Determination of local source profile for soil dust, brake dust and biomass burning sources.

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Knowledge on the main emission sources and their relative importance is essential for policy makers to define effective pollution reduction strategies. Such knowledge can be gained by receptor modeling using e.g. the chemical mass balance model (CMB). For a successful application of CMB all important sources must be known and information must be available on representative emission profiles. Speciation profiles of emission sources can be found in literature and extensive databases are available (U.S. E.P.A., 2002). However, it is preferable to use profiles representing the actual sources present in the area whenever is possible. For the Lombardy region, previous studies have demonstrated the importance of soil and fugitive dust, biomass burning and brake lining dust (Regione Lombardia, ARPA Lombardia, Fondazione Lombardia per l'Ambiente, 2008; AA.VV., 2006).

The goal of this work is to report our methodology used to determine 'local' source profiles of soil dust, domestic wood burning and brake lining dust, to be used for example in the CMB applications. To investigate the model sensitivity, simulations were carried out for several sites with different local and no-local profiles.

Introduction

The set-up of strategies for the abatement of ambient particulate matter (PM) requires quantitative knowledge on the contributions from individual sources. PM sources are many, ranging from local ones with a limited spatial impact, to sources contributing on a regional scale. Effective abatement strategies must be based upon a quantitative knowledge of the main sources. In this paper we present the methodology used to derive local emissions profiles for significant sources of PM in the Lombardy region. The obtained profiles will form the basis for source apportionment through receptor modeling.

Methods

This section describes a methodology for source sampling, which was developed to be consistent with protocols used for ambient air sampling (Chow et al., 2007) while producing homogeneous (laminar flow), thin layer samples on filters compatible with XRF analysis.

The concentrations of a range of elements and compounds in the samples were determined using different analytical methods. Ions were analyzed by ion chromatography after extraction with Milli-Q water in an ultrasonic bath. Polyaromatic Hydrocarbons (PAH) were measured by high pressure liquid chromatography ((B(a)Pyrene, B(a)Anthracene, B(b)Fluoranthene, B(k)Fluoranthene, Indeno(1,2,3-c,d)Pyrene, dB(a,h)Anthracene, Fluoranthene, Pyrene, Chrysene, B(g,h,i)Perylene)). Organic and elemental carbon (OC and EC, respectively) were determined by Thermogravimetric Analysis/Fourier Transformed Infrared Spectroscopy and by thermal/optical transmittance. The analysis of trace elements was performed using a system with a polarized X-ray beam, which allows for a significant reduction of spectral background.

1.1 Soil Dust

For the derivation of soil dust profiles for the receptor sites information related to soil utilization in the area around was collected: extension of asphalted roads, presence or absence of farming, presence of industries with emissions that can contaminate soil (e.g. cement producers and steelworks, Furthermore local observations were carried out by tracking all events than could contribute to dust re-suspension, such as cars or farming vehicles crossing over eroded road surfaces and non-asphalted road shoulders. Based on the collected information the sampling points were decided. Samplings were done during clear sky weather conditions with absence of recent strong winds and rain. Sampling was carried out with a brush and a spade, collecting a dust from about 100 cm^3 of surface. The samples were air-dried in the laboratory for at least 2 days after which, they were sieved (mesh 2 mm through 125 µm) and re-suspended in a specially designed system to collect soil dust on filters compatible with the chemical analysis. The system for re-suspension consisted of a modified 3 L tailed flask with a standard cone for Total Particle Size (TPS, complying with regulation DPR203/88) inserted through the mouth of flask with its proper grid and a homogenization chamber vertically placed (aluminum cylinder 25 cm length, diam. 50 mm) and connected trough a pipe (1.5 m length and 50 mm diameter) with two TPS cones. Into the upper standard cone was inserted the sampling filter. The flow was adjusted with a low-volume pump and the first sample was a dummy, aimed at bringing the pneumatic system to steady state and to allow suspended dust to cover all internal surfaces of the system. Further samples were collected for analyses. The system was run with the flow of 10±5 l/min and exposition time of 10-20 minutes (depending on type of dust). For each sample at least 5 filters were collected in order to verify the reproducibility of data. The filters were weighed using the same procedure as for ambient aerosol and stored at -20 ^{o}C until analysis.

1.2 Biomass burning

Domestic wood combustion is considered a major source of particulate matter in the Alpine region (Schmidl et al., 2008), but wood stoves and open fires are also used throughout Lombardy for recreational purposes. Literature provides averaged profiles for wood burning but preliminary experiments in our laboratory have yielded large differences in terms of color and smell of the collected filters indicating a strong dependence on combustion phase (lighting, embers, …) and kind of burned wood (i.e. percentage of resin). For the homologation of domestic wood stoves, emission factors are calculated but the sampling conditions are not real. The methodology used in the present project is aimed at reproducing real conditions and investigate different facets during the sampling phase in order to derive representative averaged profiles for selected kinds of burned biomass.

Realistic experiments with biomass burning were carried out in a typical house of the Valtelline valley equipped with a fireplace and a pellet stove with two independent chimneys. Local habits were studied by interviewing inhabitants of the valley. It was revealed, that in addition to wood and pellet combustion for residential heating purposes also mixed brushwood, such as gardens foliage or grapevine brushwood is usually combusted in the open air. Thus, PM samples were collected from following experiments: combustion of pine and beech wood in a closed fireplace, combustion of pellet in a proper stove and outdoor combustion of mixed biomass (brushwood).

To facilitate the cooling of the exhaust a specially designed aluminum "frame" was inserted into the chimneys (the temperature in the sampling point was below 40° C). On this frame Piteau pipes were inserted and the exhaust was pumped through transparent silicon pipes (for a visual inspection of condensation) by a pneumatic circuit connected with a low-volume pump. Repeated tests were executed with 3 simultaneous samples, in order to verify the reproducibility of data, and on different filters types compatible with the chemical and physical characterization. The chimneys were pre-heated to obtain conditions for averaged profiles. Due to the fact that the quantity emitted PM was not known ex-ante, the first set of filters were used to calibrate the sample flow and exposition time. For this reason, measurement was made with a flow of 20±5 l/min and exposition time of 10-20 minutes (depending on type of filters).

To sample PM in the outdoor combustion experiments, an aluminum frame was put on a barbecue pre-cleaned (to avoid eventual residues of previous combustions). Identical sampling methodology and instruments were used as for indoor experiment (including water cooling of exhaust). In the first series common garden brushwood was studied (leaves of chestnut and oak) and in the second series (after a proper cleaning) grapevine brushwood was studied. Individual filters were exposed either during the burning phase, or during the embers phase, which in case of brushwood can be significantly long). The filters were weighed using the same procedure as for ambient aerosol and stored at -20 ^{o}C until analysis.

The appearance in terms of color and smell of the collected filters was very different from experiment to experiment. The PM from combustion in the closed fireplace was black due to the presence of elemental carbon and the ones from the pellet stove were almost beige whereas the PM from outdoor combustion of foliage was almost yellow. In The differences in terms of smell were associable with aromatic compounds and sugar anhydrides and were specific for the different kinds of biomass.

1.3 Brakes

A brake-ware profile was also derived. In this case PM samples were collected in a mechanical shop with technical support of the staff. Using a brush, PM settled on the internal surface of the wheel rim of several vehicles (cubic capacity, age and coverage) was collected. This material was sampled to present the real mixture of PM coming from brake discs and brake pads wearing out. The fact that PM weight had no variations when heated up to 100° C and leached with water, showed that ionic components were not present in significant amounts. In addition, from the color there was no evidence for the presence of carbon. The sample was deposited on polycarbonate membranes for elemental ED-XRF analysis.

Results

In Table 1 and 2 the source types and the derived source profiles (g/g of emitted PM) are shown. When a species was below the detection limit it was attributed the value of zero in the profiles. When a species was not analysed in a particular source there is a void in the profile.

Table 1. Source Type and Code.

Source Type	Code
Suburban Paved Road (Cantù)	SUPVR-C
Urban Paved Road (Pero)	UPVR-P
Composite Rural Soil (Erba)	RSOILMIX-E
Brake Dust	BKDUST
Pellet Combustion	PELLET
Closed fireplace (Pine)	CBURN-P
Closed fireplace (Beech)	CBURN-B
Composite Wood and Pellet Combustion	MIXBURN
Open Burning (Branches of grapevine)	OBURN-GV
Open Burning (Leaves of chestnut and oak)	OBURN-CO

Table 2 Source Profiles.

Species	SUPVR-C	Source Code UPVR-P	RSOILMIX-E	BKDUST	MIXBURN
Mg	1.7E-2±6.7E-3				
Al	5.1E-2±6.3E-3	2.3E-2±4.8E-3	1.5E-2±8.4E-3	7.4E-3±1.4E-3	2.9E-3±5.5E-5
Si	1.4E-1±1.4E-2	7.6E-2±1.6E-2	5.2E-2±3.0E-2	2.2E-2±4.3E-3	6.2E-4±9.5E-5
S	4.5E-3±6.1E-4	2.0E-3±6.0E-4	1.3E-3±1.7E-3	6.8E-3±1.1E-3	3.0E-2±2.3E-4
Cl	1.5E-3±5.6E-4	3.5E-3±2.3E-3	3.4E-4±5.1E-4		1.3E-2±4.9E-4
K	1.1E-2±1.2E-3	8.4E-3±1.4E-3	6.2E-3±3.4E-3	2.1E-3±3.9E-4	1.1E-1±1.1E-2
Ca	7.3E-2±8.9E-3	2.8E-2±4.9E-3	5.1E-2±4.3E-2	1.3E-2±2.8E-3	1.4E-2±2.6E-3
Ti	4.2E-3±6.7E-4	3.5E-3±5.6E-4	1.4E-3±7.3E-4	1.1E-3±8.9E-5	6.1E-4±5.5E-5
V	1.2E-4±7.4E-5	1.7E-4±3.2E-5	9.0E-5±5.0E-5	7.4E-5±8.1E-6	
Cr	1.5E-4±5.1E-5	1.3E-4±3.2E-5	7.0E-5±6.0E-5	4.0E-3±2.3E-4	6.0E-5±1.0E-4
Mn	7.5E-4±9.2E-5	6.6E-4±1.2E-4	3.5E-4±1.7E-4	3.0E-3±2.1E-4	3.3E-3±7.8E-4
Fe	3.8E-2±7.9E-3	3.6E-2±5.8E-3	1.4E-2±6.9E-3	4.1E-1±2.9E-2	5.2E-4±1.5E-4
Ni	1.0E-4±1.5E-5	6.3E-5±1.4E-5	5.0E-5±3.0E-5	1.9E-4±1.6E-5	1.3E-5±1.7E-5
Cu	3.7E-4±7.4E-5	3.0E-4±6.3E-5	1.3E-4±1.0E-4	3.3E-2±2.1E-3	1.9E-4±5.3E-5
Zn	9.8E-4±1.3E-4	8.8E-4±2.1E-4	3.9E-4±2.7E-4	9.9E-3±6.0E-4	6.9E-3±2.9E-5

Species					
Br	2.2E-5±7.9E-7	7.7E-6±3.6E-6	2.0E-5±2.0E-5		4.7E-5±5.8E-6
Rb	8.1E-5±1.3E-5				
Pb	2.5E-4±9.5E-5	3.2E-4±7.3E-5	9.0E-5±5.0E-5	2.1E-4±2.6E-5	1.6E-4±3.2E-5
Sr	3.1E-4±1.2E-4	2.0E-4±3.3E-5	1.6E-4±9.0E-5	9.3E-5±1.8E-5	4.4E-4±5.5E-5
Sn	4.5E-5±2.9E-6		4.3E-3±2.4E-3		3.2E-3±1.2E-4
Ba	6.5E-4±1.0E-4		1.2E-4±8.0E-5	1.0E-3±2.2E-4	3.0E-4±5.8E-5
Cd			2.2E-3±2.1E-3	1.3E-3±5.0E-5	3.3E-5±1.2E-5
NH4+	3.7E-4±2.6E-4				2.3E-4±8.0E-5
Ca2+	4.2E-3±2.0E-3				
Cl-	1.1E-3±7.5E-4				2.1E-2±5.2E-3
NO3-	1.3E-3±1.3E-3				8.1E-3±1.2E-3
K+	2.7E-4±2.3E-4				
Na+	4.8E-3±2.1E-3				
SO42-	8.7E-4±2.2E-4				1.0E-1±9.7E-3
OC	1.3E-1±1.5E-2	6.9E-3±9.5E-3			3.1E-1±1.1E-1
EC	5.7E-3±1.2E-3	9.4E-3±2.3E-3			1.2E-1±5.7E-2

Table 2 Continued.

	Source Code			
Species	PELLET	CBURN-P	CBURN-B	OBURN-GV	OBURN-CO
Mg	1.7E-3±1.1E-3	1.1E-3±4.7E-4	7.4E-4±5.1E-4	0.0000±0.0000	5.3E-3±3.1E-3
Al	7.0E-3±1.4E-4	8.3E-4±1.7E-4	1.9E-3±3.6E-4	6.7E-4±1.6E-4	2.3E-3±6.1E-4
Si	1.5E-3±1.2E-4	3.0E-4±1.9E-4	4.0E-4±2.4E-4	8.5E-4±3.6E-4	4.2E-3±9.8E-4
S	7.9E-2±1.1E-3	5.2E-3±1.2E-3	1.4E-2±3.4E-3	2.9E-3±5.0E-4	1.9E-3±2.3E-4
Cl	2.7E-2±1.4E-3	4.4E-3±6.4E-4	8.5E-3±1.1E-3	1.7E-3±2.0E-4	9.4E-4±1.3E-4
K	2.9E-1±1.1E-2	2.6E-2±6.8E-3	6.8E-2±1.6E-2	1.7E-2±3.2E-3	3.5E-3±2.1E-4
Ca	3.1E-2±6.5E-3	3.8E-3±1.2E-3	5.3E-4±1.0E-4	2.9E-3±4.9E-4	2.0E-2±5.3E-3
Ti	5.6E-5±2.9E-6	3.2E-5±7.7E-6	0.0000±0.0000	1.7E-5±6.6E-6	9.3E-5±3.1E-5
V	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000
Cr	0.0000±0.0000	3.4E-5±1.6E-5	7.3E-5±4.9E-5	0.0000±0.0000	0.0000±0.0000
Mn	9.4E-3±1.5E-3	4.3E-4±2.5E-4	8.5E-5±1.4E-5	6.8E-5±2.2E-5	2.0E-3±6.1E-4
Fe	7.1E-4±1.4E-4	4.0E-4±1.3E-4	2.9E-4±2.2E-4	2.1E-4±3.2E-5	1.2E-3±4.0E-4
Ni	4.4E-5±3.1E-5	1.6E-5±3.8E-6	4.7E-5±2.3E-5	0.0000±0.0000	0.0000±0.0000
Cu	5.2E-4±8.8E-5	3.1E-5±8.2E-6	5.8E-5±9.0E-6	2.8E-5±1.8E-5	0.0000±0.0000
Zn	1.8E-2±1.6E-4	1.8E-3±2.0E-4	3.4E-4±7.8E-5	8.6E-5±2.6E-5	2.4E-4±2.8E-5
Br	1.1E-4±2.5E-6	3.6E-5±6.0E-6	3.2E-5±5.7E-6	0.0000±0.0000	3.6E-5±8.2E-6
Rb	1.3E-3±8.0E-5	1.2E-4±2.8E-5	2.3E-4±6.8E-5	3.4E-5±6.3E-6	2.2E-5±5.2E-6
Pb	0.0000±0.0000	7.0E-5±1.2E-5	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000
Ba	7.3E-4±1.0E-4	2.1E-4±5.5E-5	2.6E-4±9.0E-5	2.0E-4±7.6E-5	4.5E-4±1.3E-4
NH4+	4.3E-4±2.9E-5	1.1E-3±1.6E-4			
Cl-	1.6E-2±1.3E-3				
NO3-	1.2E-2±1.8E-3				
SO42-	1.9E-1±1.2E-2	1.2E-2±1.8E-3			
OC	7.2E-2±4.8E-3	4.2E-1±8.1E-2	5.5E-1±5.9E-2	6.2E-1±9.9E-3	6.2E-1±2.0E-2
EC	1.2E-5±1.2E-5	2.6E-1±3.8E-2	3.3E-1±5.8E-2	2.0E-2±5.8E-3	3.4E-2±9.8E-3
Ant	0.0000±0.0000	7.3E-4±1.7E-4			
Fluo	1.1E-4±9.0E-5	3.2E-3±2.9E-3			
Pyr	4.3E-4±1.9E-4	3.8E-3±1.4E-3			
B(a)A	5.2E-6±2.9E-6	3.1E-3±1.2E-3			
Chry	2.2E-5±1.7E-5	2.8E-3±8.9E-4			
B(b)F	1.5E-5±8.3E-6	2.6E-3±6.4E-4			
B(k)F	2.9E-5±6.6E-6	1.7E-3±3.8E-4			
B(a)P	2.8E-5±4.0E-6	3.0E-3±7.9E-4			
Db(ah)A	1.0E-6±3.5E-7	1.4E-4±6.3E-5			
B(ghi)P	3.0E-5±1.7E-6	2.0E-3±1.0E-3			
I(123cd)P	1.1E-4±4.2E-5	5.6E-3±2.5E-3			

The obtained profiles have been used as input for CMB modelling in various projects of the Lombardy region (using the EPA CMB 8.2 software) and performed significantly better than profiles obtained from the US-EPA Speciate library. Some examples are in references (Belis et al., 2007; Larsen et al., 2008; Colombi et al., 2008; Colombi et al., 2010).

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