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Use of proton backscattering to determine the carbon and oxygen content in fine particle samples deposited on PTFE($(CF_2)_n$) membrane disk filters

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ABSTRACT

Particulate carbon is routinely measured in the IMPROVE (interagency monitoring of protected visual environments) program by analysis of samples collected on quartz filters. The analysis is performed at Desert Research Institute using the thermal optical reflectance method. Measurements of Si, Al, Ca, Ti, and Fe by X-ray fluorescence at Crocker Nuclear Laboratory are used by IMPROVE to calculate a SOIL parameter by weighting these elements to account for the oxygen and minor elements that are not measured. It is desirable to have alternative methods to measure both carbon and oxygen for data validation purposes.

We have tested a method to measure carbon and oxygen concentrations from air samples deposited on PTFE membrane filters using the backscattered proton spectrum. The measurements were performed with a 4.5 MeV proton beam from the cyclotron of the Crocker Nuclear Laboratory during routine IMPROVE measurements of hydrogen by proton elastic scattering analysis. A surface barrier detector at 155° below the plane of the beam was employed in a Cornell geometry setup to measure the proton spectrum. We will discuss a consistent method to estimate the carbon from the PTFE $(CF_2)_n$ membrane substrate that must be subtracted from the measured carbon (filter plus deposit). This method is independent of the number and arrangement of the fibers and the unknown stretching of the substrate. The measured carbon at multiple IMPROVE sites using this new method is generally slightly higher than carbon measured using thermal optical reflectance. The sum of all elements, including the oxygen and carbon determined by proton backscattering, compares somewhat better to gravimetric mass than the same sum using carbon by TOR instead of backscattering.

1. Introduction

The Clean Air Act protects visibility in Class I Areas against impairment due to existing and future anthropogenic air pollution. The interagency monitoring of protected visual environments (IMPROVE) network (Malm, Sisler, Huffman, Eldred, & Cahill, 1994) program monitors the air quality and particulate matter composition in those areas. At each site, parallel sampling modules collect fine particulate matter ($PM_{2.5}$) on different filters for different analyses, drawing about 33 m^3 of air over 24 h, through a cyclone designed to reject particles larger than 2.5 μm in aerodynamic diameter. The

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25-mm-diameter PTFE membrane filters from one of the modules are weighed to determine total sample mass, then undergo X-ray fluorescence (XRF) analysis to determine elements heavier than neon and by forward proton elastic scattering analysis (PESA) to determine hydrogen. These analyses are performed at the Crocker Nuclear Laboratory of the University of California, Davis. The 25-mm-diameter quartz fiber filters from another module are sent to Desert Research Institute (DRI) at Reno by thermal-optical reflectance (TOR) analysis (Chow et al., 1993), which yields values for elemental, organic, and total carbon.

The quartz filters required for TOR analysis actively adsorb some of the organic gases present in ambient air, and this positive artifact complicates the determination of carbon in the particulate phase. Carbon concentrations reported by IMPROVE are adjusted for this artifact by subtracting a correction based on the median concentration observed on backup quartz filters sampled at selected sites. It would be a desirable cross-check to measure carbon in the same sample used for the mass and XRF measurements, but the PTFE filter on which this is collected is itself largely carbon (TEFLON®, or $(CF_2)_n$). Chiari et al. (2004) have reported the determination of carbon and other light elements by analysis of backward proton elastic scattering with fairly good results. We have added a second detector at the IMPROVE bean line to measure the carbon in the samples routinely analyzed with (forward scattering) PESA. The consistent stoichiometry of the PTFE membrane allows to establish its intrinsic carbon contribution to the observed total carbon loaded in the membrane by simultaneously determining the fluorine in the membrane. With this method, we find that satisfactory precision for carbon would require a PESA exposure longer than 15 s now routinely done, but that existing exposures are adequate for a direct determination of oxygen, the main (1/3 to 1/2 of total mass) element not currently reported.

2. Methods

We use the cyclotron of the Crocker Nuclear Laboratory of UC Davis to generate a proton beam of 4.5 MeV energy for the PESA analysis. The beam energy resolution was 25 KeV. The beam stability during all the time of the exposure of samples was within 40 KeV. The IMPROVE beam line was modified to include a back detector in the vertical plane at an angle of 155° to the beam direction. Fig. 1 shows the IMPROVE vacuum chamber and the geometry for the sample, detectors and Faraday cup that captures the beam. The $PM_{2.5}$ samples are deposited on PTFE (CF_2) membrane disk filters (TEFLON®, Pall Corporation) and irradiated for 15 s for PESA at an intensity of 40 nA.

The spectra were acquired with the standard IMPROVE data acquisition system and were analyzed with software not included in the IMPROVE protocol. To check the elemental separation of the light elements a LiF deposit on a Mylar ($C_{12}H_8O_4$) film was bombarded with 4.5 MeV protons. Fig. 2 shows the resulting backscattering spectrum as well as the results using the code SIMNRA. For this homogeneous deposition on a thin Mylar film, the separation for elements below fluorine is very good. The peaks for the ground state of ^{19}F, ^{16}O, ^{12}C and ^{7}Li are well separated. We also observed the higher excited states of fluorine, i.e. the lower energy structure (lower channel number), which is located in a part of the spectrum that is free of any interference from elements in the samples. This is an important feature for the extraction of C and O capture in the PTFE membrane.

Unfortunately the nonhomogeneity of the PTFE membrane causes the peaks to display an asymmetry toward the low energy edge, as seen in Fig. 3. The protons interacting deep in the substrate see more PTFE® filaments in the matrix than those that scatter closer to the surface. The protons that interact with more substrate material lose more energy and may scatter outside the solid angle subtended by the detector. The consequence of this is that the peaks are not symmetric and exhibit a lower energy tail. The spectra from the IMPROVE samples were acquired at a higher amplifier gain than in the previous example to use as much as possible the range of the Analog to Digital Converter to better resolve all light elements including Nitrogen.

As it was in the case for the LiF sample, both unloaded and loaded filter spectra show the higher excited states of fluorine at an energy interval where it does not interfere with any possible elements in the collected sample. The spectrum from the loaded filter also displays higher energy peaks produced by heavier elements in the sample.

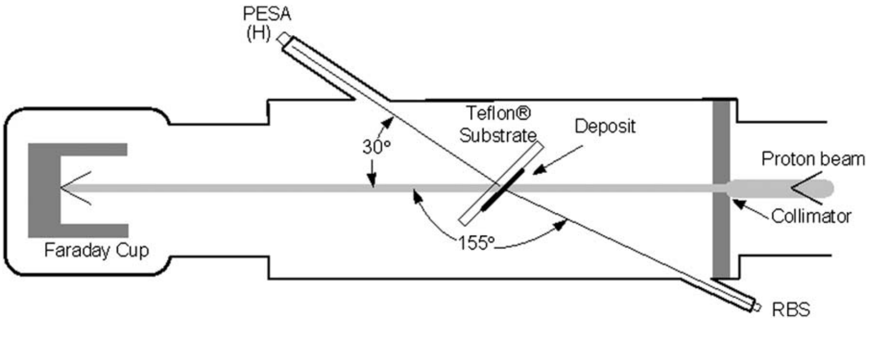

Fig. 1. PESA/PBS beam line at Crocker Nuclear Laboratory.

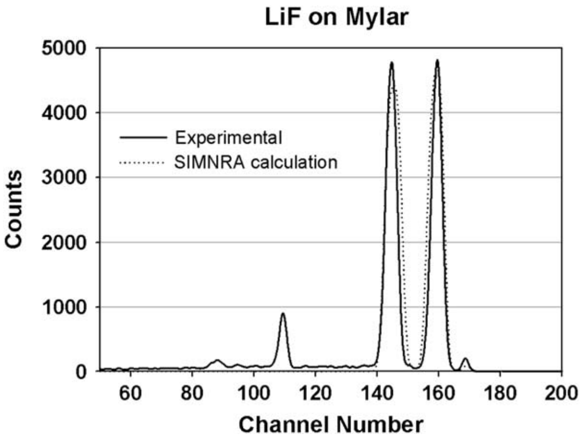

Fig. 2. LiF on Mylar. Backscatter spectrum at 155°.

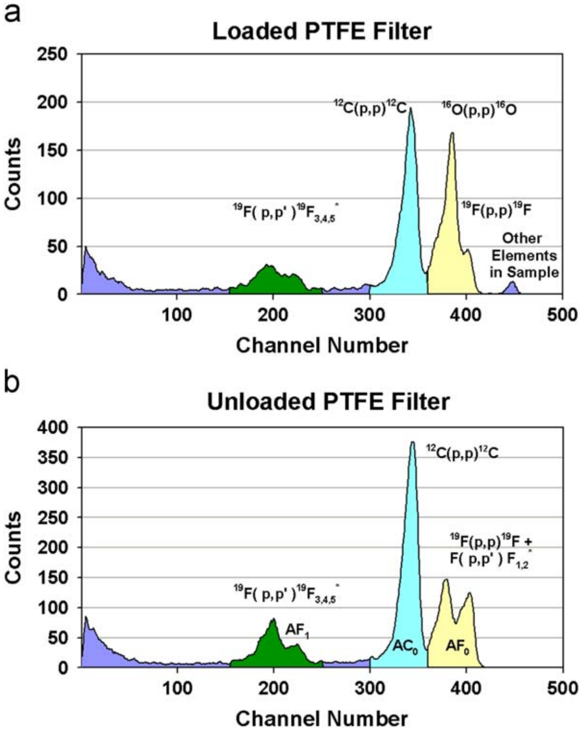

Fig. 3. Backscatter spectra from (a) unloaded and (b) loaded PTFE® (CF_2) filters.

The problem encountered in using backscattering to measure carbon from the samples on PTFE membranes is that carbon is also present in the matrix of the filter. Because of how the filters are manufactured, even filters from the same batch of PTFE® fibers may have different tension applied and consequently their areal density may be different. This means a simple subtraction of a standard unloaded filter from a loaded one is not an accurate method to determine the amount of C or O in the samples.

However, the PTFE filters contain carbon and fluorine in a known ratio. Fluorine is not present in the air sample (or is at such low concentrations it can be considered to be absent) so the carbon in the substrate of the loaded filter can be inferred from the measured fluorine. This is accomplished by integrating the peaks of fluorine from the 3rd, 4th and 5th excited states and multiplying this count by the ratio of carbon to fluorine counts in an unloaded filter. This ratio is the same for all the filters, since it depends only on the number of atoms of fluorine and carbon and on the cross section for exciting the states. The same argument applies to the region of the spectrum where the oxygen peak is superimposed on the higher energy fluorine peaks, but in this case the ratio depends only on the cross sections for the fluorine peaks. Thirty-two unloaded filters were analyzed to obtain these ratios. The values obtained were $(AC_0/AF_1)=3.2\pm0.2$ for carbon to low energy fluorine and $(AF_0/AF_1)=2.1\pm0.1$ for the high energy to low energy fluorine peaks. These factors were used to compute the C and F contributions from the substrate to be subtracted from the peaks in the loaded filters.

3. Results

The data presented here are for samples from the IMPROVE network collected in July 2005 and June 2007. A total of 1715 samples from 179 sites were analyzed for July 2005. Analyses of collocated samples from July 2005 and June 2007 were used to estimate the uncertainties of the measurements. Figs. 4 and 5 show the correlation between values from the primary and collocated samplers in June 2007 and July 2005 for oxygen and carbon. The collocated precisions for C and O for these periods were calculated using Eq. (1) in SIMNRA. For July 2005, the collocated precision was 30% for carbon and 10% for oxygen. For the June 2007 data, the results were 20% and 11%. The difference in the precisions for C and O is mainly due the statistics in the number of counts. By analyzing the blanks in the same fashion as the samples, a critical detection limit for carbon and oxygen can be estimated (Hyslop & White, 2008a, 2008b). From the analysis of 31 blanks we estimate that for carbon the detection limit is 1500 ng/m^3 and for oxygen it is 500 ng/m^3. Fig. 6 shows the distribution of blank values for the 31 samples.

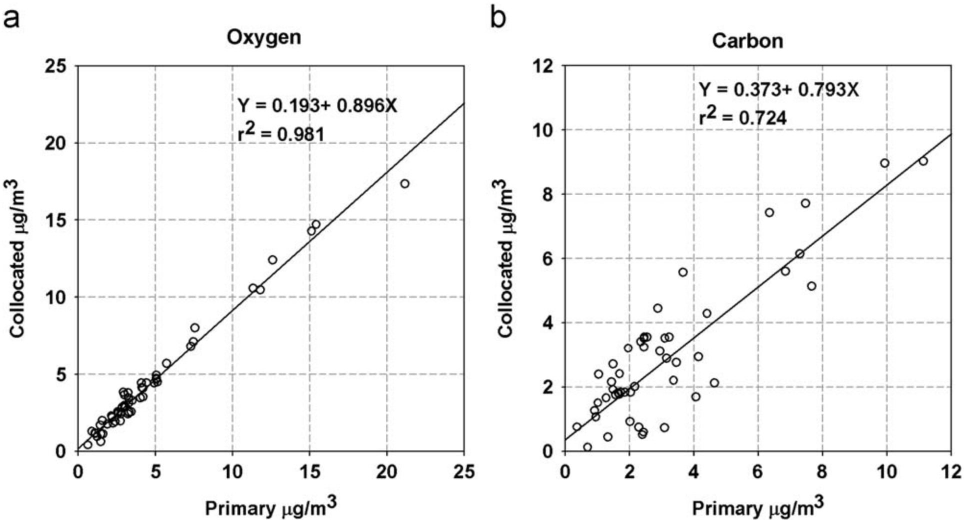

Fig. 4. Collocated comparison June 2007: (a) oxygen and (b) carbon.

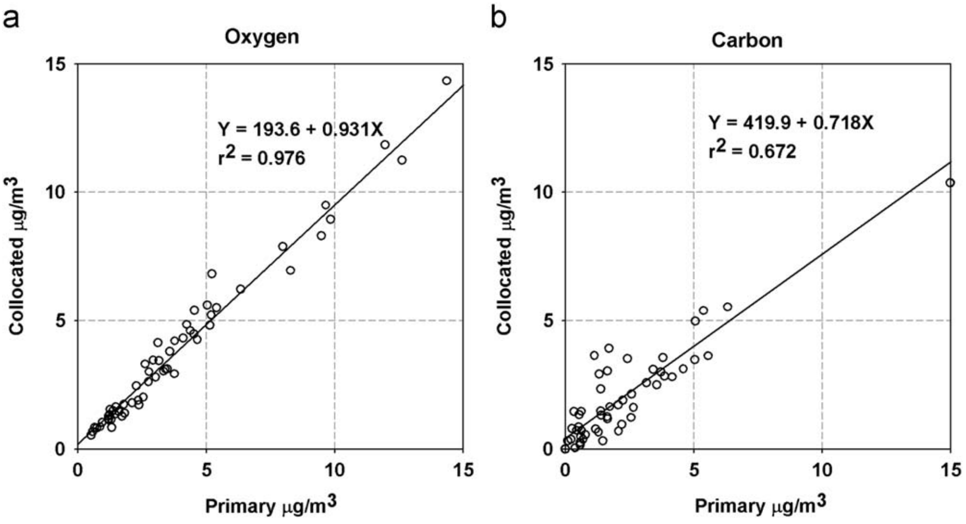

Fig. 5. Collocated comparison July 2005: (a) oxygen and (b) carbon.

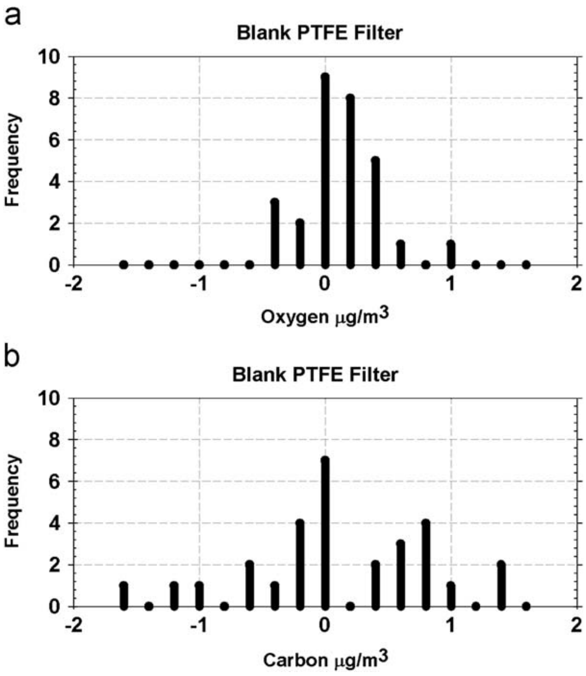

Fig. 6. Distribution of values for (a) oxygen and (b) carbon from 31 blank PTFE membranes.

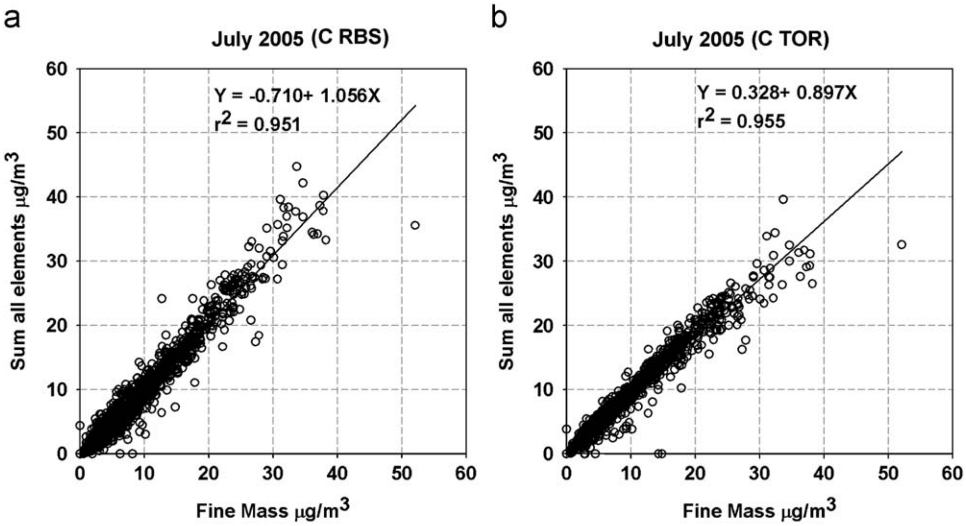

Fig. 7. (a) Sum of elements (with O and C from RBS) vs. gravimetric mass and (b) Sum of elements (with O from RBS and C from TOR) vs. gravimetric mass.

Fig. 7 displays the relationship between the sum of all elemental masses and the gravimetric mass for all 1715 points. Fig. 7a includes the carbon from backscattering and Fig. 7b uses carbon from TOR analysis. The correlation is very good in both cases, with a slightly better agreement for the TOR carbon. The TOR carbon results in a lower sum of elements than the RBS carbon. This may indicate that there is a deficit in the carbon determined by TOR, or it may be due to the artifact correction that is applied to the TOR carbon. There is no artifact correction on the RBS carbon.

Fig. 8 shows the relationship between carbon determined by RBS and TOR. At face value, there is a lot of scatter in the data, but the back scattering method, on the average, generally shows higher carbon mass than thermal optical reflectance analysis. It is possible that the different types of filters collect carbon in different amounts, although we would expect the quartz filters to show higher carbon by retaining more of the volatile carbon compounds. If one selects individual sites, there is a linear correlation between both methods of total carbon extraction. Fig. 9 shows four sites for which a linear relation between the two methods is clearly seen, but the sites shown different slopes. This inconsistency has not been resolved and could be just a matter of statistics coupled with the subtraction of the carbon in the membrane material.

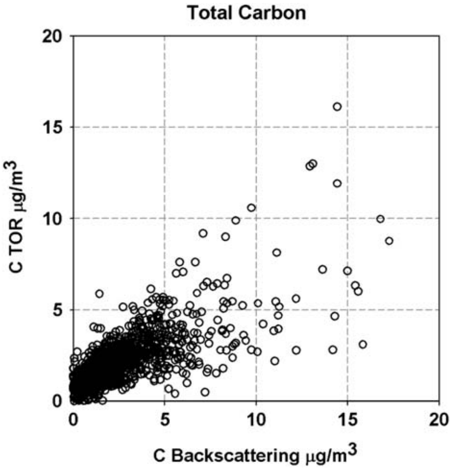

Fig. 8. Comparison of carbon from TOR to carbon from backscattering.

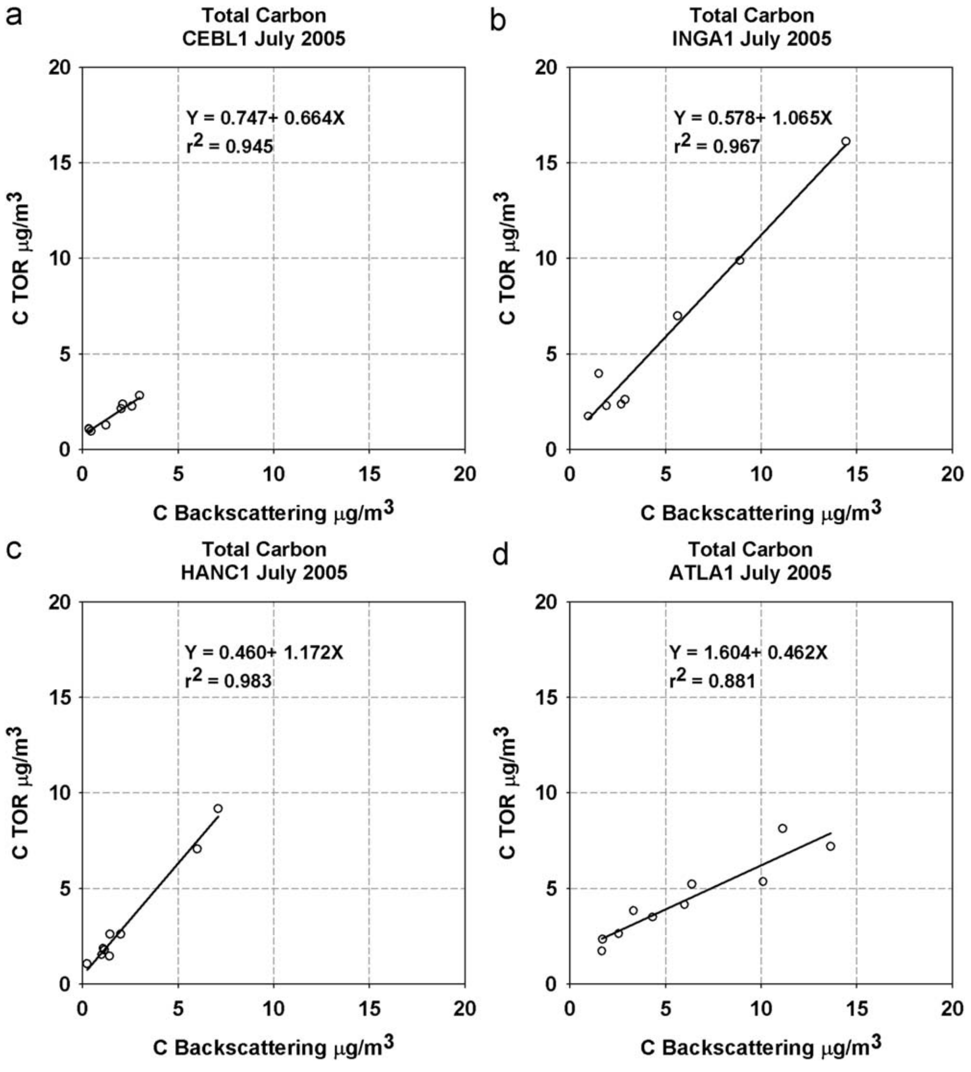

Fig. 9. Comparison of RBS carbon and TOR carbon at selected IMPROVE sites: (a) Cedar Bluff State Park, KS, (b) Indian Gardens (within Grand Canyon), (c) Hance Camp (Grand Canyon rim), and (d) Atlanta, GA.

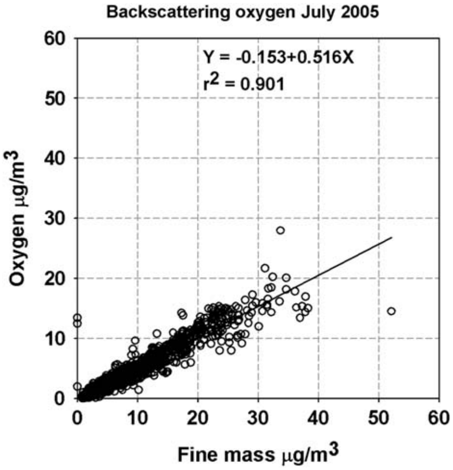

Fig. 10. Oxygen content of samples compared to gravimetric mass.

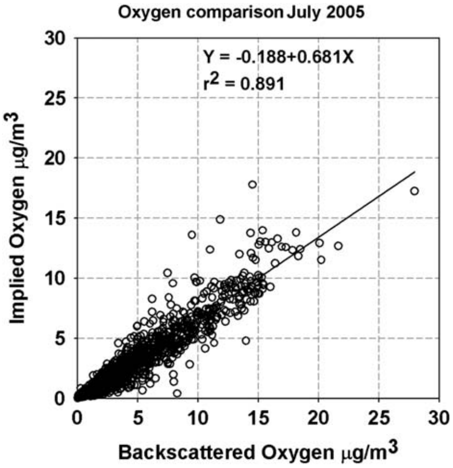

Fig. 11. Oxygen implied by soil oxides, sulfates and nitrates compared to measured oxygen.

Fig. 10 shows the oxygen content of the samples as a function of the gravimetric mass. On the average the oxygen mass accounts for 50% of the collected mass in the PTFE membrane. Fig. 11 shows the oxygen implied by the soil oxides, sulfates and nitrates as a function of the measured oxygen. On the average, it is 65% of the measured in these experiments

Fig. 12 shows how the RBS results improve when the exposure time to the beam is increased from 15 to 60 s. The sum and individual values of carbon and oxygen are compared for the 15 and 60 s exposure times. It is clear that without the constrains from the run time protocol for the IMPROVE PESA exposures, we could increase the exposure time to get better counting statistics to improve the precision for the measurements of carbon and oxygen in the samples

4. Conclusions

We have implemented a proton backscattering method to measure carbon and oxygen concentrations in particulate matter deposited on PTFE® filters in the IMPROVE network. Fluorine exhibits low energy peaks in a region of the backscatter spectrum that is free from interference by other elements in the particles, so we can subtract the background carbon in the PTFE® substrate by using the ratio of carbon to fluorine. This method is self regulating; i.e. it does not depend on consistency of substrate thickness between sample and blank. The correlation between carbon mass extracted by this method and the mass determined by thermal optical reflectance is very scattered when all the sites are examined together. Each individual site shows good correlation, and all are different. Some sites have the TOR carbon greater than the RBS carbon, but on the average we measured more carbon by RBS than is measured by TOR. The method also determines the oxygen mass contained in the sample. The oxygen mass is on average 50% of the total fine mass measured gravimetrically.

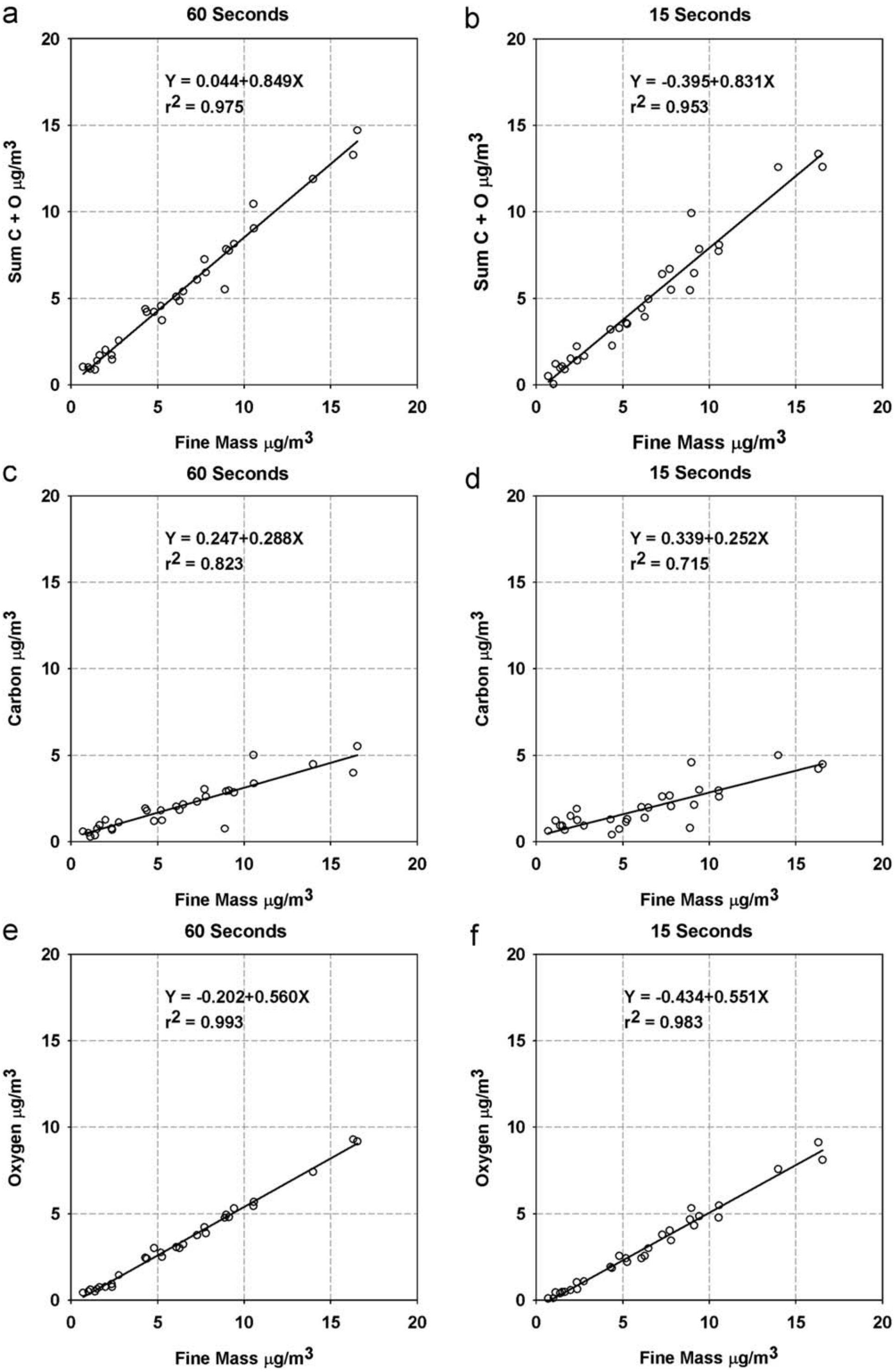

Fig. 12. Comparison between 60 s analysis time and 15 s analysis time for (a,b) sum of carbon and oxygen, (c,d) carbon alone, and (e,f) oxygen alone.

When the carbon and oxygen measured by RBS is added to all other elements present in the sample, the correlation to the total fine mass determined by gravimetric means is almost one to one. Although this method will not discriminate the components of carbon collected as TOR does, increasing the exposure time to the proton beam, could give a way to a precise alternative measurement of the total carbon in the air samples.

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