

Chemical data (photometry) at Lake Stechlin 1970-2020

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Data origin Data were collected by IGB (Uta Mallok, Marén Lentz).

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Data

Sampling site

Lake Stechlin is a deep, dimictic, formerly oligotrophic clear-water lake that has been undergoing eutrophication since the early 2000s and especially since 2010. The lake is located in a nature reserve approximately 80 km north of Berlin, Germany (53°9'5.6"N, 13°1'34.2"E) at 59 m altitude. Lake Stechlin has a maximum depth of 69.5 m, a mean depth of 23.3 m, a surface area of 4.3 km² and a volume of 96.9 x 10⁶ m³ (Casper 1985). The lake basin was formed during the last continental glaciation ca. 12,000 years ago and is today situated at the transition between temperate maritime and temperate continental climate (Fraedrich et al. 2001). The catchment has a size of 12.6 km² and is almost completely covered by managed forest (95%). The main species is Scots pine (*Pinus sylvestris*), although beech (*Fagus sylvatica*) is the dominant tree species along the shoreline. Non-forested areas are the site of a former nuclear power plant (KKW Rheinsberg) and the small village of Neuglobsow with about 300 residents (up to 1000 during the tourist season in summer), whose wastewater is diverted to a different catchment. The shoreline is largely undeveloped with no notable infrastructure except on the small beach and the boat rental, the properties of a fisherman, the Federal German Environment Agency and the Leibniz Institute of Freshwater Ecology and Inland Fisheries. The seepage lake is mainly fed by precipitation and

groundwater, resulting in a theoretical water retention time of more than 40 years (Koschel 1995, Holzbecher et al. 1999). There are no river inflows except for occasional discharge from a small stream channel that is dry in most years. The water level of Lake Stechlin is regulated. From 1966 to 1990, the lake received a total of about 300,000 m³ d⁻¹ of cooling water from the nearby nuclear power plant. The cooling water was withdrawn from neighbouring Lake Nehmitz (North basin) and discharged into Lake Stechlin at an average temperature of approximately 10 °C above the ambient surface water temperature. This resulted in an average increase in water temperature by 1-2 °C during the power plant operation (1966-1990) and decreased the retention time of Lake Stechlin. For more information, see Casper (1985), Koschel and Casper (1986), Casper and Koschel (1995), Koschel and Adams (2003) and Kirillin et al. (2013).

Time span 1970-2020

Sampling method

Water samples were taken at the deepest point of Lake Stechlin (69.5 m) situated in the main basin (53°9'19.5"N, 13°1'52.9"E), from 1985 onwards as well in the West basin (53°9'15.1"N, 13°0'30.5"E) and in the South basin (53°8'37.0"N, 13°1'14.9"E), and between 1994 and 2018 as well at the inlet of Lake Dagow (Dagowsee). The temporal resolution varied over time. In the main basin, fortnightly samples have usually been taken from May to September, however, most parameters were only measured on a monthly basis. Outside the stratification period monthly sampling was performed even throughout winter (when possible). The temporal resolution at the other sites is irregular. The spatial resolution was oriented according to thermal stratification patterns. In the epilimnion samples were taken at discrete depth in steps of 5m, according to the epilimnion depth 2-3 of these separate samples (at a depth of 0m, 5m and 10m, respectively) were taken and afterwards pooled representing the situation of the upper mixed layer (epilimnion). Several other samples were collected but not mixed in order to reflect the situation in the deeper waters (metalimnion and hypolimnion).

- Total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), nitrite (NO₂), nitrate (NO₃), ammonium (NH₄), soluble calcium (Ca), aluminium (Al), iron (Fe) and silicate (Si) were determined photometric following standardized protocols or methods outlined in the user manual of the respective instrument. Dissolved components were estimated after filtration of the sample through a 0.45 µm membrane. TP and TN were measured after wet digestion of unfiltered subsamples in an autoclave (potassium peroxodisulfate, TP 30 min., 134 °C; TN 40 min., 121 °C).
 - TP, SRP: Foss FIAstar 5000 Analyzer, Foss Analytical AB, Höganäs, Sweden; Water quality, determination of orthophosphate and total phosphorus contents by flow analysis
(FIA and CFA) - Part 1: Method by flow injection analysis (FIA) (ISO 15681-1:2003)
 - TN, NO₂, NO₃, NH₄: Foss FIAstar 5000 Analyzer, Foss Analytical AB, Höganäs, Sweden; Water quality, determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection (ISO 13395:1996)

- Ca: Foss FIAstar 5000 Analyzer, Foss Analytical AB, Höganäs, Sweden; Determination of dissolved calcium in water by FIAstar, Application note 5261, Foss Analytical AB, Höganäs, Sweden, 2003
 - Al: FIAcompact, Bestimmung des gesamten gelösten Aluminiums im Wasser. Arbeitsanleitung, Medizin- und Labortechnik GmbH, Dresden, Deutschland 2004
 - Fe: FIAcompact, Medizin- und Labortechnik GmbH, Dresden, Deutschland 2004, German standard methods for the examination of water, waste water and sludge; cations (group E); determination of iron (E 1), DIN 38404-1:1983-05
 - Si: Foss FIAstar 5000 Analyzer, Foss Analytical AB, Höganäs, Sweden; Water quality, determination of soluble silicates by flow analysis (FIA and CFA) ISO 16264:2002
- Total inorganic carbon (TIC) and non-purgeable organic carbon (NPOC) were estimated using an unfiltered sample following the methods suggested in the user manual, SHIMADZU, TOC analyser VCPH/ASI-V, Kyoto, Japan
 - Calcium carbonate (CaCO_3) was determined by filtering aliquots through membranes (cellulose acetate, pore size 0.45 μm , Sartorius, Göttingen) which were stored in a desiccator until further analysis. Samples were then dissolved in 10 % hydrochloric acid and the released CO_2 was measured using an infrared gas analyser (Infralyt 50 Saxon, Junkalor, Dessau, Germany; see Proft 1984). To recalculate from CO_2 -C into CaCO_3 a factor of 8.3 was used.
 - Alkalinity was ascertained titrimetric, Titrando 888, Metronom, Filderstadt, Germany). Water quality, determination of alkalinity - Part 1: Determination of total and composite alkalinity (ISO 9963-1:1994)
 - Chlorophyll a was measured photometric, Hitachi spectrophotometer U-2900; German standard methods for the examination of water, waste water and sludge; test methods using water organisms (group L); determination of chlorophyll a in surface water (L 16), DIN 38412-16:1985-12. Data before 1997 are only available as rounded values to the units digit, from 1997 data are provided in higher precision.

Parameters

- lake – sampled lake
- date – date of measurement [YYYY-MM-DD]
- site – measurement site
- depth – depth of measurement [m]
- tp – total phosphorus [mg L^{-1}]
- srp – soluble reactive phosphorus [mg L^{-1}]
- tn – total nitrogen [mg L^{-1}]
- no2 – nitrite [mg L^{-1}]

- no3 – nitrate [mg L⁻¹]
- nh4 – ammonium [mg L⁻¹]
- ca – soluble calcium [mg L⁻¹]
- al – aluminium [mg L⁻¹]
- fe – iron [mg L⁻¹]
- si – silicate [mg L⁻¹]
- npoc – non-purgeable organic carbon [mg L⁻¹]
- ic – total inorganic carbon [mg L⁻¹]
- doc – dissolved organic carbon [mg L⁻¹]
- caco3 – calcium carbonate [mg L⁻¹]
- chla – chlorophyll a [µg L⁻¹]
- alkalinity – alkalinity [mval L⁻¹]
- comments – comments

Data Cleaning

Non-Purgeable Organic Carbon (NPOC)

NPOC values between 1990 and 2020 were measured using a combination of four different instruments. Initially, between 1994 and 2006 the department employed a Shimadzu TOC Analyzer. In 2007 a Jena Analytik TOC Analyzer was obtained, but then a switch back to another Shimadzu TOC analyzer was made in 2009. A newer Shimadzu TOC analyzer was purchased in 2018.

Throughout operation of all four instruments, efforts were taken to ensure accurate calibration using available standards. However, we identified periods in the raw data where large deviations in the observed trend occurred compared to other measurements. In almost all cases we could trace this back to the standard curve where, although the R² values were very high > 0.98, gradients of the slopes were not consistent. We extracted for each calibration instance the slope. We then calculated the median for all calibration instances across the entire time-period. We identified calibration slope values that differed from the mean by greater than 20% and sought to correct the samples measured based on these erroneous calibrations.

Notable instances were between 2003-2006 where we identified that multiple calibration instances had slopes which were 80% of the median slope value, in 2010 where we identified a slope which was 120% of the median slope value. In 2014-2015 the technician had noted that values were elevated and had applied a correction with the assumption that the calibration slope for this period was 160% of the median slope value. From the calibration curves we estimated a lower overestimation with the observed calibration slopes over this period of 140% of the median slope value. In most cases we attribute these differences in the standard curve to issues with the storage and preparation of dilutions for constructing the standard curve. An exception to this appears to be the period between 2007-2009 where the Jena Analytik TOC Analyzer was in operation. Values during this period were 180% higher than normal and were likely attributed to differences in the instruments.

Corrections were only applied to raw data between sampling intervals where calibration slopes showed at least 20% variation from the median slope value. The correction involved dividing the measured value by the estimated correction factor, for example:

for values 2003-2006

$$1.45 \text{ mg L}^{-1} / 0.8 = 1.8125 \text{ mg L}^{-1}$$

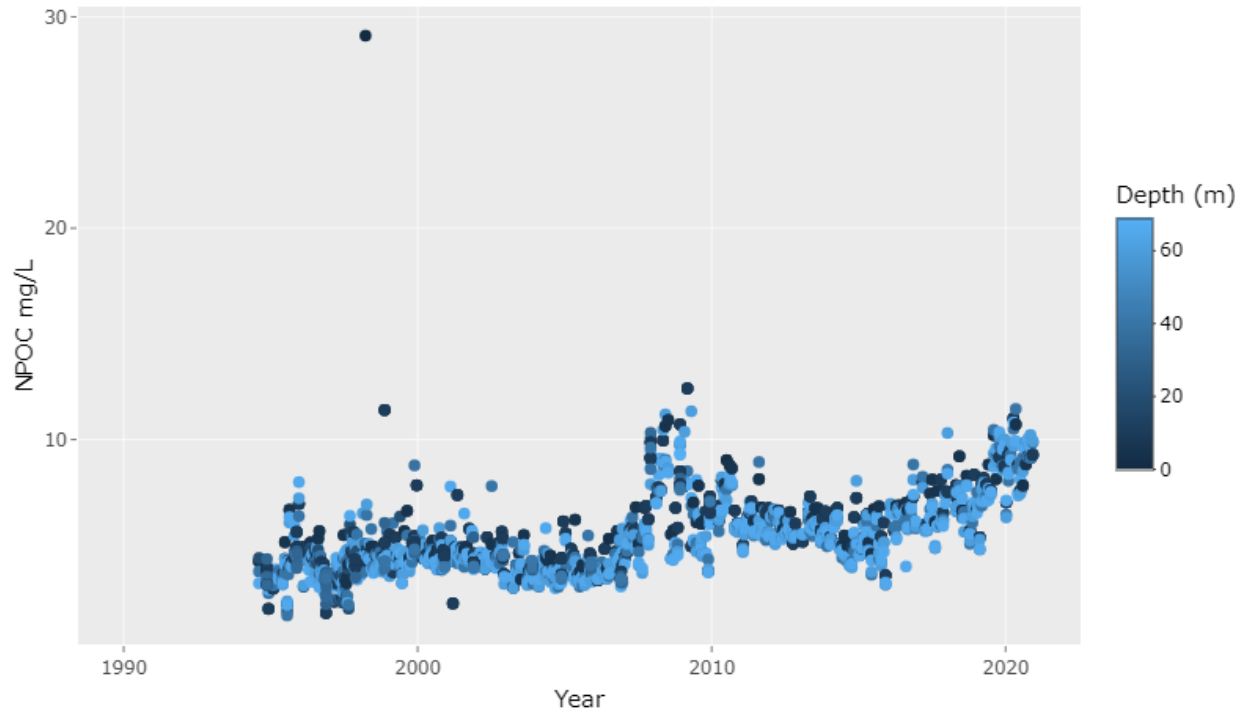
for values 2014-2015

$$1.67 \text{ mg L}^{-1} / 1.2 = 1.39 \text{ mg L}^{-1}.$$

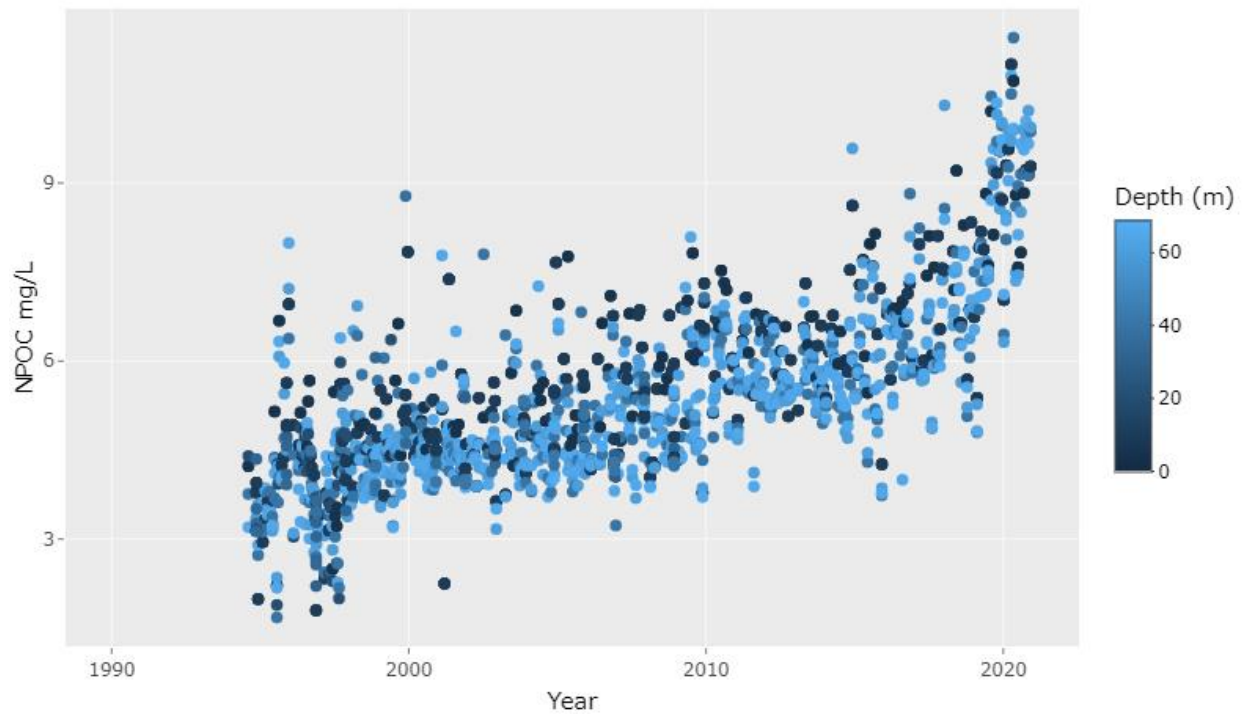
Since 2019 we have observed a consistent and large increase in the TOC values. At this stage we do not have sufficient evidence to suggest that this increase is due to technical issues in the data

collection. This increase is consistent with increases in other dissolved nutrients, including total phosphorous and coincides with large accumulations of cyanobacteria in the lake.

Lake Stechlin NPOC (Raw Data)



Lake Stechlin NPOC (Corrected Data)



Inorganic Carbon

Inorganic carbon is also measured as a function of the total organic carbon (measured without purging). Aforementioned calibration issues (see above) impacted also inorganic carbon values and these have been similarly corrected.

Calcium

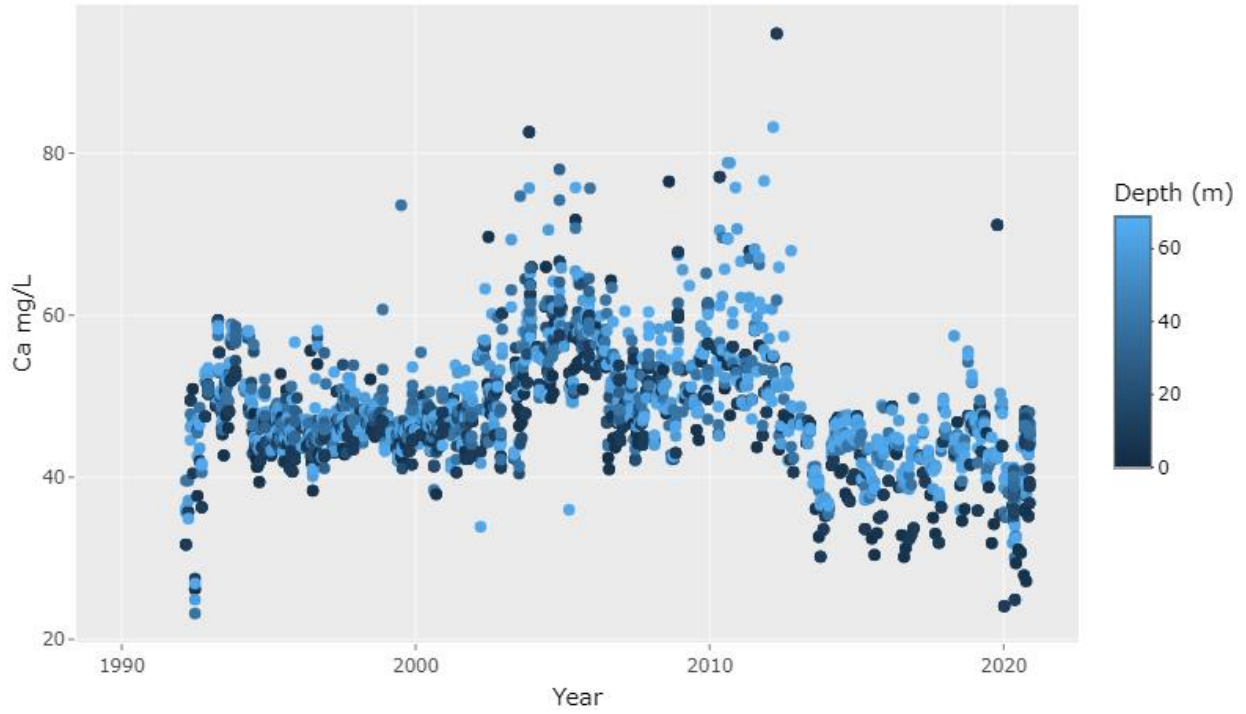
Historically total calcium has been measured using a Flow-Injection Analysis (FIA) coupled spectrophotometer. We identified an increase in FIA measured values during the period 2003-2012, but were unable to identify a clear reason. Between 2003-2012, sub-samples from the lake were also taken for measurement of multiple parameters (including Calcium) using an Ion Chromatogram system. We made a direct comparison between data from both instruments of the data collected between 2003-2012. Measurements of calcium made using the FIA were 130% higher, between 2003-2007, and 120% higher, between 2007-2012, than values from the same samples measured using the Ion Chromatogram. This discrepancy was most obvious in those lakes with lower Calcium values (i.e. Lake Grosse Fuchskuhle) and less evident in lakes with higher Calcium values (i.e. Lake Tiefwaren). We made the decision, for consistency, to continue using the FIA values and correct these during the aforementioned periods.

Values were corrected by dividing the measured Calcium value made using the FIA by the correction factor, determined based on comparison between FIA and Ion Chromatogram values.

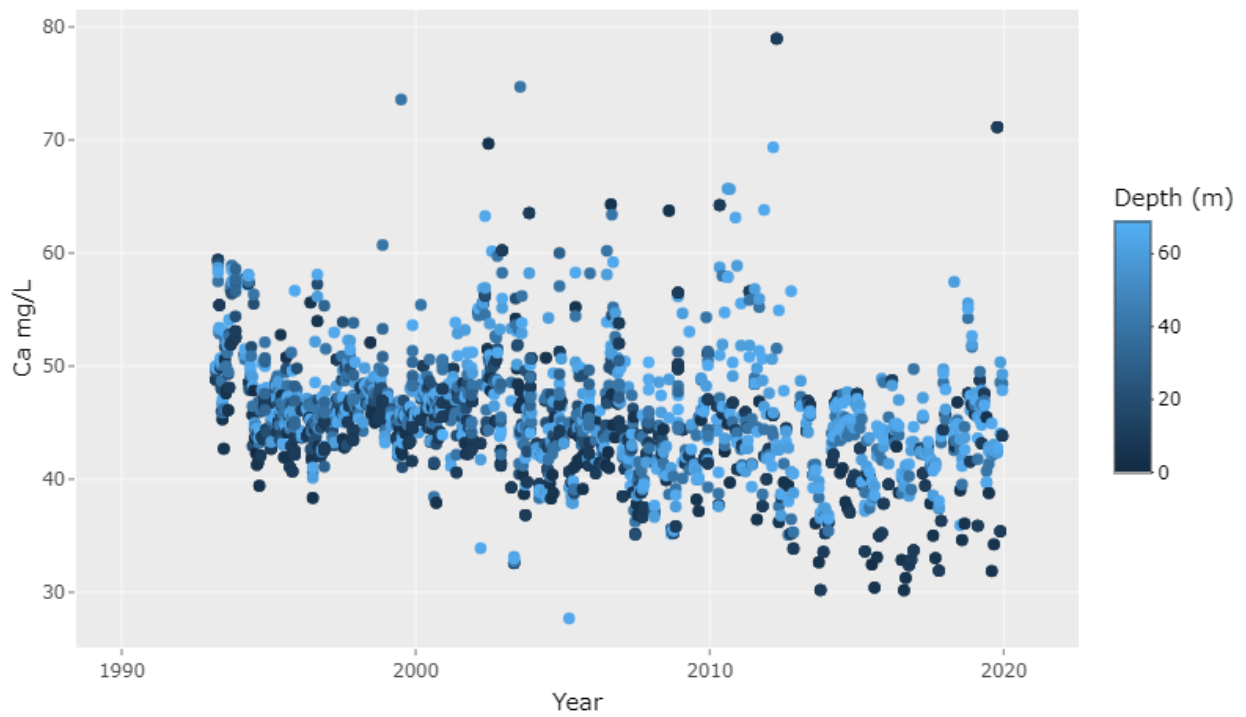
For instance, between 2007-2012 with a discrepancy of 120%

$$3.78 \text{ mg L}^{-1} / 1.2 = 3.15 \text{ mg L}^{-1}.$$

Lake Stechlin Calcium (Raw Data)



Lake Stechlin Calcium (Corrected Data)



References

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Change log

- 2020/2021 Silke R. Schmidt: Chla values should be exchanged: a higher accuracy is available in raw data, however, values were rounded to the units digits.
- 2022 Jason N. Woodhouse/Sabine Wollrab: Extensive data cleaning. NPOC, IC, Ca²⁺ values adjusted for calibration failure/instrument changes (see Data Cleaning section). Chla values from 1997 onwards have been exchanged for high resolution values.