

Chemical data (spectrophotometry) at Lake Tiefwaren

1998-2020

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Data

Sampling site

Lake Tiefwaren is a dimictic meso-eutrophic hardwater lake located on the northeastern perimeter of the town of Waren (Müritz) in the Mecklenburg Lake District, [Mecklenburg-Western Pomerania](#), Germany (53°31'40"N 12°41'30"E). The lake has a maximum depth of 23.6 m, a mean depth of 9.7 m, a surface area of 1.38 km² and a volume of 13.41 x 10⁶ m³ (morphometric data from Ministry for Climate Protection, Agriculture, Rural Areas and the Environment M-V, calculation base 2015). The catchment area has a size of 21.9 km² and is dominated by agriculture, forests, and gardens in direct vicinity of the lake (Nixdorf et al. 2004). Due to the discharge of communal, agricultural and industrial sewage waters into the lake, Lake Tiefwaren became more and more hypertrophic in the 1980s. To enhance water quality, NaAl(OH)₄ and Ca(OH)₂ were introduced into the hypolimnion in the years 2001-2005 to provoke the precipitation of nutrients. After the restoration measure, the phosphorus release from the sediments was almost completely eliminated for several years and the phosphorus concentrations in the water body drastically decreased, while secchi depth increased (Wauer et al., 2009, Gonsiorczyk et al. 2015).

Time span 1998-2020

Sampling method

Water samples for chemical analyses were taken from a buoy at the center of the lake (P1, 53°31'38.3"N, 12°41'27.8"E) between Feb 1998 and Dec 2020 (Wauer et al., 2009). 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, including (0-2.5m, 0-5m and 0-10m). Samples were also regularly collected from hypolimnic waters (20m and 22(.5)m). Commencing on the 6th Feb 2020 samples from 22 m were no longer collected, rather an additional sample at 12 m was collected. All water samples were taken using a 2.6 L or 3.5 L Limnos water sampler (Limnos Oy, Turku, Finland). Between 1998 and Nov 2012 regular monthly surface layer samples (0m) were collected from the northern inflow channel (Stadtgraben, 53° 32' 25.89"N, 12° 41' 51.33"E, which receives water from the Falkenhäger Bruch forested nature reserve (Wauer et al., 2009), as well as from an eastern inflow channel (Melzer inflow, 53°31'28.6"N 12°42'00.8"E) which receives water from Lake Melzer (Wauer et al., 2009). Regular surface water samples (0-1m) were collected from Lake Melzer since 2001, but at not part of this data package. From 2003-2005, during the deployment of an aeration device, additional samples were collected during stratified periods (Jun-Nov) from another site approximately 200 m north of the P1 buoy (P2, 53°31'48.2"N, 12°41'27.8"E) at various depths between 0-20m (Wauer et al., 2009). Between May 2010 and Nov 2012 regular monthly surface water samples were collected at an inflow point on the western shore of the lake (Neuer Graben, 53° 31' 38.61"N, 12° 41' 13.97"E) (Wauer et al., 2009).

Total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), dissolved calcium (Ca^{2+}), dissolved aluminum (Al), dissolved iron (Fe: sum of Fe^{2+} and Fe^{3+}) 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 (CaCO_3), 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, NO_2^- , NO_3^- , NH_4^+ , 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 CaCO_3 determination, were dried at 60 °C overnight and stored in a desiccator 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:

- TP, SRP: Spectrophotometry
 - From 1998 to October 2009, 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, NO₂⁻, NO₃⁻, NH₄⁺: Spectrophotometry
 - From 1998 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) according to ISO 11732.
- Ca²⁺: Spectrophotometry,
 - 1998-10/2009, 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 auflösbar Aluminums in Wasser. Arbeitsanleitung, 2004, based on APHA 3500-Al and ISO 10566
- Fe: Spectrophotometry,
 - From 1998 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,
 - From 1998 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.
 - From 2008 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,
 - 1998-2010: 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 1.2 μm pore size, Whatman, Little Chalfont, United Kingdom). Before 1997, data were rounded to the nearest integer ($\mu\text{g L}^{-1}$), thereafter to the nearest 0.1 $\mu\text{g L}^{-1}$.
 - 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}]
- alkalinity – alkalinity [mval L^{-1}]
- chla – chlorophyll a [$\mu\text{g L}^{-1}$]
- 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 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 0.144 with a median value of 10 ± 1.7 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 (15.57, 15.6, 8.14 mg/L) and the median of the interpolation (9.63, 9.76, 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: 9.65 ± 1.19 , 9.69 ± 2.19 , 9.87 ± 0.64), 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, when slopes 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 32.94 ± 5 mg/L. We calculated correction factors (1.32 and 0.74) as the difference between the median values of the originally measured (23.85 and 47.79 mg/L) and the interpolated concentrations (31.66 and 35.56 mg/L), resulting in a corrected median of 31.7 ± 4.2 and 35.4 ± 4.3 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.

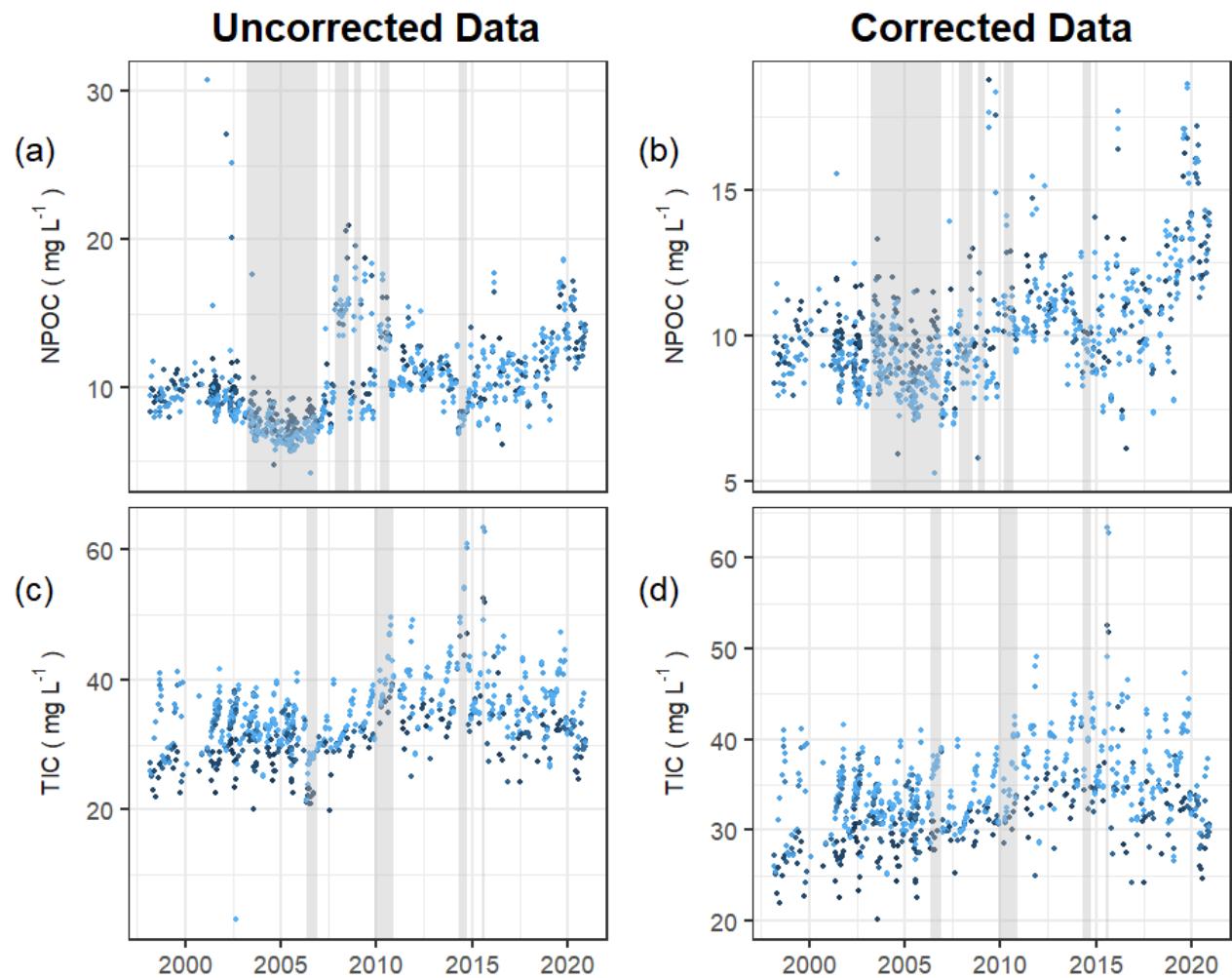


Fig. 1 Time series for NPOC (a, b) and TIC (c, d) illustrating the effect of raw data corrections on temporal dynamics. Grey shaded areas indicate affected time periods.

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 0.62
NPOC	Analytik Jena TOC Analyzer	Dec 2008 - March 2009	interpolation	x 0.62
NPOC	Shimadzu TOC-VCPh Analyzer	Dec 2009 – Sep 2010	calibration curve	x 0.62
NPOC	Shimadzu TOC-VCPh Analyzer	May 2014- Sep 2014	interpolation	x 0.74
TIC	Shimadzu TOC-5000/5050 Analyzer	May 2006-Dec 2006	interpolation	x 1.32
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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