JOURNAL OF LIMNOLOGY

SUPPLEMENTARY MATERIAL

Long-term persistence of sedimentary copper contamination in Lake Orta: potential environmental risks 20 years after liming

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Supplementary Tab. 1. Copper concentrations in digestion blanks and ranges of Cu concentrations (not blank corrected) in digested samples for the various digestion batches.

Digestion batch	Blank (µg/L)	Sample range (µg/L)	Blank to sample ratio (%)
1	7.4	87.4-7152	8.4-0.1
2	4.9	119-7020	4.1-0.1
3	BDL	69.1-1091	n.a.
4	2.7	434-1876	0.6-0.1
5	0.5	297-1134	0.2-0.04
5b	2.4	449[a]	0.5
6	BDL	363-9475	n.a.
7	BDL	711-7844	n.a.
8	0.84	260-378	0.3-0.2
9	2.7	65.5-378	4.0-0.7

BDL, below detection limit (0.2 µg L^{-1} Cu); n.a., not applicable. [a]Control analysis for a single sample only.

Supplementary Tab. 2. Copper concentrations (in µg g^{-1} dry weight) determined in aliquots of the reference material S7 (AQUANCON project *CHECK*) mineralized in the different digestion batches. The certified Cu concentration is 100±2 µg g^{-1} on a dry weight basis.

Digestion batch	Cu (µg g^{-1} d.w.)	Recovery (%)
1	94.7	94.8[a]
1bis	91.3	91.4[a]
2	86.8	86.8
3	123.8	123.9
4	99.8	99.8
5	86.3	86.4
5b	n.m.	n.a.
6	86.4	86.5
7	n.m.	n.a.
8	89.4	89.4
9	88.9	89.0

[a]Replicate measurements of the same solution. N.m., not measured; n.a., not applicable.

Supplementary Tab. 3. Chronology, percentage water content and LOI, and Cu content (mg kg^{-1} dry weight) in each section of cores ORTA 07/1A and ORTA 07/2A. Percent organic carbon (OC) has been estimated by multiplying percent LOI by 0.4 according to Lami *et al*. (2000) who report OC to be about 35 to 45% of LOI in Lake Maggiore and other alpine lakes. The ratio beween Cu and OC (in mg Cu g^{-1} OC) is a proxy for possible copper toxicity to biota when it exceeds the value of 5.5 according to Campana *et al*. (2013).

Depth (cm)	Date (AD)	Water content (%)	LOI (%)	OC (%)	Cu (mg kg^{-1}) d.w.	Cu / OC mg Cu g^{-1} OC
Core ORTA 07/1a						
0	2007[a]	---		---		
0–1	2001[a]	89.3	25.5	1.71	1331	77.7
1–2	1989[a]	84.9	23.5	1.58	2594	164.7
2–3	1975[a]	84.0	24.5	1.64	3156	192.0
3–4	1957[a]	85.3	24.8	1.66	3572	214.9
4–5	1935[a]	82.8	18.9	1.27	1401	110.5
5–6	1909[a]	80.9	16.0	1.07	332	30.9
10–11	1758[b]	77.3	14.9	1.00	40.9	4.1
20–21	1455[b]	73.1	13.8	0.93	51.7	5.6
40–41	850[b]	72.9	15.8	1.06	48.3	4.6
51.5–52.5	530[b]	73.4	16.7	1.12	34.5	3.1
Core ORTA 07/2a						
0	2007[c]	---	---	---	---	---
0–1	2005[c]	63.8	13.0	0.87	492	56.6
1–2	2001[c]	64.7	13.3	0.89	500	56.0
2–3	1996[c]	66.3	16.2	1.08	342	31.6
3–4	1992[c]	63.3	17.5	1.18	316	26.8
4–5	1986[c]	76.7	24.6	1.65	938	56.9
5–6	1980[c]	80.2	30.0	2.01	821	40.8
6–7		76.2	22.7	1.52	902	59.3
7–8		71.2	16.5	1.11	530	47.9
8–9	1971[d]	71.3	16.8	1.13	330	29.3
9–10		71.4	14.6	0.98	311	31.7
10–11		61.0	11.0	0.74	148	20.0
11–12		68.9	14.0	0.94	214	22.8
12–13	1963[d]	72.1	16.6	1.11	719	64.5
13–14		73.8	17.1	1.15	942	82.0
14–15		76.4	21.6	1.45	1670	115.0
15–16	1953	75.6	23.0	1.55	4617	298.6
16–17		79.8	20.8	1.40	3962	283.2
17–18		75.9	17.0	1.14	1548	135.3
18–19	1943[e]	77.9	16.0	1.07	348	32.4
19–20		78.4	15.9	1.07	129	12.1
20–21	1938[e]	77.6	15.8	1.06	104	9.8
25–26		69.5	13.1	0.88	43.2	4.9
35–36	1890[e]	77.2	15.5	1.04	34.2	3.3
45–46		72.5	13.7	0.92	31.4	3.4
60.5–61.5	1800[e]	64.5	10.9	0.73	38.9	5.3

[a]Dating from Piscia *et al*. (2012); [b]dating calculated by extrapolation of the sedimentation rate of 0.033 cm year^{-1} reported by Piscia *et al*. (2012) for the section 5-6 cm; [c]based on Piscia *et al*. (2011) – see Supplementary Tab. 4.

Supplementary Tab. 3. Estimated sedimentation rate for core 07/2A based on the dating reported in Figure 2b of the main text according to Piscia (2011).

Depth (cm)	Date (AD)	Estimated sedimentation rate (cm year^{-1})
0.5	2005	---
1.5	2001	0.2
2.5	1996	0.2
3.5	1992	0.25
4.5	1986	0.17
5.5	1980	0.17
8.5	1971	0.27
12.5	1963	0.5
15.5	1953	0.3
18.5	1943	0.3
20.5	1938	0.4
35.5	1890	0.32
60	1800	0.28

Calculation of the quantity of $CaCO_3$ possibly precipitating in Lake Orta after liming

According to Baudo and Beltrami (2001), about 14,800 tons of $CaCO_3$ were added over 2/3 of the lake surface. Calderoni *et al*. (1993) report that around 85% of the added $CaCO_3$ dissolved during the early stage of the intervention. This would leave around 2220 tonnes of $CaCO_3$ potentially precipitating (14,800 tonnes $\times$ 0.15). In the following calculations we will consider the water column as a homogenous system and use the total lake volume and surface for the sake of simplicity.

Let us start by assuming an homogenous dissolution of the added $CaCO_3$ into the whole lake volume (1.286 km^3; Bonacina, 2001). The added $CaCO_3$ concentration per liter of lake water would be:

$$14{,}800 \text{ tons} / 1.286 \text{ km}^3 = 11.5 \text{ g L}^{-1} \text{ of } CaCO_3 \qquad \text{(eq. 1)}$$

Given the molecular weight (MW) of $CaCO_3$ of 100.078, we have:

$$11.5 \text{ g L}^{-1} / 100.078 = 0.115 \text{ M of } CaCO_3 \text{ added to each liter} \qquad \text{(eq. 2)}$$

The solubility product of $CaCO_3$ is in the range of 10^{-9} M, with some variation according to the literature sources. Hereinafter, we will refer to the values and calculations reported in the document available at: http://www.colby.edu/chemistry/CH142/CH142B/saving.html (search for 'solubility of calcium carbonate') on the solubility of calcium carbonate (last accessed on 24 September 2015). This document report a solubility product of 5×10^{-9}.

Before calculating the solubility of $CaCO_3$ we must also consider that part of the added carbonate will hydrolyze to HCO_3^- according to the reaction:

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^- \qquad \text{(eq. 3)}$$

The equilibrium constant (hydrolysis constant – K_2) of reaction (3) is 4.8×10^{-11}.
The solubility (S) of $CaCO_3$ is then given by:

$$S = \sqrt{K_{sp}\left(1 + \left(\frac{H^+}{K_2}\right)\right)} \qquad \text{(eq. 4)}$$

Applying equation 4, we obtain a $CaCO_3$ solubility of 0.102 M at pH = 4. This value corresponds to about 89% of the added $CaCO_3$ (0.115 M; see equation 2) in good agreement with the observations of Calderoni *et al*. (1993) reporting that 85% of the added $CaCO_3$ dissolved in the lake water.

At pH 6.5, equation 4 calculates a solubility of 5.8×10^{-3} M; suggesting that $CaCO_3$ precipitation may have occurred at some time during the liming process as the pH value increased. Considering that 85% of the added $CaCO_3$ dissolved in the water column (Calderoni *et al*., 1993), we are left with:

$$0.115 \text{ M (added } CaCO_3 \text{ } per \text{ liter)} \times 0.15 \text{ (fraction of undissolved } CaCO_3\text{)} = 0.01725 \text{ M}$$
$$\text{of } CaCO_3 \text{ possibly precipitating for each liter of lake water} \qquad \text{(eq. 5)}$$

Calculation of the Cu concentration adsorbed on the precipitated CaCO$_3$

It is now a matter of checking if the amount of CaCO$_3$ depositing to the bottom of Lake Orta (eq. 5) can potentially dilute previously deposited contaminated sediments. An approximate quantitative idea of the process is described by the following calculations:

0.01725 M (non-dissolved added CaCO$_3$ *per* liter) – 5.8×10^{-3} M (CaCO$_3$ solubility at 6.5) = 0.01145 M (CaCO$_3$ in excess of the solubility product and potentially precipitating per liter of lake water)   (eq. 6)

0.01145 M (CaCO$_3$ *per* litre - equation 6) × 100.078 (PM CaCO$_3$) × (1.286 × 10^9 L) (volume of Lake Orta) = 1477 tonnes of CaCO$_3$ that could precipitate in the whole lake   (eq. 7)

Considering a Cu adsorption capacity of 0.015 mg g^{-1} for CaCO$_3$ (Aziz *et al.*, 2008), we could expect an overall total adsorption of the following quantity of Cu:

0.015 mg g^{-1} = 0.015 kg tonnes^{-1} × 1477 tons CaCO$_3$ = 22.15 kg of Cu adsorbed onto the precipitated CaCO$_3$.   (eq. 8)

In 1989, we had a dissolved Cu concentration of 40 μg L^{-1}, that is:

40 μg L^{-1} × 1.286 km^3 (volume of Lake Orta) = 51.44 kg of Cu (stock of dissolved Cu in Lake Orta before liming).   (eq. 9)

Note that, due to the acidic conditions of Lake Orta waters before liming, most of the Cu was occurring in the dissolved phase (Camusso et al., 1989). In practice, part of the Cu dissolved in lake water before liming could have adsorbed on the precipitated CaCO$_3$ and then settled to the bottom. The Cu adsorption capacity of CaCO$_3$ being relatively low, calcite deposition following liming could have caused a decrease in Cu concentrations of bed sediments.

Comparison of the sedimentation fluxes of the precipitated CaCO$_3$ and the other matter sedimenting in Lake Orta

The other factor that influences the actual importance of 'dilution' of contaminated sediments by the deposition of cleaner material is the deposition rate of particles other than those formed by precipitation of CaCO$_3$. According to Camusso *et al*. (1989) 'The average annual flux of particulate matter was 0.67 g (dry weight) m^{-2} day^{-1}' (page 70, second paragraph). The entire surface of Lake Orta is 18.2 km^2 (Camusso *et al*., 1989). Using this value (although liming was not performed over the entire lake surface) and assuming a homogenous system, we could expect a maximum of:

1477 tons CaCO$_3$ potentially precipitating / 18.2×10^6 m^2 = 8.11×10^{-5} tons m^{-2} or 81.15 g m^{-2} of calcite settling to the lake bottom   (eq. 10)

This figure is comparable with the annual particulate flux of 243 g m^{-2} year^{-1} reported by Camusso *et al*. (1989), confirming the hypothesis that deposition of CaCO$_3$ with relatively low Cu content could have contributed to the decreased of Cu levels observed in sediments after liming.

The above calculations and discussion have a purely descriptive value and do not claim to provide a detailed balance of what occurred in Lake Orta during liming. However, as mentioned also in the main text, Baudo and Beltrami (2001) report that the Ca content of the upper 2-cm of sediment grab samples collected in 1996 (post-liming) showed an increased content of Ca compared with 1985 (pre-liming) samples. This observation would support the hypothesis that some of the added CaCO$_3$ eventually precipitated to lake bottom where it could have diluted the deposited Cu.

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