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Technical note

Carbonate measurements in PM10 near the marble quarries of Carrara (Italy) by infrared spectroscopy (FT-IR) and source apportionment by positive matrix factorization (PMF)

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ABSTRACT

The concentration of carbonates in atmospheric Particulate Matter (PM) is usually quite low. The surroundings of marble quarries are peculiar sites where the impact of carbonates in PM levels can be significant. We present here the results of a PM10 sampling campaign performed in Carrara (Italy). The town lies between the famous marble quarries and the harbour: about 1000 trucks per day transport marble blocks and debris from the quarries to the harbour passing through the town centre. PM10 was collected on daily basis on PTFE filters analyzed by Energy-Dispersive X-Ray Fluorescence (ED-XRF) and Ion-Chromatography (IC). Carbonate concentration was measured by a non-destructive Infrared Spectroscopy analysis (FT-IR). Time series of elemental (Na–Pb by ED-XRF), ionic (SO_4^{2-}, NH_4^+ by ion-chromatography) and carbonate (by FT-IR) concentration values were merged in a unique data set and a PMF analysis singled out the major PM10 sources in the area. Marble transportation turned out to be the major pollution source in the town accounting to PM10 for about 36%; this corresponded to a $CaCO_3$ average level of about 8 $\mu g\ m^{-3}$ during working days. The FT-IR analysis was a crucial part of the work and an ad-hoc analytical procedure was specifically set up, calibrated, and tested as described in the text.

1. Introduction

In recent years, atmospheric aerosols have been studied extensively and strong relationships among heterogeneous chemistry, cloud formation, and climate forcing have been observed (Charlson et al., 1992; Seinfeld and Pandis, 1998; IPCC, 2007). Effects on the health of human beings are also well established and concentration limits for PM10 and PM2.5 (PM10, PM2.5 = atmospheric particulate matter with aerodynamic diameter, $D_{ae} \leq 10\ \mu m$ and $D_{ae} \leq 2.5\ \mu m$, respectively) to safeguard the human health have been recently revised in Europe with the European Directive 2008/50/EC. Large amount of PM10 concentration data are collected for regulatory purposes in several countries. Elements and/or compounds can trace specific emissions and the knowledge of the chemical composition of particulate matter can be used to evaluate the impacts of the various sources on ambient air quality. Several source apportionment strategies have been developed during time and receptor models (Gordon, 1988) are presently one of the most used approaches; among these, Positive Matrix Factorization, PMF (Paatero and Tapper, 1994) has rapidly become a reference tool. PMF is a variant of factor analysis (Heidam, 1982; Thurston and Spengler, 1985) which constrains factor loadings and factor scores to non-negative values. This important improvement does not completely avoid difficulties in resolving major sources and the more comprehensive is the PM speciation and the lower are measurement uncertainties, the more reliable is the result of the receptor model. While similar PM sources are often resolved in several sampling sites, peculiar situations ask for dedicated studies.

This paper describes the results of a particular experiment performed in the urban area of Carrara (Italy). This is a small town (about 50,000 inhabitants), not far from the Tyrrhenian Sea in Northern Italy. The site has been known since the Roman Empire age thanks to the white marble quarries located in the mountains (Alpi Apuane) just behind the urban area. This high quality marble

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is continuously extracted, loaded in large pieces as well as in small debris on trucks, transported to the nearby harbour of Marina di Carrara and then delivered all over the world. About 1000 trucks cross every day the urban area of Carrara, which lies along the road from the quarries to the harbour. In this particular condition, the concentration of Calcium Carbonate ($CaCO_3$) and other related compounds can reach unusual values but – up to now – the "marble transportation" has not been separated from other PM sources. In this work we faced the problem both developing non-conventional analytical approaches for $CaCO_3$ concentration measurement and exploiting the resolving power of PMF.

Usually, Organic (OC) and Elemental (EC) Carbon are the most abundant classes of carbonaceous compounds in PM and the Carbonate Carbon (CC, sometimes referred to as Inorganic Carbon) is often neglected (Chow and Watson, 2002; ten Brink et al., 2004). Moreover, the analytical methods for CC determination are quite scarce. Peculiar situations are reported in the literature with not-negligible CC concentration in PM10 due to erosion, sand storms, and buildings construction (Chow et al., 2003; Arimoto et al., 2004; Querol et al., 2009).

Different methods to solve the problem of the interference due to CC in OC and EC analysis have been proposed so far. Cachier et al. (1989) suggested to treat the samples with HCl smoke to remove CC before the thermal evolution analysis; with this approach, the CC concentration is obtained as the difference between Total Carbon (TC) measured in the same sample without and with the HCl pre-treatment. Presently, the most widespread method for carbon analysis is the thermal-optical determination of OC and EC (Chow et al., 1993; Birch and Cary, 1996). It should be noted that the thermal–optical analysis can be only carried out on PM collected on quartz fibre filters. Chow and Watson (2002) proposed to evaluate the CC content measuring the CO_2 produced when a portion of the filter is attacked with HCl; in this way OC, EC, and CC can be all measured in the same sample. Nevertheless, the exposure of the sample to HCl smokes increases the charring and therefore the uncertainty in the OC/EC separation (Jankowski et al., 2008). It is worthy to note that OC and EC do not correspond to any unique chemical compound and they are operationally defined with a strong dependence on the thermal protocol in use (e.g. Chow et al., 1993; Birch and Cary, 1996; Cavalli et al., 2010). Several inter-comparison studies showed that the CC concentration could be one of the reasons for the large discrepancies among EC values determined by different thermal–optical protocols (Jankowski et al., 2008; Karanasiou et al., 2010).

Jankowski et al. (2008) compared the CC values measured by a particular thermal–optical protocol with the CC concentration evaluated by ionic balance. Actually, the ionic balance is a simple and widely used method for CC quantification: with this approach the possible anionic deficit is totally ascribed to CC (Mihalopoulos et al., 1997; Bardouki et al., 2003; Nicolás et al., 2009). However, there are several drawbacks (Jankowski et al., 2008) like the possible residual acidity in PM, the presence of organic anions (oxalates, short-chain organic acids, etc), and compounds produced by phytoplankton activity in the sea (as MSA, methanesulfonic acid). Moreover, it is not clear if the water-extraction of PM samples can be completely effective with $CaCO_3$. According to Jankowski et al. (2008), $CaCO_3$ is completely soluble using only diluted MSA as solvent and, in this case, the ionic balance would not be applicable with water-extracted samples.

Recently, Perrone et al. (in press) have proposed to quantify carbonates using a new method to deconvolve the evolution curves obtained by thermal–otpical analysis.

Fourier transform infrared spectroscopy (FT-IR) has been used by many authors for the characterization and quantification of PM components (Gilardoni et al., 2009; Maria et al., 2002; Reff et al., 2005, 2007; Russell et al., 2009; Tsai and Kuo, 2006). Coury and Dillner (2008) developed a multivariate calibration method by using the attenuated total reflectance FT-IR (ATR-FTIR) spectroscopy to quantify aerosol organic functional groups and inorganic compounds. Maria et al. (2003) carried out quantitative measurements of organic and inorganic components in submicron aerosol samples. FT-IR has been also applied so far to identify the presence of carbonate in PM samples (Shaka' and Saliba, 2004; Kouyoumdjian and Saliba, 2006; Perrone et al., in press) but – to our knowledge – there are no studies on FT-IR spectroscopy for carbonate quantification in PM collected on Teflon filters.

The novel approach to $CaCO_3$ quantification in PM samples by transmittance FT-IR is the main methodological issue discussed in this work.

2. Material and methods

2.1. Sampling

PM10 samples were collected in a site in the centre of Carrara along the road connecting the quarries to the harbour (Fig. 1). We used a sequential low-volume PM sampler designed according to the US-EPA standard for PM10 (i.e. flow rate $= 1\ m^3\ hour^{-1}$) placed at about 3 m above the ground. We collected 50 PM10 daily samples between July and September 2007. The sampling started every day at midnight and PM was collected on 47 mm Teflon (PTFE) filters with pore size of 2 μm. During the sampling period the trucks flow transporting the marble was about 1000 vehicles per day during working days while became zero in the week-ends and holidays.

2.2. Laboratory analyses

Filters were pre-conditioned for 2 days in a controlled room (temperature: 20 ± 1 °C, relative humidity: 50 ± 5%) and weighed using an analytical balance (sensitivity: 1 μg, electrostatic effects were avoided using a de-ionizing gun). The weighing procedure included several reproducibility tests and controls with certified weights, resulting in a typical accuracy of 3–5 μg and being the PM deposit on each filter in the range 300–2000 μg.

The elemental composition of PM10 was detected by energy-dispersive X-ray fluorescence (ED-XRF) using an ED-2000 spectrometer by Oxford Instruments (Ariola et al., 2006). In the ED-2000 spectrometer the primary X-rays beam is produced by a Coolidge tube ($I_{max} = 1$ mA, $V_{max} = 50$ kV, with an Ag anode). The primary X-ray spectrum can be optimized as for the background to peak ratio

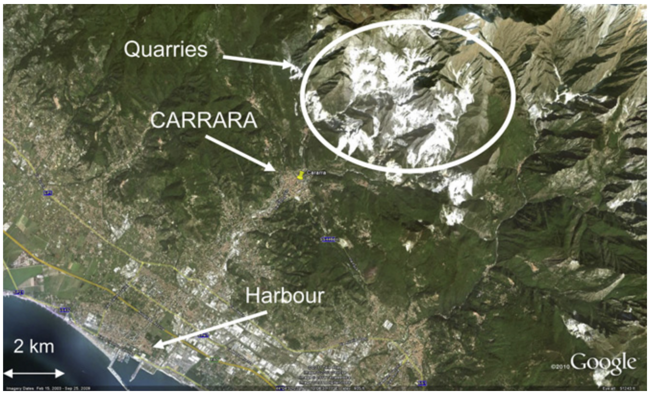

Fig. 1. The study area with the position of the quarries, the urban area of Carrara, and the harbour of Marina di Carrara on the Tyrrhenian Sea (i.e. the portion of the Mediterranean Sea between Italy and the islands of Corsica, Sardinia, and Sicily).