

DOI: [10.4081/jlimnol.2016.1232](https://doi.org/10.4081/jlimnol.2016.1232)

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 ($\mu\text{g/L}$)	Sample range ($\mu\text{g/L}$)	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 ($0.2 \mu\text{g L}^{-1}$ Cu); n.a., not applicable. ^aControl analysis for a single sample only.

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

Digestion batch	Cu ($\mu\text{g g}^{-1}$ 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

^aReplicate 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 between 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).

Core ORTA 07/1a						
Depth (cm)	Date (AD)	Water content (%)	LOI (%)	OC (%)	Cu (mg kg ⁻¹) d.w.	Cu / OC mg Cu g ⁻¹ OC
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						
Depth (cm)	Date (AD)	Water content (%)	LOI (%)	OC (%)	Cu (mg kg ⁻¹) d.w.	Cu / OC mg Cu g ⁻¹ OC
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

^aDating from Piscia *et al.* (2012); ^bdating 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; ^cbased 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

Possible contribution of liming to the decrease of Cu concentrations in sediment deposited after the 1990s in cores 07/1A and 07/2A

Calculation of the quantity of CaCO₃ possibly precipitating in Lake Orta after liming

According to Baudo and Beltrami (2001), about 14,800 tons of CaCO₃ were added over 2/3 of the lake surface. Calderoni *et al.* (1993) report that around 85% of the added CaCO₃ dissolved during the early stage of the intervention. This would leave around 2220 tonnes of CaCO₃ potentially precipitating (14,800 tonnes × 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 CaCO₃ into the whole lake volume (1.286 km³; Bonacina, 2001). The added CaCO₃ concentration per liter of lake water would be:

$$14,800 \text{ tons} / 1.286 \text{ km}^3 = 11.5 \text{ g L}^{-1} \text{ of CaCO}_3 \quad (\text{eq. 1})$$

Given the molecular weight (MW) of CaCO₃ of 100.078, we have:

$$11.5 \text{ g L}^{-1} / 100.078 = 0.115 \text{ M of CaCO}_3 \text{ added to each liter} \quad (\text{eq. 2})$$

The solubility product of CaCO₃ 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 CaCO₃ we must also consider that part of the added carbonate will hydrolyze to HCO₃⁻ according to the reaction:



The equilibrium constant (hydrolysis constant – K₂) of reaction (3) is 4.8×10⁻¹¹.

The solubility (S) of CaCO₃ is then given by:

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

Applying equation 4, we obtain a CaCO₃ solubility of 0.102 M at pH = 4. This value corresponds to about 89% of the added CaCO₃ (0.115 M; see equation 2) in good agreement with the observations of Calderoni *et al.* (1993) reporting that 85% of the added CaCO₃ dissolved in the lake water.

At pH 6.5, equation 4 calculates a solubility of 5.8×10⁻³ M; suggesting that CaCO₃ precipitation may have occurred at some time during the liming process as the pH value increased. Considering that 85% of the added CaCO₃ dissolved in the water column (Calderoni *et al.*, 1993), we are left with:

$$0.115 \text{ M (added CaCO}_3 \text{ per liter)} \times 0.15 \text{ (fraction of undissolved CaCO}_3\text{)} = 0.01725 \text{ M of CaCO}_3 \text{ possibly precipitating for each liter of lake water} \quad (\text{eq. 5})$$

Calculation of the Cu concentration adsorbed on the precipitated CaCO₃

It is now a matter of checking if the amount of CaCO₃ 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:

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

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

Considering a Cu adsorption capacity of 0.015 mg g^{-1} for CaCO₃ (Aziz *et al.*, 2008), we could expect an overall total adsorption of the following quantity of Cu:

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

In 1989, we had a dissolved Cu concentration of $40 \mu\text{g L}^{-1}$, that is:

$40 \mu\text{g L}^{-1} \times 1.286 \text{ km}^3 \text{ (volume of Lake Orta)} = 51.44 \text{ kg of Cu (stock of dissolved Cu in Lake Orta before liming)}$. (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 CaCO₃ and then settled to the bottom. The Cu adsorption capacity of CaCO₃ 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 CaCO₃ 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 CaCO₃. According to Camusso *et al.* (1989) 'The average annual flux of particulate matter was $0.67 \text{ g (dry weight) m}^{-2} \text{ day}^{-1}$ ' (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:

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

This figure is comparable with the annual particulate flux of $243 \text{ g m}^{-2} \text{ year}^{-1}$ reported by Camusso *et al.* (1989), confirming the hypothesis that deposition of CaCO₃ 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 CaCO₃ eventually precipitated to lake bottom where it could have diluted the deposited Cu.

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