Continuous Flow Analysis of Total Organic Carbon in Polar Ice Cores

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Ice cores are a widely used archive to reconstruct past changes of the climate system. This is done by measuring the concentration of substances in the ice and in the air of bubbles enclosed in ice. Some species pertaining to the carbon cycle (e.g., CO₂, CH₄) are routinely measured. However, information about the organic fraction of the impurities in polar ice is still very limited. Therefore, we developed a new method to determine the content of total organic carbon (TOC) in ice cores using a continuous flow analysis (CFA) system. The method is based on photochemical oxidation of TOC and the electrolytic quantification of the CO₂ produced during oxidation. The TOC instrument features a limit of detection of 2 ppbC and a response time of 60 s at a sample flow rate of 0.7 mL/min and a linear measurement range of 2–4000 ppbC. First measurements on the ice core from Talos Dome, Antarctica, reveal TOC concentrations varying between 80 and 360 ppbC in the 20 m section presented.

Introduction

For many years, the analysis of ice cores has been recognized as an important source of information for the understanding of the global climate system and in quantifying the range of past natural and anthropogenic changes in atmospheric chemistry and composition (1). Much information about conditions and processes of the past climate are archived at high temporal resolution in ice cores and cover a relatively large geographical area of the outer part of the Earth. This is why ice cores are extensively used to study past climate and the chemistry of the atmosphere as well as the impacts of human activities on the Earth’s climate system (2).

Organic compounds play an important role in cloud formation and atmospheric acidification (4, 5). Furthermore, they can make up the majority of the total suspended particle mass in some parts of the world and can significantly contribute to the global radiation budget (6). In contrast to the content of major ions of polar snow and ice (7), organic material is one of the least understood fractions of the aerosol load deposited on a polar ice sheet. This despite the fact that the content of organic impurities of ice cores can outweigh the sum of ions (7).

Due to the extreme diversity of different organic compounds present in the atmosphere (8) and thus in polar ice cores (9, 10), it is very challenging to characterize the composition of the organic carbon content. Only a minor fraction has been specified so far and existing studies mainly focus on individual compounds such as formaldehyde (11, 12), methansulfonate (13), low molecular weight organic acids (14), or fatty acids (15, 16). The goal of this work is to address this lack of measurements of organic carbon in polar ice, and to develop a new device to determine total organic carbon (TOC) by continuous flow analysis (CFA).

One of the major advantages of the CFA technique (17, 18) is the ability to provide a meltwater stream which was melted continuously under controlled conditions and was never exposed to the atmosphere (19). For this, an ice sample with a typical square cross section of 32 × 32 mm² and a length of 1 m is placed on top of a melt head to create a continuous melt flow which consists of a water flow segmented by the air present in the ice. The upper surface of the melter head is divided into two concentric parts, and to prevent any contamination, only the debubbled sample water from the inner part is used for the CFA methods as well as the TOC analysis described here.

Because of the presence of organic compounds in the drilling fluid, laboratory air, and packing materials, decontamination of discrete samples for organic analysis is challenging and very time-consuming. CFA is thus in general much more efficient compared to discrete sampling methods, typically allowing a depth resolution of ~1 cm over the full length of a deep ice core (~3 km). However, CFA methods require a very high sensitivity adequate for the low impurity concentrations present in polar ice cores, a fast response time (seconds to at most a couple of minutes) and very low water consumption (maximum of ~1 mL/min typically available per channel).

The analysis of TOC includes the conversion of organic compounds to CO₂ and its subsequent quantification. For the conversion either high-temperature combustion, chemical- or UV-oxidation can be used (20, 21), whereas the CO₂ is measured using conductometry or IR absorption spectrometry. For all these methods commercial analyzers are available but they do not meet all of our requirements such as continuous flow operation, sample and reagent consumption, precision, response time, portability, and customer serviceability, which is critical during field deployments.

In this work, we present a new CFA method designed for measuring the concentration of total organic carbon (TOC) in polar ice cores. The method is based on a continuous photochemical oxidation of organic molecules in the sample water flow with subsequent quantification of the CO₂ produced. This is performed by measuring the electrolytic conductivity. The method was successfully embedded into our established CFA system (17, 18) and applied during a measurement campaign. Below we describe the new method and its analytical characteristics and present the first measurements made on the ice core from Talos Dome, Antarctica.

Materials and Methods

Analytical Setup. The detection of TOC in the air-free sample water stream provided by the melting system (17) consists of three steps: The UV oxidation, the transfer of the CO₂ produced into a carrier flow, and its subsequent detection by measuring the electrolytic conductivity.

After mixing the sample flow with the reagent (0.4 M phosphoric acid), it is split in two channels determining the content of total carbon (TC) and total inorganic carbon (TIC), respectively (Figure 1). TIC includes the inorganic CO₂
including the additional CO$_2$ produced by the oxidation of
originating from the ice and the air bubbles, TC further
(arrow boxes), flow rates in mL/min (numbers in the arrow
measuring cells (MF) for the electrolytic conductivity ($\sigma$ in white circles), waste (W)).

Both channels are virtually identical, except for the photo-
the organic material in the TC line, using a strong UV
source (Figure 1, see the Oxidation Reactor section). If
organic carbon (dissolved organic carbon, DOC, and
particulate organic carbon, POC) is oxidized, TOC can be
calculated as the difference of the two signals as

\[
\text{TOC} = \text{TC} - \text{TIC}
\]

(1)

this is, strictly speaking, the UV-oxidizable OC of our sample.
The whole analytical manifold is made of 1/16" × 0.5 mm
PFA and PEEK tubing (from Omnilab and Upchurch). Tygon
tube is used in a peristaltic pump (both from Ismatec SA)
for all flow lines.

The continuous sample flow of 0.7 mL/min is acidified
with the reagent at a flow rate of 0.1 mL/min to reduce the
pH of the sample stream to pH $< 2$. The reagent and the
standard solution are from Merck and prepared with ultra
pure Milli-Q water from Millipore Gradient A10 (resistance
of $\geq 18.2$ M$\Omega$/cm) with integrated UV lamp to reduce the
organic content of the water to the lower ppbC range.

Special attention was directed to minimizing mixing
volumes as well as tubing length in order to keep the
dispersion, which limits the temporal resolution and thus
the depth resolution in the ice, as small as possible.

**Oxidation Reactor.** The TOC content of the sample flow
is converted to CO$_2$ by UV oxidation. The oxidation reactor
consists of a custom-made octagonal glass coil (17 windings)
made of quartz capillary (Ismatel G, length of 150 cm; i.d.
0.6 mm; o.d., 1.0 mm, from Quarzscheible Ilmenau). In one
of the two channels, the coil is exposed to UV light from a
low-pressure mercury UV lamp (wavelength of 254 and 185
nm, NNQ8/18, from Hereaus). The optical transmissivity of
the coil is above 0.95 at both wavelengths, due to a very small
wall thickness. The sample residence time in the reactor is
about 1 min at the chosen flow rate of 0.41 mL/min of the
sample-reagent mixture.

A custom-made connection between the thin-walled
quartz capillary tube and the PEEK tubing, using an adhesive
agent with very low outgassing properties (TorrSeal, from
Varian), was deployed because equivalent connectors are
not commercially available.

Ozone has strong optical absorbing properties for UV light
and would reduce the efficiency of the reactor. Therefore,
and to eliminate the potential health hazard of ozone, the
reactor body is flushed with an unreactive gas like N$_2$ or He
preventing ozone production from ambient air. It is critical
to avoid an unequal cooling of the UV lamp as this would result
in a blow out of the lamp. The radiation intensity is monitored by a GaP-UV-photodiode (EPD-150–0, from Roithner) to ensure constant oxidation conditions.

The photochemical processes during the UV oxidation
affect the organic molecules in two ways. While the 185 nm-
irradiation produces highly reactive radicals like OH and HO$_2$
by the radiolysis of water and oxygen, the 254 nm-irradiation
attacks mainly UV-sensitive areas of organic molecules (22).
In contrast to existing instruments, the oxidation efficiency
in the reactor was not further enhanced with persulfate reagents (23) or additional heating. Although the oxidation
time of $\sim$1 min is relatively short compared to other UV
photo-oxidation methods (24) the determined oxidation
efficiencies for the various chemical compounds tested (see
the Characteristics section) indicate a rather complete
oxidation. This result was checked by a filtering experiment
and a comparison with a commercially available analyzer
(see Characteristics section).

**Extraction of CO$_2$.** After the oxidation reactor, the CO$_2$
are extracted in the TC and also in the TIC channel by a selective
membrane unit and redissolved in a high purity water flow
(carrier flow, see Figure 1). This is necessary to remove the
background conductivity stemming from the ions present in
the ice core and the reagent to remove potential interferences
of byproducts other than CO$_2$ formed during the oxidation.
To enhance the extraction efficiency and maintain constant pH conditions, the meltwater is acidified
to pH $< 2$ so that the dissolved carbonates are present as
CO$_3^-$.

The membrane unit consists of a silicone rubber tube
(110 mm; i.d., 0.5 mm; o.d., 0.7 mm, from Labomatic) which
divides the inner volume of a Pyrex glass tube (150 mm; i.d.,
1.0 mm) into two parts. The sample water flow inside the
rubber tube is pumped in opposite direction to the carrier
flow in the volume between the rubber and glass tube.
Because silicon rubber has a high permeability for CO$_2$
compared to other gases (25, 26), CO$_2$ is selectively extracted
from the sample flow and transferred into the carrier flow.

To reduce wall thickness and thus to enhance the CO$_2$
permeation through the membrane, the silicone rubber tube
is stretched by about a third in length. Before installation,
the silicone rubber tube has to be rinsed thoroughly with
Milli-Q water to ensure a good wetting of the membrane
surface, to avoid micro bubbles sticking on the surface and
hence disturbing the flow and the membrane diffusive
characteristics.

Prior to the extraction membrane, the carrier flow (Milli-Q
water) is decarbonated in a carbonate removal unit. Therein,
a silicon rubber tube (3 m i.d., 0.5 mm; o.d., 0.7 mm) is
immersed in NaOH solution (0.2M) which acts as a trap for
CO$_2$. To monitor the purification, the electrolytic conductivity
is subsequently measured (see Figure 1 and the Detection
section for details) which indicates a TIC content of a sub-
ppbC level.

**Detection.** After the extraction of CO$_2$ from the sample
flow and redissolution into the carrier flow, the carbonate equilibria

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^- \rightarrow 2\text{H}^+ + \text{CO}_3^{2-}
\]

(2)

are established. Subsequently, the electrolytic conductivity
$\sigma$ of the carrier flow is measured and thus the carbon content
can be calculated (27). For this, two conductivity meters
(AS1056) are used in combination with two Micro Flow Cells
(Nr.529, with a cell constant of 100 cm$^{-1}$ and a volume of 120
µL, both from Amber Science), one for each of the TIC and
TC line (Figure 1). The value of TOC is then determined as
the difference of TC and TIC (see the Convolution of the

**FIGURE 1. Schematic setup of the TOC detection system.** After
continuous mixing with reagent, the sample water is divided
into two lines: “TC” equipped with an UV lamp and “TIC”
constructed in the same way as “TC” but without lamp. The
TOC value is calculated as the difference between total carbon
(TC) and total inorganic carbon (TIC). Abbreviations and
symbols: reagent (Rea), solenoid valve (small white circle),
working standards (Sta), pump tubing and flow directions
(arrow boxes), flow rates in mL/min (numbers in the arrow
boxes), measuring cells (MF) for the electrolytic conductivity
($\sigma$ in white circles), waste (W)).
RAPIDLY with increasing concentrations likely due to saturation (ppbC). Above 4000 ppbC, the rise of the signal diminishes the standard deviation of the signal of Milli-Q water (Supporting Information). LOD is calculated as three times the limit of detection (LOD) of 2 ppbC to 4000 ppbC (see standard, the parameters of both signals differ at most by 1 s. An example is shown in Figure 2B, where the TC signal has been convolved with a transfer function (e.g., TC in Figure 2), so that the rise times are identical and the midpoints t(50%) are coincident. For the transfer function f we assume

$$f(t) = a \times \exp(-t/b), \quad t > 0$$

the parameters a and b were optimized so that $\Delta t_{(10\%-90\%)}$ and $t_{(50\%)}$ of both signals differ at most by 1 s. An example is shown in Figure 2B, where the TC signal has been convolved and the under- and overshooting of the TOC signal has vanished. For every standard run performed with a TOC standard, the parameters a and b in eq 3 are redetermined which is especially important after maintenance of the system or repair. We estimate the influence of different parameters to our TOC data, determined by different calibrations, to about $\pm 2\%$ (see Supporting Informations for details).

**Results and Discussion**

**Characteristics.** The new TOC analysis unit features excellent linearity ($r^2 > 0.998$) over the whole measurement range from the limit of detection (LOD) of 2 ppbC to 4000 ppbC (see Supporting Information). LOD is calculated as three times the standard deviation of the signal of Milli-Q water ($\sim$50 ppbC). Above 4000 ppbC, the rise of the signal diminishes rapidly with increasing concentrations likely due to saturation effects of the semipermeable membrane. The standard series was measured with different dilutions of a TOC standard (1000 mg/L, from Merck), containing potassium hydrogen phthalate ($C_8H_5KO_4$), which is likely stabilized with sodium azide (NaN$_3$) to minimize biological activity (information is not released from Merck). The precision was determined by measuring alternately two standards of 48.8 and 126.1 ppbC for 10 times and calculating the standard deviation which yielded values of 1.1 and 3.0 ppbC, respectively. The interference of other compounds was checked with various species of ions and molecules such as Na$^+$, NH$_4^+$, Ca$^+$, K$^+$, H$_2$O$_2$, NO$_3^-$, Cl$^-$ at concentrations which are commonly found in ice cores. Very low interferences of those species in the range of the resolution of the TOC measurement were found, indicating that matrix effects in the meltwater are negligible.

In order to investigate the efficiency of the oxidation processes of different organic molecules, various chemical compounds with different functional groups, bond structures and chain lengths were analyzed (Figure 3). The resulting efficiencies are relative to the efficiency of the TOC standard (set to 100%) and range from 86 to 139%. Especially for abundant species in ice cores like formic acid and acetic acid (7), the oxidation efficiencies are very close to the TOC standard.

The temporal resolution of the method defined as the time the signal needs to rise from 10 to 90% of a concentration step from Milli-Q water to a standard solution level is about 60 s. This corresponds to a depth resolution of $\sim$3.5 cm at a typical melting speed of 3.5 cm/min. This is a considerably higher value than for other analytical CFA units (17) due to a long flow path and the membrane unit, which involves diffusive processes. However, at the same time, the depth resolution is much higher than what can be achieved in the same time by a discrete method, and can, e.g., still provide subannual resolution at high accumulation sites.

For a further characterization of our data, a filtering experiment with a natural water sample (melted ice from the Dye-3 ice core, Greenland) was conducted. We used a hydrophilic PTFE filter (0.45 µm, Millex-LCR from Millipore) to remove POC from the sample. The unfiltered sample revealed a TOC value of 204.1 ppbC and 7% less (189.9 ppbC) for the filtered sample. This POC content is consistent with previous measurements (26) showing that our instrument measures TOC and not only the DOC. However, these results suggest that POC in Polar ice cores only contributes a minor fraction to the TOC.
In order to compare our TOC instrument with existing analyzers, we performed measurements with a natural water sample (melted ice from the Dye-3 ice core, Greenland) with a Sievers 900 TOC analyzer. The results are 144.6 ppbC for our system and 154.7 ppbC for the Sievers 900 (results are mean values of three measurements). There is no significant difference between the measured values, also considering the necessary transfer of the sample to specific vials for the Sievers 900 (certified to 10 ppbC).

These results indicate that our new system quantitatively measures TOC.

First Measurements. The first meters of the Talos Dome ice core drilled in 2006 (29), were measured with the new TOC instrument. Measurements of a section of 20 m from a depth of 328–348 m (of an age of ~4500 yr BP) are shown in the upper panel of Figure 4. TOC values range from 80 to 360 ppbC with a small but significant decreasing trend with depth. The CFA system, including TOC, was calibrated every 4 m of ice (i.e., ~every 2 h). Therefore we can exclude that the trend is a measurement artifact. On the same ice core, the components of Ca$^{2+}$, Na$^+$ and NH$_4^+$ were measured with CFA and for comparison with TOC data the section from 329 to 330 m is shown in the lower panel of Figure 4. NH$_4^+$ in Antarctic ice cores is thought to represent the marine biological activity in the Southern ocean (30), whereas Na$^+$ is interpreted as a proxy for sea ice extent and production (31). Ca$^{2+}$ has been corrected according to the empirical calibration by (32) for the sea salt contribution to the total calcium content. The remaining nssCa$^{2+}$ represents the mineral dust fraction to total Ca$^{2+}$. Neither the trend nor the high-frequency variations of TOC are correlated with any of the other records measured. For example, a significant TOC peak at 329.1 m is not imprinted in the other records and vice versa clear peaks in Na$^+$ and nssCa$^{2+}$ have no counterparts in the TOC record indicating different sources, seasonality of the sources, and/or transport and deposition patterns. In the future we plan to measure specific organic compounds such as HCHO and organic acids or oxidizing compounds such as H$_2$O$_2$ with our CFA system in parallel to TOC to study their contribution to the TOC record.

Clearly illustrated in the enlargement in Figure 4 is the lower spatial resolution of the TOC measurement compared to the other species. While Na$^+$ and nssCa$^{2+}$ would in principle allow resolving annual cycles at Talos Dome (with an annual snow accumulation of about 7.5 cm ice equivalent), this is not possible with the TOC sensor. Note, however, that the resolution of annual cycles in ice cores is not only dependent on the nominal resolution of the method but is also limited by the amplitude of seasonal cycles at a specific site and on the degree of snow reworking, as reflected in the weak seasonal variability of those species in Figure 4. Longer-term variations on multiannual to orbital time scales, however, can be reliably resolved in TOC and other species. With a further tuning of the response time, the developed system has the potential to resolve annual cycles.

The new TOC analyzer has a measurement range 2–4000 ppbC and a temporal resolution of about 1 min, thus fulfilling the requirements for CFA on Polar ice cores with respect to time resolution and sensitivity. Interferences from major ions are low enough not to be relevant for Polar ice core analyses. The instrument was embedded into an existing CFA setup and first measurements have been carried out successfully on the Talos Dome ice core. Comparison measurements with a commercially available TOC analyzer imply accurate TOC.
values of our new system. Measured TOC values varied between 80 and 360 ppbC over the 20 m of data shown. Obtained values are in good agreement with results from other studies which report discrete values in the same order of magnitude for polar snow and ice (10, 33, 34). Quantification of the organic content of polar ice cores will be very helpful in further characterizing past changes in the carbon cycle.

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Supporting Information Available

This information is available free of charge via the Internet at http://pubs.acs.org

Literature Cited


