

Sulfur Profiles of the Twentieth Century in Peat Bogs of the Swiss Midlands Measured by ICP-OES and by IC

Philipp Jeker and Urs Krähenbühl*

Abstract: The growth rates of ombrotrophic peat bogs are controlled solely by the atmospheric input of nutrients. Such systems serve as archives for the emission of anthropogenic pollutants close to urban centers. Goal of the present investigation was to unravel the history of the deposition of sulfur during the twentieth century. In two peat bogs of the Swiss Midlands peat cores were collected and dated using the lead isotope ^{210}Pb . After a wet digestion of the sample material in pressure bombs by microwave excitation the resulting solutions were measured for their S concentrations by ICP-OES or by IC.

The S concentrations vary between 1–5 g/kg of dry sample mass. The comparison with the estimated total sulfur emissions for Switzerland from the BUWAL shows an excellent correlation with two maximal values around the years 1960 and 1980, respectively. The fact that the same deposited amount of pollutant is determined in the two peat bogs situated 50 km apart indicates that the measured signals are not controlled by local sources.

Keywords: Archives · Dating by ^{210}Pb · Microwave wet digestion · Peat bogs · Sulfur

1. Introduction

Systems which conserve consecutive deposition of information are very convenient for the investigation of any variations of emissions in history. Shotyk *et al.* [1] demonstrated that peat bogs recorded lead emissions over the last 2000 years and Säggerer [2] measured the deposition of Cd, Zn, and Pb from the beginning of industrialization (150 years) in Swiss peat bogs. Ombrotrophic peat bogs obtain all their nutrients from the atmosphere and show a rather constant growth

rate. The radioactive isotope ^{210}Pb is the daughter of the constantly emanating noble gas Rn and has a half-life of 22.3 years. This isotope is well-suited to date archives of the last 200 years. In the present work it is demonstrated that peat bogs are also capable of recording the deposition of sulfur species, an important component responsible for acid rain. Novak *et al.* have presented studies on peat bogs in the USA and in Czechoslovakia [3][4].

Peat cores were collected in Düringen (570 m a.s.l., close to Fribourg) and in Burgäschli (470 m a.s.l., close to Herzogenbuchsee). The two locations lie 50 km apart. Every ombrotrophic peat bog shows a local structure of hollows and hummocks with different growth behavior. Therefore, by comparing the results of the two sites, material of the same structural type was always considered.

It is well known that reliable sulfur measurements for organic material are quite difficult [5]. It is essential that all sulfur is transformed to the same species. For measurement by ICP-OES (inductively coupled plasma optical emission spectroscopy) or IC (ion chromatography) sulfate is the ideal form, which is often obtained by a wet digestion [6–8].

2. Experimental Procedures

The collected peat core material was frozen, cut into slices of 1 cm, freeze-dried and powdered in a ball mill. The powdered material was then ready for chemical characterization.

2.1. Wet Digestion of Organic Material

Transformation of sulfur in organic material into the sulfate was performed in Teflon® pressure bombs in the presence of nitric acid and perhydrol under microwave excitation. The complete transformation of S-bearing material into the corresponding amount of sulfate was tested by the digestion of methionine and cysteine and the inorganic salts Na_2SO_4 , Na_2SO_3 or Na_2S . In early experiments no constant values were obtained due to losses. Sulfate recovery became total for organic material when some MgO was present during the digestion. The following procedure works very well for the transformation of all types of S-bearing material into the equivalent amount of sulfate: 100 mg sample material is placed into a 100 ml pressure bomb

*Correspondence: Prof. Dr. U. Krähenbühl
Department of Chemistry and Biochemistry
University of Bern
Freiestrasse 3
CH-3012 Bern
Tel.: + 41 31 631 4265
Fax: + 41 31 631 4220
E-Mail: kraehenbuehl@iac.unibe.ch

together with 2 mg of MgO and contacted with 4 ml conc. HNO₃ and 3 ml H₂O₂ 30%.

The microwave heating system, MLS ETHOS 1600, enabled controlled heating, which reached a temperature of 195 °C after 20 min. This temperature was maintained for a further 20 min. The peak pressure reached a value of 17 bar.

2.2. Sulfur Measurement by IC

Ion chromatographic measurements (IC) were performed on a Dionex DX 120 system using the following separation columns: pre-column IonPac AG 12A and an anion chromatographic column IonPac AS12A. The conductivity of the eluent was reduced by a self-regenerating suppressor. As eluent a solution of 2.7 mM Na₂CO₃, 0.3 mM NaHCO₃ was used. The system was calibrated using sulfate standard solutions. The retention time for sulfate in the samples and in the standards was 10.2 ± 0.2 min. The evaluation of the chromatogram was made by applying the Peaknet software of Dionex. Since ion chromatographic measurements are sensitive to the total concentrations of ions in a solution, the acid from the wet digestion had to be eliminated. White residue, which remained after the digestion of peat material (silicates), was filtered off through 0.5 µm Millipore membranes. The resulting solution was evaporated to dryness. The residue was taken up in water and evaporated again (twice). Finally, the residue was dissolved in 50 ml of H₂O and 2 ml used for the measurement by IC.

2.3. Sulfur Measurement by ICP-OES

After wet digestion of the material to be analyzed, the silicate residue was removed as for the IC measurements. The filtered solution was diluted to 100 g total weight. This resulted in an acid concentration of 3% in HNO₃ which is optimal for the direct measurement by inductively coupled plasma optical emission spectroscopy (ICP-OES). The measurements were made on a Varian Liberty 150 AX Turbo ICP-OES instrument. For the measurement 2 ml/min of the solution to be analyzed were nebulized by a Cetac U5000AT ultrasonic nebulizer. The aerosol thus formed was further dried by a heating device, followed by a cooling section for the recondensation and removal of some water vapor.

Sulfur is measured at the emission lines 182.036 nm and 180.734 nm. Since the optical path is not evacuated in the

applied ICP-OES instrument, oxygen had to be purged due to the huge optical absorption of O₂ below 200 nm. For the calibration of the measurement the same S standard solutions were used as for the IC determinations. The evaluation of the results was made using the Varian software Plasma96.

3. Sample Locations and Dating

The investigated peat cores were collected using a stainless steel auger (either of the Eijkelkamp Agrisearch type, diameter 4.6 cm or by a corer of 7 cm diameter made in our mechanic shop) in the Düringen Moos, canton Fribourg (coordinates 579 700/ 188 580, 580 m a.s.l.) and in the Chlepfibeerimoos, canton Solothurn (coordinates 617 750/224 600, 470 m a.s.l.). Both locations are situated in the Swiss Western Midlands about 50 km apart. The two sites were selected to see to what extent the results would be dependent on local sources.

The recovered cores had a length of 40–60 cm representing material grown in the time span of about 1920 to the present. The material was sliced and freeze-dried. The actual age of the individual slice within the core was dated using ²¹⁰Pb. This isotope has a half-life of 22.3 years and is a daughter of the noble gas ²²²Rn (T_{1/2} = 3.6 d) which itself originates from the decay of the long-lived radioactive mother ²³⁸U and emanates steadily from ground into the atmosphere. In earlier investigations it was demonstrated that the deposition of ²¹⁰Pb into natural archives (ice, lake sediments, peat bogs) is quite constant [9]. So, the decrease of its activity with time can be used to date the investigated material. The activity of ²¹⁰Pb is evaluated by measuring its gamma line of 46.5 keV in a well-tube Ge detector coupled to a multi-channel analyzing system.

4. Results and Discussion

4.1. Verification of the Experimental Procedure

Sulfur-containing compounds were measured by ICP-OES with and without wet digestion in a closed system by microwave excitation. The two methods gave very different results. Only the measurement of S after the digestion to sulfate gave a recovery of 100% for a solution of Na₂S. Tests with S-bearing amino acids by wet digestion showed large losses and poor reproducibility. For methionine the S recovery amounted to 36% ± 20% when measured by ICP-OES. In the case of IC measurements the recovery was even lower, 6% ± 22%, because the excess nitric acid from the digestion had to be removed by evaporation before the measurement with the ion chromatographic technique. The losses of S during the digestion could be stopped by the addition of excess amounts of MgO with respect to the expected amounts of SO₄²⁻ [6].

From each 1 cm peat layer three individual fractions were analyzed for sulfur. The average of the resulting three values shows an error of 4%.

4.2. Sulfur Profile in Dated Peat Bogs

The dating of the peat core of Düringen using ²¹⁰Pb gave a maximal age of 80 years.

All the measured parameters are given in Table 1 for the evaluation of the age of the individual peat layers. The gamma measurement for the individual sample was continued until the counting error was less than 10%. This gave then for the old layer a deviation of ± 8 years. This fact has to be taken in account in the discussion of the S profiles.

In Fig. 1 the results are presented for the S concentrations in the two peat bogs

depth:	massdepth:	activity (sample):	activity (calculated):	age:
[cm]	[g/cm ²]	[dpm/g]	[dpm/g]	[aD]
1	0.08	14.7	23.0	1999
5	0.60	20.0	17.1	1992
11	1.12	15.8	12.8	1986
16	1.69	13.1	9.3	1979
23	3.37	2.8	3.6	1958

Table 1. Dating parameters of the peat profile in Düringen.

from Düdingen and Burgäschi. Excellent correlations are found for the two sites despite the fact they are located 50 km apart. The values for both locations for the last 25 years are given in Table 2. This indicates that the measured signal is not controlled by local emissions but records the pollution situation for the Swiss Midlands. The average sulfur concentrations in peat samples from the 1940s are 1.5 g/kg dry mass. This value increases in the following years to 2.5 g/kg dry mass and reaches, after another

Table 2. Comparison of the sulfur contents in corresponding samples in Düdingen and Burgäschi.

age:	S content [g/kg]:	
	Düdingen	Burgäschi
1995	1.1	1.3
1990	2.1	1.9
1985	2.5	3.1
1980	4.2	3.7
1975	3.6	3.7

distinct increase, a value of more than 4 g/kg dry mass in the early 1960s. After some decrease at the beginning of the 1970s a maximal concentration of 4.8 g S/kg dry mass is measured for 1980. In the following ten years the measured S concentrations decrease to the lowest values of the last centuries of 1g/dry mass. An excellent correlation is observed when comparing these results with the total sulfur emissions estimated by the BUWAL (Fig. 2) for Switzerland for the same period [10].

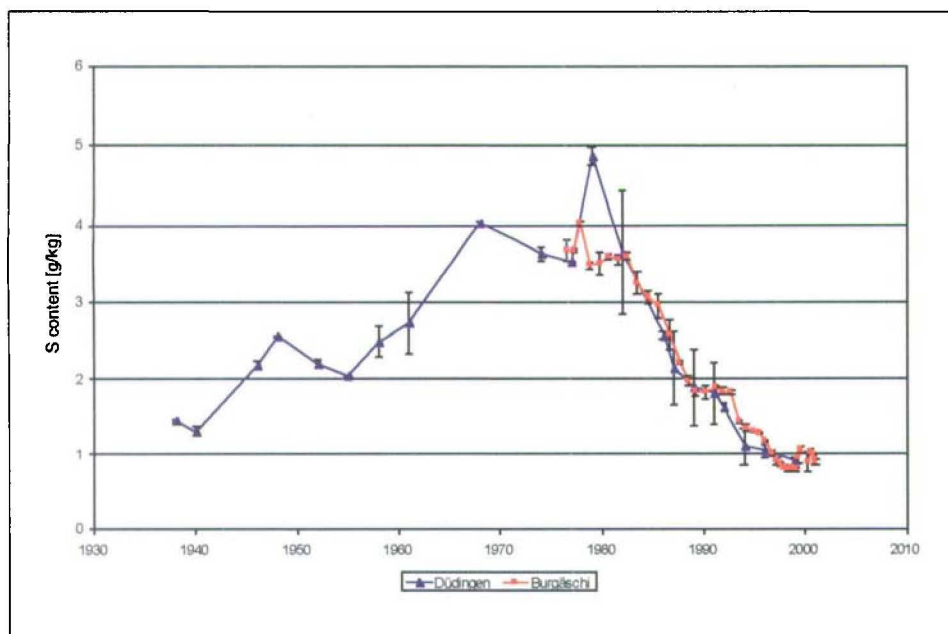


Figure 1. Sulfur profiles of the peat bogs from Düdingen and Burgäschi.

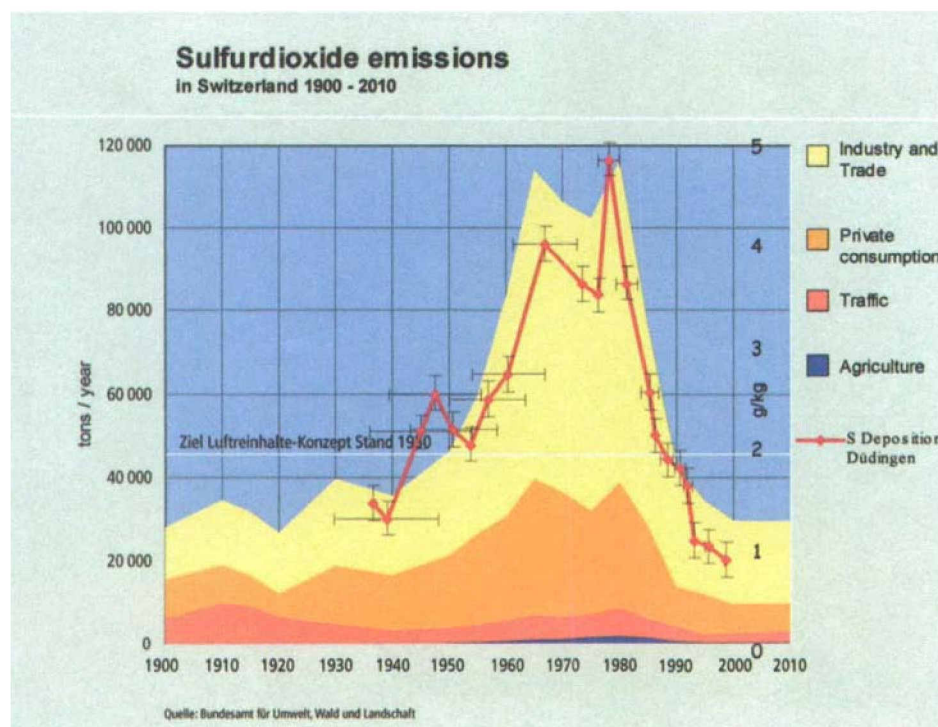


Figure 2. Sulfur profile from Düdingen compared with the SO₂ emissions estimated by the federal administration for Switzerland [10].

The emissions data reflect the increased consumption of fossil energy after the second world war with high values for the SO₂ emissions in the early 1960s. The decrease at the beginning of the 1970s is due to the oil crisis in this time span, which is followed by the maximal emission in the early 1980s. Measures were introduced for a reduction of SO₂ emissions by substituting fuels with high S concentrations with ones with a lower S content. This was achieved by the replacement of coal and 'heavy' heating oil by 'extra-light' quality and by natural gas [10]. In addition measures were enforced to limit the emissions of SO₂ of distinct emittents such as cell wool production plants or refineries. All these steps led to a reduction of the SO₂ emissions in Switzerland to about 30000 t/year after a maximal value of about 100000 t/year in the time span 1965–1980. Similar measures were introduced in the neighboring countries with the same effects as in Switzerland. It is also interesting to compare the estimated emission signature of SO₂ for Switzerland with the one in France, Germany and Italy (Table 3) [11]. There is no surprise that the best correlation is found with the emission produced in this country. This is an interesting finding since the pattern of measured sulfur concentrations in ice core samples from the Monte Rosa in Switzerland resemble more the emissions in France. This is due to the fact that the deposition of pollutants in high-alpine regions are more dominated by long-range transport: the most dominant wind direction for our country is the one from France [12].

Finally it is evident that environmental archives not only record the pollution situation but also react quickly and demonstrate improvements in air quality due to limitation of emissions by legislation measures.

tion of the organic material in Teflon pressure bombs and microwave excitations. It could be shown that peat bogs are suitable archives to record emissions of SO₂.

For the peat bog of Düringen, two maximal sulfur concentrations are found: for the early 1960s and the 1980s. This measured trend follows closely the total emissions of SO₂ for Switzerland estimated by the public administration.

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Table 3. Correlation coefficients from the comparison of the sulfur contents in the Düringen peat bog with the estimated SO₂ emissions in Switzerland and neighboring countries [10][11].

r ²	Düringen
Switzerland	0.93
France	0.78
Germany, Fed. Rep.	0.53
Italy	0.68

5. Conclusions

Concentrations of sulfur were measured reliably either by ICP-OES or by IC in peat material after complete wet diges-