# Chemical data (photometry) at Grosse Fuchskuhle 1976-2020

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

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# Data

## Sampling site

Lake Große Fuchskuhle (Brandenburg, Germany) is a naturally acidic, residual bog lake, situated in dense pine forests south of the Lake Stechlin area (53°06‘20“N, 12°59‘05“E). The catchment area has a size of 0.25 km$^2$. With a size of 0.015 km$^2$, a mean depth of 3.5 m, a maximum depth of 5.5 m and a volume of 53 x 10$^3$ m$^3$, the lake belongs to the smaller ones of this area which were formed during the post-glacial period (Krey 1985). Lake Große Fuchskuhle is characterized by low pH and conductivity, high content of humic matter and low nutrient concentrations. There are no inflowing streams and no connection to the ground water (Ginzel and Handke 1995). Initially, the lake was subdivided into two basins (1986), and later (1990) into four experimental compartments of approximately the same size by means of large plastic curtains (Kasprzak et al. 1988; Kasprzak 1993). Because of the division, the interaction between lake and swamp is now mainly restricted to basins in the western part, causing differences in pH and the DOC pools. The water of the two basins adjacent to the bog body are brownish in color indicating input of allochthonous humic matter. In the east-basins, the pH is usually higher (Šimek et al.

1998). Two of these basins, one from the eastern part (Northeast, NE with a contiguous pine forest) and one from the western part (Southwest, SW adjacent to the peat bog), have been regularly monitored since their establishment.

**Time span** 1976-2020

**Sampling method**

Initially samples for dissolved inorganic nutrients (NO3, NH4, PO4, Si) were collected from the center of the lake at 4 depths (0.5, 1, 2.5 and 3.5 m) using a small boat and a Ruttner water sampler. Sampling of the undivided lake continued, at semi-regular intervals, mostly restricted to spring and summer stratified periods, with the additional of additional parameters. Sampling depths were not consistent but typically comprised an epilimnic sample (0-1 m), a sample of the oxycline (2.5 m) and one or more hypolimnic samples (3-4.5 m). No sampling was conducted in in 1983 and 1984 and only one sampling was performed in February of 1985. In 1986 preparations took place to divide the lake into four basins, samples were collected in February and May of 1986 prior to the separation of the lake into two halves. Samples from the two basins were first taken in August 1986 with regularly monthly sampling at 0, 2.5 and 4 m occurring until July of 1989. No sampling was performed in 1990, partially due to political instability and also to permit for the final division of the lake into four basins. The first samples from each of the four basins were collected in Feb 1991 at depths of 0, 2 and 4 m. Samples were taken from the basin using a platform suspended over the center of the lake that can be reached via small boat via the NE basin. Regular monthly sampling of the four basins at these depths continued until 1998 with some exceptions for specific parameters (for instance no dissolved nitrogen species were measured in 1995). In summer 1998 a decision was made to focus on the two most distinct basins (NE and SW). Since 1998 the NE and SW basins have been sampled at on a regular monthly basis until present day. As previously, three discrete depth samples were collected corresponding to a surface water sample (0 m) epilimnic sample (1m or 2m) and a hypolimnic sample (typically 4m but occasionally 4.5 m).

**Water-chemical analyses**

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)

- DOC: catalytic oxidation, NDIR, TOC Analyzer (Shimadzu VCPH analyzer, Kyoto, Japan), determination of CO2 release from pre-filtered (0.45 µm pore size, filters as described above)) 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: 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 $L^{-1}$]
- ic – total inorganic carbon [mg $L^{-1}$]
- doc – dissolved organic carbon [mg $L^{-1}$]
- chla – chlorophyll a [µg $L^{-1}$]
- 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 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 three other clear-water lakes (Lake Stechlin, Breiter Luzin and Lake Tiefwaren) as a part of the 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 high variability in NPOC concentrations particular a strong decrease in concentrations in the South-West basin, which we speculate is due to decreased precipitation and a drying of the fen (see Fig. 1A-D). Due to large differences between the North-East and

South-West basin we decided it was appropriate to calculate the correction coefficients for each basin individually. For the North-East basin, the linear regression yielded an $R^2$ of 0.46 with a median value of 15.8±3.7 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 (21.98, 23.52, 28.82 mg/L) and the median of the interpolation (14.94, 15.52, 18.78 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: 14.92±1.87, 15.52±1.11, 18.73±1.66), while maintaining the full variability of the original data (Table 2, Fig. 1A,B). For the South-West basin, the linear regression yielded an $R^2$ of 0.50 with a median value of 38.89±14.16 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 (59.19, 56.37, 61.97 mg/L) and the median of the interpolation (32.91, 35.26, 48.38 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: 32.91±5.18, 35.29±2.75, 48.40±5.62), while maintaining the full variability of the original data (Table 2, Fig. 1A,B).

## Dissolved calcium

The spectrophotometric analyses of dissolved calcium (Ca2+) indicated increased concentrations between October 2002 and July 2006, and between Jan 2007 and December 2012 that were not apparent in the ion chromatographic analyses. Specifically, the spectrophotometrically determined data exceeded those determined by ion chromatograph by 50% during both periods. The reported spectrophotometric data have been corrected for the two periods, resulting in 50% reduced concentrations than originally measured (Fig. 1C,D).

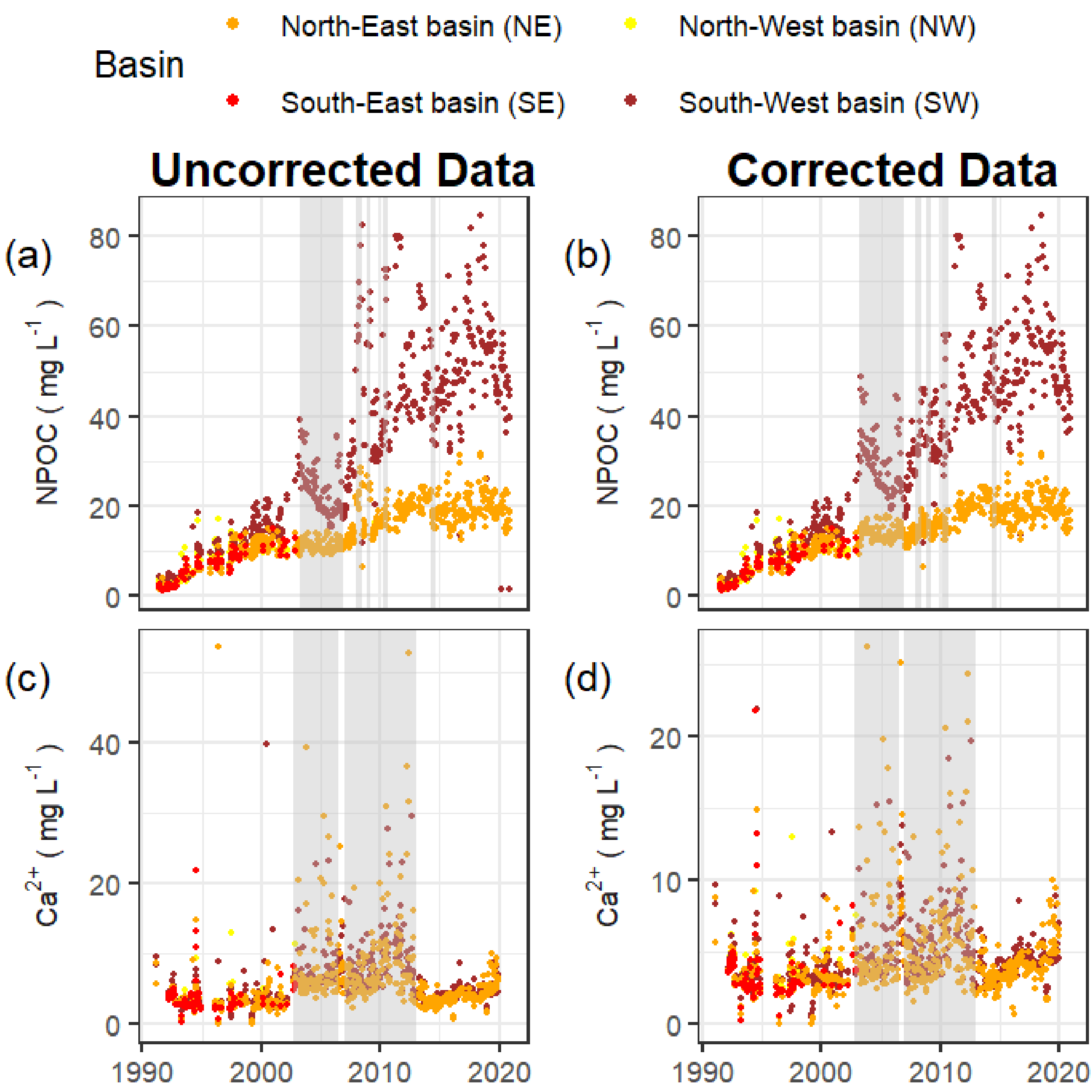

**Fig. 1** Time series for NPOC (A, B), and Ca (C, D) illustrating the effect of raw data corrections on temporal dynamics. Shaded areas indicate affected time periods.

**Table 1** Corrections of NPOC 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 (NE)<br>x 1.25 (SW) |
| NPOC | Analytik Jena TOC Analyzer | Nov 2007 -July 2008 | interpolation | x 0.679 (NE)<br>x 0.556 (SW) |
| NPOC | Analytik Jena TOC Analyzer | Nov 2008 - March 2009 | interpolation | x 0.66 (NE)<br>x 0.626 (SW) |
| NPOC | Shimadzu TOC-VCPH Analyzer | Mar 2010 – Sep 2010 | calibration curve | x 0.8 (NE)<br>x 0.8 (SW) |
| NPOC | Shimadzu TOC-VCPH Analyzer | April 2014- Sep 2014 | interpolation | x 1.06 (NE)<br>x 1.27 (SW) |

## 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.