Supplementary Information: Preventing CO_2 overestimation from mercuric or copper (II) chloride preservation of dissolved gases in freshwater samples

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Table S1. Water chemistry analyses of Lake Svartkulp sample.

Determinants	Standard (NIVA method)	Result	Units	MU	LOQ
Alkalinity	NS-EN ISO 9963-1:1996 (C1-4)	127	μmol L^{-1}	20%	30
Ammonium	NS-EN ISO 10304-1:2009 (anion) NS-EN ISO 14911:1999 (cation) (C4-4)	3	μg N L^{-1}	20%	2
Nitrate	NS-EN ISO 10304-1:2009 (anion) NS-EN ISO 14911:1999 (cation) (C4-4)	5	μg N L^{-1}	20%	2
Colour	NS-EN ISO 7887:2011 (A5-2)	59	mg L^{-1} Pt	20%	2
Phosphate	Mod. NS 4724:1984 (D1-3)	1	μg P L^{-1}	30%	1
pH	NS-EN ISO 10523:2012 (A1-5)	6.73	pH units	±0.2	3.5
pH temperature	NS-EN ISO 10523:2012 (A1-5)	23.9	°C		
TOC	Mod. NS-EN 1484:1997 (G4-2)	8.9	mg C L^{-1}	20%	0.1
Total nitrogen		230	μg N L^{-1}	20%	10
Total phosphorus	Mod. NS 4725:1984 (D2-1)	9	μg P L^{-1}	20%	1
Aluminum*	Mod. NS-EN ISO 17294-1:2007 (E8-4)	66.6	μg L^{-1}	20%	0.1
Calcium*	Mod. NS-EN ISO 17294-1:2007 (E8-4)	2.34	mg L^{-1}	20%	0.005
Chloride*	NS-EN ISO 10304-1:2009 (C4-4)	1.91	mg L^{-1}	20%	0.005
Copper*	Mod. NS-EN ISO 17294-1:2007 (E8-4)	1.23	μg L^{-1}	25%	0.04
Iron*	Mod. NS-EN ISO 17294-1:2007 (E8-4)	51.6	μg L^{-1}	20%	0.3
Magnesium*	NS-EN ISO 14911:1999 (C4-4)	0.43	mg L^{-1}	20%	0.002
Manganese*	Mod. NS-EN ISO 17294-1:2007 (E8-4)	53.5	μg L^{-1}	15%	0.03
Nickel*	Mod. NS-EN ISO 17294-1:2007 (E8-4)	0.22	μg L^{-1}	15%	0.04
Potassium*	NS-EN ISO 14911:1999 (C4-4)	0.19	mg L^{-1}	20%	0.003
Sulfate*	NS-EN ISO 10304-1:2009 (C4-4)	1.63	mg L^{-1}	20%	0.005
Zinc*	Mod. NS-EN ISO 17294-1:2007 (E8-4)	6.5	μg L^{-1}	25%	0.15

*determined in water from nearby lake Store Åklungen (60.000; 10.722; 3 km North of Lake Svartkulp, within the same watershed) in August 2020. TOC = total organic carbon, MU = measurement uncertainties, LOQ = limit of quantification

Table S2. Effect of time and treatment on dissolved gases (two way anova, with *F* test and *P* value). Bonferroni correction for multiple testing α=0.05/5=0.01.

	Treatment		Time		Treatment × Time	
	F	*P*	*F*	*P*	*F*	*P*
O_2	204	$<2\times10^{-16}$	199	$<2\times10^{-16}$	61	$<2\times10^{-16}$
CO_2	215	$<2\times10^{-16}$	165	$<2\times10^{-16}$	61	$<2\times10^{-16}$
CH_4	121	$<2\times10^{-16}$	3.4	0.039	0.74	0.62
N_2O	8.9	6×10^{-5}	84	$<2\times10^{-16}$	6.3	4×10^{-5}
N_2	1.5	0.22	0.5	0.61	0.9	0.53

Table S3. CO_2 diffusion fluxes (F_{CO2}, mol m^{-2} d^{-1}) from Lake Lundebyvannet estimated from $HgCl_2$-fixed and unfixed samples following Cole and Caraco (1998; CC98), Vachon and Prairie (2013; VP13) and Crusius and Wanningkhof (2003; CW03).

Preservatives		Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Ice-free season
CC98	$HgCl_2$	0.10	0.07	0.01	0.15	0.11	0.23	0.37	0.48	0.17
	None	0.20	0.21	0.16	0.34	0.29	0.47	0.57	0.77	0.35
	Diff (%)	97 %	188 %	2163 %	130 %	162 %	99 %	55 %	62 %	108 %
VP13	$HgCl_2$	0.15	0.11	0.01	0.22	0.16	0.35	0.52	0.71	0.24
	None	0.30	0.32	0.24	0.50	0.42	0.69	0.80	1.14	0.51
	Diff (%)	97 %	186 %	2101 %	130 %	164 %	99 %	56 %	62 %	109 %
CW03	$HgCl_2$	0.02	0.01	0.00	0.02	0.01	0.04	0.02	0.09	0.02
	None	0.03	0.03	0.02	0.04	0.02	0.07	0.04	0.15	0.04
	Diff (%)	88 %	178 %	1783 %	136 %	163 %	103 %	59 %	63 %	112 %
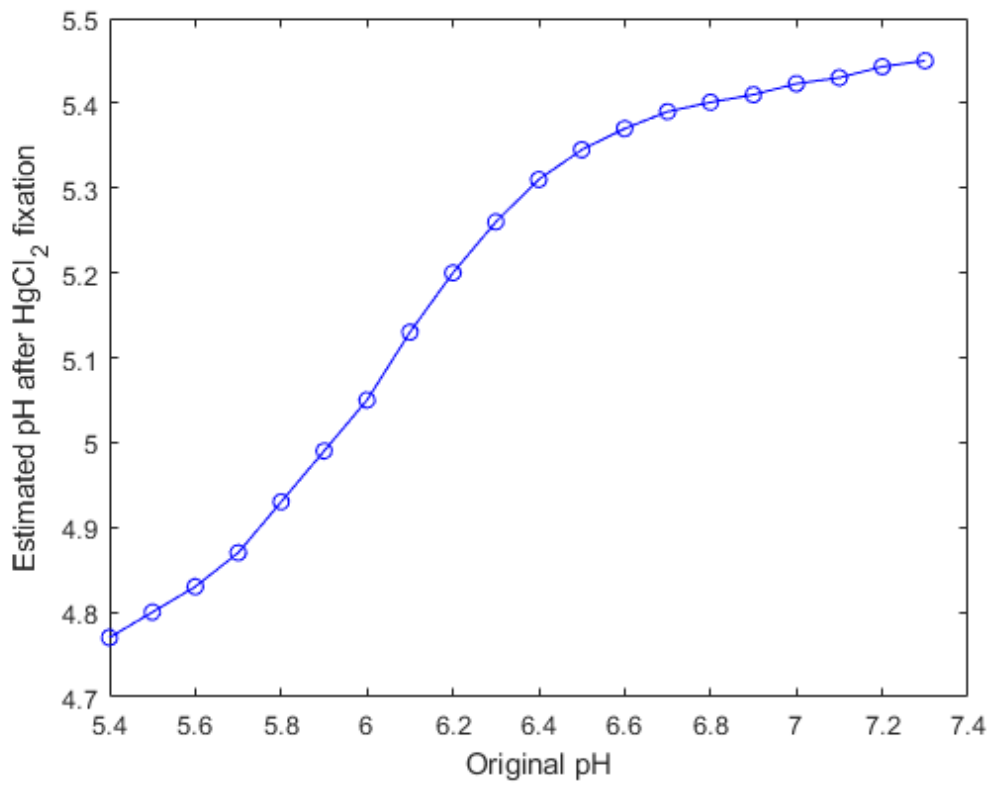
Fig S1. Comparison of in-situ and PHREEQC-estimated pH after HgCl$_2$ fixation in Lake Lundebyvannet samples.
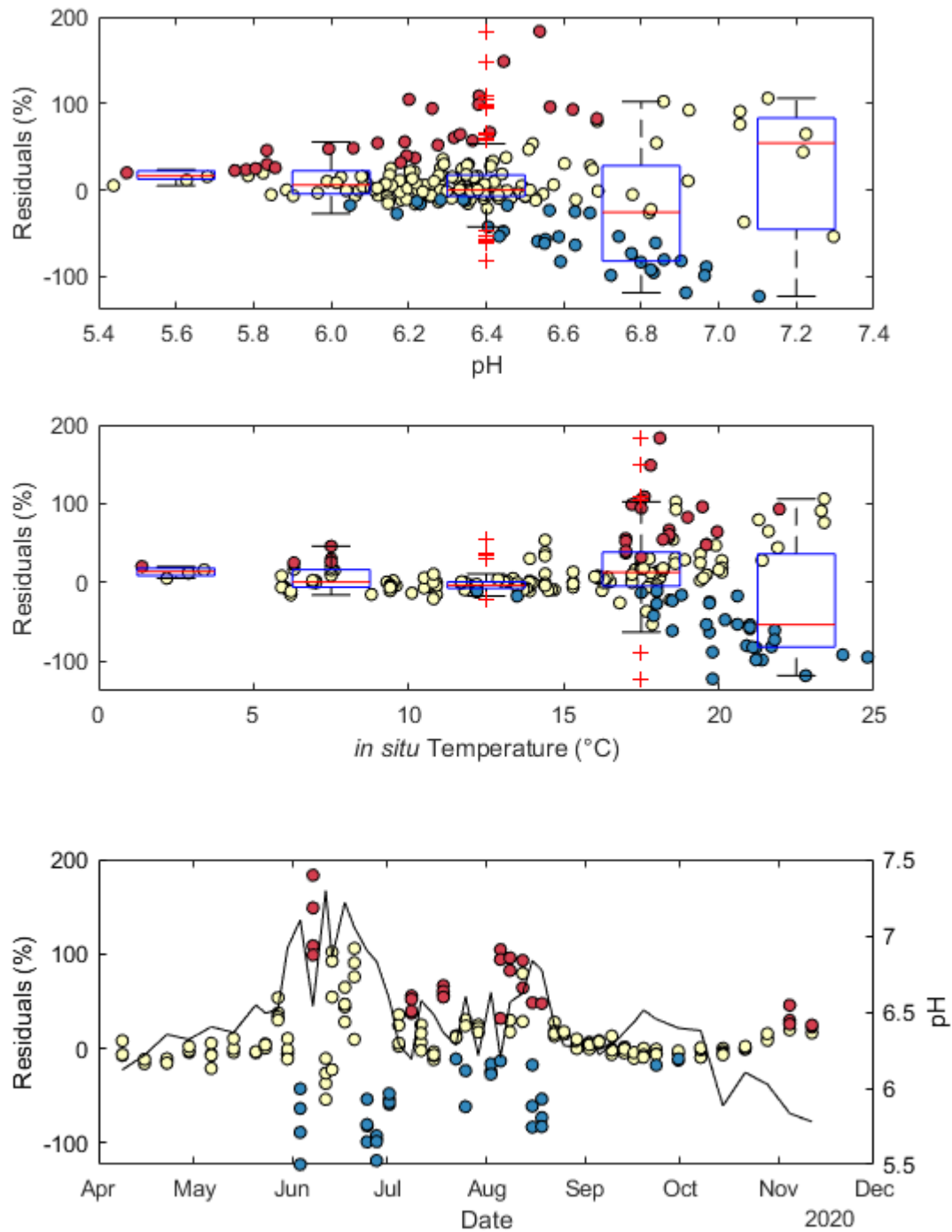
Fig S2. E model residuals as a function of pH (top), *in situ* water temperature (middle) and date (bottom) in Lake Lundebyvannet. Residuals are determined by the difference between E predicted with Eq. 11 and empirically determined E with Eq. 7. Timeseries of pH is also shown in the bottom panel. For each 0.4 pH unit bin and 5°C temperature bin, a box plot was drawn. Blue and red symbols are samples for which values of $[HCO_3^-]_i - [CO_2]_{ex}$ were larger than (or equal to) 20 µM and smaller than (or equal to) − 20 µM, respectively.
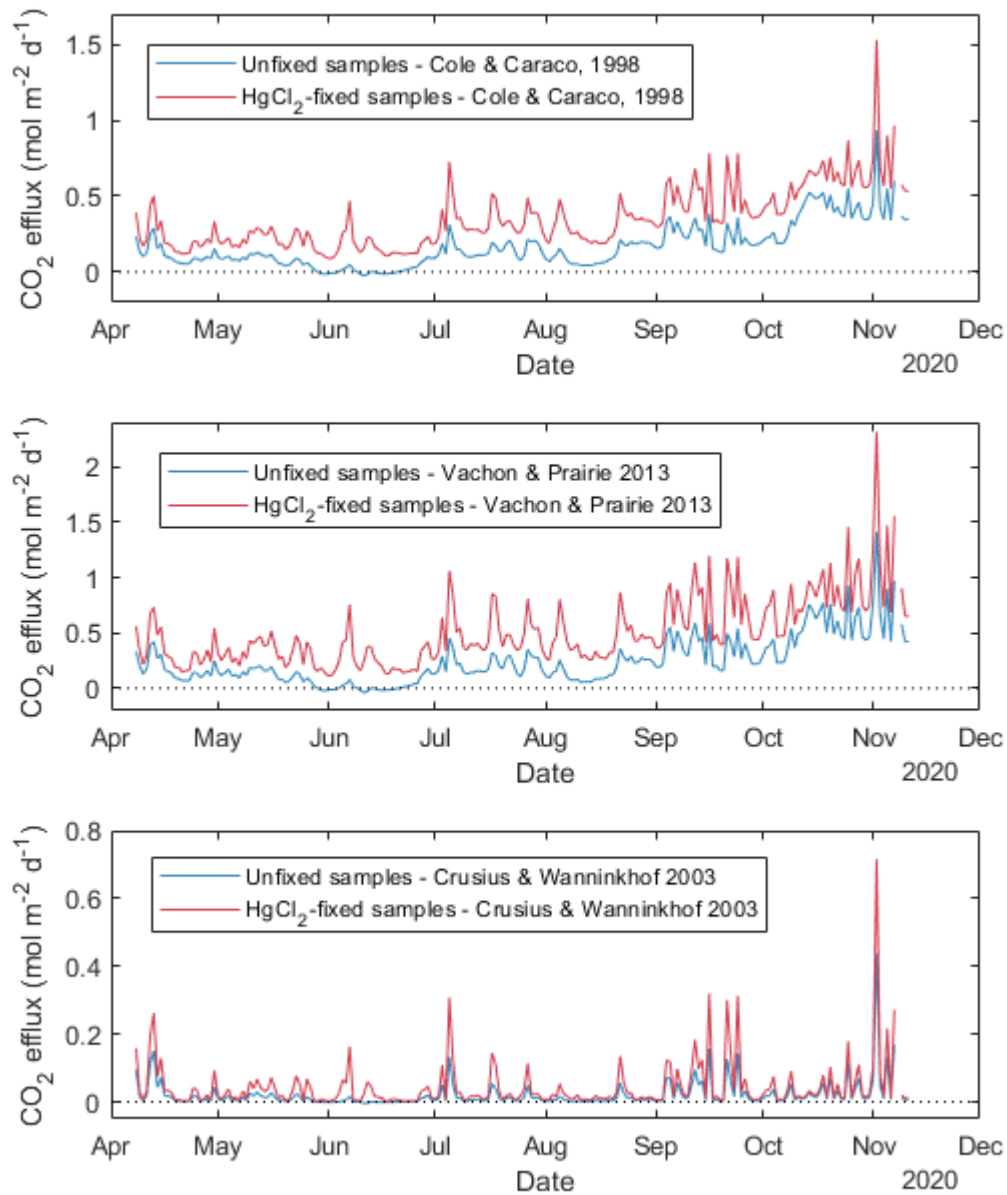
Fig S3. Daily and monthly diffusion fluxes at the water-atmosphere interface from Lake Lundebyvannet. Diffusion fluxes were calculated following Cole & Caraco (1998; top panel), Vachon and Prairie (2013; middle panel) and Crusius and Wanninkhof (2003; bottom panel).