limited. However, uncertainty regarding the inputs through the Leyse River
349 remains nonnegligible. The quantification limits communicated by “Agence de l’eau RMC” for
350 individual PCBs were elevated (i.e., from 0.3 to 1.2 ng·L⁻¹). Therefore, the substantial number of
351 nondetectable values (replaced by LQ/2 in the calculations) in the dataset could have led to an
352 overestimation of the PCB concentration, and consequently, to an overestimation of PCB inputs.
353 However, the sediment concentration of the Leyse river sediments recorded by “Agence de l’eau
354 RMC” (5 – 33.5 ng·gD·W⁻¹) for the period 2013 to 2017 and the concentration measured in the Leyse
355 River plume zone in Lake Bourget (75 ng·gD·W⁻¹) in 2005⁴⁰ are important. These results support the
356 high levels of PCB contamination recorded in the water and strengthen our hypothesis that the
357 Leyse River is currently the major source of PCBs in Lake Bourget.

358 **3.2 Internal flows**

359 *Settling*

360 Samples representing an integrative settling particle flux for a full year (July 2016 to June 2017) could
361 be retrieved from the automatic sediment trap and analyzed. The total sediment dry weight

362 collected was 1400 g, and the settling rate was $0.14 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$. The mean PCB concentration in the
363 settling particles from the three sediment traps across the lake ($n = 5$) was $56 \pm 39 \text{ ng}\cdot\text{g}_{\text{DW}}^{-1}$ and was
364 assumed to be representative of the whole lake. The PCB congener profile was mainly composed of
365 heavy PCBs (PCB 153, 138, 180 > 75% $\Sigma 7\text{PCB}_i$). Hence, the annual flux of PCBs to the sediment
366 through settling was estimated at $1721 \pm 1214 \text{ g}\cdot\text{yr}^{-1}$.

367 *Resuspension*

368 The resuspension of PCBs from the sediment was calculated for zones I – V to account for
369 discrepancies in sediment PCB concentration at the five sampling locations (Tab. 1). Resuspension
370 from the sediment concerned mostly PCBs with a high affinity for organic matter (i.e., PCB153, 138,
371 180 > 75%). By adding the results for zones I – V, an annual resuspension flux of $1648 \pm 549 \text{ g}\cdot\text{yr}^{-1}$ was
372 deduced.

373 *Diffusive water/sediment PCB exchange flux*

374 Diffusive water/sediment PCB exchange flux was estimated for zones I to V. Every PCB congener
375 showed sorption to surficial sediment in every zone except for PCB28, which diffused from the
376 sediment to the water in zones II, IV and V. Generally, the PCB flux profile was relatively similar
377 between sites and was dominated by PCB101 (20%) and PCB138 (25%) (Fig. S4 in SI). The sorption
378 rates of PCBs were similar in zones I, II, III and V, with a flux of $3.25 - 4 \text{ }\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$. However, a lower
379 flux was calculated for zone IV ($1.7 \text{ }\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$). This was due to the higher PCB concentration in the
380 sediment of zone IV compared to the other zones. Overall, the sorption flux from water to sediment
381 was estimated at $143 \pm 62 \text{ g}\cdot\text{yr}^{-1}$.

382 Error propagation analysis was performed and included a measurement in the uncertainty of C_w , C_s ,
383 f_{OM} , K_{ow} and δbl . An uncertainty of 76–100% was associated with the flux of PCBs in every zone
384 except zone IV (191%). The relative contribution of input parameter uncertainty to the sorption flux
385 uncertainty was investigated. The flux uncertainty was mainly associated with C_w (45%), δbl (16%)
386 and K_{ow} (14%). In the case of the diffusion from sediment to water, the flux uncertainty was related
387 to C_s (41%), K_{ow} (26%), C_w (15%) and δbl (14%). Thus, it is critical to correctly assess C_s and C_w to
388 perform the modeling of this flux, but a wise choice of δbl and K_{ow} values also enhances the accuracy
389 of the model.

390 Overall, the internal flux ($F_{\text{set}} + F_{\text{sw}} - F_{\text{res}}$) was $70 \pm 1334 \text{ g}\cdot\text{yr}^{-1}$. Therefore, this system could be
391 considered at equilibrium and was not included in the net PCB mass budget hereafter.

392 **3.3 Outputs**

393 *Air/water gaseous PCB exchange*

394 The model showed a mean net PCB volatilization of $54 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ from the surface of Lake Bourget.
395 Every PCB congener outgassed, and the volatilization profile was evenly represented by low- and
396 high-molecular weight PCBs (i.e., mainly PCB28, 52 and 153, Fig. S5 in SI). A seasonal pattern was
397 observed since monthly fluxes of PCB volatilization were on average 35% higher in the period of May
398 to August than in the rest of the year. However, the PCB volatilization profile remained fairly
399 constant throughout the year. The higher fluxes observed in the summer were due to (i) a warmer
400 lake water temperature and (ii) a lower gaseous PCB concentration (i.e., mean $\Sigma 7\text{PCB}_i$ (summer) =
401 $35.0 \text{ pg}\cdot\text{m}^{-3}$ and mean $\Sigma 7\text{PCB}_i$ (winter) = $127.3 \text{ pg}\cdot\text{m}^{-3}$).

402 The influence of the input parameters can vary depending on the direction of the flux (i.e.,
403 volatilization or absorption), as recently demonstrated by Liu et al.⁹ Therefore, measurement errors

404 regarding the input parameters or an unwise choice in H values for computing could critically affect
405 the flux calculation because it could lead to great uncertainties in the resulting flux. According to Liu
406 et al.⁹, when volatilization dominated, the main input parameters influencing the flux were C_w and
407 K_{oi} .

408 To identify the relative contribution and the effects of the uncertainty from the input parameters to
409 the flux uncertainty, an error propagation analysis was performed for individual PCB congeners.
410 Overall, an uncertainty of 55% was computed for the yearly flux of PCB. This output was similar for
411 Lake Ontario and Lake Erie⁹. The relative contribution of parameter uncertainty to the flux
412 uncertainty was mainly related to C_w (86%) and K_{oi} (13%). This result was consistent with the control
413 of C_w and K_{oi} over the flux intensity in the case of volatilization⁹. Nonetheless, the importance in the
414 choice of H value for modeling should not be minimized. Indeed, flux modeling with the minimum
415 and maximum individual PCB H values (among those retained for this study ($n = 10$) from the Henry's
416 law compilation from Sander²⁹) led to a variation of 209% in the PCB volatilization flux when every
417 other input parameter was fixed. Altogether, the volatilization flux of PCBs was $861 \pm 473 \text{ g}\cdot\text{yr}^{-1}$.

418 *Sediment burial*

419 The sediment burial flow was calculated for the accumulation zone of Lake Bourget (i.e., 11 km^2). The
420 PCB congener profile of the buried sediment was mainly composed of heavy PCBs (PCB153, 138, 180
421 > 80%, Fig. S6), as could be expected from the high affinity of these highly chlorinated molecules for
422 organic particles. An annual flux definitively incorporating the anoxic sediment of $3408 \pm 2404 \text{ g}\cdot\text{yr}^{-1}$
423 was estimated. This elevated flux was mainly due to the intensity of the accumulation rate as a result
424 of a high settling rate combined with an important resuspension of SPM-bound particles eventually
425 accumulated at the bottom of the lake.

426 *Outflow*

427 Outflow was only possible through the Savières Canal. The mean water flow was $13.4 \text{ m}^3\cdot\text{s}^{-1}$, and the
428 total lake water concentration was $518 \pm 96 \text{ pg}\cdot\text{L}^{-1}$. Therefore, the average annual flow of PCBs
429 exiting the lake was estimated to be $220 \pm 41 \text{ g}\cdot\text{yr}^{-1}$.

430 *Output through fishing activity*

431 The mean PCB concentration in fish filets for the period 2013-2017 was $258 \pm 90 \text{ ng}\cdot\text{gW}\cdot\text{W}^{-1}$ and $47 \pm$
432 $26 \text{ ng}\cdot\text{gW}\cdot\text{W}^{-1}$ for arctic char and whitefish, respectively. The average annual capture (professional
433 and recreational) of arctic char and whitefish was 4 and 95 tons, respectively, for the period 2014-
434 2017 (S. Cachera, personal communication). Therefore, the annual output through fishing activity
435 was $5 \pm 1 \text{ g}\cdot\text{yr}^{-1}$.

436 **3.4 PCB inventory in Lake Bourget**

437 The net flow of PCBs in Lake Bourget exiting the lake water column for the period 2013-2017 was
438 $3701 \pm 2452 \text{ g}\cdot\text{yr}^{-1}$ and was mainly due to sediment burial and volatilization (Fig. 1). This net output
439 was consistent with a diminution of the lake contamination, as suggested by the decreasing PCB
440 contamination observed in the biota since 2008²⁷.

441 The stock of PCBs in the lake water column was estimated from the water total PCB concentration
442 and the volume of the lake. A stock of $1865 \pm 353 \text{ g}$ of PCBs was estimated to remain in the water
443 column, both in dissolved and particulate form, potentially susceptible to bioaccumulation in the
444 biota. This stock is expected to decline due to the negative net flow of PCBs in Lake Bourget. The
445 residence time of PCBs in the water column was estimated at 231 ± 72 days. This results is similar to

446 that of Guo et al. (2017)⁴¹ in Lake Michigan and highlights the relatively rapid dynamics of PCBs in
447 water. A stock of PCBs in the lake surficial sediment (0-4 cm) for zones I to V of 181 ± 60 kg was
448 estimated. This represents the quantity of PCBs potentially available for resuspension, bioturbation
449 or diffusion to the water column. Moreover, the residence time of PCBs in the surficial sediment was
450 estimated at 36 ± 20 years. Therefore, the high quantity of PCBs in the sediment associated with a
451 long residence time cannot be neglected and raises concern even though this stock is expected to
452 become progressively lower with the progressive deposition of cleaner sediment due to the
453 continuous decrease in the PCB concentration in the water column.

454 In this work, photo-degradation of PCBs in the euphotic zone as well as biodegradation processes in
455 the anoxic compartment of the sediment were considered negligible. Therefore, the impact of these
456 processes in the removal of PCBs from these two compartments were neglected.

457

458 **3.5 Main fluxes driving PCB decontamination in Lake Bourget**

459 *Importance of PCB loads from tributaries to perialpine lake contamination*

460 The input of PCBs into Lake Bourget was mainly due to inflow from contaminated tributaries rather
461 than from atmospheric inputs (i.e., dry and wet deposition + gaseous absorption). This is in contrast
462 with other lakes, such as lake Michigan and Lake Superior, where atmospheric inputs contribute
463 more than tributaries^{2,3}. Two possible explanations are (i) the catchment area over the lake surface
464 area ratio was 13 for Lake Bourget and 0.6–1.5 for the American Great Lakes, which enabled a larger
465 contribution from atmospheric deposition in the latter and (ii) the much higher water residence time
466 (i.e., 99 years in Lake Michigan and 8 years for Lake Bourget) could justify the lower PCB input
467 through tributaries. However, our results were consistent with those of Gevaio et al.⁴ for a small rural
468 lake (Lake Cumbria) in the UK with a high catchment area to lake surface area ratio (i.e., 17). As
469 expected, the contribution of the Tillet River was very low ($21 \text{ g}\cdot\text{yr}^{-1}$) and diminished drastically
470 compared to the prior sediment clean-up ($1500 \text{ g}\cdot\text{yr}^{-1}$). Consequently, the Leysse River should
471 currently be considered as the main source of PCBs in Lake Bourget.

472 Altogether, our results suggest that as in the American Great Lakes^{2,3}, losses through sediment burial
473 and volatilization largely overcame any other fluxes. This observation was rather consistent with
474 previous studies reporting the PCB mass budget of several American Great Lakes exhibiting high
475 levels of PCBs in the water column. However, some discrepancies about the relative contributions of
476 these fluxes to the PCB net losses were noted.

477 *Sediment burial as a driver for the loss of PCBs*

478 The sediment burial contribution was larger in Lake Bourget (i.e., 76%) than in the American Great
479 Lakes (i.e., 27%²). This observation was mainly related to dissimilarities in the accumulation rates
480 rather than in the PCB contamination of surficial sediment. The high accumulation rate recorded in
481 Lake Bourget could be related to the fact that despite a constant decrease since the peak
482 eutrophication in the 1970s, Lake Bourget primary production remains higher than in the American
483 Great Lakes (Chlorophyll α concentration = $3.3 \text{ mg}\cdot\text{m}^{-3}$ vs $0.75 \text{ mg}\cdot\text{m}^{-3}$, respectively⁴² and total
484 phosphorus = $9 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ vs $7 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ respectively^{16,43}). Therefore, the effect of the biological pump
485 coupled with a high settling flux that drives organic contaminants from the euphotic zone to the
486 sediment could partly explain the intensity of the sediment burial flux of PCBs. In addition, the
487 important SPM loads from the tributaries contributed in part to the high accumulation rate.
488 Furthermore, the binding of the more hydrophobic PCBs to the suspended particles should directly

489 impact the intensity of the sediment burial of PCBs and its contribution to lake decontamination. If
490 the efforts towards reoligotrophication remains effective in the future, primary production and PCB
491 sediment burial flux should continue to decline. However, in the context of climate change, an
492 increase in the water temperature could enhance the primary production and counterbalance or
493 overcome the former effect.

494 *Impact of volatilization in the lacustrine decontamination process: observations and* 495 *perspectives*

496 The estimated net volatilization rate of $54 \pm 30 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ was high compared to Lake Erie and Lake
497 Ontario (2.9 and $9 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, respectively)⁴⁴ but was on the same order as that of Lake Michigan ($52 \pm$
498 $22 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)² and Lake Cumbria⁴ ($192 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$). This net volatilization is closely related to the
499 dissimilarities in PCB water concentration because it is the main parameter driving the flux intensity
500 in the case of volatilization, as stated earlier. Indeed, the water concentrations were low in Lake Erie
501 and Lake Ontario (33.9 and $29.1 \text{ pg}\cdot\text{L}^{-1}$, respectively)⁴⁴ compared to Lake Michigan ($190\text{-}300 \text{ pg}\cdot\text{L}^{-1}$)²
502 and Lake Cumbria ($2000 \text{ pg}\cdot\text{L}^{-1}$)⁴⁵. Considering that the surface area/volume ratio of Lake Bourget is
503 comparable to Lake Michigan (12.8 and 11.8 , respectively) and that the volatilization rate is of the
504 same order, volatilization contributes similarly to the PCB decontamination of the water column in
505 both lakes. The higher average water surface temperature in Lake Bourget compared to Lake
506 Michigan (i.e., 15.5°C and 10°C , respectively)^{16,46} did not significantly impact the magnitude of the
507 volatilization process or its relative contribution to the loss of PCBs from the lake. Even though it was
508 not investigated in this study, a seasonal variability of the volatilization process is expected to occur.
509 Indeed, volatilization has been shown to be related to processes that are season-dependent such as
510 temperature⁴⁷, thermal stratification^{48,49} or plankton abundance^{50,51}.

511 An important rise in the water temperature is expected in the near future. These trends will be
512 magnified in small- to medium-sized water bodies, such as perialpine lakes, which are more sensitive
513 to variations in the air temperature than large lakes. An increase in surface water temperature will
514 impact the biogeochemical processes of PCBs. Among the perturbation of other mechanisms such as
515 partitioning to particulate matter or enhanced uptake by the biota such as described in the work of
516 Meijer et al.⁵², an increase of temperature could also thermodynamically favor the volatilization of
517 PCBs. Therefore, it could ultimately enhance the relative contribution of this flux to the overall PCB
518 mass budget.

519 This PCB mass budget revealed important discrepancies compared to previously investigated
520 ecosystems (i.e., the American Great Lakes and high-altitude lakes) and brings new insights into the
521 processes ruling PCB dynamics in perialpine lakes. Most of the perialpine lakes in Europe present
522 similar characteristics (i.e., high catchment basin/lake surface area ratio, similar surface area/volume
523 ratio, low water residence time, highly urbanized and industrialized watershed) to Lake Bourget.
524 Therefore, the PCB mass budget investigated in this work should be applicable to similar lakes across
525 the world (e.g., Lake Geneva, Lake Maggiore).

526 *Impact of uncertainties in the estimation of PCB fluxes*

527 The contribution of uncertainties in the PCB concentration of environmental samples to the modeled
528 flux uncertainties highlighted the importance of an accurate determination of PCB concentration in
529 every studied matrix. As an example, PCB concentration in sediment must be precisely measured for
530 the calculation of diffusion at the water/sediment interface and sediment burial fluxes. Similarly,
531 measurements of the truly dissolved PCB concentration for air/water exchange modeling are also
532 recommended since only truly dissolved PCBs are available for volatilization. This measurement

533 remains challenging, and it has been shown that ~35% of PCBs were not retained by conventional
534 filtration of particles due to binding to colloids⁵³. Colloid-bound PCBs included in the dissolved PCB
535 fraction would lead to an overestimation of the dissolved PCB concentration and volatilization flux.
536 Therefore, the determination of the water-dissolved PCB concentration using passive sampling
537 techniques is recommended and leads to robust results^{44,54}. These cheap and easily operated
538 techniques should encourage the performance of triplicate measurements to reduce measurement
539 uncertainties. Moreover, these techniques allow time-weighted average concentration
540 measurements and could be used to obtain mean water concentration with a moderate temporal
541 resolution within a timeframe of a few weeks. The error propagation analysis also highlighted the
542 importance of the wise choice of constants for the accurate estimation of modeled fluxes.
543 Consequently, a careful, exhaustive review of the literature available should be performed before
544 assigning H and K_{ow} values to the flux calculation. Relying on at least a review paper rather than on
545 only one source is highly recommended. When possible and appropriate, field measurements should
546 be performed to lessen the use of inconsistent constant values or partition coefficients in flux
547 modeling.

548

549 Author information

550 Corresponding author:

551 *Tel: +33 479 758 898; email: Thibault.masset@univ-smb.fr

552 References:

- 553 (1) Rossmann, R. Results of the Lake Michigan Mass Balance Project: Polychlorinated Biphenyls
554 Modeling Report. **2006**.
- 555 (2) Guo, J.; Romanak, K.; Westenbroek, S.; Li, A.; Kreis Jr, R. G.; Hites, R. A.; Venier, M. *Environ. Sci.*
556 *Technol.* **2017**, *51* (21), 12455–12465.
- 557 (3) Jeremiason, J. D.; Hornbuckle, K. C.; Eisenreich, S. J. PCBs in Lake Superior, 1978-1992:
558 Decreases in Water Concentrations Reflect Loss by Volatilization. *Environ. Sci. Technol.* **1994**,
559 *28* (5), 903–914.
- 560 (4) Gevao, B.; Hamilton-Taylor, J.; Jones, K. C. Towards a Complete Mass Balance and Model for
561 PCBs and PAHs in a Small Rural Lake, Cumbria UK. *Limnol. Oceanogr.* **2000**, *45* (4), 881–894.
- 562 (5) Grimalt, J. O.; Fernandez, P.; Berdie, L.; Vilanova, R. M.; Catalan, J.; Psenner, R.; Hofer, R.;
563 Appleby, P. G.; Rosseland, B. O.; Lien, L.; et al. Selective Trapping of Organochlorine
564 Compounds in Mountain Lakes of Temperate Areas. *Environ. Sci. Technol.* **2001**, *35* (13),
565 2690–2697. <https://doi.org/10.1021/es000278r>.
- 566 (6) Nellier, Y.-M.; Perga, M.-E.; Cottin, N.; Fanget, P.; Malet, E.; Naffrechoux, E. Mass Budget in
567 Two High Altitude Lakes Reveals Their Role as Atmospheric PCB Sinks. *Sci. Total Environ.* **2015**,
568 *511*, 203–213. <https://doi.org/10.1016/j.scitotenv.2014.12.052>.
- 569 (7) Blais, J. M.; Schindler, D. W.; Sharp, M.; Braekevelt, E.; Lafrenière, M.; McDonald, K.; Muir, D.
570 C.; Strachan, W. M. Fluxes of Semivolatile Organochlorine Compounds in Bow Lake, a High-
571 altitude, Glacier-fed, Subalpine Lake in the Canadian Rocky Mountains. *Limnol. Oceanogr.*
572 **2001**, *46* (8), 2019–2031.
- 573 (8) Meijer, S. N.; Dachs, J.; Fernandez, P.; Camarero, L.; Catalan, J.; Del Vento, S.; Van Drooge, B.;
574 Jurado, E.; Grimalt, J. O. Modelling the Dynamic Air–Water–Sediment Coupled Fluxes and
575 Occurrence of Polychlorinated Biphenyls in a High Altitude Lake. *Environ. Pollut.* **2006**, *140* (3),
576 546–560.

- 577 (9) Liu, Y.; Wang, S.; McDonough, C. A.; Khairy, M.; Muir, D.; Lohmann, R. Estimation of
578 Uncertainty in Air-Water Exchange Flux and Gross Volatilization Loss of PCBs: A Case Study
579 Based on Passive Sampling in the Lower Great Lakes. *Environ. Sci. Technol.* **2016**.
580 <https://doi.org/10.1021/acs.est.6b02891>.
- 581 (10) Totten, L. A.; Gigliotti, C. L.; Offenberg, J. H.; Baker, J. E.; Eisenreich, S. J. Reevaluation of
582 Air–Water Exchange Fluxes of PCBs in Green Bay and Southern Lake Michigan. *Environ. Sci.*
583 *Technol.* **2003**, *37* (9), 1739–1743. <https://doi.org/10.1021/es026093x>.
- 584 (11) Corvi, C.; Majeux, C.; Vogel, J. Les Polychlorobiphényles et Le DDE Dans Les Sédiments
585 Superficiels Du Léman et de Ses Affluents. *Rapp Comm Int Prot Eaux Léman Contre Pollut*
586 *Camp.* **1986**, *1985*, 207–216.
- 587 (12) Thomas, R. L.; Vernet, J. P.; Frank, R. ΣDDT, PCBs, and HCB in the Sediments of Lake Geneva
588 and the Upper Rhône River. *Environ. Geol.* **1983**, *5* (3), 103–113.
589 <https://doi.org/10.1007/BF02381268>.
- 590 (13) Loizeau, E.; MAKRI, S.; ARPAGAU, P.; FERRARI, B.; CASADO-MARTINEZ, C.; BENEJAM, T.;
591 MARCHAND, P. Micropolluants Métalliques et Organiques Dans Les Sédiments Superficiels Du
592 Léman (Metallic and Organic Micropolluants in the Surface Sédiments of Lake Geneva. *Rapp*
593 *Comm Int Prot Eaux Léman Contre Pollut Camp.* **2016**, *2017*, 143–198.
- 594 (14) Bettinetti, R.; Quadroni, S.; Boggio, E.; Galassi, S. Recent DDT and PCB Contamination in the
595 Sediment and Biota of the Como Bay (Lake Como, Italy). *Sci. Total Environ.* **2016**, *542*, 404–
596 410.
- 597 (15) Guzzella, L. M.; Novati, S.; Casatta, N.; Roscioli, C.; Valsecchi, L.; Binelli, A.; Parolini, M.; Solcà,
598 N.; Bettinetti, R.; Manca, M. Spatial and Temporal Trends of Target Organic and Inorganic
599 Micropollutants in Lake Maggiore and Lake Lugano (Italian-Swiss Water Bodies):
600 Contamination in Sediments and Biota. *Hydrobiologia* **2018**, 1–20.
- 601 (16) Jacquet, S., D. Barbet, C. Barbier, S. Cachera, M. Colon, L. Espinat, C. Girel, J. Guillard, V.
602 Hamelet, J.C.; Hustache, D. Lacroix, L. Laine, B. Leberre, J. Neasat, G. Paolini, M. Perga, P.
603 Perney, F. Rimet. Suivi Environnemental Des Eaux Du Lac Du Bourget Pour l’année 2017. **2018**.
- 604 (17) Balvay, G.; Laurent, M. Evolution Quantitative à Long Terme Des Rotifères Au Cours de
605 l’eutrophisation Du Lac Léman. *Aquat. Sci.-Res. Boundaries* **1990**, *52* (2), 162–175.
- 606 (18) Balvay, G. Eutrophisation et Phytoplancton Du Lac d’Annecy. *Terre-Vive* **1971**, 13–16.
- 607 (19) Morabito, G.; Manca, M. Eutrophication and Recovery of the Large and Deep Subalpine Lake
608 Maggiore: Patterns, Trends and Interactions of Planktonic Organisms between Trophic and
609 Climatic Forcings. *Eutrophication Causes Econ. Implic. Future Chall. Environ. Sci. Lambert Roux*
610 *C Eds* **2013**, 183–214.
- 611 (20) Galbán-Malagón, C.; Del Vento, S.; Cabrerizo, A.; Dachs, J. Factors Affecting the Atmospheric
612 Occurrence and Deposition of Polychlorinated Biphenyls in the Southern Ocean. *Atmospheric*
613 *Chem. Phys.* **2013**, *13* (23), 12029–12041.
- 614 (21) Nizzetto, L.; Gioia, R.; Li, J.; Borgå, K.; Pomati, F.; Bettinetti, R.; Dachs, J.; Jones, K. C. Biological
615 Pump Control of the Fate and Distribution of Hydrophobic Organic Pollutants in Water and
616 Plankton. *Environ. Sci. Technol.* **2012**, *46* (6), 3204–3211.
- 617 (22) Dumas, M. D. Changes in Temperature and Temperature Gradients in the French Northern
618 Alps during the Last Century. *Theor. Appl. Climatol.* **2013**, *111* (1–2), 223–233.
- 619 (23) Cottin, N. ContaSed2015; Monte Verità, Ascona (Switzerland), **2015**.
- 620 (24) Agence de l’eau RMC. Base de Données Micropolluants Du Programme PCB. Agence de l’eau
621 RMC, FRANCE **2008**.
- 622 (25) Jenny, J.-P. Réponses Des Grands Lacs Périalpins Aux Pressions Anthropiques et Climatiques
623 Récentes: Reconstitutions Spatio-Temporelles à Partir d’archives Sédimentaires. **2013**.
- 624 (26) Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. Using Passive Air Samplers To
625 Assess Urban–Rural Trends for Persistent Organic Pollutants. 1. Polychlorinated Biphenyls and
626 Organochlorine Pesticides. *Environ. Sci. Technol.* **2004**, *38* (17), 4474–4483.
627 <https://doi.org/10.1021/es040302r>.

- 628 (27) Masset, T.; Frossard, V.; Perga, M.; Cottin, N.; Piot, C.; Cachera, S.; Naffrechoux, E. Trophic
629 Position and Individual Feeding Habits as Drivers of Differential PCB Bioaccumulation in Fish
630 Populations. *Sci. Total Environ.* **2019**.
- 631 (28) Dargnat, C.; Fisson, C. Les PolyChloroBiphényles (PCB) Dans Le Bassin de La Seine et Son
632 Estuaire. March **2010**.
- 633 (29) Sander, R. Compilation of Henry's Law Constants (Version 4.0) for Water as Solvent. *Atmos*
634 *Chem Phys* **2015**, *15* (8), 4399–4981. <https://doi.org/10.5194/acp-15-4399-2015>.
- 635 (30) Corcoran, M.; Sherif, M. I.; Smalley, C.; Li, A.; Rockne, K. J.; Giesy, J. P.; Sturchio, N. C.
636 Accumulation Rates, Focusing Factors, and Chronologies from Depth Profiles of 210Pb and
637 137Cs in Sediments of the Laurentian Great Lakes. *J. Gt. Lakes Res.* **2018**, *44* (4), 693–704.
- 638 (31) Vinçon-Leite, B.; Groleau, A.; Sarazin, G.; Quiblier, C.; Paolini, G.; Tassin, B. Fonctionnement
639 Biogéochimique Du Lac Du Bourget: Phosphore, Phytoplancton Calcite et Taux de
640 Sédimentation; La page blanche, **2006**; pp 65–73.
- 641 (32) Eadie, B. J.; Vanderploeg, H. A.; Robbins, J. A.; Bell, G. L. Significance of Sediment
642 Resuspension and Particle Settling. In *Large Lakes*; Springer, **1990**; pp 196–209.
- 643 (33) Eisenreich, S. J. The Chemical Limnology of Nonpolar Organic Contaminants: Polychlorinated
644 Biphenyls in Lake Superior. *Adv. Chem. Ser. USA* **1987**.
- 645 (34) Blais, J. M.; Kalff, J. The Influence of Lake Morphometry on Sediment Focusing. *Limnol.*
646 *Oceanogr.* **1995**, *40* (3), 582–588.
- 647 (35) Rowe, M. D.; Perlinger, J. A. Micrometeorological Measurement of Hexachlorobenzene and
648 Polychlorinated Biphenyl Compound Air-Water Gas Exchange in Lake Superior and
649 Comparison to Model Predictions. *Atmos Chem Phys* **2012**, *12* (10), 4607–4617.
650 <https://doi.org/10.5194/acp-12-4607-2012>.
- 651 (36) Fang, M.-D.; Lee, C.-L.; Jiang, J.-J.; Ko, F.-C.; Baker, J. E. Diffusive Exchange of PAHs across the
652 Air–Water Interface of the Kaohsiung Harbor Lagoon, Taiwan. *J. Environ. Manage.* **2012**, *110*,
653 179–187.
- 654 (37) Chang, F.; Pagano, J. J.; Crimmins, B. S.; Milligan, M. S.; Xia, X.; Hopke, P. K.; Holsen, T. M.
655 Temporal Trends of Polychlorinated Biphenyls and Organochlorine Pesticides in Great Lakes
656 Fish, 1999–2009. *Sci. Total Environ.* **2012**, *439*, 284–290.
- 657 (38) Epa, U. *Guidance for Data Quality Assessment. Practical Methods for Data Analysis. Office of*
658 *Environmental Information*; EPA QA/G-9, QA00 Version Washington, DC, **2000**.
- 659 (39) Helsel, D. R. Fabricating Data: How Substituting Values for Nondetects Can Ruin Results, and
660 What Can Be Done about It. *Chemosphere* **2006**, *65* (11), 2434–2439.
- 661 (40) Jung, S.; Chebbo, G.; Lorgeoux, C.; Tassin, B.; Arnaud, F.; Bonte, P.; Winiarski, T. Temporal
662 Evolution of Urban Wet Weather Pollution: Analysis of PCB and PAH in Sediment Cores from
663 Lake Bourget, France. *Water Sci. Technol.* **2008**, *57* (10), 1503–1510.
- 664 (41) Guo, J.; Romanak, K.; Westenbroek, S.; Li, A.; Kreis Jr, R. G.; Hites, R. A.; Venier, M. Updated
665 Polychlorinated Biphenyl Mass Budget for Lake Michigan. *Environ. Sci. Technol.* **2017**, *51* (21),
666 12455–12465.
- 667 (42) Fahnenstiel, G. L.; Sayers, M. J.; Shuchman, R. A.; Yousef, F.; Pothoven, S. A. Lake-Wide
668 Phytoplankton Production and Abundance in the Upper Great Lakes: 2010–2013. *J. Gt. Lakes*
669 *Res.* **2016**, *42* (3), 619–629.
- 670 (43) Pauer, J. J.; Anstead, A. M.; Melendez, W.; Taunt, K. W.; Kreis Jr, R. G. Revisiting the Great
671 Lakes Water Quality Agreement Phosphorus Targets and Predicting the Trophic Status of Lake
672 Michigan. *J. Gt. Lakes Res.* **2011**, *37* (1), 26–32.
- 673 (44) Liu, Y.; Wang, S.; McDonough, C. A.; Khairy, M.; Muir, D. C. G.; Helm, P. A.; Lohmann, R.
674 Gaseous and Freely-Dissolved PCBs in the Lower Great Lakes Based on Passive Sampling:
675 Spatial Trends and Air-Water Exchange. *Environ. Sci. Technol.* **2016**, *50* (10), 4932–4939.
676 <https://doi.org/10.1021/acs.est.5b04586>.
- 677 (45) Gevao, B.; Hamilton-Taylor, J.; Jones, K. C. Polychlorinated Biphenyl and Polycyclic Aromatic
678 Hydrocarbon Deposition to and Exchange at the Air–Water Interface of Esthwaite Water, a
679 Small Lake in Cumbria, UK. *Environ. Pollut.* **1998**, *102* (1), 63–75.

- 680 (46) NOAA (National Oceanic and Atmospheric Administration). NOAA CoastWatch, Great Lakes
681 Node. **2016**.
- 682 (47) Hornbuckle, K. C.; Jeremiason, J. D.; Sweet, C. W.; Eisenreich, S. J. Seasonal Variations in Air-
683 Water Exchange of Polychlorinated Biphenyls in Lake Superior. *Environ. Sci. Technol.* **1994**, *28*
684 (8), 1491–1501. <https://doi.org/10.1021/es00057a018>.
- 685 (48) Dueri, S.; Castro-Jiménez, J.; Zaldívar, J.-M. Modelling the Influence of Thermal Stratification
686 and Complete Mixing on the Distribution and Fluxes of Polychlorinated Biphenyls in the Water
687 Column of Ispra Bay (Lake Maggiore). *Chemosphere* **2009**, *75* (9), 1266–1272.
- 688 (49) Jurado, E.; Zaldívar, J.-M.; Marinov, D.; Dachs, J. Fate of Persistent Organic Pollutants in the
689 Water Column: Does Turbulent Mixing Matter? *Mar. Pollut. Bull.* **2007**, *54* (4), 441–451.
- 690 (50) Dachs, J.; Eisenreich, S. J.; Baker, J. E.; Ko, F.-C.; Jeremiason, J. D. Coupling of Phytoplankton
691 Uptake and Air–Water Exchange of Persistent Organic Pollutants. *Environ. Sci. Technol.* **1999**,
692 *33* (20), 3653–3660. <https://doi.org/10.1021/es990168o>.
- 693 (51) Jeremiason, J. D.; Eisenreich, S. J.; Paterson, M. J.; Beaty, K. G.; Hecky, R.; Elser, J. J.
694 Biogeochemical Cycling of PCBs in Lakes of Variable Trophic Status: A Paired-Lake Experiment.
695 *Limnol. Oceanogr.* **1999**, *44* (3part2), 889–902.
696 https://doi.org/10.4319/lo.1999.44.3_part_2.0889.
- 697 (52) Meijer, S. N.; Grimalt, J. O.; Fernandez, P.; Dachs, J. Seasonal Fluxes and Temperature-
698 Dependent Accumulation of Persistent Organic Pollutants in Lakes: The Role of Internal
699 Biogeochemical Cycling. *Environ. Pollut.* **2009**, *157* (6), 1815–1822.
- 700 (53) Baker, J. E.; Capel, P. D.; Eisenreich, S. J. Influence of Colloids on Sediment-Water Partition
701 Coefficients of Polychlorobiphenyl Congeners in Natural Waters. *Environ. Sci. Technol.* **1986**,
702 *20* (11), 1136–1143.
- 703 (54) Vrana, B.; Allan, I. J.; Greenwood, R.; Mills, G. A.; Dominiak, E.; Svensson, K.; Knutsson, J.;
704 Morrison, G. Passive Sampling Techniques for Monitoring Pollutants in Water. *TrAC Trends*
705 *Anal. Chem.* **2005**, *24* (10), 845–868. <https://doi.org/10.1016/j.trac.2005.06.006>.
706

Compartment	n	Monitoring period	Mean ± sd
Water, tributary (ng.L⁻¹)			
Terre-Nue canal	2	2014-2015	5.3 ± 1.0
Leyse River	4	2010-2014	3.5 ± 0.5
Tillet River (dissolved fraction only)	3	2017	1.8 ± 0.2
Water, Lake (dissolved) (pg.L⁻¹)	5	2015-2016	384 ± 170
Water, Lake (total) (pg.L⁻¹)	3	2015-2016	518 ± 96
Air, gas (pg.m⁻³)	9	2014-2016	47 ± 18 (summer) 106 ± 70 (winter)
Sediment core, Lake (0 – 1cm) (ng.g_{DW}⁻¹)			
Zone I	2	2013-2015	47 ± 43
Zone II	1	2015	52
Zone III	2	2013-2015	59 ± 64
Zone IV	3	2013-2016	121 ± 15
Zone V	3	2013-2016	61 ± 82
Fish filet (ng.g w.w⁻¹)	248	2013-2017	258 ± 90 (arctic char) 47 ± 26 (whitefish)
Water Temperature (°C)	24	2015-2016	18 ± 4 (summer) 8.1 ± 2.3 (winter)
Wind speed (m.s⁻¹)	24	2015-2016	2.1 ± 0.3 (summer) 2.4 ± 0.4 (winter)

Table 1: $\Sigma 7\text{PCB}_i$ concentrations in the Lake Bourget ecosystem and meteorological parameters used for model computation (n = number of samples, sd = standard deviation).

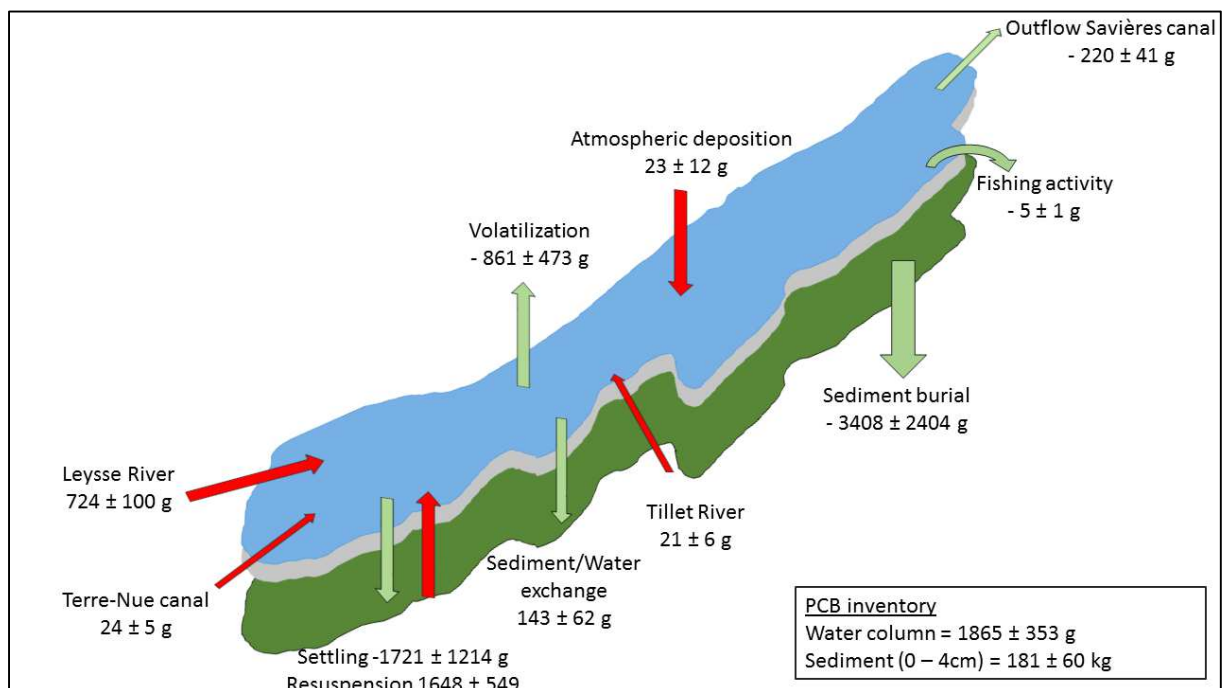


Fig. 1: PCB mass budget (mean ± sd) of Lake Bourget (2013-2017). The green area represents the surficial sediment of the lake.

