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^{14}C analysis of filter samples for source apportionment of carbon in PM in the Netherlands

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The filter samples in Petten were collected by G. Kos and Hans van 't Veen. Also the weight of the collected PM10, resp. the PM mass-concentration, was determined by weighing the filters before and after sampling.

We courteously thank Dave de Jonge (GGD-Amsterdam) for providing the filter samples from the Overtoom. A large number of filters were received of which ten were analyzed but part of the other samples was used earlier in the year 2009 at IMAU for optimizing their preparation procedure.

Abstract

We tested the feasibility of ^{14}C analysis of carbon in PM in the Netherlands. This allows a first assessment of the sources of the carbon: PM-carbon that derives from modern sources has a ^{14}C content similar to that of atmospheric carbon dioxide, while carbon that comes from (incomplete combustion) of fossil fuel does not contain ^{14}C.

Twenty filter samples were analysed for ^{14}C in the so-called Organic Carbon fraction only. The reason is that it is already known that the other carbon-fraction, Elemental Carbon, derives from fossil fuel.

There is a long preparation procedure for the samples and this gave rise to a loss of five of the samples. Nonetheless sufficient data remained for a first evaluation.

A first look at the results indicates that, on average, 70% of the Organic Carbon is modern, that means from living material like plants and trees, including wood combustion. The remainder of the OC comes from fossil fuel sources.

The samples coming from a rural site contained on average 75% modern carbon; these samples were collected in summer with presumably the highest biogenic activity. The samples coming from an urban site had an average percentage modern carbon of 64%; these were collected in the winter-spring season.

This was a preliminary exercise in which some of the samples were rather dated; furthermore, it is known that the filters not only collect OC but also volatile organic compounds. This artifact was not quantified. It is, hence, highly recommended to perform a more comprehensive study with respect to selection of sites and season; also the sampling artifact should then be addressed.

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Summary

Filter samples loaded with Particulate Matter (PM10) were analyzed for their content of the carbon isotope ^{14}C. Analysis of this isotope enables a first apportionment of the sources of the carbon in the PM. Carbon constitutes a major fraction and the sources are not (well) known.

The source apportionment of the carbon via ^{14}C analysis can be made because the fraction deriving from fossil fuel does not contain ^{14}C. The carbon coming from so-called contemporary sources has a ^{14}C content that is similar to that of atmospheric carbon dioxide. The amount of ^{14}C in a sample thus directly reveals the percentage of contemporary carbon in the PM.

Contemporary sources of carbon include emissions from living material and combustion of wood and we cannot distinguish between the two sources unfortunately. It is custom not to use the term contemporary carbon but rather “modern” carbon than in this field of research and this wording is also chosen in this report.

As in all analyses of the carbon also here a split is made into Organic Carbon and Elemental Carbon (EC). The reason is that the sources of EC are known: EC almost completely derives from emissions of fossil fuel sources, in fact, diesel traffic. EC therefore does not contain ^{14}C. For OC the situation is different. It is not known to what extent OC derives from emissions of modern carbon and how much comes from fossil fuel sources. As mentioned above, the relative amount of ^{14}C in a sample is a measure of the percentage modern OC. The rest of the OC thus derives from fossil fuel sources.

In order to analyze the ^{14}C a complex preparation of the filter samples has to be performed. First the carbon is separated into OC and EC. This is done via a standardized two-step combustion process. This combustion is done at two different temperatures. In the combustion process carbon dioxide is produced that is collected for further preparation and analysis. The carbon dioxide produced at the lower temperatures, the first step, is that from the OC and this carbon dioxide is collected. (Incidentally, the similar two-step oxidation method was also used in the separation and analysis of OC and EC in the recent national BOP-program.)

The combustion of the filter samples and the separation of the carbon dioxide from interfering gases were performed by partner IMAU, while converting the carbon dioxide in graphite which is the actual component analysed and the analysis itself were done by the University of Groningen. The preparation process is a very time consuming and complex affair and some samples were lost in the process. Hence a total of fifteen samples could be analyzed.

There were two sets of filter samples of ten filters each. One set came from an urban site in Amsterdam and was taken in the period from January to June (in the year 2006). Other, recent, filters were taken at the rural site of Petten near the North Sea, 50 km north-west of Amsterdam. These samples were deliberately collected in the summer season so that the contribution of wood combustion to the OC would be minimal.

The results of the analyses are provided as percentage modern OC according to their relative content of ^{14}C. A first look at the data indicates that, on average, 70% of the Organic Carbon is contemporary. The remainder of the OC therefore comes from fossil fuel sources. There is a differences with respect to the location at which the samples were taken. The rural samples contained on average 75% modern carbon, while the urban samples had a percentage modern carbon of 64%.

It should be mentioned that this investigation was a very preliminary exercise, with fifteen samples analyzed for their ^{14}C content. Furthermore, the samples from Amsterdam were rather dated. It is hence recommended to perform a more thorough study in which the differences in ^{14}C content should be investigated for samples taken on the same day at a relatively close distance at a rural, urban and street-site.

Care should also be taken to minimize the sampling artifacts caused by adsorption of volatile organic compounds to the filters. This could either be done by using a back-up filter or, to have an estimate of the artifact, by analyzing a series of so-called field blanks. These are filters on which no PM is sampled but which are in the filter holder for a similar period of time as used for collection of the PM.

1. Introduction

Carbon is a major component of PM10 and especially PM2.5 in the Netherlands [ten Brink et al., 2009]. Its contribution is around 25%. In contrast to the other major components of PM the sources of the carbon are hardly known. The carbon is most often split into two components, viz., Organic Carbon (OC) and Elemental Carbon (EC). EC is known to derive almost completely from emissions of fossil fuel sources, in fact, diesel traffic in our region. Therefore the sources of OC are the ones that are not known.

A first indication of the sources is provided via analysis of the content of the isotope ^{14}C in the OC-fraction in the sample. From such an analysis a good estimate can be made of the contribution of modern carbon versus carbon that derives from fossil fuels. Modern carbon, which derives from living material like wood, plants and their debris, contains an amount of ^{14}C that is similar to that of the carbon dioxide in the air. Carbon deriving from fossil fuel is so old that it does not contain this isotope because the lifetime of ^{14}C is too limited to live that long when stored. For that reason analysis of Elemental Carbon for ^{14}C is not meaningful, also given the costs of analysis.

From the ratio of the unstable isotope ^{14}C to that of the stable ^{12}C the relative amount of modern carbon in the OC-fraction is obtained. Currently such analysis of ^{14}C in PM filter samples is being carried out by a number of scientists in Europe to make such a first assessment of the sources of the Organic Carbon fraction of PM. Most of the analyses are made in the leading institute in Europe (PSI, Switzerland; Szidat and coworkers), which is working in this field now for quite a number of years now [Szidat et al, 2004].

The most complete analysis was made for samples collected in the city of Zurich and it was observed that on average some 65% of the Organic Carbon derived from what was called in their publications “modern” carbon.

We had anticipated that in the more densely populated Netherlands this percentage would be lower. However the first preliminary results show otherwise, as discussed below.

2. Experimental methods

The PM-samples to be analysed were collected with High-Volume samplers. With such samplers sufficient material could be collected for analysis. This limited the number of samples available.

A number of samples derived form an older measuring campaign by the GGD-Amsterdam (courtesy Dave de Jonge) at an urban site in 2006 in Amsterdam, know as Overtoom. The site is approximately 30 m from a busy main street but separated by a 5-storey building from the road. The samples had been collected in the period January to June (2006).

Because samples taken in the winter time could contain carbon from wood combustion it was decided to undertake a special sampling campaign in summer when no wood combustion occurs. This would possibly enable a proper first estimate of the contribution of true living, biogenic, sources to the OC. This campaign was therefore also carried out at a rural setting to maximize the contribution of biogenic OC. The sampling was performed sources at ECN, in Petten, a rural site near the coast of the North Sea, 50 km north-west of Amsterdam. The samples in this campaign were collected in the period July to September 2009.

As for the collected samples, these were stored in a refrigerator to prevent evaporation of Semi Volatile Organic Carbon. The filter samples were brought to the preparation lab in Utrecht, in October 2009, packed in aluminum foil.

The first preparation of the samples was performed at IMAU (Institute for Marine and Atmospheric Research Utrecht). This comprised combustion of the filter samples and separation of the carbon dioxide from interfering gases and solidifying these for easy shipping and further preparation. These purified carbon dioxide canisters were then transferred to the University of Groningen, Centrum voor Isotopen Onderzoek (CIO). There the carbon dioxide was transferred to solid graphite, which is the proper material for analysis.

It should be mentioned that in the preparation procedure the separation is made between OC and EC by a two-step oxidation of the carbon. This process is very similar to the one used by Szidat et al., (2004). This was a for awhile the standard protocol, however there is a present a discussion with which combustion protocol the most optimal split between OC and EC can be attained. Incidentally, two-step combustion is also the way analysis of OC and EC was done in the recent BOP-program in which the OC and EC content of PM was determined in a year-round study [ten Brink et al., 2009] and from which the percentage carbon in PM derived that was quoted above.

Details on the rather complex preparation route and analysis procedures are provided in the appendix. Because of the long preparation route, necessary before analysis, there are steps that are quite risky. And indeed of the samples five were lost so that (only) the result of the analysis of 15 samples is available.

3. Results and discussion

An overview of the results is provided in table 1. The actual result is tabulated in column 4 as percentage modern OC. Together with the analysis data, some details of the sampling conditions are provided.

Table 3.1 *Results of the percentage modern carbon, column 4, of the indicated samples*

Sample-code	Date	ug OC	% modern OC	Notes
A679	19-1-2006	159	70.4	
A681	5-4-2006	116	57.0	
A683	28-3-2006	214	57.9	
A685	20-3-2006		49.0	
A688	12-3-2006	236	72.9	
A694	19-5-2006	174	67.9	
A696	27-5-2006	121	61.6	
A698	4-6-2006	140	90.6	
A699	12-6-2006	185	45.8	
A700	8-6-2006	x		Failed to graphitize
Amsterdam AVERAGE			64%	SD = 13%
P1	29-7-2009	158	81.6	
P2	30-7-2009	141	63.4	
P3	1-8-2009	222	75.4	
P4	3-8-2009	257	71.6	
P5	12-8-2009	142	91.4	
P6	26-8-2009	x		Failed to graphitize
P7	17-9-2009	x		Failed to graphitize
P8	18-9-2009	143	67.6	
P9	19-9-2009	*75*	*11.7*	*Outlier: not considered in average*
P10	20-9-2009	158		Lost during measurement
Petten AVERAGE			75%	SD = 9%

A=Amsterdam

P=Petten

It is seen that the samples deriving from the rural site have more modern carbon (around 75%) than those from the urban site (65%). It should be cautioned that the number of data is limited and furthermore that the result of the analysis of one sample (P9 in table 1) was obviously not reliable.

It should also be considered that the samples were taken at different periods of the year with typically different emission activities. Furthermore the urban samples had been stored for over three years.

It should be further indicated that this was a preliminary study with fifteen samples analyzed for their ^{14}C content. Furthermore, the filter samples from Amsterdam were rather dated and also taken in another period of the year.

Another issue addressed at length in the BOP-study mentioned before [ten Brink, et al., 2009] is that part of the OC on the filter derives from adsorbed gaseous compounds. In the BOP-study a large number of blank filters was used to assess the amount of adsorbed material. Such data cannot be translated to this study because the sampling approach was quite different. Hence, in case a new study would be commenced, care should be given to this artifact.

Even with all the caveats given above, it is remarkable that the percentage modern carbon in Amsterdam is quite similar to that reported by the leaders in the field (Szidat and coworkers, e.g., 2004) in Zurich. Szidat et al. claim that the rather high percentage is due to the fact that Zurich is amidst a very rural setting with quite some woods. With this first quite surprising result it might be highly advisable to repeat the investigation this year, however with the following in mind.

The follow-up study (to be performed this year) profits from the experience built up in this study here, and will be more thorough. In the new investigation the differences in ^{14}C content should be investigated for samples taken on the same day at a relatively close distance at 1) a rural, 2) urban and 3) a street-site. Also care will be taken to assess the sampling artifact, discussed above.

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Appendix A Analysis and preparation method

For ^{14}C measurements of the organic aerosol fraction, pieces of aerosol filter samples are combusted in O_2. Specifically the organic fraction is thereby combusted to CO_2. The CO_2 is cryogenically separated from O_2 and other gases produced in the combustion of the aerosol sample, and finally reduced to graphite. The fraction of modern carbon in the graphite sample is measured using an Accelerator Mass Spectrometer (AMS). The details of the experimental procedures are described in the following sections.

A.1 The combustion system

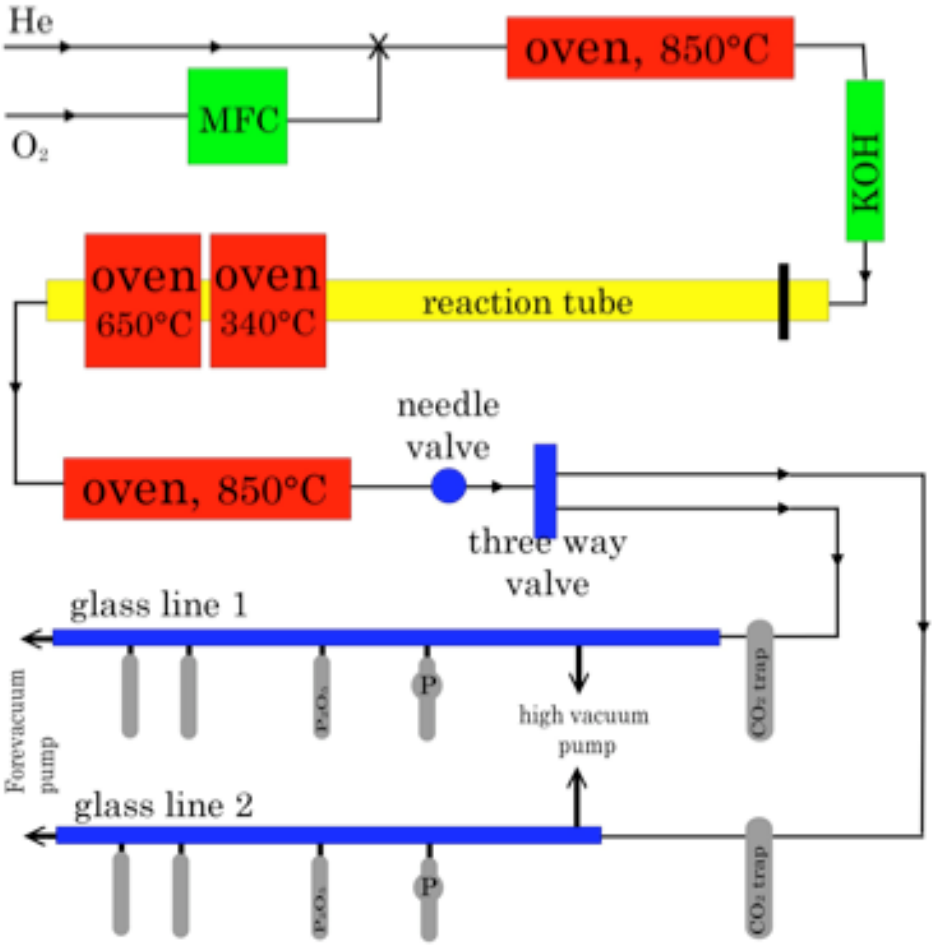

Figure A.1 *Schematic representation of the setup used for the combustion of organic and elemental carbon*

A schematic view of the combustion system is given in figure A.1. This system is very similar to the one used by Szidat et al., (2004). The combustion reaction takes place in the reaction tube, which has a total volume of approximately 300 ml. A sample holder with a filter is inserted into the tube, and moved into the ovens with a magnet. In the first oven at 340 °C, the main fraction of the organic carbon is combusted to CO_2 in pure pre-cleaned O_2, while elemental carbon remains on the filter.

The gas mixture resulting from the combustion of the aerosol flows first through a second oven

at 650 °C which is normally used to combust EC. Also at 650 °C, sulfix ® is used to remove SO_2 and other sulfur compounds and a Pt catalyst to oxidize possible CO or other incomplete combustion products. The CO_2 is then further purified in an oven containing a NiO wire at 850 °C. The flow through the reaction tube is regulated by a needle valve. The pressure inside the reaction tube is slightly higher than the ambient atmospheric pressure, while the pressure in the extraction trap and glass line after the needle valve is approximately 15 mbar.

The glass line contains a CO_2 trap that can be cooled with liquid nitrogen for CO_2 extraction, a flask with phosphorus pentoxide (P_2O_5) for the removal of water vapor, a calibrated volume with pressure sensor to determine the amount of CO_2 manometrically, and break-seals or other flasks for storage of the samples.

A.2 Procedure for the combustion of the organic carbon

At the beginning of the experiment an aerosol filter is put into the sample holder and is placed in the reaction tube. The fore vacuum pump on the excess glass line is opened, and the helium flow is started for ten minutes to flush the system through glass line 2. After ten minutes of flushing, the CO_2 trap at sample glass line 1 is cooled with liquid nitrogen. The flow is switched to oxygen at a flow rate of 65 ml/min, and the three-way valve is switched to glass line 1. After three minutes, when the reaction tube is filled with O_2, the filter is moved to the 340 °C oven for 15 minutes. After 15 minutes, the three-way valve is switched to excess glass line and the filter is taken out of the oven.

The CO_2 that is collected in the CO_2 trap during the 15 min of organic carbon combustion is purified further. First the CO_2 is sublimated from the trap, and then frozen into the flask with P_2O_5 to remove water vapor. From the P_2O_5 flask, the CO_2 is frozen to the calibrated volume equipped with a pressure sensor to measure the amount of CO_2 manometrically. Last, the CO_2 is frozen into a break-seal or an empty flask for storage.

A.3 Removal of N2O

The combustion of ammonium nitrate, a major inorganic aerosol constituent can lead to the formation of N_2O. N_2O cannot be separated from CO_2 cryogenically, since it has a similar freezing temperature. N_2O is removed offline from the sample by equilibrating the CO_2-N_2O mixture with a CeO_2 catalyst at 850 °C. The amount of N_2O removed is determined by comparing the sample pressure in the calibrated volume before and after treatment.

A.4 Standards and backgrounds

Standards and background samples were produced by combusting HOxII samples (nominal activity: 134.06%) and anthracite samples (nominal activity: 0%) in oven 2 for one hour. The extraction and purification of the sample follows the procedure of OC. A removal of N_2O was not necessary in this case.

A.5 Graphitization of the samples

Graphitization and AMS measurements are performed at the AMS facility of the Centrum voor Isotopen Onderzoek (CIO) in Groningen, and at the Robert van der Graaff laboratory in Utrecht.

In Groningen, the CO_2 sample is heated with sulfix, a mixture of cobalt oxide and silver oxide, at 500 °C for three hours before the graphitization to remove possible sulfur compounds, because sulfur compounds poison the catalyst used during the graphitization.

The graphitization system consists of a cold finger, a small reaction tube, and a pressure sensor. The system has a total volume of 2.6 ml and is connected to a glass line containing a high vacuum pump. Samples containing 50 – 100 microgram of carbon can be graphitized with this system. For the graphitization, 1.5 mg iron powder is pressed as a porous iron pellet with a diameter of 1.3 mm (de Rooij et al., 2009). The iron pellet is placed in the reaction tube and the system is evacuated. Then, a CO_2 sample is added to the system. The pressure of CO2 in the system is determined, and CO_2 is frozen into the cold finger with liquid nitrogen.

Hydrogen is added to the system, so that the molecular ratio H_2/CO_2 is 2.5. Adding too much hydrogen would cause side reactions like the formation of methane. Then, the liquid nitrogen is removed, the cold finger is heated, and the oven is placed around the reaction tube for one night at 600 °C. Meanwhile, Peltier cooling elements cryogenically removed the water vapor formed during the graphitization reaction. After one night, graphite is formed on the iron. For the small samples from 25 to 300 µg C, the graphitization yield is 80 to 93%. Using the iron pellet technique, the reaction time for small samples was 60 to 90 minutes. After graphitization, the pellet is pressed into 1.5 mm target holders from the back with a small silver pellet behind it.

A.6 The AMS system

The AMS system is a high-throughput mass spectrometer, dedicated to ^{14}C. It consists of a 59-sample ion source, a recombinator as injector, a 2.5 MV tandetron accelerator, a high-energy mass spectrometer (110° magnet, 33° electrostatic deflector and a 90° magnet) and an AE/E ionization chamber. To obtain the required high precision in ^{14}C, the three carbon isotopes (^{12}C, ^{13}C, ^{14}C) are accelerated simultaneously. This ensures a continuous diagnostic tool, wherein the three isotopes travel along the same path, thereby minimizing mass fractionation.

A.7 Data evaluation and correction

The Groningen ^{14}C AMS system simultaneously measures the $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios of the samples, the HOxII standards and background samples. The $^{14}C/^{12}C$ ratios of the sample are reported relative to the HOxII standards and normalized for fractionation to $\delta^{13}C = -25‰$.

During the extraction, graphitization, and AMS measurement an increase in activity of the backgrounds and a decrease of the HOxII standards with decreasing sample size is observed. This is due to modern and dead contamination, respectively. These effects are reproducible. Therefore, we can find the ^{14}C activity of the samples by using a mass-dependent background correction. With the present set-up the modern carbon contamination during the graphitization process is in between 0.15 and 0.35 µgC.

Without pre-cleaning the iron pellet, e.g. reduction of the iron pellet at 400°C in 1 atmosphere of hydrogen, the dead carbon contamination during the graphitization process is in between 0.5 and 2 µgC. For samples < 40 µgC it is around 0.75 µgC, whereas for larger samples it seems to increase to 1.5 µgC.

Since the standard and background samples were extracted exactly as the aerosol filter samples, the correction method outlined above also corrects for typical contamination during extraction and combustion.