Measurement and source apportionment of ubiquitous soot black carbon in sediments

Marie Elmquist
Abstract

The pyrogenic particles formed from incomplete combustion of organic matter are often termed black carbon (BC) and they partake in many important biogeochemical processes. For instance, BC in water and sediment affects the solid-water partitioning of hydrophobic organic pollutants reducing their bioavailability.

The key objective of this thesis was to test the chemothermal oxidation method (CTO) to quantify soot-BC in sediments. In the CTO method, sedimentary BC is isolated by removing non-pyrogenic organic matter through thermal combustion at 375°C under active airflow and subsequent removal of inorganic carbonates by adding hydrochloric acid. The CTO method was here shown to work well for quantifying the thermally more stable soot-BC phase.

Another objective was to study sediment samples to measure the historical and spatial distribution of combustion products. First, historical fluxes of BC and polycyclic aromatic hydrocarbons (PAH) were investigated in a Swedish lake sediment. Increasing fluxes of BC and PAH were seen in sediment dated to the industrial revolution in the 1850s, the high coal usage in the early 1900s lead to a 5 time increase in BC flux relative to the pre-industrial flux, and the switch from coal to oil usage in the 1950s lead to a 46 time increase in PAH flux relative to the pre-industrial flux. Further, lower fluxes came from stricter emission controls in the 1960s, improvements in combustion technology and the usage of catalytic filters from mid-1980s. Modern sediment measured 20% lower BC flux and 5 times higher PAH flux relative to the pre-industrial fluxes.

Secondly, the spatial distribution and sources of sedimentary soot-BC were studied in rivers in the Arctic region. The estimated BC flux was highest in the McKenzie (99 kton yr⁻¹) whereas it was lowest in Yukon (1.1 kton yr⁻¹). Contemporary biomass-derived BC was detected for the Yenisey, whereas fossil fuel derived BC was found for the Lena, Yukon and McKenzie.
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List of papers

I. Quantification of sedimentary black carbon using the chemothermal oxidation method: an evaluation of ex situ pretreatments and standard additions approaches
Elmquist Marie, Gustafsson Örjan, Andersson Per.

II. Distinct oxidative stabilities of char versus soot black carbon: Implications for quantification and environmental recalcitrance
Elmquist Marie, Cornelissen Gerard, Kukulska Zofia, Gustafsson Örjan.

III. A 700-year sediment record of black carbon and polycyclic aromatic hydrocarbons near the EMEP air monitoring station in Aspvreten, Sweden
Elmquist Marie, Zencak Zdenek, Gustafsson Örjan.
2007, submitted manuscript, Environmental Science and Technology.

IV. Source apportionment of black carbon in surface sediments off seven large Pan-Arctic rivers using natural abundance radiocarbon and molecular markers
Elmquist Marie, Semiletov Igor, Guo Laudong, Gustafsson Örjan.
2007, manuscript.

Paper I is reprinted with permission from the American Chemical Society (ACS) and Paper II with permission from the American Geophysical Union (AGU).

In Paper I and Paper II, I had full responsibility for experimental set-up and main evaluation of data. In Paper III, I had main responsibility for the sediment sampling, the analysis and data evaluation. In Paper IV, I was involved in the laboratory work and had main responsibility for data-evaluation. I wrote the first drafts for Paper I-IV. Collection of sediment samples for papers I and IV was performed by co-authors as well as part of the laboratory analysis in papers II and IV.
Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>BC</td>
<td>Black carbon</td>
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<tr>
<td>CTO</td>
<td>Chemothermal oxidation method</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>Radiocarbon</td>
</tr>
<tr>
<td>1,7-DMP</td>
<td>1,7-dimethylphenanthrene</td>
</tr>
<tr>
<td>2,6-DMP</td>
<td>2,6-dimethylphenanthrene</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
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<tr>
<td>kton</td>
<td>Kiloton, $10^9$ g</td>
</tr>
<tr>
<td>MP</td>
<td>Methylphenanthrene</td>
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<tr>
<td>P</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
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<tr>
<td>PCDD/F</td>
<td>Polychlorinated dibenzo-p-dioxins and dibenzofurans</td>
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<tr>
<td>Tg</td>
<td>Terragram, $10^{12}$ g</td>
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<td>TOC</td>
<td>Total organic carbon</td>
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1 Introduction and scope of thesis

The term black carbon (BC) is used to describe relatively inert carbon particles originating from incomplete combustion. They are ubiquitous in nature and mainly consist of carbon atoms [1]. The carbon-based fuel that produce these type of particles can broadly be separated into i) solid materials such as coal, charcoal, wood, grass, leaves, ii) fluid materials such as oil, gasoline, diesel, and iii) gaseous materials. These particles are released into the atmosphere and distributed throughout the biogeosphere. BC in nature may have both positive effects (e.g., sorption of organic pollutants, soil fertilization and long-term storage of carbon) and negative effects (e.g., human health, global warming).

The scientific scope of this thesis is divided into testing of the CTO method that is used to quantify sedimentary BC, and application of this technique to natural sediment. The testing of the CTO method was done by (i) investigating several wet-chemical pre-treatments prior to the basic CTO method as proposed by Gelinas and co-workers [2], (ii) examining a standard additions technique and (iii) creating thermograms to reveal the oxidative stabilities on a variety of environmental carbon phases. The evaluated CTO method was used to study historical BC-variations in lake sediments from south of Stockholm. In combination with radiocarbon and molecular markers, the CTO method was also applied to investigate the spatial BC distribution and source apportionment in a Pan-Arctic climosequence.
1.1 BC sources

The most prominent BC sources are natural wild-fires and anthropogenic combustion within major cities. In cities, vehicles and domestic home heating are primary BC sources. So, even though BC is found all around the planet, the concentrations are elevated close to cities and in areas close to where large forest fires have been burning. A study conducted in Gothenburg on the Swedish West Coast, showed a 10 time decrease in soot spherules concentration at 100 km distance from the city center [3]. This was still a 10 times higher BC concentration than what was measured in Lapland, a rural area in the northern part of Sweden.

In remote environments, the direct anthropogenic influence is less noticeable. Instead, natural sources such as forest fires may produce the BC particles. The BC may also be emitted from fossil fuel combustion in urban areas and thereafter transported to the remote areas. It has been estimated that vegetation fires contribute 50-270 terragram Tg BC per year to the environment [4]. This can be compared with the almost 10 times lower contribution from burning of fossil fuels with 13-24 Tg BC per year [5].

Wild-fires or uncontrolled fires, are common in all different vegetation zones. Two specific environmental settings that are frequently subjected to wild-fires are the African Savannas and the dry tundra and taiga landscapes of the Far East Russian region. This is due to their specific climatic and vegetation characteristics. Vast amounts of BC are released to the surrounding environment from these regions [6,7]. In the less populated areas in the high latitudes, the most dominant ignition source is lightning, whereas in more densely populated regions in lower latitudes mainly humans start the fires.
2 BC characteristics

2.1 The combustion continuum

BC is not one chemical compound or a group with well-defined characteristics, but can best be understood with the “combustion continuum model” (Fig. 1) [8,9]. Depending on factors such as fuel material, oxygen flow, temperature of the fire and formation phase, the BC particle will have different physical and chemical properties.

![Figure 1. The combustion continuum model [10] where T is temperature; P is pressure; O/C is the oxygen to carbon ratio.](image)

The combustion products from a fire range from slightly charred, biodegradable material to highly condensed, refractory soot-BC. All BC matter shares a common origin of being combustion-derived products, which
separates them from other types of organic-rich material. Two important sub-groups of BC particle types are char-BC and soot-BC.

### 2.2 Distinction between soot-BC and char-BC
Char-BC is the residual phase left after combustion. These particles are larger than soot-BC and formed at lower temperatures, which means that the source material is not fully destroyed and some morphological features can be retained [11-13]. It is common that structure from the original wood piece can be seen in the char-BC particle when the micron-sized particle is further investigated with a microscope. The diameter of char-BC particles generally ranges from 1 to 100 µm. The surface areas of synthetically produced char-BC matter are highly variable (1.3 to 424 m² g⁻¹) and are dependent upon starting material, combustion temperature and duration of combustion [13].

Soot-BC on the other hand, is formed in the gas-phase resulting in smaller sized primary particles (30-40 nm), aggregated into micron-sized clusters and generally having surface areas of 100 m² g⁻¹. No morphological feature from the original fuel material is retained during soot-BC formation.

### 2.3 Micro structure of soot-BC
Soot-BC consists of sub-micron particles formed at high temperatures from the condensation of hydrocarbons in the gas-phase (Fig. 2). This condensation is followed by stacking of aromatic layers, which conglomerate into grape-like structures and leading to a BC particle constituting of a randomly ordered inner core and a more crystallized outer shell (Fig. 2) [14-17].
Figure 2. Soot formation from polycyclic aromatic sheets to primary soot particles and conglomeration of primary BC particles into large secondary particle agglomerates.

The soot-BC spherules are joined together by shared carbon deposits to form loose aggregates of 0.1 to 1 µm size (Fig. 2). The soot-BC particles are covered with a thin oily film, which condenses on the particle when the temperature decreases further away from the combustion flame [18]. HRTEM analysis of primary soot spheres revealed a mean fringe length (i.e., length of polycyclic aromatic layers) of ~1.0 nm [16,19]. The majority of the polycyclic aromatic planes are stacked by 2 to 4 units with interlaying spaces of 0.39–0.43 nm (i.e., the distance between two neighboring polyaromatic layers). The parallel layering is observed over dimensions of nanometers with disorder over large scale. In contrast, graphitic material, which has a geological origin and is formed during high temperature and pressure, has a perfectly ordered structure and interlayer spacing that is shorter (~0.33 nm).
3 Quantification of BC in sediments

There are several analytical methods currently used to quantify BC in sedimentary matrices. They all rely on chemical or thermal oxidation to remove non-BC phases, such as inorganic carbonates and organic matter from the matrix, before quantifying the remaining carbon as BC. The oxidation may be performed either with strong oxidants in liquid solution (so-called chemical oxidation) or in an oxidizing atmosphere (e.g., air or O₂) under controlled temperature (so-called thermal oxidation). This chemical/thermal oxidation is accompanied with various forms of treatments to remove carbonates and to minimize matrix effects, such as encapsulation of organic matter by secondary minerals. Since there are no well-defined boundaries between different BC phases but rather a continuum, it is crucial to find the oxidative strength of the non-pyrogenic organic matter vs. the strength of the pyrogenic BC material. The lack of certified BC standards makes the testing of the used analytical methods complicated and therefore reported BC concentration is currently method dependent rather than an exact value.

The chemical oxidation methods [20-24] have the advantage over the thermal oxidation methods that there is lower risk of charring of organic matter. However, the oxidative strength (i.e., cut-off between BC and non-BC matter) is difficult to control since it depends on many factors such as type of oxidant applied and reaction time [20,23]. In addition, these methods may be extremely time consuming. Also, this type of wet-chemical treatment requires several clean-up steps with repeated washing and handling of the sample, creating several opportunities for soot-BC to be lost [2,25].
The thermal oxidation methods [2,16,22,26-28] have the advantage over the chemical oxidation methods that there is lower risk of losses of BC by avoidance of washing and handling steps. Further, the temperature and gas flow can be easily monitored during combustion and thus the oxidation strength is under more control.

3.1 The chemothermal oxidation method (CTO)

The chemothermal oxidation method (CTO) is commonly used to quantify BC in marine sediments since its introduction in the mid-1990s [e.g., 2,13,16,22,25-30]. The method includes a thermal oxidation step at 375°C during 18 hours with active airflow of 200 mL min\(^{-1}\) and subsequent removal of inorganic carbonates by acidification (Fig. 3).

**Figure 3.** The different treatment steps during the chemothermal oxidation method (CTO).

Sediment
- dried, ground 20 min in ball grinder (≤ 100 µm)
- sample size: < 10 mg g\(^{-1}\); < 200 µg TOC

Combustion
- (i.e., removal of organic material)
- 375 °C in active air flow, 18h

Acidification
- (i.e., removal of inorganic carbonates)
- 1M HCl in situ

Quantification
- CHN Elemental analysis
- 1030 °C, 28 s O\(_2\) boost
The sediment is ground to fine powder in an automatic ball grinder. Then, sub-samples of about 10 mg are weighed into small silver capsules (5 x 9 mm), and thereafter placed into an aluminum boat (10 x 5 cm). The boat is placed in a tube furnace and the temperature is increased to 350°C with 10°C min\(^{-1}\) and then to 375°C with 0.5°C min\(^{-1}\). The first higher heating rate is used to avoid charring of non-BC phases, which is favored if the temperature increases slowly. The second lower heating rate is used to achieve 375°C without overshooting the target temperature, which could lead to removal of less stable BC phases. The small sample size enhances oxygen accessibility.

3.2 Comparison of CTO-BC with \(^{14}\)C dating of molecular markers and distribution of PAHs and PCDD/Fs

The CTO method relies on a thermal discrimination between the non-pyrogetic TOC and the BC compartments within the analyzed matrix with BC being significantly more resistant to heat. If the BC is not thermally resistant enough it will not be quantified as BC. The CTO method has been subjected to extensive testing both with field data from sediments and in the laboratory with standard materials. The soot-BC is suggested to be the most important BC phase for instance for sorption of organic pollutants \([27,31]\) and the CTO method has been developed to quantify this phase. Recent intercomparison studies demonstrate that the CTO method quantifies the carbon residue that is the most thermally stable, i.e., soot-BC \([32,33]\).

Studies of sediment samples have provided geochemically consistent measures of BC: (i) radiocarbon dating of CTO isolated BC was well separated from the radiocarbon date of the bulk TOC signal, but had a radiocarbon value similar to polycyclic aromatic hydrocarbon (PAH) combustion markers \([30]\), (ii) the environmental distribution of PAHs and
polychlorinated dibenzo- \textit{p}-dioxins and dibenzofurans (PCDD/Fs) are better correlated with CTO estimates of BC than with TOC, both in lake sediment cores [27] and geographically in surface sediments [34,35], (iii) the solid-water and solid-air distribution of PAHs and PCDD/Fs are better explained by CTO quantified BC than by bulk TOC [27,35-39]. These separate tests of the CTO method tell us that the BC portion extracted with the CTO-method from the sediment more resembles the PAH than the TOC fraction, i.e., there has not been any significant “charring” during the CTO procedure that falsely include TOC in the BC residue. However, this type of testing cannot be used to determine if there have been any losses during the thermal treatment.

3.3 Thermal stability of environmental carbon forms

Thermograms, constructed by plotting the mass percent carbon remaining in the residue after combustion over a broad temperature interval (Fig. 4) can be used to evaluate the stability of different carbon phases during combustion. They are used to determine the cut-off temperature between non-pyrogenic organic carbon (OC) and black carbon (BC) [13,16,26,27]. In this study, the materials were divided into positive BC materials (containing both OC and BC material) and negative materials (containing OC but are essentially void of BC matter). The thermograms show that the positive BC materials start to oxidize at higher temperature than the negative BC materials.

When quantifying BC at the cut-off temperature of 375ºC (dashed line in Fig. 4), it can be seen that 78% of the bulk diesel particulate matter (from forklift truck) is detected as BC whereas the \textit{n}-hexane soot (laboratory produced) contain about 44% BC. For soot-BCs, it is mainly the oily coating that is removed during the thermal treatment. When instead looking at the
two tested chars (laboratory produced), the relative amount of BC quantified at 375°C is close to 0% because all the carbon within the sample has already been oxidized at lower temperatures before measuring the residual carbon.

**Figure 4.** Resulting thermograms for positive (A) and negative (B) BC materials [10]. Dashed vertical line indicates the cut-off temperature of 375°C between OC and BC currently used in the CTO-375 method.
Why is char more thermally labile than soot? To answer this question, the microstructure of the respective BC particle type has to be looked upon and their relative behaviour towards oxidation. Important key factors that control the oxidative nature of the BC particle are (i) density of reactive sites (i.e., how many atoms types embedded within the structure), (ii) number of fringe carbons (i.e., carbon atoms sticking out from the large aromatic sheet structure being easier to attack by O₂), and (iii) the internal microporosity of the particle. Chars have higher density of reactive sites, more fringe carbon atoms and greater microporosity than soots and therefore react easier with oxygen in air leading to chars being more thermally labile than soots [10].

There is at present not one single method able to quantify the entire continuum of BC particles. The CTO method detects carbonaceous material of high thermal-oxidative resistance and is therefore well suited for quantification of soot-BC.
4 Source apportionment of BC particles

Tools are needed to determine the relative contribution of different sources to the BC particles found in the environment. A technique previously used to decide the BC particles origin includes using the texture and micro-structure of the BC surface to distinguish between combustion from oil, coal and wood [11]. Another way to source apportion the BC particles is to measure their radiocarbon ($^{14}$C) content [30]. In this way, BC formed from fossil fuel combustion can be separated from BC particles formed during burning of recently synthesized biomass. Furthermore, information about the BC sources can also be achieved by analyzing other combustion-derived compounds formed simultaneously in the fire, such as the polycyclic aromatic hydrocarbons (PAHs).

4.1 Radiocarbon source apportionment

Radiocarbon ($^{14}$C, half-life of 5730 years) is formed in the atmosphere and taken up by green plants during photosynthesis. The $^{14}$C content of a BC particle mirrors the $^{14}$C signal from the carbon source that has been combusted. Here, two main source distinctions can be made. First, combustion of recently synthesized modern organic material (i.e., wood from trees, grass, leaves) results in BC particles having a contemporary $^{14}$C signal (Fig. 5). Secondly, if instead fossil fuels (i.e., gasoline, diesel, oils etc) are used to produce the BC particle, the particle will have a fossil $^{14}$C signal (Fig. 5). This fossil signal comes from the long time passed between petroleum formation until the actual combustion in vehicles, home heating
systems etc. As a result, BC particles formed from combustion of fossil fuels will have low $^{14}$C content and a fossil signal.

**Figure 5.** Radiocarbon content measured for BC particles varies from contemporary (burning of recently synthesized biomass) to fossil (combustion of fossil fuels). The two end-members are mixed within the atmosphere and transported to the sediment.

The $^{14}$C signal of BC harvested with the CTO-method have been shown to have similar $^{14}$C signal as single PAHs extracted from a urban sediment in the Northeast USA [30]. This shows that there are similarities between BC particles and PAHs and also that radiocarbon apportionment is applicable to describe the original source of the BC particles.
4.2 Application of PAHs for BC source apportionment

In addition to BC particles, other combustion-derived products are the PAHs, which are formed simultaneously in the gas-phase. Since they share a common origin, PAHs can be used for source apportionment of the produced BC particles. For this source apportionment, different types of ratios can be used since some of the PAH congeners are formed from specific fuel types. For instance, the methylphenanthrene to phenanthrene ratio (MP/P) has been used to ascertain whether the PAHs are combustion-derived (e.g., pyrogenic) or if they originate from oil spills or oil seepages (e.g., petrogenic) [27]. Pyrogenic MP/P usually have values of 0.4 to 0.7, whereas the PAHs of petrogenic origin have MP/P values of 5 or higher [34]. Another commonly used diagnostic PAH ratio is the relative abundance of 1,7-dimethylphenanthrene (1,7-DMP) over the 2,6-dimethylphenanthrene (2,6-DMP) [27,40,41]. The 1,7-DMP congener is only formed when burning softwood (i.e., pine, fir, juniper, larch) and is absent when burning hardwood (i.e., oak, birch). Pure softwood combustion gives a 1,7-DMP over 2,6-DMP ratio of 0.90 or higher. This ratio is used to distinguish PAHs from combustion of fossil fuels (value below ~0.45) from coal combustion (values ranging between 0.65 and 0.68) and softwood combustion (ratio over 0.90) [41].
5 Summary of thesis

5.1 Paper I

Different BC-quantification methods give highly variable results raising ambiguity whether this reflects limitations of the used method, or that different methods simply mirror different parts of the BC spectrum. To address this issue, thorough testing of the two wet-chemical pre-treatments steps proposed by Gélinas and co-workers [2] prior to the basic CTO method were examined by using a soot-BC standard in both ex situ and in situ systems. Furthermore, to estimate the BC concentrations in both freshwater and marine sediments, the standard additions approach was tested. The wet-chemical pre-treatments tested gave lower BC concentrations as compared with the CTO method without the chemical pre-treatments. This probably stems from losses of the hydrophobic soot-BC phase during the extensive handling and washing of the sediment. The wet-chemical pre-treatments can thus not be recommended. In contrast to the wet-chemical pre-treatments, the standard additions approach proved to be useful as it gave linear regressions between added soot-BC standard and measured BC concentration, from which the recovery of added soot-BC standard could be calculated. The BC concentration determined with this approach closely matched the BC concentration determined with the original CTO method, and therefore the less laboratory intense original CTO method is recommended for BC quantification.
5.2 Paper II
There is neither a common technique for quantifying BC nor is there a certified standard material with well-characterized BC concentration. Several environmental and laboratory produced materials were tested for their thermal oxidative characteristics when being subjected to the CTO method over a large range of combustion temperatures (50°C-600°C). The soot-BC had higher thermal stabilities as compared with char-BC and non-pyrogenic organic material. The CTO method is thus well suited for quantifying the recalcitrant soot-BC phase. Further, it distinguished between soot-BC and char-BC phases and had only small interferences for other relevant organic carbon phases (coals, natural organic matter, shale, melanoidin). The oxidative stabilities also play a role when it comes to the longevity of different BC forms in the environment. Based on the results from the oxidative stabilities of various BC forms, soot-BC and char-BC produced at high combustion temperatures such as in scrubland and forest fires, will have higher environmental recalcitrance than char-BC produced at lower combustion temperatures such as in smoldering grassland fires.

5.3 Paper III
The decadal-millenial scale historical variations in sedimentary BC and PAH fluxes were deduced from sediment core studies and compared to variations in fuel usage. Seven distinct features of the BC and PAH records were revealed and could be related to varying historical energy consumption patterns. At certain times the BC and PAH fluxes were coupled, but at other times they were asynchronous. For the BC flux, high values were measured in the 1920s (5 times the pre-industrial flux) due to high coal and coke usage and in the late 1950s (4 times the pre-industrial flux) caused by high oil consumption. Lower BC fluxes were detected in 1930-1950 (3.3-3.9 times the pre-industrial flux). Further, steady decreasing fluxes were seen in 1960-
1990, and a more constant value was seen from 1990 until today being 20% lower than the pre-industrial flux. The PAH flux started to increase rapidly between 1920 and 1960 where a maximum value (46 times the pre-industrial flux) was reached probably due to high oil consumption. Thereafter, the PAH flux fell during a short period probably caused by stricter emission controls. From the 1980s to 1990s, the PAH flux decreased by from being 26 times to be about 5 times higher than the pre-industrial flux, and then reached a more constant value until today (3 times the pre-industrial flux). The observed declines in BC and PAH fluxes in modern sediment can be linked to improvements in combustion technology of home heating systems as well as in vehicles.

5.4 Paper IV

BC in the Arctic region may alter the atmospheric energy balance. The effect may be greater here than at other locations due to the strong albedo reduction, resulting from BC deposition onto snow or ice-covered land. The sources of the BC seen in this region have been studied for several years. However, ambiguity persists especially on how large the influence is from combustion in southern Asia. Source apportionment of BC was made by $^{14}$C dating of CTO harvested BC from surface sediments off the major Arctic rivers. Furthermore, the BC fluxes were calculated for each of the seven rivers studied and a total $^{14}$C signal was calculated for the Arctic region. The $^{14}$C signal of BC spanned between 88% contemporary biomass contribution (Yenisey River) to 5-15% contemporary biomass contribution (Lena, Yukon and McKenzie Rivers). The soot-BC export ranged between 99 kton yr$^{-1}$ (McKenzie River) to 1.1 kton yr$^{-1}$ (Yukon River). Further, the contemporary biomass soot-BC was calculated to be 21% of the total soot-BC export, which was low compared to a atmospheric model-based value calculated to 59% contemporary biomass contribution. This discrepancy may be caused
by the high influence of McKenzie River when contributing with ~50% of the total soot-BC flux decreasing the total $^{14}$C signal, or that the measured data is representing several more years of BC deposition than the model-based value.
6 Conclusions

- The CTO-375 method is distinct among BC methods for quantifying the thermally stable soot-BC apparently without significant interference from natural organic matter. Soot-BC may also be a key portion of BC.

- The cut-off temperature of 375°C should not be lowered to account for more of the thermally unstable char-BC since that may cause inclusion of non-pyrogenic organic matter in the BC compartment.

- *Ex situ* wet-chemical pre-treatments upstream the CTO-375 method should be avoided since the small, hydrophobic soot-BC is easily lost during washing and handling of the sample.

- The BC and PAH fluxes could be related to historical changes in main fuel used (wood, coal, oil), legislations to cut down the emissions and improvements in combustion technology.

- Radiocarbon together with molecular markers showed to be a strong tool to source apportion the BC phase harvested for the seven rivers studied in the Arctic region.
Partiklar som bildas under ofullständig förbränning av organiskt material kallas ofta för *black carbon* (BC). Dessa partiklar deltar i flera viktiga biogeokemiska processer. Ett exempel är i sediment, där BC påverkar fördelningen av hydrofoba organiska miljöföroreningar mellan vatten och fasta sedimentfaser. Föroreningarna fastnar på partikelytor vilket minskar halten i vattenfasen och därigenom så reduceras deras biotillgänglighet.


Det andra målet med avhandlingen var att studera hur den historiska och geografiska fördelningen av förbränningsprodukter ser ut. Historiska flöden av BC och polycykliska aromatiska kolväten (PAH) under de senaste 700 åren undersöktes i ett svenskt sjösediment som hämtats nära Naturvårdsverkets luftprovtagningsstation i Aspvreten söder om Stockholm. Flera olika utmärkande drag kunde urskiljas i BC och PAH-flödena. Halten av BC och PAH började stiga i en snabbare takt från mitten av 1850-talet


Alla på ITMx tackas för diverse hjälp med analytiska problem och trevligt sällskap under luncher, fikastunder och vår konferensresa till Verona. Tack! Kajjorna på 6:an förtjänar en rad liten rad också. Tack för pubar och andra tillställningar som gör många glada!


_Familjen Kruså_ tackas för trevliga middagar, samt för vistelser till både Ornö och Dominikanska. Sist men inte minst, Martin…tack för det där vinet som blev starten på vår historia. Vad hade jag gjort utan dig?
9 References


