Supplementary information (SI)

Supplementary Text: Lake Site description (extended)

I. Lake Greifen

5 By 1900 the anthropogenic activity acting on Lake Greifen had increased strongly (higher population, more infrastructure and traffic) and already between 1918 to 1932, 7 mass deaths of fish were reported. Since 1930 severe eutrophication started in Lake Greifen. Between 1965 and 1977 water treatment plants were build, developed and later on (1981 to 1986) equipped with phosphorus (P) precipitation systems. Still around 1970 the highest P concentrations were measured and in 1987 high water column chlorophyll *a* concentrations were recorded (Liechti, 1994; Känel, 2012). In 1999 an anoxic event lead to a massive

10 fish die-off. In 2009 an artificial ventilation system with air was introduced to improve lake water conditions. Thereby air is pumped down into the lake water column and released with distributors creating fine bubbles, which enrich the water with oxygen and support mixing. Nevertheless, in 2010 high P concentration were measured due to multiple winters with weak circulation. Today the tributaries of the lake remain highly contaminated with nutrients and pollutants from sewage and agriculture. The thermal stratification lasts approximately from May to December. During summer stratification (June to

15 December) the hypolimnion becomes anoxic below 10 m water depth (Kümmerlin and Matzinger, 2008; Känel, 2012).

II. Lake Baldegg

Clear signs of eutrophication have been evident in Lake Baldegg since the late 19th century, with the first cyanobacterial blooms (*Oscillatoria rubescens*) reported in the 1870s, and bottom water anoxia documented below 60m water depth around 1885

20 (Lotter, 1998; Teranes et al., 1999; Lotter, 2001). As anthropogenic activity increased further in the early 20th century due to industrialization and increased human settlement, an increasing volume of water was diverted into the lake from industry and villages. This lead to seasonal anoxia below 40 m water depth by 1940 (Liechti, 1994). From 1965 onward, agricultural use of the lake drainage area intensified (e.g. stock of swine), which lead to over-fertilization and an increase of nutrients in the lake. In 1967 the water treatment started. In 1970 anoxia was found to occur below 10 m water depth and in 1974 the highest P

25 concentrations were measured (Buergi and Stadelmann, 2000). In 1980 additonal water treatment plants were added and equipped with P precipitation systems. Thereby P is co-precipitated with coagulants, usually metals like Fe and or Al and removed afterwards. Since 1982/3 the net circulation of the lake is enhanced using pressured air in winter to mix the lake completely, in summer fine bubbles of O_2 are introduced (Stadelmann and Escher, 2002). Since O_2 levels increased, macrofauna can be found again in the lake sediments.

30

III.   Lake Zug

Lake Zug was influenced by anthropogenic activities already between 1830 and 1860 by construction of the first factories followed by strong increase in population from 1850 onwards. First sights of eutrophication in 1898 by the occurrence of algae blooms occurred. Agriculture activities increased from 1940 onwards and population increasing strongly as well as animal stock. Since 1940/50: low O_2 or even anoxic conditions occur at greater depths. In 1953 water treatment plants are build and extended in 1968, between 1973 to 1977 more water treatment plants are added (Liechti, 1994). From 1980 onwards animals stock is decreasing again as well as usage of fertilizers. Between 1993 and 1999 agriculture techniques develop towards higher ecological responsibility. Since 1994 eutrophication decreased slightly (Maerki et al., 2009). Nowadays, Lake Zug has an annually mixed water column to a depth of 50-80 m (rarely exceeding 100 m). At the sediment water interface O_2 decreases sharply.

IV.   Lake Zürich

Lake Zürich sedimentary records reveal massive blooms of algae because of eutrophication already in 1896 and 1898 (Livingstone, 2003; Jankowski and Weyhenmeyer, 2006). Before 1955 low bottom water (BW) O_2 due to eutrophication was recorded. Also in 1955 water treatment plans were introduced. Better conditions established from 1970 onwards, less P input and higher O_2 in BW due to better-implemented P removal (AWEL 2014) was achived. Between 1967 and 1970, the water treatment plants were equipped with P precipitation systems and from 1994 onwards they were extended with special flocculation/coagulation filtration ((Liechti, 1994), AWEL 2014). Due to the water treatment actions, the lake changes from a eutrophic to mesotrophic state. Since 2000 O_2 declined again, probably related to climate change and the increasing temperature related to it (Cole et al., 2007). Thus, mixing intensities are reduced because of stratification, which reduced BW O_2 renewal. Today the "Untersee" of lake Zürich is mixed regularly until 80 m water depth but only every few years to the ground (Känel, 2012). During summer high thermal stratification occurs, with a thermocline between 7.5 and 12.5 m (Gammeter et al., 1997; Gammeter et al., 2002).

V.   Lake Lucerne

Since 1860 the catchment area of Lake Lucerne was influenced by higher population densities, which influenced water quality. At the end of the 19th century the city of Luzerne develop towards an international tourismus metropole which lead to the extension of the canalization system and the discharge of sewage water into the lake (BAFU, 2013). In 1931 the first water treatment plant was build. Since 1966 the lake water nutrients increased significantly (Staub et al., 1981). More protection of the lake was introduced since 1971-1999 to reduce nutrients loadings by building and extending water treatment plants (Liechti, 1994). Nowadays a complete overturn occurs every 6 years (BFS 2010 and BAFU, 2013). The water column is naturally oxygenated and in general Lake Lucerne has low nutrient concentrations but relatively high Nitrate concentrations can be found (63 µM) in the water column (Vissers et al., 2013).

Supplementary Text: Detailed description of redox state analysis of the sediment

Mediated electrochemical reduction (MER) and oxidation (MEO) was performed in electrochemical cells (Glassy carbon crucibles (GAZ1; Sigradur G, HTW, Germany), that also served as the working electrodes, and were filled with 6 ml of anoxic buffer (pH 5, 0.01 M acetate, 0.1 M KCl). A Pt wire served as counter electrode and was placed in a compartment separated

5 from the working electrode by a porous glass frit. Potentials applied to the working electrodes were measured against Ag/AgCl reference electrodes (Bioanalytical Systems Inc., USA) but are reported herein versus standard hydrogen electrode (E_h= -0.65 V and +0.58 V for MER and MEO, respectively). The MER and MEO cells contain the dissolved electron transfer mediators 1,1'-Ethylene-2,2'-bipyridinium dibromide (diquat) and 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt, respectively, to facilitate electron transfer between the working electrode of the electrochemical cells and

10 the redox-active constituents in the sediment. Addition of 50 µl of sample slurries to the MER and MEO cells resulted in reductive and oxidative current responses that were integrated (software ORIGIN 9.1) to yield the number of electrons transferred to and from the sediment samples, as detailed before (Kluepfel et al., 2014; Klupfel et al., 2014; Sander et al., 2015).

Supplementary Text: Focusing Factor calculation

15 However focusing factors (FF) were calculated for comparison using the ratio of the measured inventory of ^{210}Pb (I_m) in Bq/cm^2 and the expected inventory of ^{210}Pb (I_e) in Bq/cm^2 after the following formula (Hermanson and Christensen, 1991):

$$I_m = \sum_i^N p_i \ s_i \ \Delta z_i \qquad \textbf{(1)}$$

$$I_a = \sum_i^N F_i \ e^{-\lambda t} \qquad \textbf{(2)}$$

Where i is the core layer, N is the deepest layer where the ^{210}Pb was found, pi is dry bulk density (g/cm^3), si is activity (Bq/g) and Δzi is layer height (cm) of the ith layer. Fi is atmospheric input of ^{210}Pb and was estimated from precipitation (average local weather stations, 1961-2010). λ is the decay constant for the nuclide and t is the number of years the nuclide was in the sediment

20 (Hermanson and Christensen, 1991). The FF is then calculated as FF=I_m/I_a.
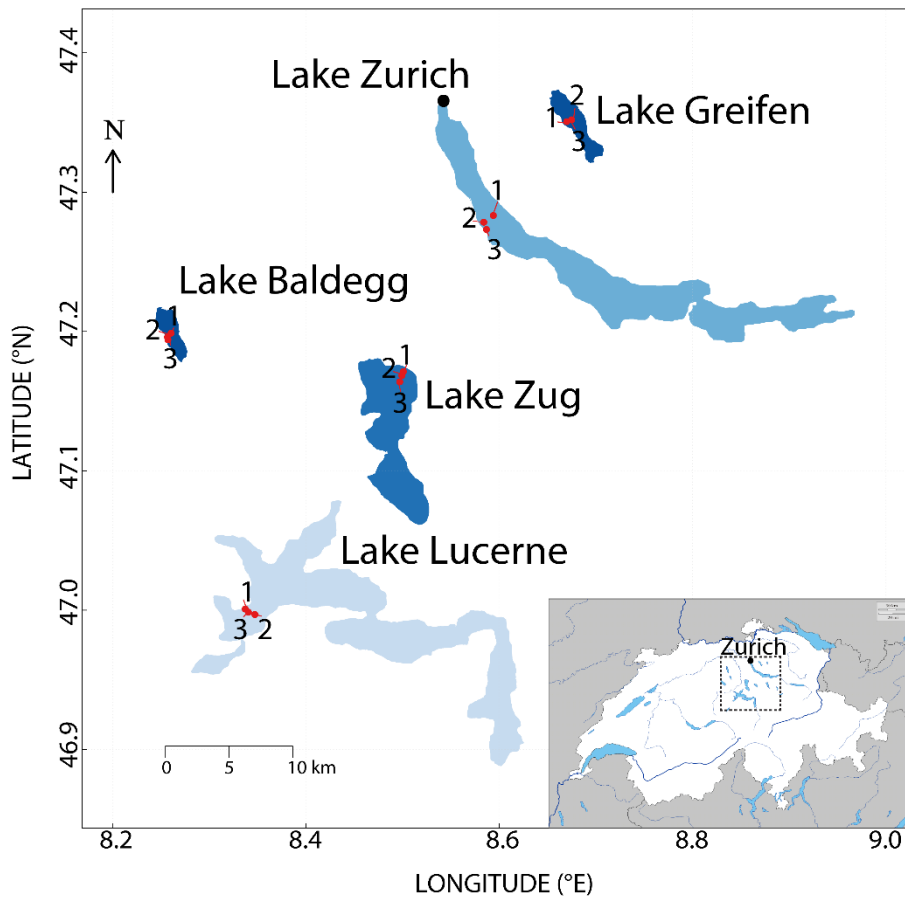
Figure S1: Map of the study area. The sampling stations within each of the five lakes are indicated by red dots and numbered 1 to 3. Color indicates trophic state from light blue (oligotrophic) to dark blue (eutrophic). This map contains data based on aerial images from DigitalGlobe (CO) and CNES/Airbus (France) as provided by Google (CA) and was created with the software R (South, 2011). Small insert map from d-maps (https://www.d-maps.com/carte.php?num_car=2648&lang=en).
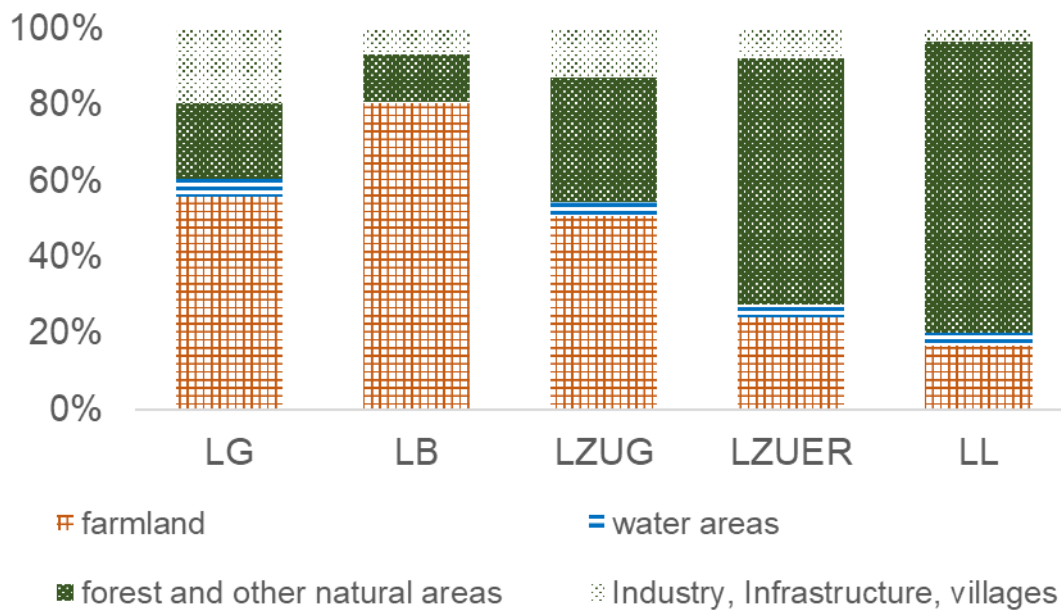
Figure S2: Present-day land use of lake drainage area in %, LG (Lake Greifen), LB (Lake Baldegg), LZUG (Lake Zug), LZUER (Lake Zurich), LL (Lake Lucerne). Data were provide by the EEA (2010), Swiss Federal Office of the Environment (BAFU (2013)). https://www.bafu.admin.ch/bafu/en/home/topics/water/info-specialists/state-of-waterbodies/state-of-lakes/water-quality-in-lakes.html
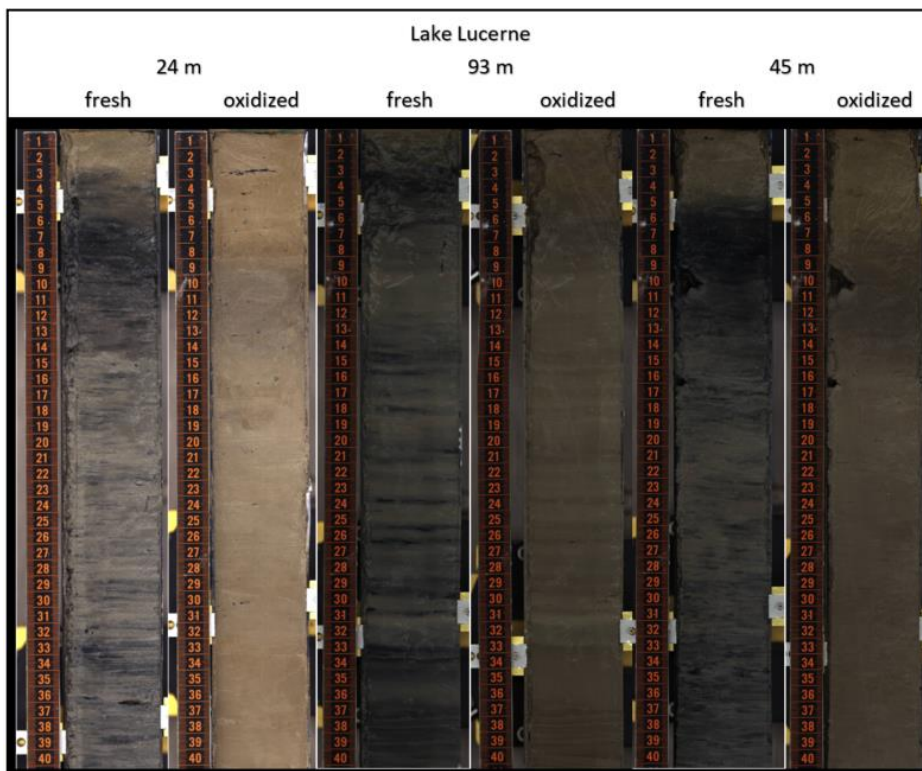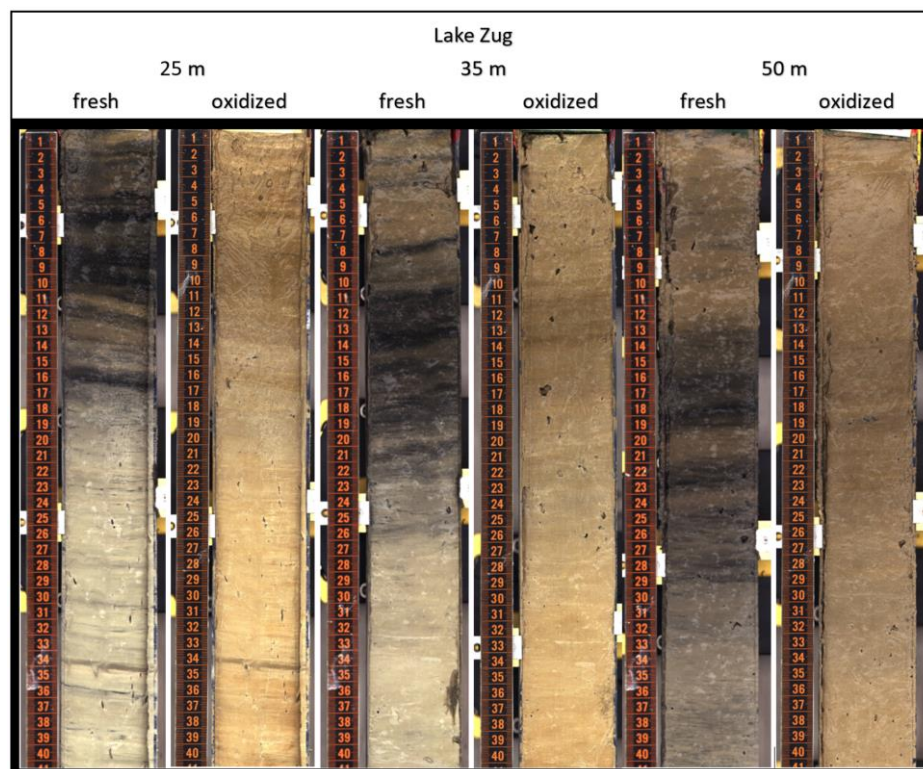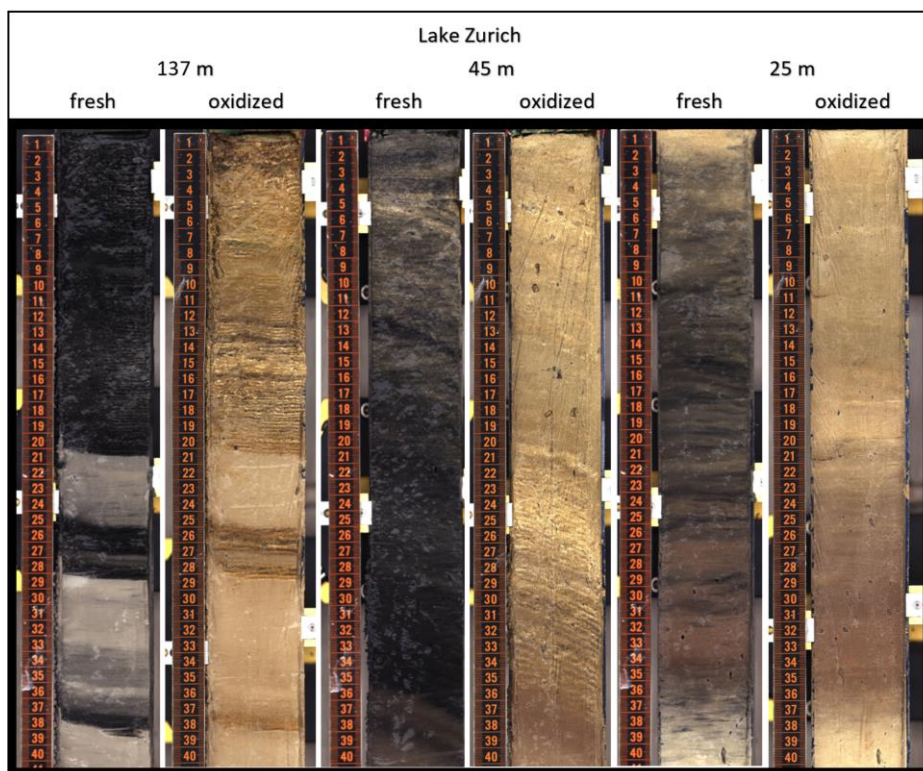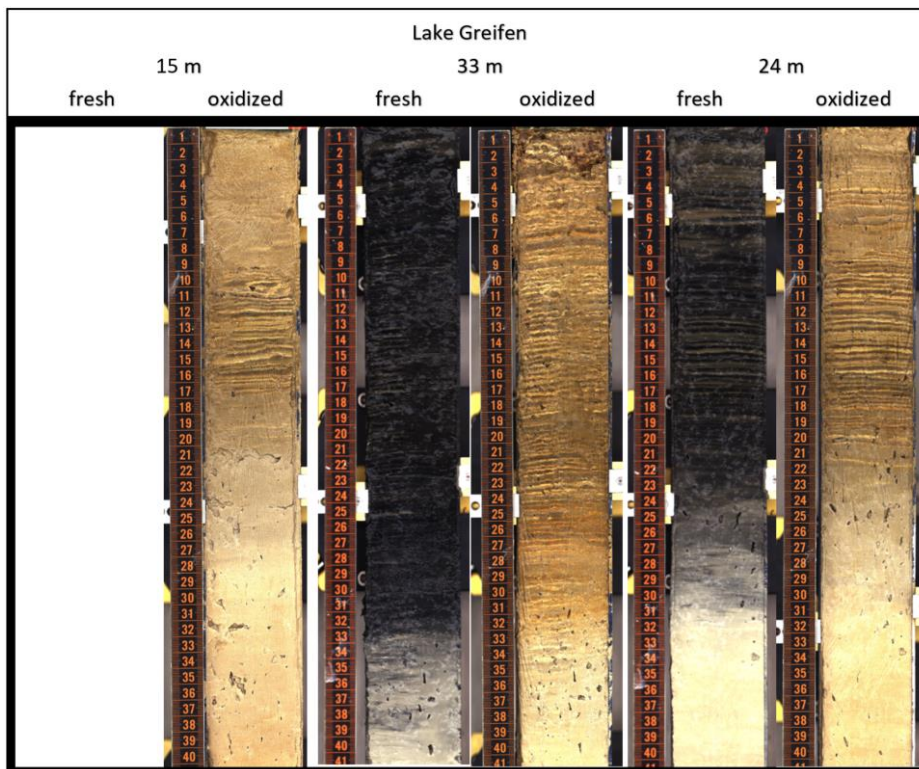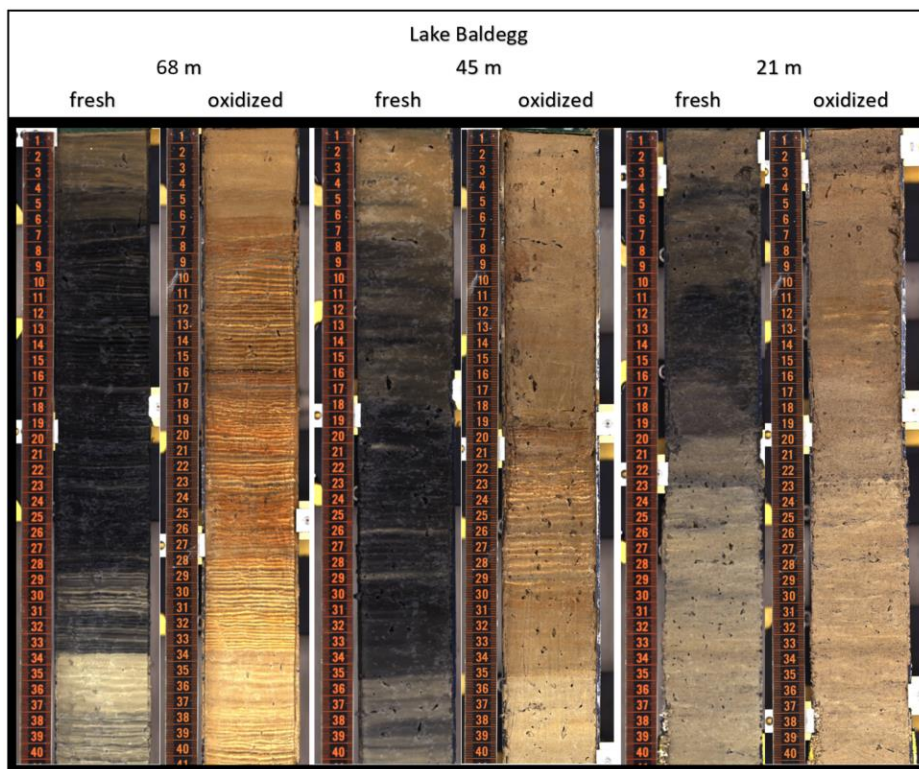
Figure S3: Core pictures for each station, directly after opening (fresh) and after stored opened in air (oxidized). Lake Name and water depth are indicated for each lake (Lake Lucerne, Lake Zurich, Lake Zug, Lake Baldegg, Lake Greifen).
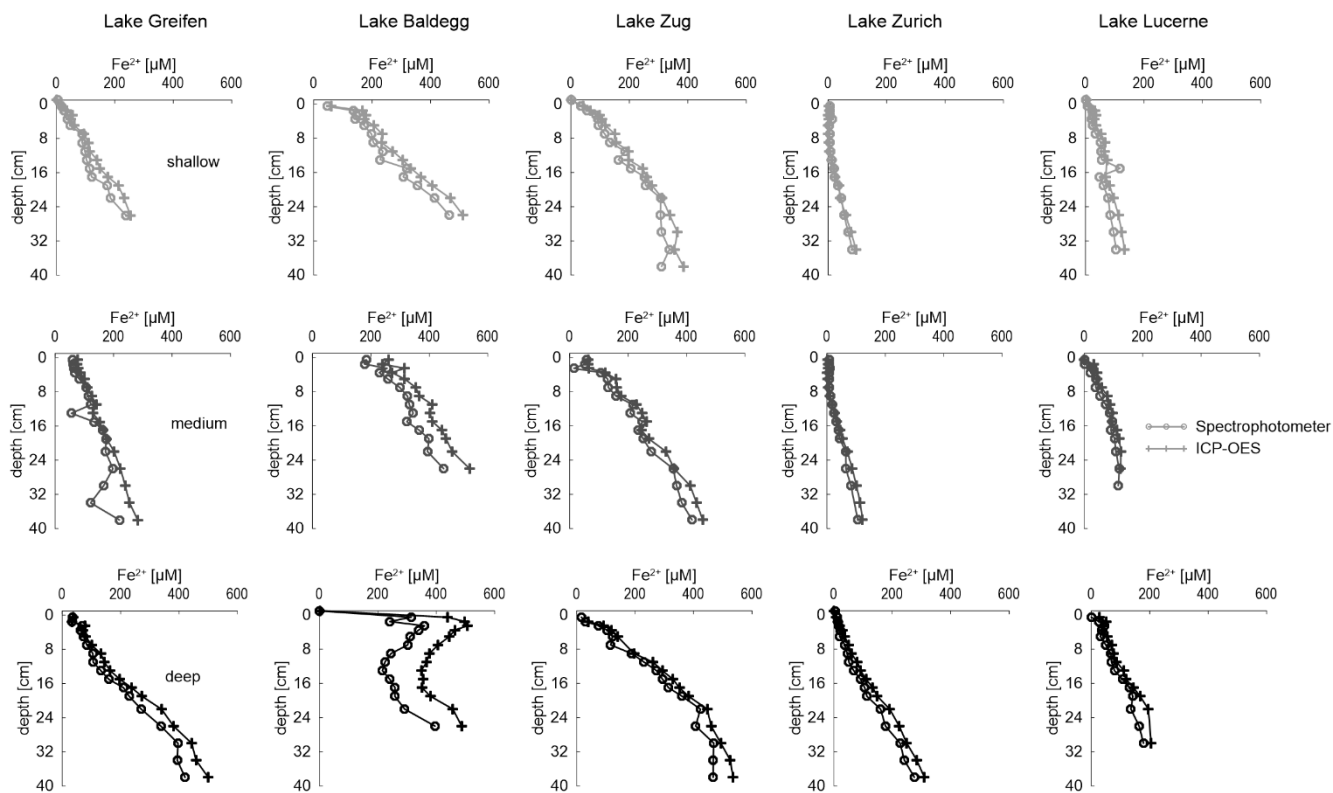
Figure S4: Porewater concentrations of Fe^{2+} (µM) determined photometrically (circles) and by ICP-OES (plus signs) for each station. Stations are ordered according to water depth from shallow to deep and by eutrophication from highly eutrophic Lake Greifen to Lake Lucerne.
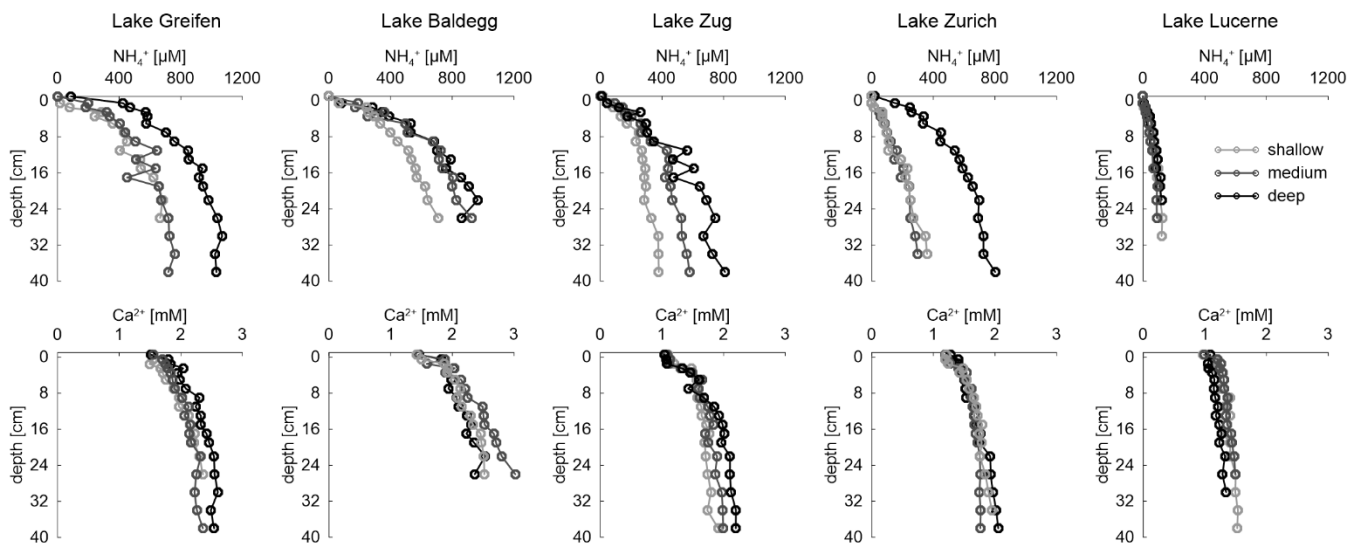
Figure S5: Porewater concentrations of NH$_4^+$ (µM) and Ca^{2+} (mM) vs. sediment depth (cm). All three stations per lake are shown in each subplot.
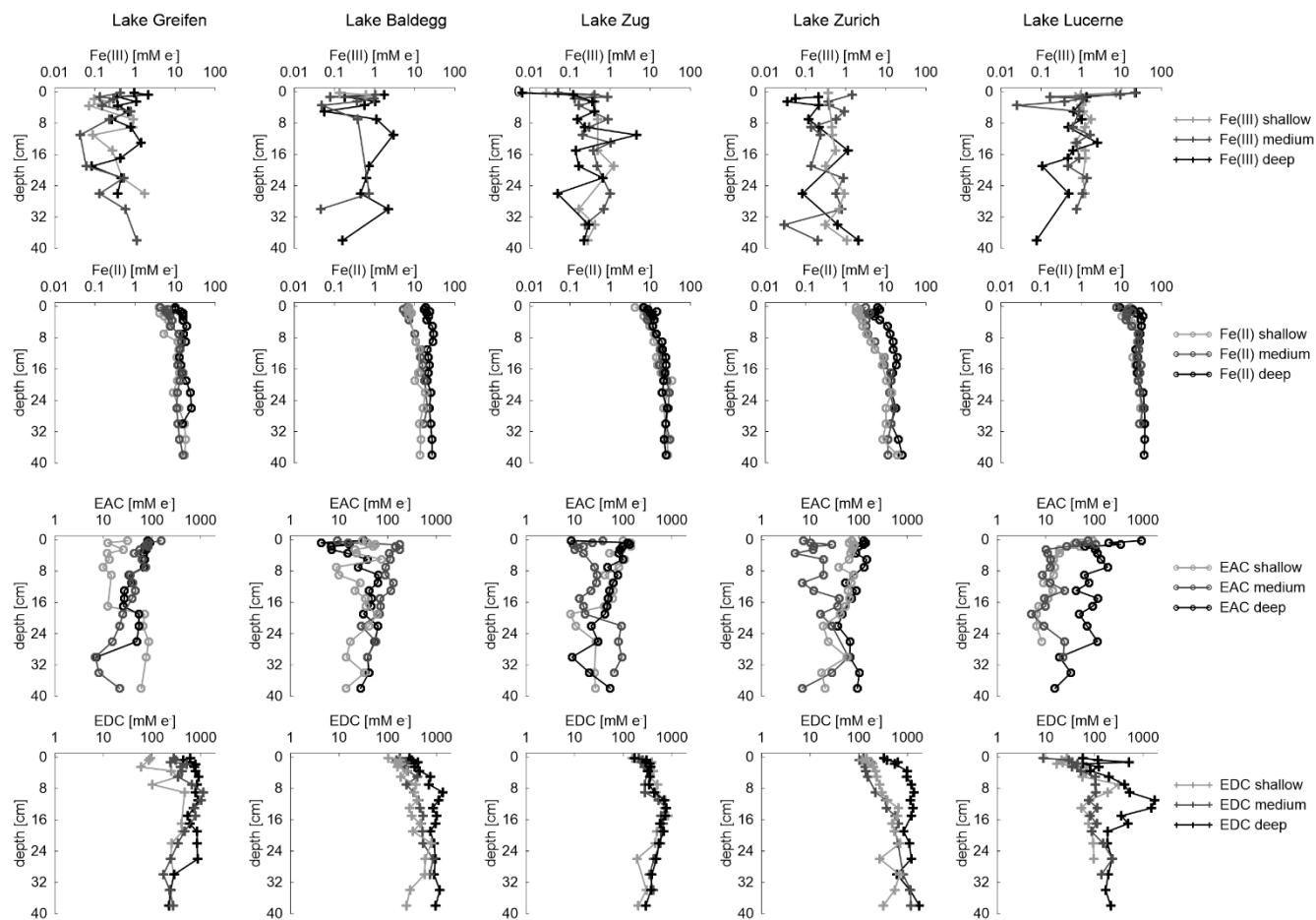
Figure S6: Bioavailable solid phase Fe(II) and Fe(III) as well as EDC and EAC for each lake. Each subplot shows 3 stations per lake. Note concentrations are per liter of wet sediment.
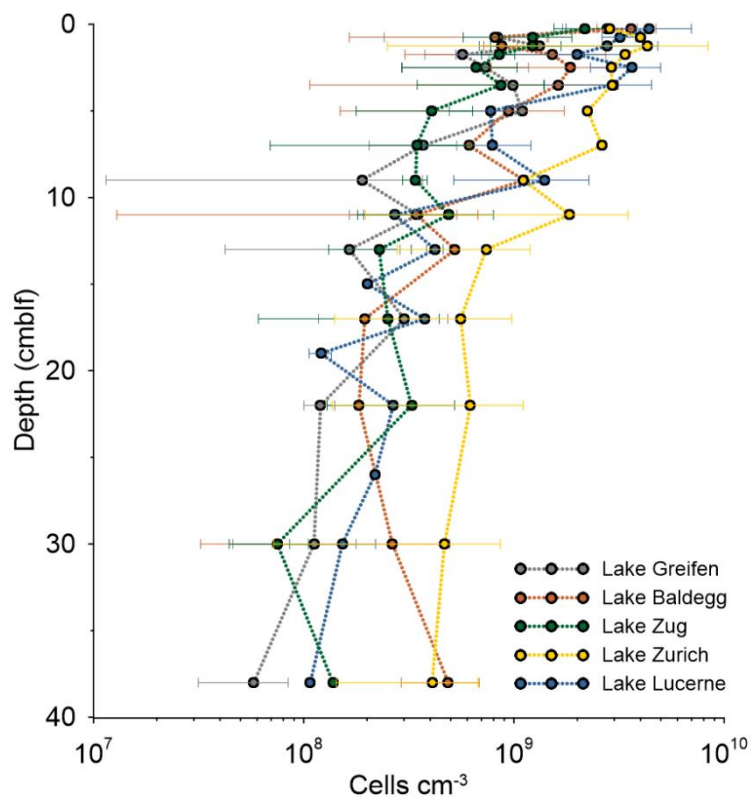
Figure S7: Average cell numbers (3 station average) vs depth. Error bars indicate standard deviations for the average of the 3 stations.
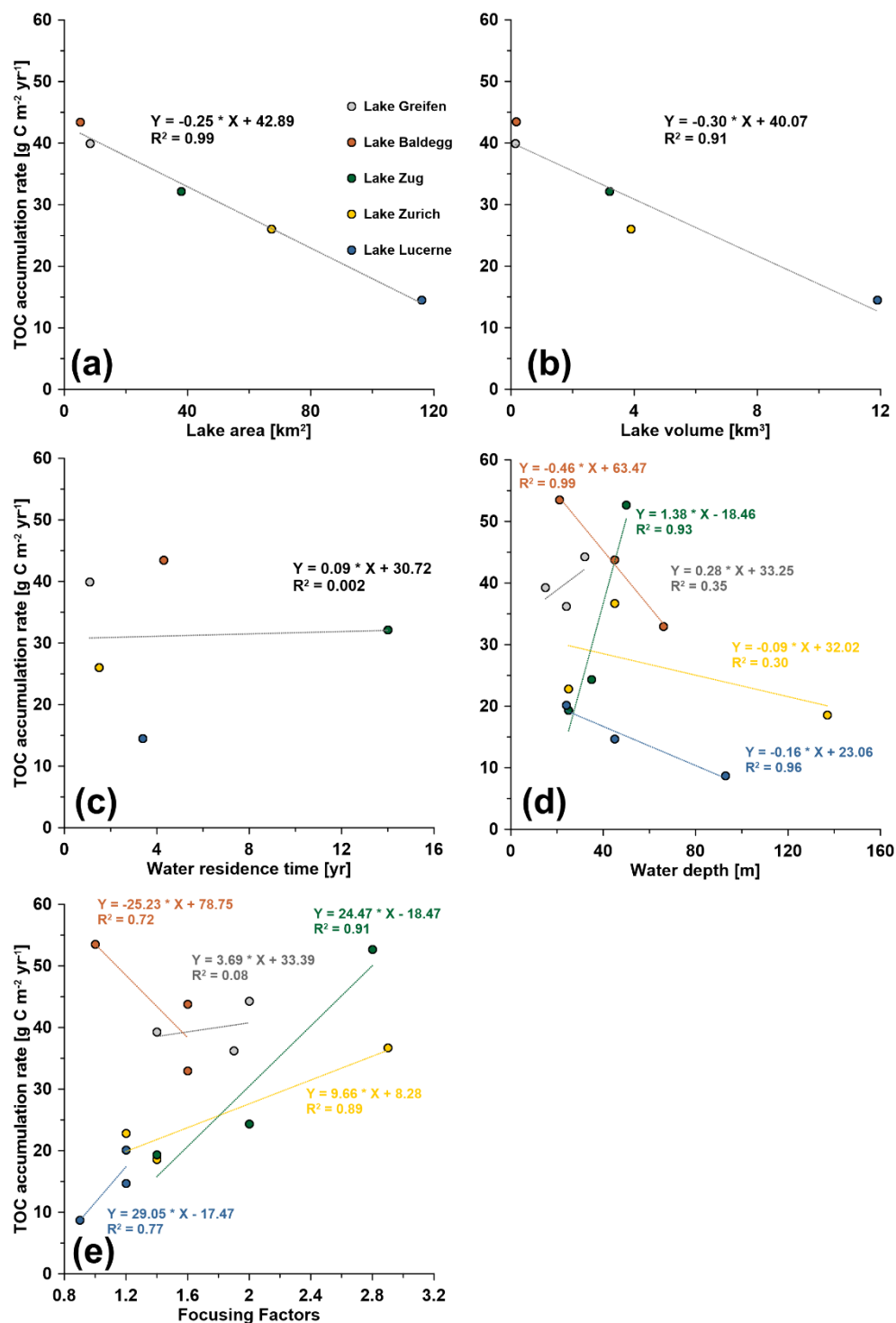
Figure S8: TOC accumulation rates (1840–2016) vs. (a) lake area, (b) lake volume, (c) water residence time, (d) water depth, and (e) focusing factors. Linear correlation equations and R^2 are indicated in each subplot. For a, b and c, TOC accumulation rates of the 3 stations per lake are averaged.

Table S1: Lake characteristics used for relations of average TOC accumulation rate (1840-2016) in g C m^{-2} yr^{-1} vs. lake area, lake volume, water residence times, water depth and focusing factors.

	Area (km^2)	Volume (km^3)	Water residence time [yr]	St. (#)	Water depth (m)	FF	TOC accum. rates	AV TOC accum. rates
Lake Greifen	8.4	0.148	1.1	2	33	2.0	44.3	39.9
				3	24	1.9	36.2	
				1	15	1.4	39.3	
Lake Baldegg	5.2	0.173	4.3	1	68	1.6	33.0	43.3
				2	45	1.6	43.8	
				3	21	1.0	53.5	
Lake Zug	38	3.2	14	3	50	2.8	19.3	32.1
				2	35	2.0	24.3	
				1	25	1.4	52.7	
Lake Zurich	67.3	3.9	1.5	1	137	1.4	22.8	26.0
				2	45	2.9	36.7	
				3	25	1.2	18.5	
Lake Lucerne	116	11.9	3.4	2	93	0.9	8.7	14.5
				3	45	1.2	36.7	
				1	24	1.2	22.8	

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