

Chemical data (photometry) at Lake Stechlin 1970-2020

Version 2024-06-19

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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 The cooling water was withdrawn from neighbouring Lake Nehmitz (North basin) and discharged into Lake Stechlin at an average temperature of approximately 10 °C above the ambient surface water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 for chemical analyses have been taken at the deepest point of the lake (69.5 m) in the main basin (53°9′19.5″N, 13°1′52.9″E) since 1970. Additional samples were collected in the west (53°9′15.1″N, 13°0′30.5″E) and south (53°8′37.0″N, 13°1′14.9″E) basin from 1985 onwards, complemented between 1994 and 2018 by samples from the eastern bay that occasionally received surface flow. Sampling frequency varied over the years. In the main basin, fortnightly samples were usually taken from May to September, although various measurements were only made monthly. Monthly samples were also taken during the rest of the year, unless winter ice conditions prevented access to the sampling sites either by boat or on foot. In the south and west basin, sampling was restricted to the end of summer stratification in either November or December. Both basins have been sampled four times a year in 2020. All water samples were taken from the surface mixed layer using a 1 L or 2 L Ruttner-sampler from 1970-1990, and a 2.6 L or 3.5 L Limnos water sampler (Limnos Oy, Turku, Finland) from 1991 onwards. From 1985 onwards occasionally a 5 L Hydrobios water sampler was used. Epilimnion (surface mixed layer) samples were taken in 2.5 m intervals from 0 to 10 m depth before 1992 and separately analyzed. Since 1992 they were taken at 5 m increments and then pooled, containing the samples from 0 and 5 m depth, and additionally a sample from 10 m when the epilimnion was deep enough, occasionally, for periods with a very shallow epilimnion depth a pooled sample from 0 and 2.5 m depth was used. Hypolimnetic water was collected at 15, 20, 40, 60 and 65 m depth before 1992, and at 40, 60 and 65 m depth since 1992 until 2008. These discrete deep-water samples were separately analyzed. Since 2009, additional discrete samples have been taken during summer stratification at 5 m intervals between 15 and 55 m depth.

Total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), ammonium (NH₄⁺), nitrite (NO₂⁻), nitrate (NO₃⁻), dissolved calcium (Ca²⁺), dissolved aluminum (Al), dissolved iron (Fe: sum of Fe²⁺/Fe³⁺) and dissolved silicon (Si), total inorganic carbon (TIC), non-purgeable organic carbon (NPOC) (i.e. the fraction of organic carbon remaining after sparging an acidified aqueous sample with gas to remove all volatile carbon constituents), dissolved organic carbon (DOC), calcium carbonate (CaCO₃), total alkalinity (alkalinity) and chl *a* were determined following

standard methods or protocols outlined in the user manual of the respective instrument (see below for details).

If not analyzed immediately after filtration, samples were stored at -20°C. Filters for CaCO₃ determination were dried at 60°C overnight and stored in an exicator until analysis, while filters for Chl-a analysis were stored at -20°C. TP and TN were measured after wet digestion of unfiltered aliquots in an autoclave using 10 g L⁻¹ potassium peroxodisulfate as oxidant (30 min at 134 °C for TP; 45 min at 120 °C for TN).

Details of the analytical methods are as follows:

- TP, SRP: Spectrophotometry
 - Before 1992, manual spectrophotometric analysis as described in Vogler 1965, 1966a,b, Mothes 1974, Mothes 1981
 - From 1992 to October 2009, flow-injection analysis with spectrophotometric detection: FIAstar (Tecator AB, Höganäs, Sweden) Application Note 60/83, ASN 60-02/83 (Determination of orthophosphate in water by flow injection analysis) and ASN 60-04/83 (Determination of total phosphate in water by flow injection analysis)
 - Since November 2009 flow-injection analysis with spectrophotometric detection FIAstar 5000 Analyzer (Foss Analytical AB, Höganäs, Sweden). Application Notes 5240 (Determination of ortho-phosphate in water by FIAstar 5000) and 5241 (Determination of total phosphorus in water by FIAstar 5000) according to ISO 15681-1.
- TN, NO₂⁻, NO₃⁻, NH₄⁺: Spectrophotometry
 - Before 1992, flow stream analysis as described in Vogler 1975a,b, which was conducted by Wasserwirtschaftsdirektion Havel, Potsdam, German Democratic Republic (Mothes 1981)
 - From 1992 till October 2009, flow-injection analysis with spectrophotometric detection: FIAstar (Tecator AB, Höganäs, Sweden) Application Note 62/83, ASN 110-01/92 (Determination of the sum of nitrate and nitrite in water by flow injection analysis) and ASN 110-03/92 (Determination of total nitrogen in water by flow injection analysis); and Application Note 50/84, ASN 151-01/92 (Determination of ammonia nitrogen in water by flow injection analysis according to DIN 38406 (E23))
 - Since November 2009 flow-injection analysis with spectrophotometric detection FIAstar 5000 Analyzer (Foss Analytical AB, Höganäs, Sweden). Application Notes 5201 (Determination of sum of nitrate and nitrite in water by FIAstar 5000) according to ISO 13395-1996, Application Note 5202 (Determination of total oxidized nitrogen in water by FIAstar 5000) according to ISO 11905 and ISO 13395, and Application Note 550 (Determination of ammonium in water by FIAstar 5000) according to ISO 11732.

- Ca^{2+} : Spectrophotometry,
 - 1992-10/2009, flow-injection analysis with spectrophotometric detection: FIAstar (Tecator AB, Höganäs, Sweden) Application Note 48/83, ASN 48-03/84 (Determination of calcium in water by flow injection analysis)
 - since 11/2009 flow-injection analysis with spectrophotometric detection FIAstar 5000 Analyzer (Foss Analytical AB, Höganäs, Sweden). Application Note 5261 (Determination of dissolved calcium in water by FIAstar 5000) according to DIN 38406-3
- Al: Spectrophotometry, FIAcompact (Medizin- und Labortechnik GmbH, Dresden, Germany). Bestimmung des gesamten auflösbaren Aluminiums in Wasser. Arbeitsanleitung, 2004, based on APHA 3500-Al and ISO 10566
- Fe: Spectrophotometry, FIAcompact (Medizin- und Labortechnik GmbH, Dresden, Germany). Bestimmung des Gesamt-Eisens/Eisen(II) in Wasser/Abwasser), 2004, based on DIN 38406-1:1983-05 with ferrozine used instead of ortho-phenanthroline
- Si: Spectrophotometry,
 - Before 1992, flow stream analysis as described in Vogler (1975c), which was conducted by Wasserwirtschaftsdirektion Havel, Potsdam, German Democratic Republic (Mothes 1981)
 - 1992-2009, flow-injection analysis with spectrophotometric detection: FIAstar (Tecator AB, Höganäs, Sweden) Application Short Note 4/92 (Determination of silica in water by flow injection analysis)
 - since 2009 flow-injection analysis with spectrophotometric detection FIAstar 5000 Analyzer (Foss Analytical AB, Höganäs, Sweden). Application Note 5240 (Determination of silicate in water by FIAstar 5000) according to ISO 16264
- TIC and NPOC: catalytic oxidation, NDIR, TOC analyzer (TOC-5000/5050 Analyzer (Shimadzu, Kyoto, Japan) between 1994 and 2008, multi N/C 3100 Analyzer (Analytik Jena, Jena, Germany) from 2007 to 2009, TOC-VCPH analyzer (Shimadzu, Kyoto, Japan) between 2009 and 2018, and TOC-LCPH analyzer (Shimadzu Kyoto, Japan) between 2019 and 2020, quantification of CO_2 released at high temperature from unfiltered water samples before and after acidification following the procedures described in the user manual.
- DOC: catalytic oxidation, NDIR, TOC analyzer (Shimadzu VCPH analyzer, Kyoto, Japan), determination of CO_2 release from 0.45 μm pre-filtered water samples, following the methods described in the user manual.
- CaCO_3 : infrared gas analyzer (Infralyt 50 Saxon, Junkalor, Dessau, Germany) (Proft 1984, Lenz 2018), determination of CO_2 released from dry filtration (cellulose acetate membrane filter, pore size 0.45 μm ; Sartorius, Göttingen, Germany) residue of water samples after dissolution in 10% hydrochloric acid. CO_2 -C was converted to CaCO_3 by applying a multiplication factor of 8.3, according to the stoichiometry of CaCO_3 .

- Alkalinity:
 - Before 1991: Titrimetric by p- and m-value (Legler 1986)
 - 1991-2010: Titrimetry, Titroprocessor 686 (Metrohm, Filderstadt, Germany), Titration to pH 4.3, according to ISO 9963-1:1994
 - Since 2011 Titrimetry, Titrand 888 (Metrohm, Filderstadt, Germany), Titration to pH 4.3, according to ISO 9963-1:1994
- Chl *a*: Spectrophotometry after overnight extraction in 90% acetone (Perkin Elmer Lambda 2 spectrophotometer until 2008, Hitachi spectrophotometer U-2900 since 2009) modified from Strickland and Parsons (1968) and Kasprzak (2008) using membrane filters (ME 28, 47 mm 1,2µm, Whatman, USA). Data before 1997 were rounded to the nearest integer (µg L⁻¹), thereafter data are reported to the nearest 0.1 µg L⁻¹).

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]
- tic – 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]
- epi_int_depth – indicating the integrated depth of the epilimnion sample [m]
- comments – comments

Data Cleaning

Laboratory workflows followed standard protocols. Laboratory measurements were documented in laboratory note books and manually entered into a local database. Quality assurance of analytical procedures involved occasional participation in round-robin tests with multiple laboratories. The data were checked by an automated procedure to identify values beyond reasonable bounds as well as by visual inspection. In cases of doubt, data entries were compared with the original records in laboratory note books. Discontinuities in trends were detected for three spectrophotometrically determined parameters (NPOC, TIC, Ca²⁺), the breakpoints coinciding with times when methods or instruments were changed. The data curation for these three parameters is described in detail in the following sections:

Non-Purgeable Organic Carbon (NPOC)

Non-purgeable organic carbon (NPOC) concentrations were measured on four different instruments, a Shimadzu TOC-5000/5050 Analyzer between 08/1994 and 10/2007, an Analytik Jena TOC Analyzer multi N/C 3100 from 11/2007 to 11/2009, a Shimadzu TOC-VCPH analyzer between 12/2009 and 12/2018, and a Shimadzu TOC-LCPH analyzer between 01/2019 and 12/2020. Good laboratory practices were ensured throughout, including routine calibrations. Nevertheless, five periods stood out where the measured concentrations deviated by more than 20% from the values expected based on the long-term trendlines (Table 2), whereas similar deviations were not observed for any other variables. Furthermore, NPOC concentrations during these periods departed from the long-term trends also in two other clear-water lakes (Breiter Luzin and Lake Tiefwaren) and a brown-water lake (Grosse Fuchskuhle) included in IGB's lake monitoring program. These discrepancies suggest that measurement errors occurred during the five suspicious periods.

For the two periods from April 2003 to December 2006 and December 2009 to September 2010, the slopes of the calibration curves differed by more than 20% from the slopes obtained both before and after these periods (Table 2). Consequently, we recalculated all concentrations based on the calibration slopes determined before and after the suspicious periods, resulting in 25% higher and 20% lower concentrations than originally measured during the first and second critical period, respectively.

In 2014, NPOC and TIC concentrations, which were measured on the same instruments, both deviated from the respective long-term trends, suggesting instrument rather than calibration issues, an explanation that is also likely for the two periods from 2007-2008 and 2008-2009, because potential calibration errors could not be identified. To correct the NPOC data for these three periods, we first calculated an overall linear regression for the period from January 2004 to December 2017, ignoring all periods with identified issues. The last three years of the time series were not included due to an increasingly steep rise in concentration (see Fig. 1A-D). The linear

regression yielded an R^2 of 0.13 with a median value of 5.8 ± 1.0 mg/L. Next, we interpolated the missing values based on the linear regression and then calculated ratios of the median values of the originally measured concentrations (8.745, 9.12, 7.9 mg/L) and the median of the interpolation (5.48, 5.53, 6.03 mg/L) for each of the respective periods (2007-2008, 2008-2009, and 2014). Multiplication of these ratios with the originally measured concentrations resulted in corrected concentrations consistent with the long-term trend (median of respective time periods after correction: 5.51 ± 0.75 , 5.54 ± 0.94 , 6.34 ± 0.5), while maintaining the full variability of the original data (Table 2, Fig. 1A,B).

Total Inorganic Carbon (TIC)

Total inorganic carbon (TIC) concentrations were determined with the same instruments used for the NPOC analyses. However, since different methods and calibration curves were used and calibrations were not always performed at the same time, periods with TIC calibration issues differed from those identified for NPOC (Table 1, Fig. 1C,D). An exception was in 2014 when the instrument issue affected both measurements. A calibration issue was identified for TIC samples taken between December 2009 and December 2010, differed by more than 20% from the slopes obtained both before and after this period. For this period, concentrations were recalculated based on a calibration curve established in February 2011, resulting in 40% reduced concentrations than originally measured during the critical period. For the periods from May until December 2006 and April until September 2014, we used the interpolation approach as described for NPOC, based on an overall linear regression calculated over the period from 2004 until 2017, with both suspicious periods excluded, resulting in a median of 21.5 ± 2.1 mg/L. We calculated correction factors (1.33 and 0.74) as the difference between the median values of the originally measured (16.4 and 29.1 mg/L) and the interpolated concentrations (21.7 and 21.5 mg/L), resulting in a corrected median of 21.8 ± 3.2 and 21.5 ± 2.6 mg/L for 2006 and 2014, respectively. In contrast to the NPOC data, no deviation from the general trend was observed for TIC concentrations during the operation of the Analytik Jena instrument between 2007 and 2009, probably because frequently encountered problems with the combustion tube or catalyst affected NPOC but not TIC measurements.

Dissolved calcium

The spectrophotometric analyses of dissolved calcium (Ca^{2+}) indicated increased concentrations between January 2003 to May 2003, August 2003 to July 2006 and January 2007 to December 2012, that were not apparent in the ion chromatographic analyses. Specifically, the spectrophotometrically determined data exceeded those determined by ion chromatograph by 30% between 2003 and 2007 and by 20% between 2007 and 2012. The reported spectrophotometric data have been corrected for the three periods, resulting in 30%, 30% and 20% reduced concentrations than originally measured (Fig. 1E,F).

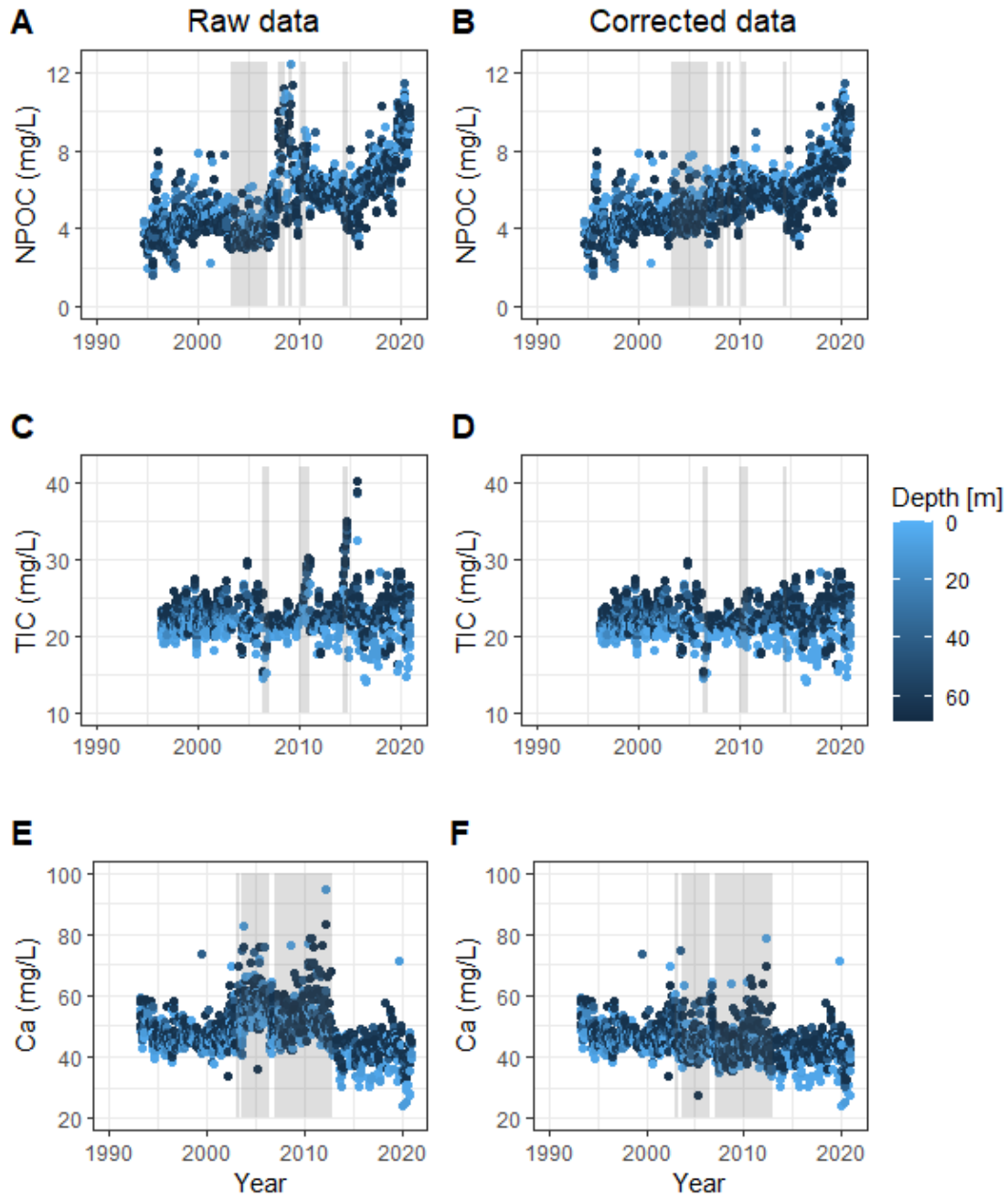


Fig. 1 Time series for NPOC (A, B), TIC (C, D) and spectrophotometrically determined calcium concentrations (E, F), illustrating the effect of raw data corrections on temporal dynamics. Coloured areas indicate affected time periods.

Table 1 Corrections of NPOC and TIC concentrations applied for different time periods

Parameter	Instrument	Period	Basis of correction	Correction factor
NPOC	Shimadzu TOC-5000/5050 Analyzer	April 2003 - Dec 2006	calibration curve	x 1.25
NPOC	Analytik Jena TOC Analyzer	Nov 2007 -July 2008	interpolation	x 0.8
NPOC	Analytik Jena TOC Analyzer	Dec 2008 - March 2009	interpolation	x 0.63
NPOC	Shimadzu TOC-VCPH Analyzer	Dec 2009 – Sep 2010	calibration curve	x 0.58
NPOC	Shimadzu TOC-VCPH Analyzer	May 2014- Sep 2014	interpolation	x 1.25
TIC	Shimadzu TOC-5000/5050 Analyzer	May 2006-Dec 2006	interpolation	x 1.33
TIC	Shimadzu TOC-VCPH Analyzer	Dec 2009-Dec 2010	calibration curve	x 0.86
TIC	Shimadzu TOC-VCPH Analyzer	April 2014 – Sep 2014	interpolation	x 0.74

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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, TIC, Ca²⁺ values adjusted for calibration failure/instrument changes (see Data Cleaning section). Chla values from 1997 onwards have been exchanged for high resolution values.
- 2024 Christine Kiel/Sabine Wollrab: update of metadata description, specifically on sampling procedures and changes in methods over time.
- 2024 Jason N. Woodhouse/Sabine Wollrab: Update on correction of identified issues and data cleaning procedures for NPOC, TIC, and Ca²⁺ data (see updated text in Data Cleaning section).