Chemical data (spectrophotometry) at Lake Breiter Luzin 1979-2020

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

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Data

Sampling site

Lake Breiter Luzin is a mesotrophic hard-water lake located in the Feldberg Lake District Nature Park (Naturpark Feldberger Seenlandschaft), Mecklenburg-Western Pomerania, Germany (53°21‘19“N, 13°27‘55“E). The lake has a maximum depth of 58.3 m, a mean depth of 22.8 m, a surface area of 3.37 km^2 and a volume of 76.89 x 10^6 m^3. The catchment area has a size of 22.6 km^2 ((morphometric data from Ministry for Climate Protection, Agriculture, Rural Areas and the Environment M-V, calculation base 2015). Lake Breiter Luzin is divided into two basins. The Northwestern shore is relatively steep and mainly populated with beech, the opposite shore exhibits a well-developed reed bed (Nixdorf et al. 2004).

Time span 1979-2020

Sampling method

Samples were taken from a buoy at the center of the lake (Deep measurement point, (BL), 53°21’31.1“N, 13°28‘0.7“E) between 1979 and 2020. The temporal resolution varied over time.

Samples were taken monthly, although fortnightly samples are occasionally available between May and September. The spatial resolution was oriented according to thermal stratification patterns. 2-3 separate samples were taken and afterwards pooled representing the situation of the upper mixed layer (epilimnion, usually 0-10m). Samples were also regularly collected from hypolimnic waters (40m and 50m) and very rarely at 20-35m. Between 1994 and Nov 2012 regular monthly surface layer samples (0m) were collected from the southern outflow channel (Schmaler Luzin outflow, 53°20'37.2"N, 13°27'36.8"E), which flows into the adjacent Schmaler Luzin lake. Regular monthly epilimnic and hypolimnic water samples were collected from multiple locations in both the upstream Feldberger Haussee (53°20'44.4"N, 13°26'35.2"E) and downstream Schmaler Luzin (53°19'14.1"N, 13°26'15.3"E) since 1978, but are not part of this data package. All water samples were taken using a 2.6 L or 3.5 L Limnos water sampler (Limnos Oy, Turku, Finland).

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+ and 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), calcium carbonate (CaCO3), total alkalinity (alkalinity) and Chlorophyll a (chl a) were determined following standard methods or protocols outlined in the user manual of the respective instrument (see below for details). All analyses of dissolved components (SRP, NO2-, NO3-, NH4+, Ca, Al, Fe, Si) were performed on water samples passed through NC60 membrane filters (0.6 µm pore size, Whatman, Little Chalfont, United Kingdom) before July 2010, cellulose nitrate membrane filters (0.45 µm pore size, Whatman, Little Chalfont, United Kingdom) between July 2010 and April 2012, and cellulose acetate membrane filters (0.45 µm pore size, Sartorius AG, Göttingen, Germany) since May 2012. Unless analysed immediately after filtration, samples were stored at -20 °C. The residual filters were used for CaCO3 determination, were dried at 60 °C overnight and stored in adesiccator 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 50 g L-1 potassium peroxodisulfate as oxidant for TP (30 min at 134 °C) and oxidizing decomposition reagent (Oxisolv®,Merck, Germany) for TN (45 min at 120 °C).

Details of the analytical methods are as follows:

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- TP, SRP: Spectrophotometry
    - Before 1992, manual spectrophotometric analysis as described in Vogler 1965, 1966a,b, Mothes 1974, Mothes 1981
    - From 1992 to December 2005, flow-injection analysis with spectrophotometric detection: FIAstar (Tecator AB, Höganäs, Sweden) Application Note 60/83, ASN 6002/83 (Determination of orthophosphate in water by flow injection analysis) and ASN 60-04/83 (Determination of total phosphate in water by flow injection analysis)

  - From January 2006 to December 2014, flow-injection analysis with spectrophotometric detection: FIAcompact (Medizin- und Labortechnik GmbH, Dresden, Germany). Arbeitsanleitung Orthophosphat in Wasser/ Abwasser/ Bodenextrakten, fotometrisch über Phosphomolybdat und Reduktion zu Molybdänblau, 2005, based on DIN EN ISO 15681-1
  - Since January 2015 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, NO_2^-, NO_3^-, NH_4^+: 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 11001/92 (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) accordin 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,
    - From 1996 until August 2005, flow-injection analysis with spectrophotometric detection: FIAstar (Tecator AB, Höganäs, Sweden) Application Note ASN 72-01/84 (Determination of iron in water by flow injection analysis (TPTZ method))
    - Since September 2005, flow-injection analysis with spectrophotometric detection: FIAcompact (Medizin- und Labortechnik GmbH, Dresden, Germany). Arbeitsanleitung Gesamt-Eisen/Eisen (II) in Wasser/Abwasser, Labormethode für FIAcompact, Laboranleitung für FIAcompact, 2004, based on DIN 38406 Part 1 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)
    - From 1992 until 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, nondispersive infrared sensor (NDIR), quantification of CO2 released at high temperature from unfiltered water samples before and after acidification following the procedures described in the user manual.
    - Between 1994 and October 2007, TOC-5000/5050 Analyzer, (Shimadzu, Kyoto, Japan)
    - From November 2007 to November 2009, multi N/C 3100 Analyzer (Analytik Jena, Jena, Germany)
    - Between December 2009 and 2018, TOC-VCPH Analyzer (Shimadzu, Kyoto, Japan)

    - Between 2019 and 2020, TOC-LCPH Analyzer (Shimadzu Kyoto, Japan)

- $CaCO_3$: 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: Titrimetry,
    - Before 1991: Manual titrimetric analysis with methylorange or phenolphthalein (Legler 1986)
    - 1991-2010: Titroprocessor 686 (Metrohm, Filderstadt, Germany), titration to pH 4.3, according to ISO 9963-1:1994
    - Since 2011: Titrando 888 (Metrohm, Filderstadt, Germany), titration to pH 4.3, according to ISO 9963-1:1994

- Chl a: Spectrophotometry after overnight extraction in 90% acetone modified from references Strickland & Parsons (1968), Kasprzak et al. (2008), using membrane filters (ME 28, 47 mm 1.2µm pore size, Whatman, Little Chalfont, United Kingdom). Before 1997, data were rounded to the nearest integer (µg L-1), thereafter to the nearest 0.1 µg L-1.
    - Until 2008, Lambda 2 spectrophotometer (Perkin Elmer, Waltham, MA, USA)
    - Since 2009, U-2900 spectrophotometer (Hitachi, Tokio, Japan)

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}]
- 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 two spectrophotometrically determined parameters (NPOC, TIC), 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 1), 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 (Stechlin 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 impacted 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 0.04 with a median value of 7.3±1.4 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 (10.93, 10.63, 5.65 mg/L) and the median of the interpolation (7.28, 7.29, 7.43 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: 7.32±1.83, 7.33±1.01, 7.03±1.05), while maintaining the full variability of the original data (Table 1, 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, April until September 2014, and July until September 2015 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 erroneous periods excluded, resulting in a median of 29.8±3.32 mg/L. We calculated correction factors (1.18, 0.77 and 0.68) as the difference between the median values of the originally measured (24.28, 39.65 and 44.96 mg/L) and the interpolated concentrations (28.65, 30.41 and 30.65 mg/L), resulting in a corrected median of 28.64±4.0, 30.53±3.66 and 30.57±4.64 mg/L for 2006, 2014 and 2015, 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. Consequently, 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).

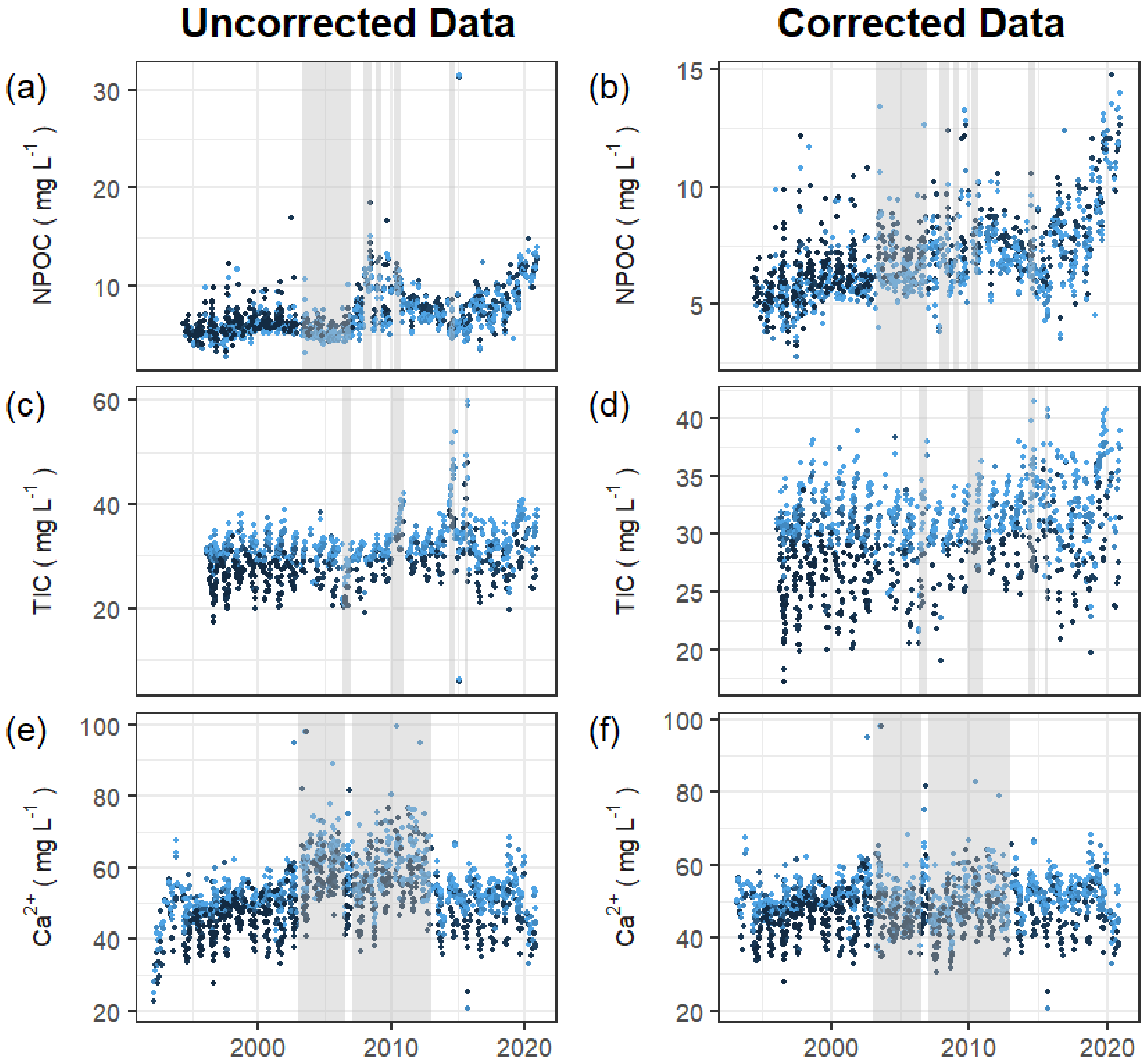

Fig. 1 Time series for NPOC (A, B), TIC (C, D), and Ca (E, F) illustrating the effect of raw data corrections on temporal dynamics. Grey shaded areas indicate affected time periods.

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 0.67
NPOC	Analytik Jena TOC Analyzer	Nov 2008 - March 2009	interpolation	x 0.69
NPOC	Shimadzu TOC-VCPH Analyzer	Mar 2010 – Sep 2010	calibration curve	x 0.8
NPOC	Shimadzu TOC-VCPH Analyzer	Apr 2014- Sep 2014	interpolation	x 0.76
TIC	Shimadzu TOC-5000/5050 Analyzer	May 2006-Dec 2006	interpolation	x 1.18
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 0.77
TIC	Shimadzu TOC-VCPH Analyzer	Jul 2015 – Sep 2015	interpolation	x 0.68

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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).
- 2024 Sabine Wollrab: Minor corrections on chla data, sometimes value for 5m was missing if integrated measure between 0 and 10m was taken. Figure 1 was updated as for TIC some data were previously not displayed.
- 2025/01 Christine Kiel/ Sabine Wollrab: Correction of metadata information on iron, TP and SRP detection method and on preparations of samples for TP and TN detection. Rights of usage has been updated.
- 2025/05 Sabine Wollrab: changed format of csv file from semi-colon to comma separated, added column with English translation of original (German) comments, additional comments recorded with the higher precision chla values have been merged with original comments on chemistry data