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THE ACTUAL CARBON EMISSIONS FROM BB DOMESTIC HEATING IN THE ALPS AND THEIR IMPACT ON AIR QUALITY

Edited by PP2 ARPA Valle d'Aosta   18. 12. 2019

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1. Biomass burning effects in the Alpine Region

The Alpine area is characterized by a climate with cold winters that leads its inhabitants to invest huge resources for domestic heating. In recent years, due to the high price of liquid and gaseous fossil fuels, there has been a progressive return to the use of wood fuel of lower cost and easier to find thanks to the woods available in these regions.

As regards the environmental impacts, this activity has an ambivalent effect: if due to climate change the use and consequent production of wooden resources makes it possible to contain and balance the emissions of carbon dioxide that generate Climate Change, due to the air quality this combustion involves the emission of particulate matter containing micro-pollutants that are harmful to the environment and health.

The Environmental Protection Agencies present in the Alpine regions have the task of monitoring the emissions of greenhouse gases and the concentrations of pollutants in the atmosphere; their data therefore allows to verify the impacts of wood combustion due to residential heating.

2. Pollutants emissions in the project area

The emissions of pollutants into the atmosphere are not "measured" data in the environment, but are calculated on the basis of the emission sources present in a given territory. These calculated data are stored in the so-called "emission inventories" which contain the data divided by pollutant, type of emission source, territorial unit (typically the municipality) and reference year.

To quantify the emissions of pollutants from the different sources, both direct measurements (for example for industrial plants with chimney measurements) and estimates based on the definition of an activity indicator and an "emission factor" are carried out (in particular for diffuse sources such as heating systems and road traffic).

Once data related to the indicators of the considered activity have been collected, it is possible to estimate the pollutants emissions using appropriate emission factors with the formula

$$E = A \times F$$

where

• E is the emission produced (expressed as a mass in tons or kilograms);

• A is an activity indicator (for example the quantity of fuel used for heating systems or the number of vehicles transiting on a road section);

• F is the emission factor for that activity expressed in grams / unit of activity.

To have a representation relative to the entire Alpine arc, from West to East, the data of the total annual emissions of the following regions were collected:

- Auvergne – Rhône Alpes (France)
- Valle d'Aosta (Italy)
- Piemonte (Italy)
- Lombardia (Italy)
- Veneto (Italy)
- Provincia di Bolzano (Italy)
- Provincia di Trento (Italy)
- Friuli Venezia Giulia (Italy)
- Steiermark (Austria)
- Slovenia (only national data)

The map below shows the regions of the BBClean project partners.
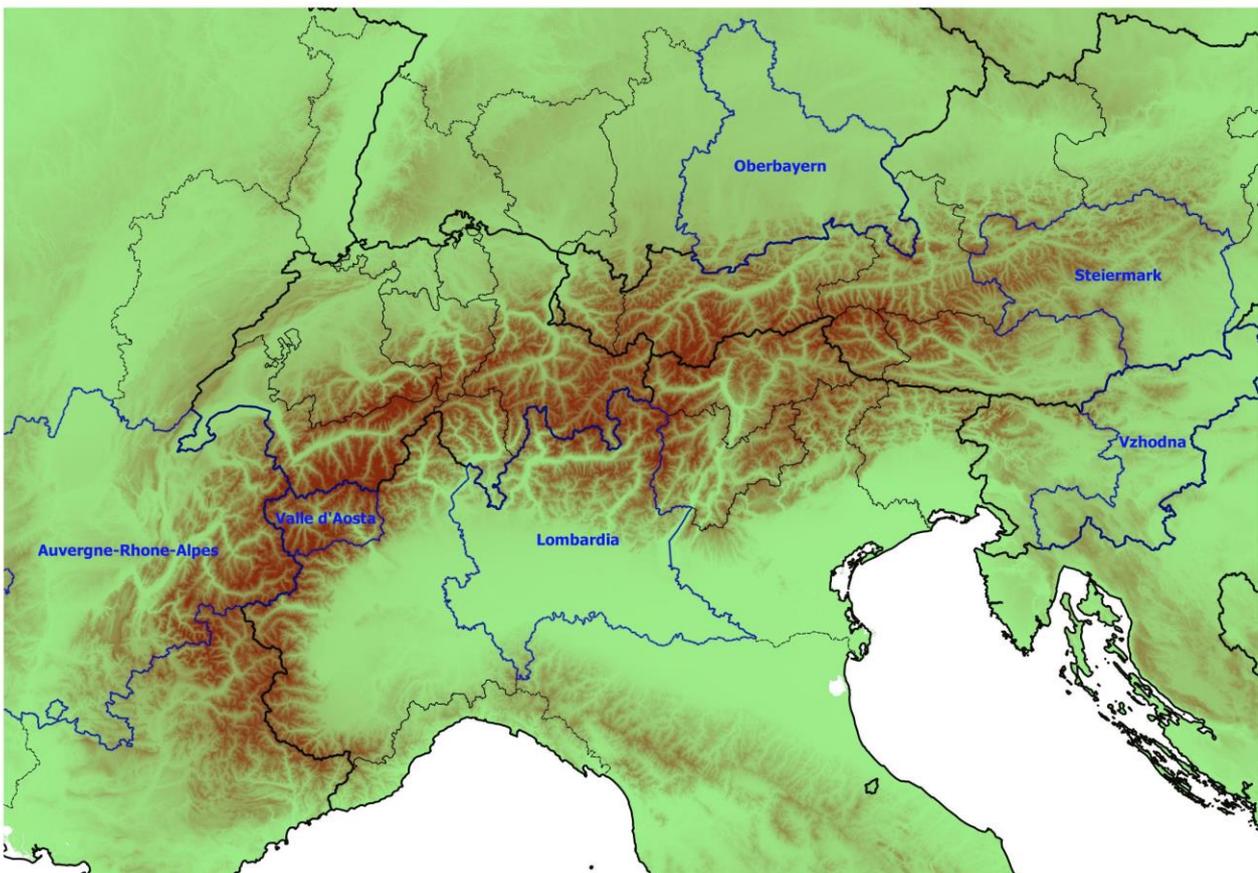

Fig. 1 – The Regions of the project Partners

Since the regional territories often include mountain areas, but also lowland areas, only the emissions data for the municipalities belonging to the Alps have been requested.

The following air pollutants have been considered along with one greenhouse gas:
- Nitrogen Oxydes (NO$_x$)
- Particulate matter (PM10 and PM2.5)
- Policyclic Aromatic Hydrocarbons (PAH)
- Carbon dioxide (CO$_2$)

The emission sources have been categorized under the following groups:
- Domestic heating with biomass
- Domestic heating not wood
- Road traffic
- Agriculture and Manure
- Other sources

the following graphs and tables show the data referring to the different emissions divided into regions, sectors and reference year.

- **Nitrogen Oxydes (NO$_x$)**

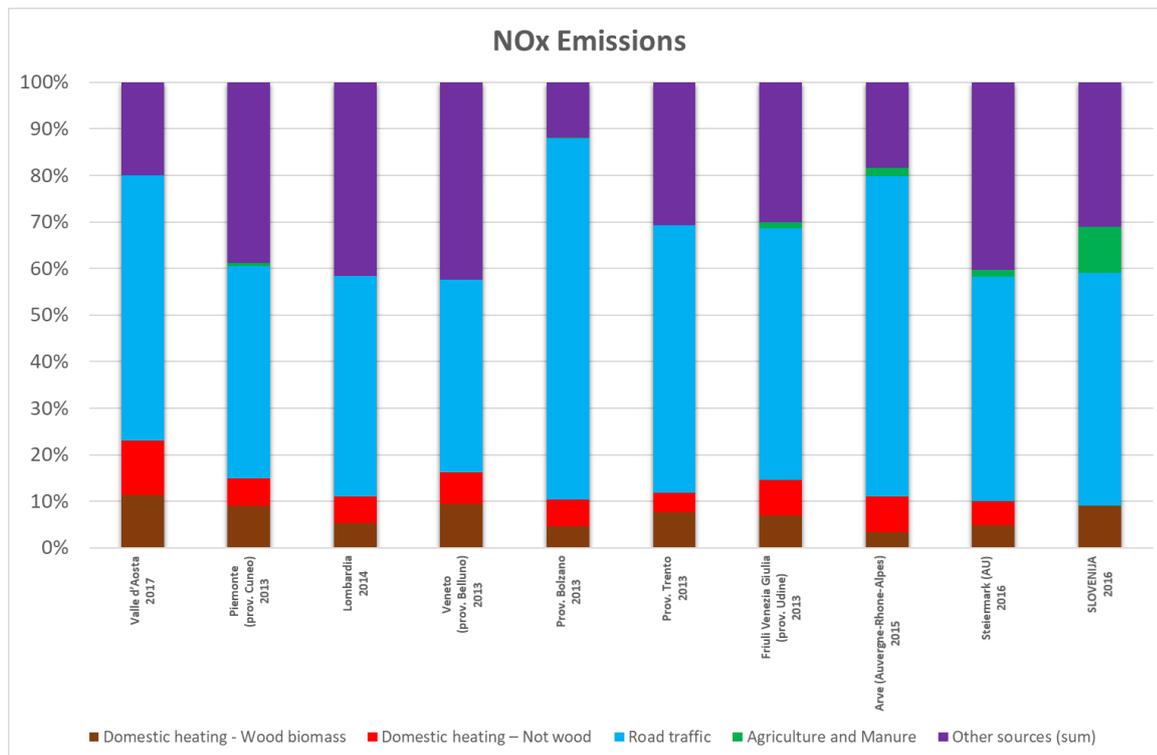| NOx emissions (tonn/year)	Valle d'Aosta 2017	Lombardia 2014	Veneto – Belluno 2013	Prov. Trento 2013	Arve (Auvergne-Rhone-Alpes) 2015	Steiermark (Austria) 2016	SLOVENIJA 2016
Domestic heating Wood biomass	171	954	321	720	66	1026	3330
Domestic heating – not wood (sum)	177	1016	236	394	150	1075	
Road traffic	862	8512	1422	5408	1342	10043	18500
Agriculture and Manure	0	5	1	6	33	306	3700
Other sources (sum)	301	7476	1457	2882	359	8384	11470
TOTAL	1511	17963	3437	9411	1950	20834	37000

Fig. 2 – Sectorial contributions of NOx emissions per alpine region

Data collected clearly show that the main source of nitrogen oxide emissions is road traffic. Wood-burning residential heating contributes less than 10%.

- **Particulate matter PM10**

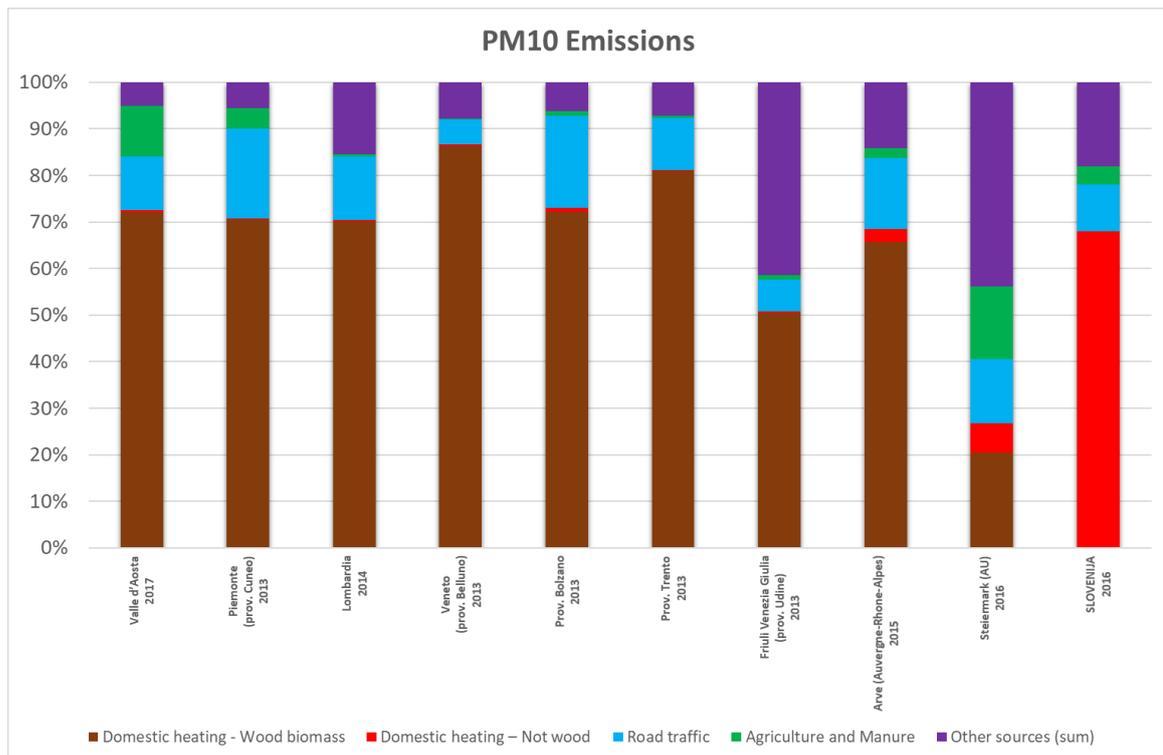| PM10 emissions (tonn/year)	Valle d'Aosta 2017	Lombardia 2014	Veneto – Belluno 2013	Prov. Trento 2013	Arve (Auvergne-Rhone-Alpes) 2015	Steiermark (Austria) 2016	SLOVENIJA 2016
Domestic heating Wood biomass	501	3277	1413	2524	399	1007	8840
Domestic heating – not wood (sum)	3	20	7	5	17	318	
Road traffic	80	638	87	351	92	2949	1300
Agriculture and Manure	76	19	3	16	13	1050	520
Other sources (sum)	35	725	128	223	86	1550	2340
TOTAL	695	4679	1638	3119	606	6874	13000

Fig. 3 – Sectorial contributions of PM10 emissions per alpine region

For PM10 the major contribution (around 70%) comes from domestic wood heating.
The Austrian data are affected by a relevant domestic heating under-estimation.
Slovenian domestic heating emissions data do not distinguish the type of fuel.

http://www.alpine-space.eu/projects/bb-clean
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- **Particulate matter PM2.5**

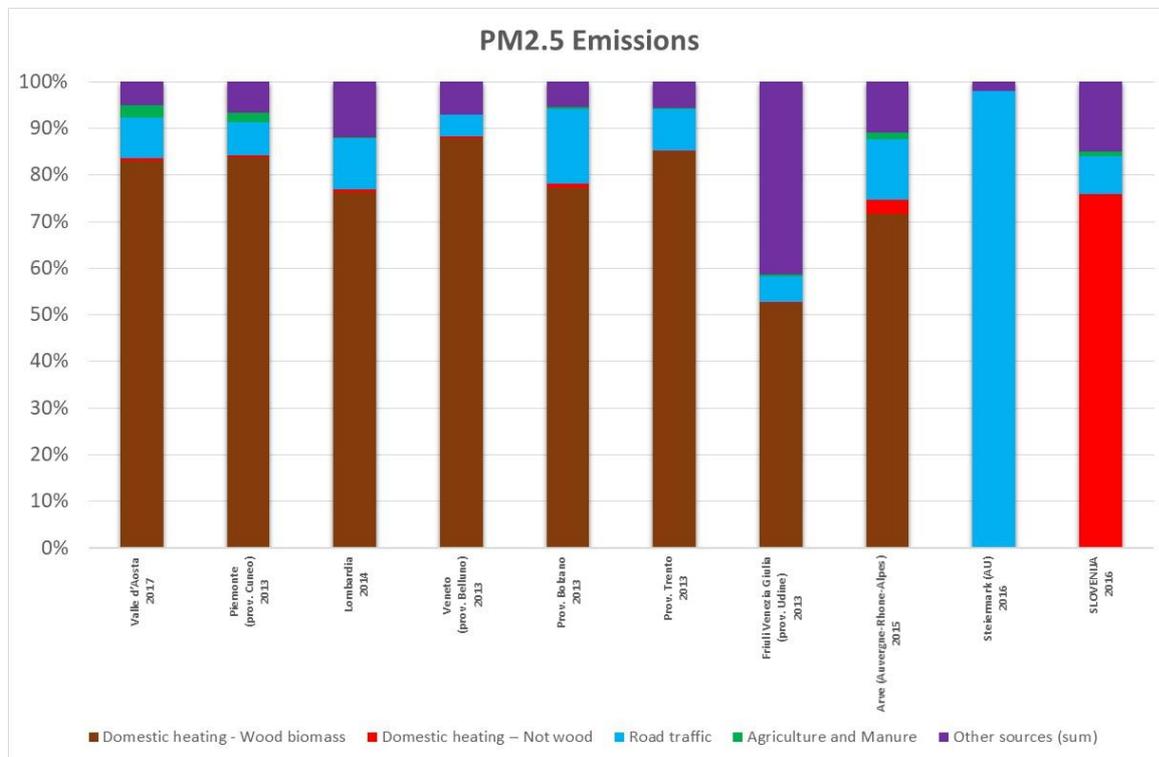| PM2.5 emissions (tonn/year)	Valle d'Aosta 2017	Lombardia 2014	Veneto – Belluno 2013	Prov. Trento 2013	Arve (Auvergne-Rhone-Alpes) 2015	Steiermark (Austria) 2016	SLOVENIJA 2016
Domestic heating Wood biomass	491	3196	1398	2494	390	*	9100
Domestic heating – not wood (sum)	3	20	7	5	16	*	
Road traffic	52	462	74	261	71	1114	960
Agriculture and Manure	15	8	1	7	8	0	120
Other sources (sum)	30	500	111	166	59	22 (*)	1800
TOTAL	591	4185	1590	2933	544	1136	12000

Fig. 4 – Sectorial contributions of PM2.5 emissions per alpine region

As for PM10, the strong link between wood-fired domestic heating and PM emissions is evident.
For the Steiermark region the domestic heating is reported in "other sources", and the under-estimation of the domestic heating emissions is always relevant.
Slovenian domestic heating emissions data do not distinguish the type of fuel.

- **Policyclic Aromatic Hydrocarbons (PAH)**

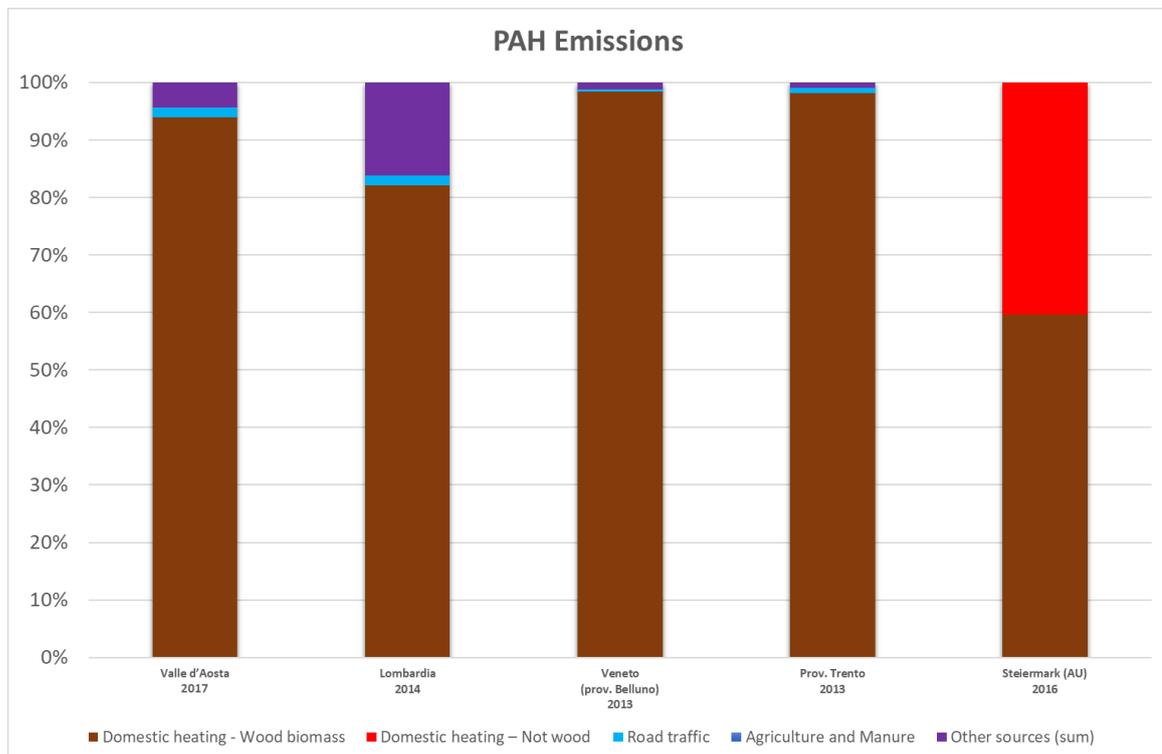| PAH emissions (kg/year)	Valle d'Aosta 2017	Lombardia 2014	Veneto – Belluno 2013 (BaP)	Prov. Trento 2013	Steiermark (Austria) 2016 (BaP)
Domestic heating Wood biomass	341	3124	567	3520	767
Domestic heating – not wood (sum)	0	1	0,1	0	519
Road traffic	6	64	2	35	
Agriculture and Manure	0	0	0	0	
Other sources (sum)	16	618	7	33	
TOTAL	363	3806	576	3588	1286

Fig. 5 – Sectorial contributions of PAH emissions per alpine region

The Polycyclic Aromatic Hydrocarbons are almost entirely emitted from domestic wood appliances, so that they represent their atmospheric "tracer" in the alpine areas.

- **Carbon dioxide (CO₂)**

CO₂ emissions (tonn/year)	Valle d'Aosta 2017	Lombardia 2014	Veneto – Belluno 2013	Prov. Trento 2013	Arve (Auvergne-Rhone-Alpes) 2015	Steiermark (Austria) 2016
Domestic heating Wood biomass	87610 *	0	327700 *	0	0	0
Domestic heating – not wood (sum)	258440	1495	357803	824	204	1406
Road traffic	290782	2299	386118	1309	347	3257
Agriculture and Manure	0	0	0	0	4	172
Other sources (sum)	183727	3676	480175	204	170	6388
TOTAL	820559	7470	1224096	2337	724	11223

(*) emissions assessed, but offset by forest absorption
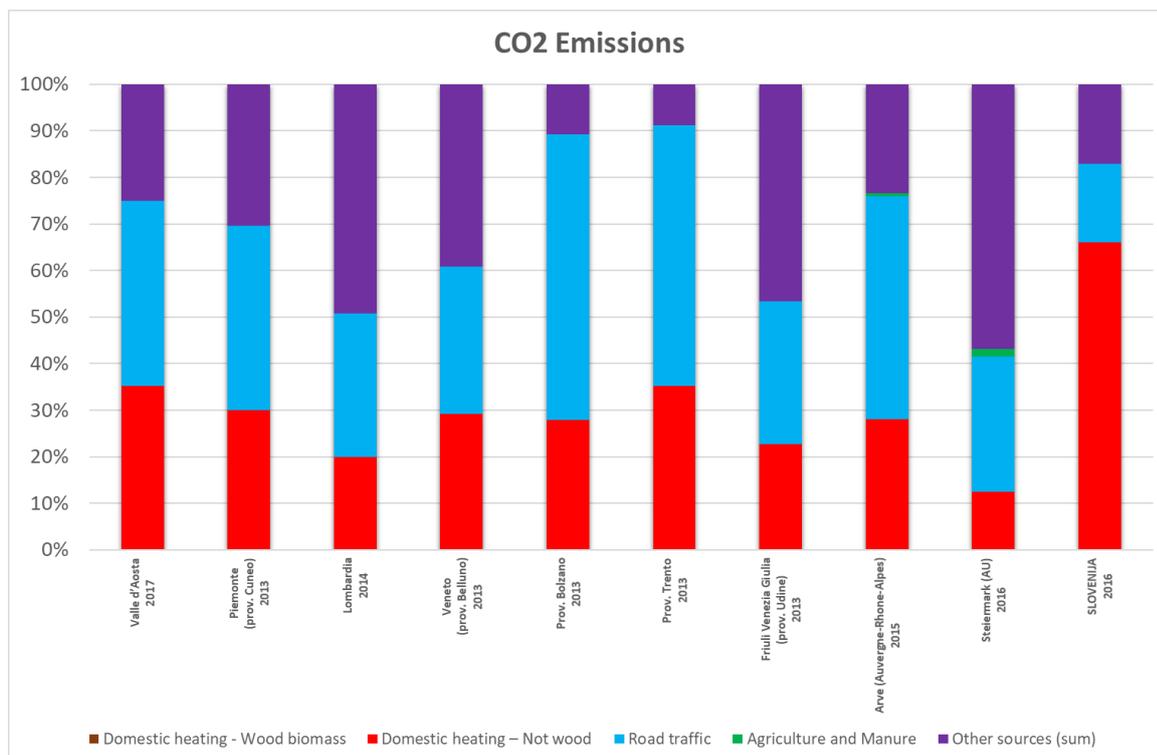

Fig. 6 – Sectorial contributions of CO₂ emissions per alpine region

The local emissions of carbon dioxide in the Alpine areas considered are highly differentiated: they are mainly due to road traffic, for the Italian regions, to domestic heating for Slovenia and to industry (other sources) for the Austrian side.

3. Air quality monitoring data collection

From the analysis of the emission inventories for the alpine areas previously presented, the following pollutants are particularly correlated to residential wood combustion:

- ➢ Particulate matter (PM10 and PM2.5)
- ➢ Benzo-a-Pyrene (the most important Policyclic Aromatic Hydrocarbon)

For this analysis we collected data on average annual concentrations measured in the air quality monitoring stations present in the mountain areas of the regions of the BBClean Partners and of some Observers.

The monitoring stations considered are those shown in the table with the indication of the monitored compounds and the reference year for the measurements.

Localisation	Region	PM10	PM2.5	B(a)P
Passy	AURA - France	2018	2018	2018
Sallanches	AURA – France	2018		
Chamonix	AURA – France	2018		
Aosta – p.zza Plouves	Valle d'Aosta – Italy	2018	2018	2018
Aosta – via Liconi	Valle d'Aosta – Italy	2018	2018	2018
Etroubles	Valle d'Aosta – Italy	2018	2018	
Darfo	Lombardia – Italy	2017	2017	2017
Moggio	Lombardia – Italy	2017	2017	2017
Bormio	Lombardia – Italy	2017	2017	
Sondrio	Lombardia – Italy	2017	2017	2017
Belluno	Veneto – Italy	2018	2018	2018
Feltre	Veneto – Italy	2018	2018	2018
Pieve di Alpago	Veneto – Italy	2018		
Trento PSC	Trentino – Italy	2018	2018	2018
Rovereto	Trentino – Italy	2018	2018	
Borgo Valsugana	Trentino – Italy	2018	2018	
Kapfenberg	Steiermark – Austria	2018		
Bruck an der Mur	Steiermark – Austria	2018		
Mürzzuschlag	Steiermark – Austria	2018		
Zeltweg	Steiermark – Austria	2018		
Judenburg	Steiermark – Austria	2018		
Liezen	Steiermark – Austria	2018		

Localisation	Region	PM10	PM2.5	B(a)P
Bad Hindelang	Bavaria – Germany	2018		
Oberaudorf	Bavaria – Germany	2018		
Lindau	Bavaria – Germany	2018		
Velenje	Vzhodna – Slovenia	2018		
Celje	Vzhodna – Slovenia	2018		
Zavodnje	Vzhodna – Slovenia	2017		

The following graphs show the annual average concentration values measured in the monitoring stations compared to the European regulatory limit (EU Directive 2008/50/EC) and to the most restrictive one of the WHO concerning human health.
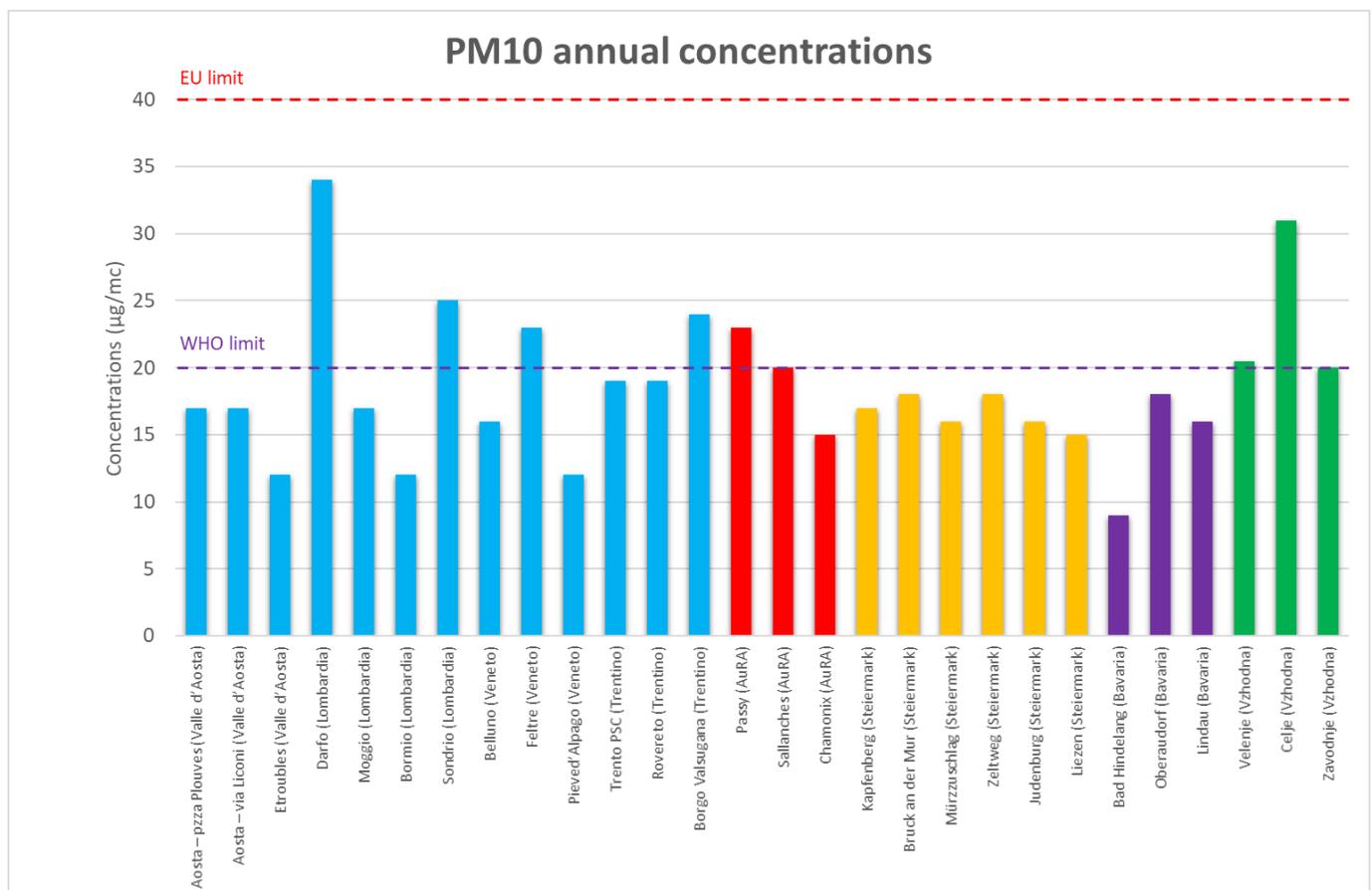
Fig. 7 – Annual mean concentrations of PM10 measured in the alpine regions

PM10: the measured values are all lower than the European regulatory limit, but many data exceed or come close to the WHO limit demonstrating how, even for areas that are sparsely inhabited such as the Alpine ones, PM emissions must be carefully monitored.
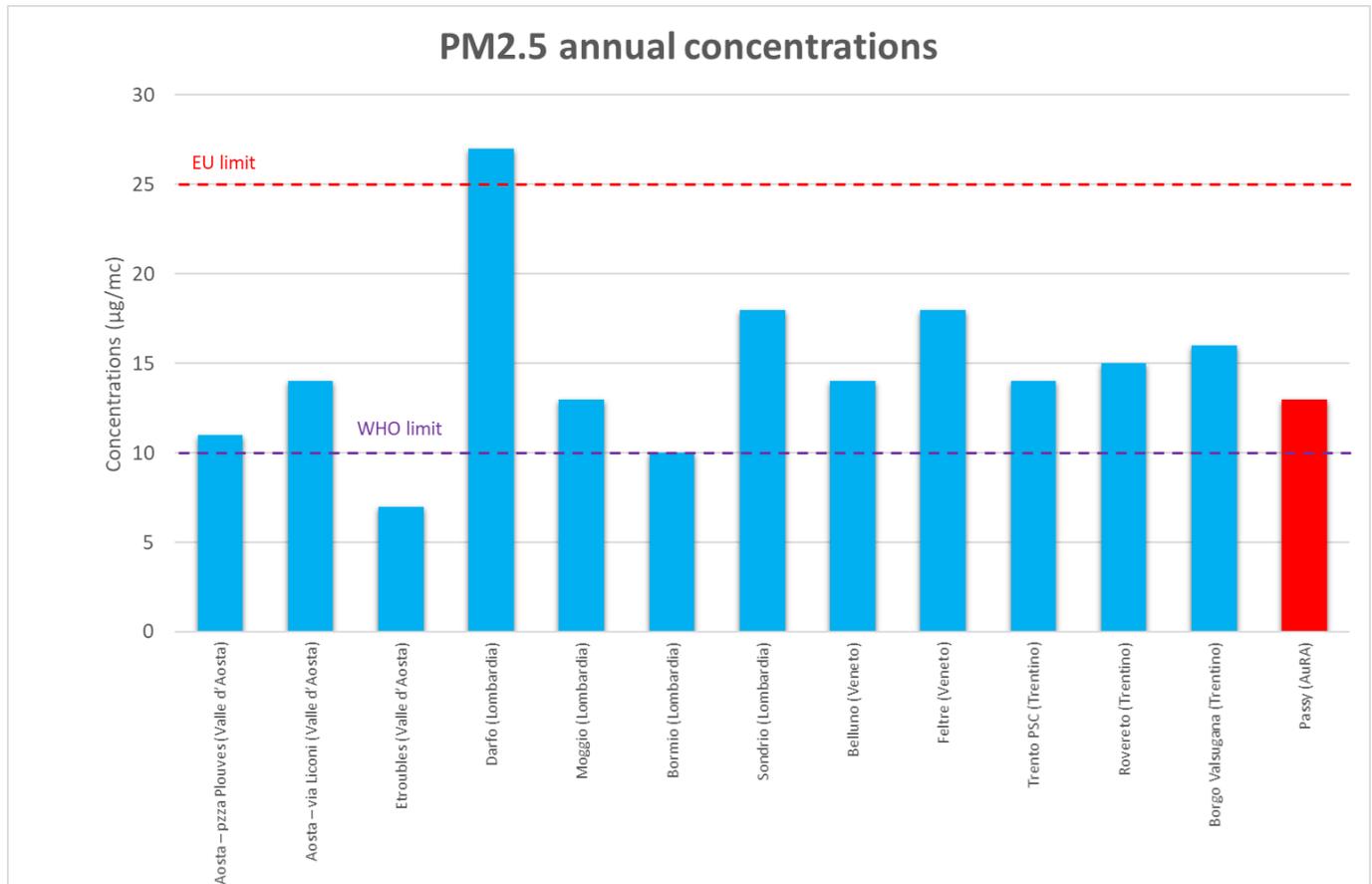
Fig. 8 – Annual mean concentrations of PM2.5 measured in the alpine regions

PM2.5: for the finest particle size measurements of particulate matter, which are those most closely linked to combustion activities, the situation is more critical than for PM10: a monitoring station in Lombardy exceeds the European limit and almost all exceed the WHO limit.
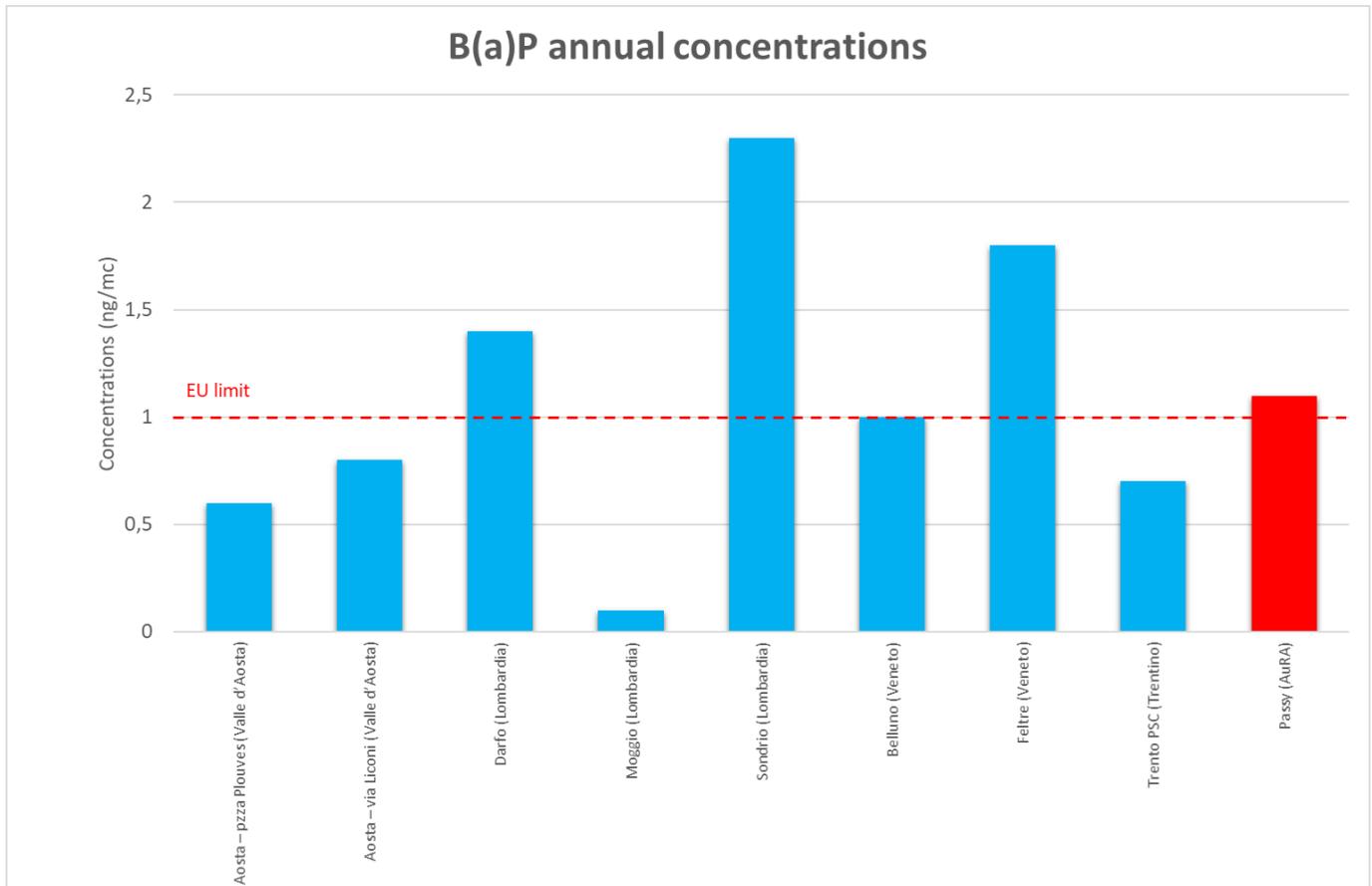
Fig. 9 – Annual mean concentrations of B(a)P measured in the alpine regions

Benzo-A-Pyrene: in five of the nine monitoring stations considered in alpine areas, the European regulatory limit is exceeded.

Given that this micro-pollutant is emitted almost exclusively from the combustion of wood and derivatives, Benzo-A-Pyrene shows us how the impact of that human activity is particularly important for the environment and people's health of the Alpine region.

After analysing the situation of emissions and concentrations measured in the Alpine area, in the following session of the report the results of a a monitoring campaign that was implemented in an Aosta Valley town are presented with the aim of identifying the contribution of the wood residential heating in the recorded concentrations data.

4. The pilot area of Saint Marcel

Biomass covers a large share of heat demand in the Alpine region which can reach 90% for small municipalities in the Alps. It is a renewable energy source but its combustion, in addition to be often inefficient from an energetic point of view, unfortunately involves critical aspects related to emissions of atmospheric particulate matter (PM), polycyclic aromatic hydrocarbons (PAH) and volatile organic compounds (VOC). The pollution becomes more intense in the alpine areas since wood is a widely used fuel and the environmental conditions, the orography and the intense cold of winters, favor the stagnation at ground level of the pollutants emitted.

In this context, a monitoring campaign was launched in October 2018 in the municipality of Saint-Marcel in Valle d'Aosta, a region located entirely in the Alps, in the extreme north-west of Italy. This municipality was chosen as a pilot area for its characteristics:

•   the main inhabited center of the municipality (1360 inhab.) is located at 625 m of altitude, about 10 km from the regional capital (Aosta), and can be considered representative of the aur quality in the central valley, where the most of the Aosta Valley population lives;

•   the only significant source of air pollution is represented by domestic heating with a large use of wood;

•   the site is in an orographic shadow situation during the winter period and consequently there are frequent phenomena of thermal inversion and stagnation of pollutants;

•   possibility to compare the results of this study with those deriving from a previous monitoring campaign carried out in 2017 by ARPA Valle d'Aosta.
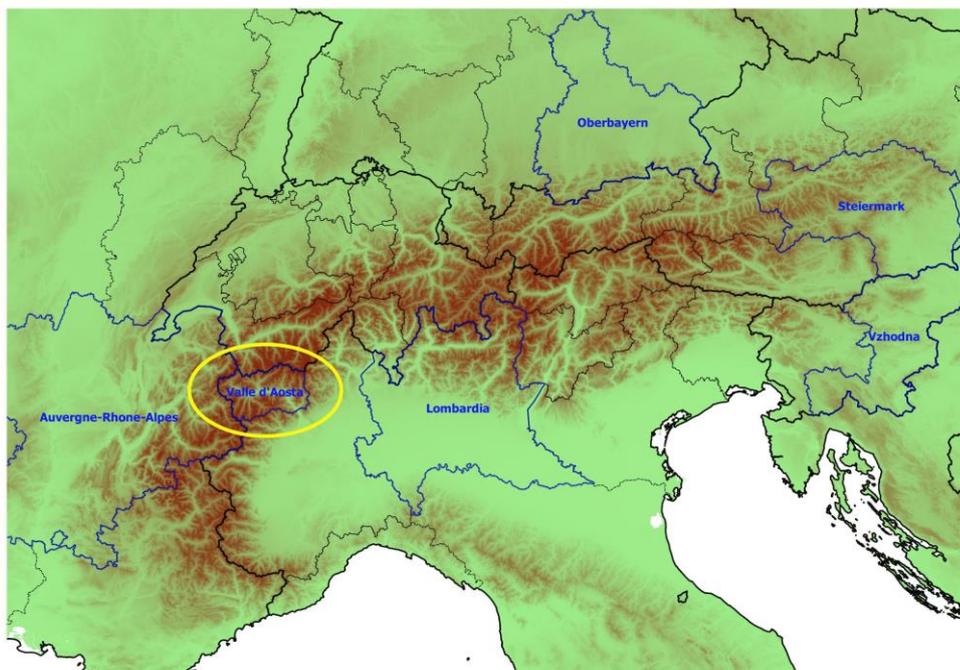

Fig. 10 - Location of the pilot site: Saint-Marcel - Aosta Valley Region (Italy)

In order to deepen the characterization of the site, within the BBCLEAN project, a "door-to-door" survey was prepared for the collection of information related to residential heating systems locally installed. These data will update the survey on the diffusion of wood-based biomass appliances, carried out throughout the region, as part of the strategic European territorial cooperation project 2007 - 2013 "RENERFOR".

The emission inventory at municipal level, updated annually by ARPA Valle d'Aosta, for the Municipality of Saint Marcel shows that around 50% of PM10 emissions and almost all CO (carbon monoxide) emissions come from domestic heating.
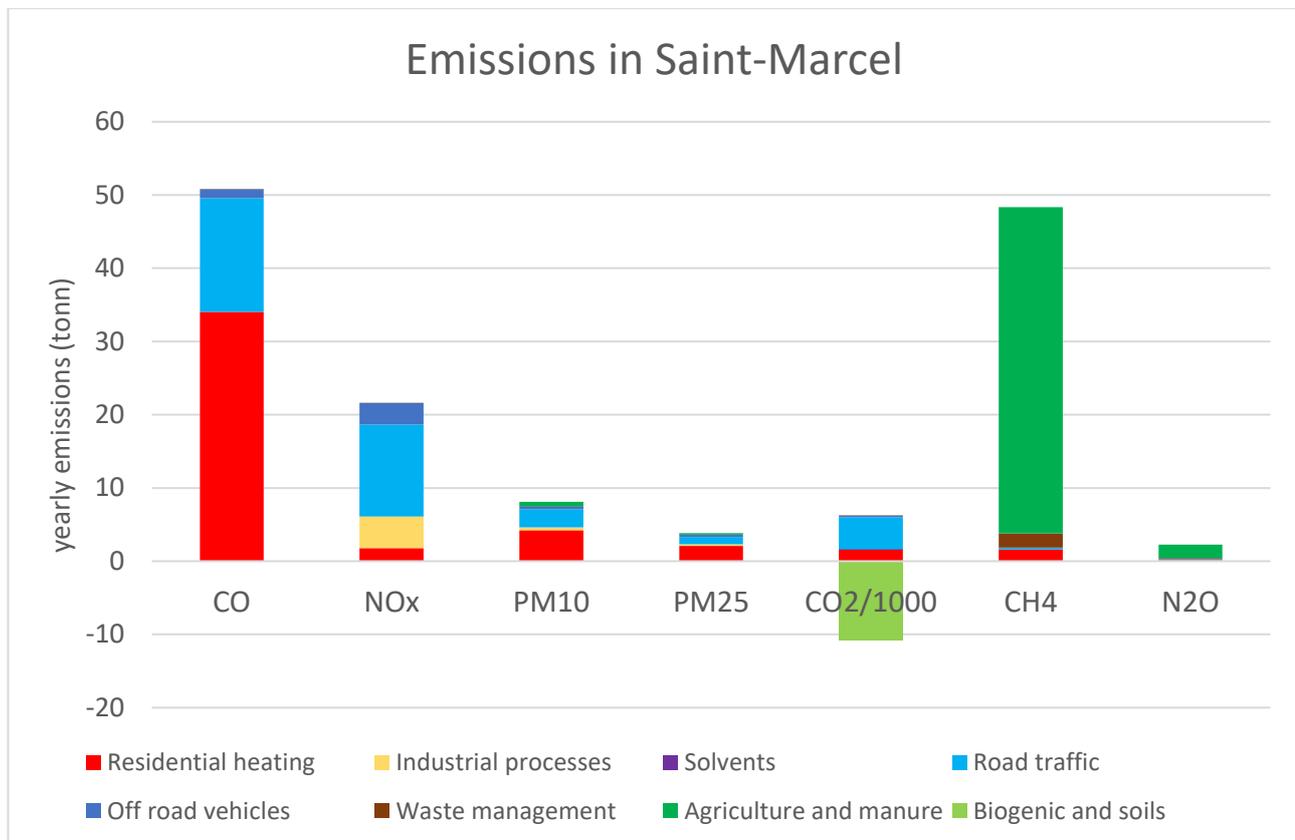

Fig. 11 - Contributions of the emission sources for the main pollutants in the municipality of Saint-Marcel (2017)

The results of the survey conducted in 2011 as part of the RENERFOR project showed that in the municipalities of the Valle d'Aosta area located in the 601-900 m altitude range, 53% of the users had a wood support system, with a preponderance of wood stoves (80% wood logs) and pellets boilers.
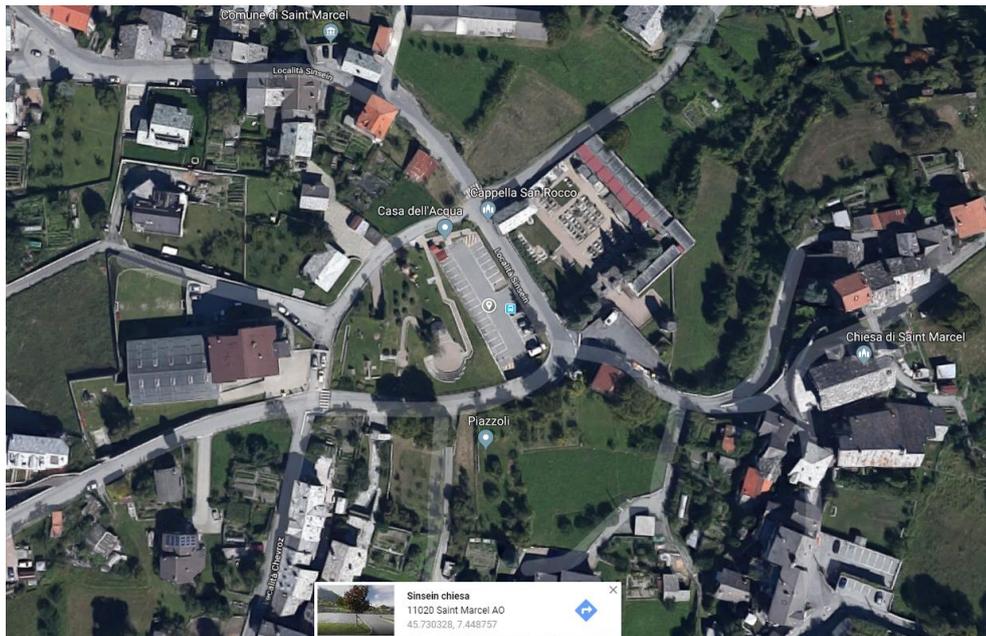
Fig. 12 - Location of the pilot site in the village of Saint-Marcel

4.1 Objective of the monitoring campaign

The purpose of the measurement campaign was to assess the air quality in the pilot area and the impact of domestic heating, with particular attention to emissions related to the use of wood biomass. The pollutants monitored were nitrogen oxides and PM10. In particular, we proceeded with the chemical speciation of PM10 and to the study of carbon particles on PM10 (black carbon or black smoke), with the aim to discriminate the share coming from the combustion of wood biomass from that produced by fossil fuels (mainly traffic).

4.2 Description of the monitoring protocol

The monitoring site consists of a mobile monitoring station equipped for measuring nitrogen oxides and black carbon and a mobile laboratory for measuring mass concentrations of PM10 and chemical speciation. Measurements of nitrogen oxides and black carbon cover the entire period of the campaign, while PM10 measurements are every other month (guaranteeing the representativeness of the different seasons).
As the measures were carried out over 12 months, it is possible to obtain data on an annual basis.

The monitoring periods were as follows:

- 01/10/2018-31/10/2018
- 01/12/2018-31/12/2018
- 01/01/2019-31/01/2019
- 01/02/2019-28/02/2019

- 01/04/2019-30/04/2019
- 01/06/2019-30/06/2019
- 01/08/2019-31/08/2019

The monitoring of the "real time" parameters (NOx, BC, meteorological data) was carried out without interruptions, covering the entire monitoring period (October 2018 - September 2019). Detail of the monitoring protocol are shown in the following table:

Date		PM10	PM10 Composition				NItrogen oxides (NO /NO₂/NOx)	BC (Aethalometer)	Meteo Data
			EC/OC	PAHs	Levo	Ions			
2018	october	X	x	x	x	x	x	X start 27/10	
2018	november						X	X	X
2018	december	X	X	X	X	x	X	X	X
2019	january	X					X	X	X
2019	february	X	X	X	X	X	X	X	X
2019	march						X	X	X
2019	april	X	X	X	X	X	X	X	X
2019	may						X	X	X
2019	june	X	X	X	X	X	X	X	X
2019	july						X	X	X
2019	august	X	X	X	X	X	X	X	X
2019	september						X	X	X

The following table shows the measured parameters, with the indication of the instrumentation and / or the methods used for their determination.

Parameter	Instrument	Method	Measure unit
NOx (NO / NO2)	Nitrogen oxides analyser API200E Teledyne	Chemiluminescence	$\mu g/m^3$
PM10	Low-volume sampler 2,3 m3/h (MCZ)	Gravimetric determination	$\mu g/m^3$
	OPSIS SM200	Beta attenuation	$\mu g/m^3$
OC/EC	Sunset Laboratory inc. analyser	TOT thermal–optical transmission method EUSAAR2 protocol	$\mu g/m^3$
PAH	Sistema HPLC SHIMADZU Nexera-i Mod LC-2040C Plus	HPLC	ng/m^3
Levoglucosan	GC/FID Trae 1300	GD-FID	ng/m^3
Ions (Anions /Cations)	AQUION/ICS-1000 modules	Ion chromatography	$\mu g/m^3$
Black Carbon (BC) BCbb (from biomass burning) BCff (from fossil fuel)	Aethalometer AE33 (Magee Scientific)	Optical measurement on 7 wavelenght	$\mu g/m^3$
Parametri meteo: Temp , Wind speed and direction, RH	Meteo mulitiparametric sensor Lufft WS500 + WS100	-	-

PM10 mass concentration was determined using two different instruments and methodologies: during the first months (from October 2018 to January 2019) PM10 was determined with the gravimetric method according to EN 12324 on PM10 filters sampled with low volume sampler (MCZ) with flow setted at 2,3 m³/h and quartz fiber filters. For the following period of the campaign a beta - gauge analyser (OPSIS SM200) was used. Both instruments provided daily averages of PM10 mass concentration.

The collected PM10 samples were analysed on a daily basis for the determination of the chemical composition of particulate:

- **Carbounaceous compounds: Elemental/organic carbon/Total carbon (EC/OC/TC) and black carbon (BC),**
- **Polycyclic Aromatic Hydrocarbons (PAHs)**
    - Benzo(a)Pyrene
    - Chrysene
    - Pyrene
    - Fluoranthene
    - Benz(a)Antracene
    - Benzo(b)Fluoranthene
    - Benzo(k)Fluoranthene
    - DiBenz(a.h)Anthracene
    - Benzo(g,h,i)Perylene

- **Levoglucosan**
- **Water-soluble inorganic ions:**
  - Calcium (Ca+)
  - Nitrates (NO3-)
  - Sulphates (SO4-)
  - Potassium (K+)
  - Chlorine (Cl-)
  - Sodium (Na+)
  - Ammonium (NH4+)
  - Magnesium (Mg++)

Fig. 13   Saint-Marcel pilot site - View of the equipped mobile monitoring station and the mobile laboratory

Fig. 14 - Saint-Marcel pilot site - View of the equipped mobile monitoring station and samplers for PM10

For a description of the parameters and the details of the individual analytical and measurement methods used, see the paragraph 4.3 related to the individual parameters.

Although the measurement campaign within the BBCLEAN project ended at the end of September 2019, it was decided to keep the measurement site active until the end of 2019 to have data for a whole calendar year (and therefore comparable with the normative references) and for further months (autumn and winter) most significant for the pollution episodes deriving from domestic heating.

4.3 Measurement data analysis

In the following paragraphs the results of the air quality assessment in the pilot area will be presented and discussed for each pollutant monitored.

4.3.1 Nitrogen oxides

Nitrogen, combining with oxygen, gives rise to different compounds called nitrogen oxides (NOx). Among these, the most important for air pollution are nitrogen oxides NO and nitrogen dioxide NO_2. Nitric oxide is a colorless and odorless gas. It is formed in any combustion process in which the air is used as a comburent, by reaction between oxygen and nitrogen at high temperatures. About 10% of NO, once placed in the atmosphere, is transformed into nitrogen dioxide by the action of solar

radiation. Moreover, in conditions of strong radiation, nitrogen oxides participate in photochemical reactions that originate secondary pollutants (ozone, photochemical smog). Nitrogen oxides also contribute to the formation of acid rain and favor the accumulation of nitrates on the ground which can, in turn, significantly alter the ecological environmental balance.

Nitrogen dioxide (NO_2) is a reddish-brown gas, slightly soluble in water, toxic, with a strong, pungent odor and strong irritant power. It is a pollutant with a predominantly secondary component, as it is the product of the oxidation of nitrogen monoxide (NO); only in a minor proportion is it emitted directly into the atmosphere. The main source of emission of nitrogen oxides is road traffic. Other sources are civil and industrial heating systems, power plants for energy production and a wide range of industrial processes. Nitrogen dioxide is a widespread pollutant that has negative effects on human health, causes eutrophication and acid rain. Together with nitrogen monoxide, it contributes to the phenomena of photochemical smog: it is a precursor for the formation of secondary pollutants such as tropospheric ozone and secondary fine particulate matter.

Reference values

The Italian and European legislation indicates limit values for both human protection and critical levels for the protection of ecosystems as shown in the following table.

	Reference	Parameter	Limit value
NO_2	Limit value for the protection of human health	Hourly mean	200 μg/m3, not to be exceeded more than 18 times a calendar year
	Limit value for the protection of human health	Annual average of hourly mean	40 μg/m^3
	Alert value	Hourly mean	400 μg/m^3
NOx	Limit value for the protection of vegetation for NOx expressed as NO2	Annual average of hourly mean	30 μg/m^3

Measurement method

The Italian reference standard for air quality is the Legislative Decree 155/2010 which is the implementation of the European Union Directive 2008/50 / EC which provides as a reference method the technical standard UNI EN 14211: 2012 "Normalized method for the measurement of nitrogen dioxide and nitrogen monoxide concentration by chemiluminescence ".

Results

The graph below shows the monthly average NO_2 values measured during the campaign in comparison with the values measured in the Aosta - Piazza Plouves urban station in the same period. The average annual value (October 2018-September 2019) is 10 μg /m^3.
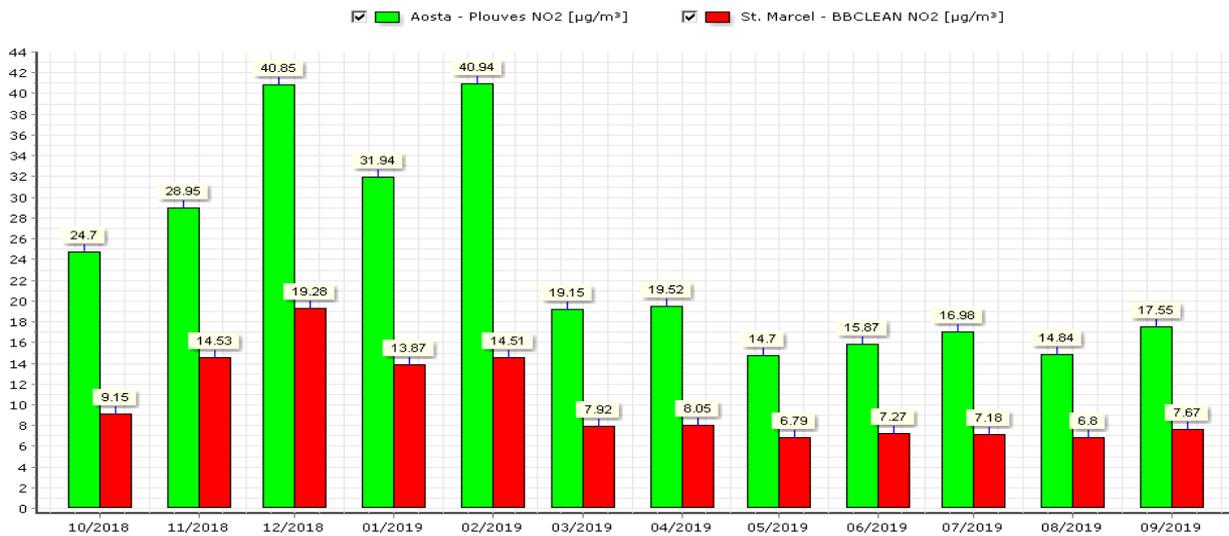
Fig 15 - Monthly average concentration of NO₂ registered in Saint-Marcel (red) and urban background site Aosta – Plouves (green)

The months with the highest concentrations are from December to February, the coldest months, during which the emissions of domestic heating are greater and the weather conditions favor the accumulation of pollutants. Nevertheless, the measured levels are very low, both when compared to those measured in Aosta (the average value for the same period is equal to 24 µg/m³), where the emission component due to traffic is much higher, both compared to the equal limit value at 40 µg/m³ (annual average).

4.3.2 Particulate matter (PM10)

PM10 is defined as the solid or liquid particulate suspended in the atmosphere which is composed of particles with an aerodynamic diameter of less than 10 µm (1 µm = 0.001 mm) and PM2.5 that consists of particles with an aerodynamic diameter of less than 2.5 µm. Particulate matter has different effects on human health depending on the chemical composition and particle size. For this reason, the legislation has taken into consideration the selective measures of PM10 and PM2.5, establishing specific reference values for them. The finer the particles are, the longer the residence times in the atmosphere and can therefore be transported even at a great distance from the point of emission. The particulate is partially emitted in the atmosphere as it is (primary particulate) and, in part, is formed in the atmosphere through chemical reactions between other polluting species (secondary particulate matter).

Reference levels

The Italian reference standard for air quality is the Legislative Decree 155/2010 is the implementation of the European Union directive 2008/50 / EC. For PM10 it provides two parameters characterized by a limit value:

- number of days in a calendar year when the average daily concentration exceeds 50 µg/ m3;
- annual average concentration.

	Reference	Parameter	Limit value
PM10	Limit value for the protection of human health Max 35 days per year admitted	Daily average	50 µg/m3
	Limit value for the protection of human health	Annual average	40 µg/m3

Measurement method

The PM10 measurements were carried out according to the UNI EN 12341: 2014 method, required by Legislative Decree 155/2010 or equivalent in compliance with UNI EN 16450: 2017

Results

The figures below show the trend for the concentration of PM10 and a statistical representation of the distribution of the values recorded by period.
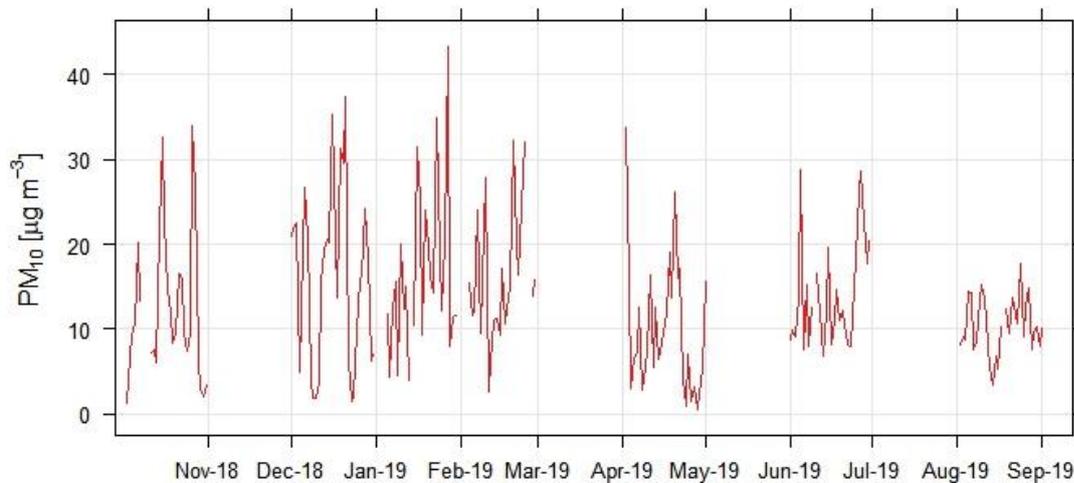

Fig. 16– Trend of daily mean concentration of PM10

The table below shows the average concentration values in the measurement periods and the comparison with the values of the 2017 campaign.

period	Average PM10 [ug/m3] BBCLEAN campaign 2019	Average PM10 [ug/m3] ARPA VDA campaign 2017
campaign	**14**	**15**
October	12,6	18,7
December	15,9	18,8
January	16,5	-
February	16,0	17,5
April	9,7	9,6
June	14,2	12,6
August	9,6	12,6

In summary:

- the average annual value is 14 $\mu g/m^3$, in accordance with the 2017 value, well below the annual limit (40 $\mu g/m^3$) and lower than the WHO reference value (20 $\mu g/m^3$);
- there were no exceedances of the daily limit value of 50 $\mu g/m^3$ (the maximum daily value was 43.4 $\mu g/m^3$ on 27/01/2019);
- the highest concentration values were recorded during the winter months, a more critical period due to both the weather conditions and the greater emission load.

4.3.3 PM10 chemical speciation

In the following paragraphs results of chemical speciation of the PM10 collected on filters will be presented and discussed, for each monitored compound.

- **Carbonaceous matter in PM10: elemental carbon (EC), organic carbon (OC) and brown carbon (BrC)**

The term Elemental carbon (EC), usually implying a near-elemental soot-carbonlike composition, refers to the fraction of carbon that is oxidized in combustion analysis above a certain temperature threshold, and only in the presence of an oxygen-containing atmosphere.
All sources that emit elemental carbon also emit other carbonaceous compounds, generally defined in literature as "organic aerosols" (OA) or "organic material" (OM). It can be both primary organic aerosol (POA), as well as secondary organic aerosol (SOA) through phase-gas reactions in the atmosphere.

Organic aerosols mass on PM samples is not directly measured, but organic carbon (OC) mass is determined through thermal-optical transmittance analysis (TOT). OC refers to the carbon molecules mass within the organic matter, not taking into account the associated oxygen and hydrogen content.

Consequently the ratio between OA and OC mass (OA:OC) depends on the oxygen mass present in the organic molecules. This ratio has, from literature studies, a variability from about 1,1 and 2,2 depending on the combustion source, with lowest values from coal or diesel and highest values from biomass combustion.

In general organic compounds are not light absorbers, but some of them absorb visible light, the so-called "brown carbon". It's a complex mixture of organic compounds.

Brown carbon, a subset of OA, is a complex mixture of organic compounds lacking a formal analytical definition. Its light absorption is weak, (with MAC less than 1 m^2g^{-1} at 550 nm, but has a strong wavelength dependence [Kirchstetter et al., 2004; Chakrabarty et al., 2010]. This strong wavelength dependence can be used to distinguish its absorption from that of BC [Wonaschütz et al., 2009]. Brown carbon particles and BC are similar in size.

Reference level

The European and national legislation does not provide for any reference value for these compounds.

Measurement method

Organic and elemental carbon was determined on a PM10 sample punch (1 cm^2) punch using the thermal–optical transmission (TOT) method (Birch and Cary, 1996) and following the EUSAAR-2 protocol (Cavalli et al., 2010) according to the EN 16909:2017.

Results

The figures below show the trend of OC and EC concentrations measured during the campaign and a statistical representation of the distribution of values recorded by period.
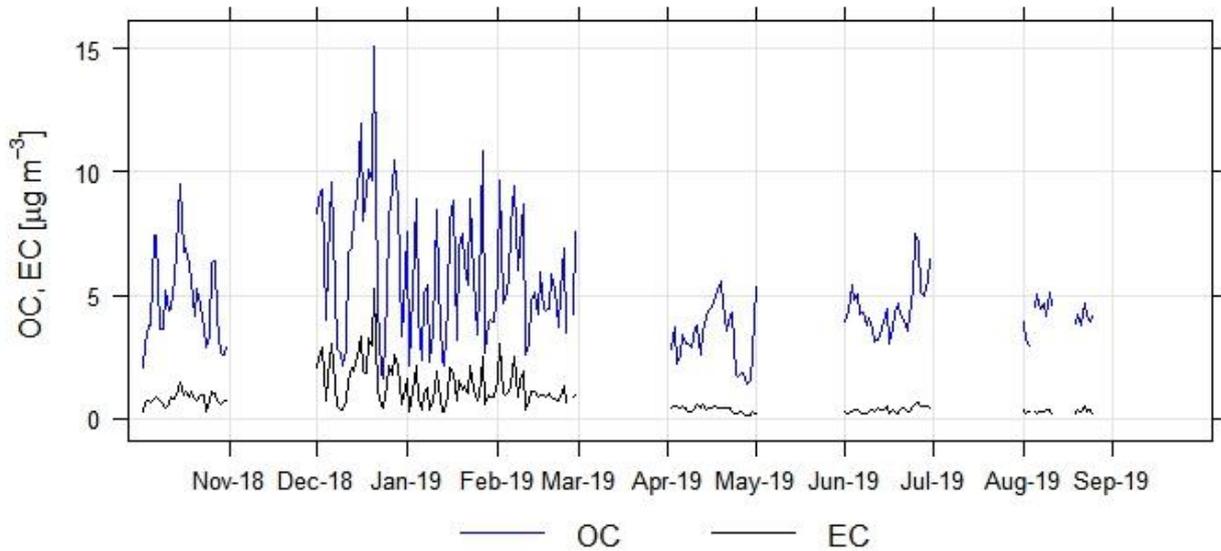
Fig. 17 – Trend of daily mean concentrations of organic carbon (OC) and elemental carbon (EC)

The table below shows the periods during which the measurement campaign was conducted and the relative average concentration values by period.

period	Average OC [ug/m3]	Average EC [ug/m3]
campaign	**5,02**	**0,88**
October	4,83	0,79
December	7,02	1,85
January	5,28	1,11
February	5,65	1,15
April	3,35	0,36
June	4,51	0,34
August	4,20	0,29

The OC and EC values are higher in the winter months as well as the OC/EC ratio. This is in agreement with the other measured parameters, and in particular with the concentrations of levoglucosan, due to the emissions from combustion of biomass linked to residential heating in the cold season. Higher EC values in winter months are due to the meteorological conditions that favor the accumulation of pollutants emitted in greater quantities in the valley during the winter months.

- **Black carbon and its source apportionment**

When designing the monitoring campaign, it was decided to include Black Carbon among the parameters to be monitored.

Black Carbon (BC) represents the carbon component consisting of more or less complex chains of carbon spheres, not linked to other atoms, which has the optical property of absorbing light radiation in the visible spectrum.

This physical property justifies the growing scientific interest within the scientific community and the inclusion of specific automatic analyzers within the measurement networks for the assessment of air quality. In fact, the ability to absorb solar radiation makes this carbonaceous fraction one of the factors that, together with climate-altering gases, has a greater impact on the radiative balance of the atmosphere.

BC mass concentration in air is not directly measurable on PM samples like gravimetric method for the determination of PM mass concentration, weighting the PM sample's filter or the elemental carbon. It must be determined indirectly, usually using thermal methods combined with optical properties (as described above for EC measurement), optical method and laser-induced incandescence.

In the present campaign, using an aethalometer, the method refers to optical properties of carbonaceous particles.

The Aethalometer model AE33 collects aerosol particles continuously by drawing the aerosol-laden air stream through a spot on the filter tape. It analyzes the aerosol by measuring the transmission of light through one portion of the filter tape containing the sample, versus the transmission through an unloaded portion of the filter tape acting as a reference area. This analysis is done at seven optical wavelengths spanning the range from the near-infrared to the near-ultraviolet. The Aethalometer calculates the instantaneous concentration of optically-absorbing aerosols from the rate of change of the attenuation of light transmitted through the particle-laden filter.

Fig 18 -   The Aethalometer® Model AE33.

In the Model AE33 Aethalometer, two measurements are obtained simultaneously from two sample spots with different rates of accumulation of the sample.

Both spots derive their samples from the same input air stream. The two results are combined mathematically to eliminate nonlinearities and provide the compensated particle light absorption and BC mass concentration.

The determination of the Black Carbon mass concentration is based on the measurement of light absorption on a filter loaded with aerosols.

The optical absorption is measured at seven wavelengths simultaneously.

The data obtained from channel 6 (measurement at 880 nm) is the defining standard used for reporting black carbon concentration:

BC = BC6

Data from the other channels are used for the source apportionment of BC. Their wavelengths and the Mass Absorption Cross-sections used in the calculations are as follows:

Channel	Measurement wavelength (nm)	Mass absorption cross-section (m^2/g)
1	370	18.47
2	470	14.54
3	520	13.14
4	590	11.58
5	660	10.35
6	880	7.77
7	950	7.19

Source apportionment of black carbon emissions is based on the Sandradewi et al. (2008) model, with optical absorption coefficient being a sum of biomass burning and fossil fuel burning fractions. Model is based on the difference in absorption coefficient wavelength dependency assuming that absorption due to from fossil fuel and biomass emissions follow λ^{-1} and λ^{-2} spectral dependencies, respectively (Sandradewi 2008). The exponents which describe the spectral dependence are called Ångström exponents: α_{ff} for fossil fuel and α_{bb} for biomass.

The algorithm of the model is based on the following equations:

$$\frac{b_{abs}(470\,nm)_{ff}}{b_{abs}(950\,nm)_{ff}} = \left(\frac{470}{950}\right)^{-\alpha_{ff}} \quad ,$$

$$\frac{b_{abs}(470\,nm)_{bb}}{b_{abs}(950\,nm)_{bb}} = \left(\frac{470}{950}\right)^{-\alpha_{bb}} \quad ,$$

$$b_{abs}(470\,nm) = b_{abs}(470\,nm)_{ff} + b_{abs}(470\,nm)_{bb}$$

$$b_{abs}(950\,nm) = b_{abs}(950\,nm)_{ff} + b_{abs}(950\,nm)_{bb}$$

where

- $b_{abs}(\lambda)$ is the absorption coefficient

- λ is the wavelength,
- $b_{abs}(\lambda)_{ff}$ is fossil fuel fraction and $b_{abs}(\lambda)_{bb}$ is biomass burning fraction of absorption coefficient

The solution of the previous system of equations allows to determine the percentage contribution of the biomass burning (BCbb)and fossil fuel (BCff) to the total BC, through the following equations:

$$BB(\%) = \frac{b_{abs}(950\,nm)_{bb}}{b_{abs}(950\,nm)}$$

$$BC_{bb} = BB * BC \qquad ,$$
$$BC_{ff} = (1 - BB) * BC$$

Reference level

As for elemental carbon (EC), European and national legislations do not provide any reference value for Black Carbon
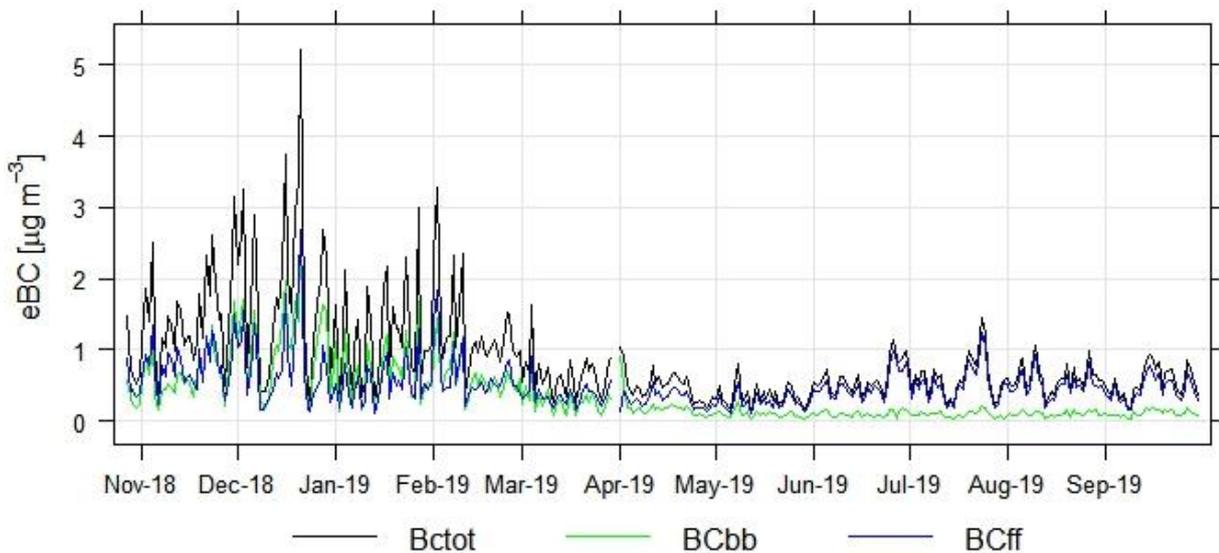
Results

Fig. 19 – Trend of daily mean concentrations of total black carbon (BCtot), BC from biomass burning (BCbb) and BC from fossil fuel (BCff)

The highest BC values were measured in the winter months, particularly in December, with a greater contribution from biomass burning; in the warmer months, on the other hand, as expected given the lower emission load and meteorological conditions favorable to the dispersion of pollutants, the BC has maintained very low concentration levels, with a modest contribution of biomass burning.
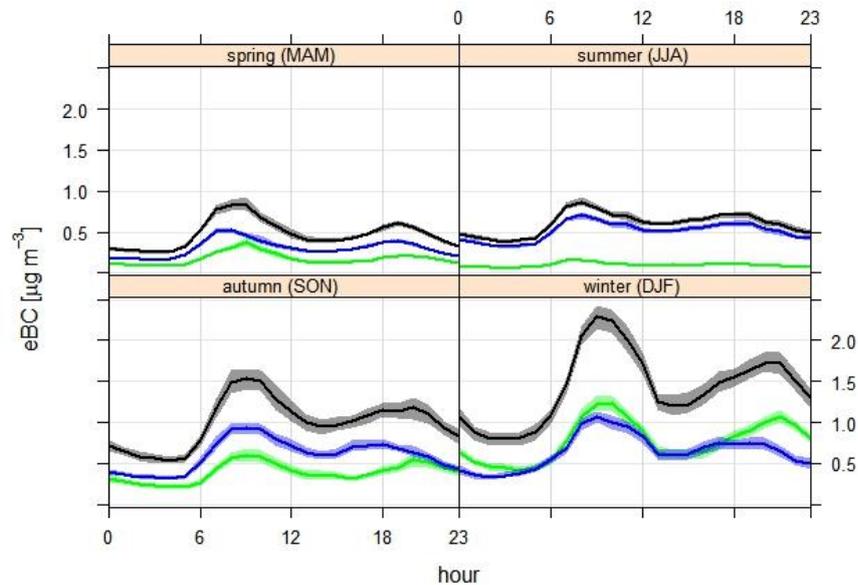
Fig.20 – Hourly trends of BC concentrations (black line), BCbb (green line) e BCff (blue line), in the typical day divided by season

Analyzing the hourly trend of BC concentrations in the typical day for the different seasons, it is interesting to note that, in the evening hours of the cold months, the BC component linked to the biomass burning shows a peak, not detectable in the fossil fuel component, attributable to the switching on of wood-burning systems and appliances for residential heating.

- **Levoglucosan**

Levoglucosan is an organic compound belonging to the anhydrous sugar family. It is a product of the pyrolysis of cellulose and hemicellulose contained in wood biomass, at temperatures greater than 200 °C. It is therefore universally used as a tracer in ambient air of biomass combustion emissions and it is considered relatively stable in the atmosphere.

Reference level
The European and national legislations do not provide any reference value for this compound, as it is neither harmful to human health nor to ecosystems.

Measurement method
Levoglucosan is determined on a PM10 sample through chemical treatment and analytical determination using gas-chromatography with FID detector (GC-FID).

Results

The figures below show concentration trends of levoglucosan detected during the campaign and a statistical representation of the distribution of the values recorded by period
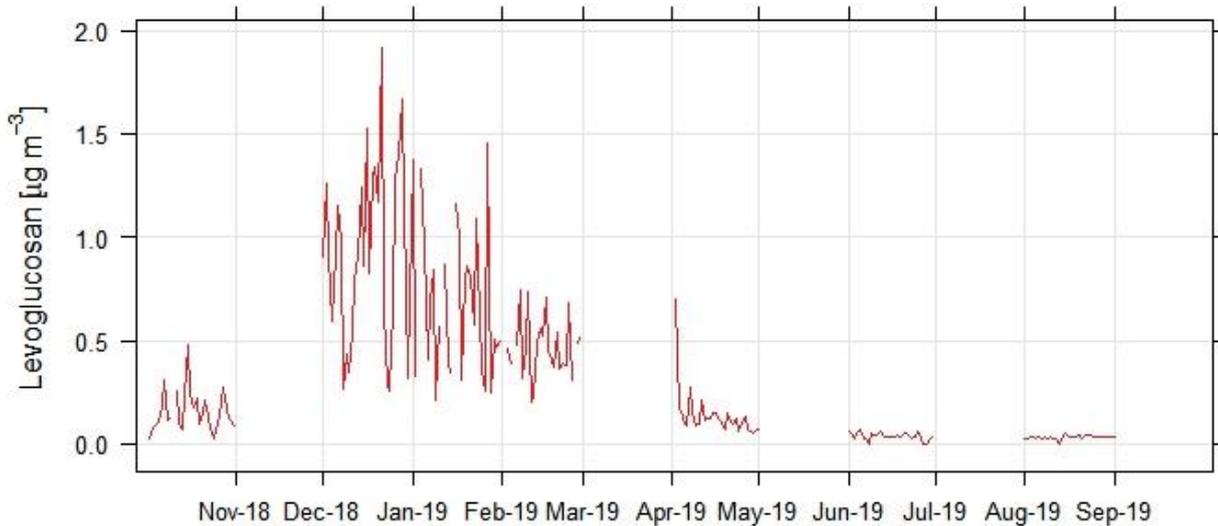

Fig. 21 – Trend of average daily concentrations of levoglucosan

The table below shows the periods during which the measurement campaign was conducted and the relative average concentration values by period.

period	Average levoglucosan [µg/m3] BBCLEAN campaign 2019
campaign	**0,34**
October	0,16
December	0,92
January	0,69
February	0,47
April	0,14
June	0,04
August	0,03

Levoglucosan highest concentrations were recorded, as expected, in the winter period (in particular in December) in correspondence with the period of ignition of the heating systems.

- **Polycyclic Aromatic Hydrocarbon (PAHs)**

Polycyclic aromatic hydrocarbons, also known by the acronym PAH, are hydrocarbons consisting of two or more benzene rings joined together, in a single generally flat structure. They are found naturally in coal and oil. They are emitted into the atmosphere as residues of incomplete combustion in some industrial activities (coke ovens, production and processing of graphite, treatment of hard coal) and in boilers (especially those fueled with solid fuels and heavy liquids). They are also present in vehicle emissions (both from diesel and petrol engines) and in emissions from biomass combustion (stoves or boilers for heating, agricultural activities that involve combustion of brushwood or forest fires).

In general, the emission of PAHs in the environment is very variable depending on the type of source, the type of fuel and the quality of the combustion.

PAHs are very often associated with suspended particles. In this case, the particle size is the main parameter that favor its entry and deposition in the respiratory system and therefore its toxicity. Present in the urban aerosol, they are generally associated with particles with an aerodynamic diameter of less than 2 microns and, therefore, able to easily reach the alveolar region of the lung and hence the blood and tissues. Although they represent a minimal fraction of the PM10 mass, it is essential to analyze their presence and concentration in the air because prolonged exposure can have toxic effects on human health.

A characteristic that makes them dangerous is their tendency to accumulate in some tissues of living beings (bioaccumulation), causing negative effects on human health.

In the atmosphere, exposure to PAHs is never linked to a single compound but to a mixture generally adsorbed on particulate matter.

The IARC (International Agency for Research on Cancer) has established that Benzo(a)Pirene, B(a)P is carcinogenic to humans (group 1: substances for which there is established evidence in relation to the induction of tumors in humans) . Since it has been shown that the relationship between Benzo (a) Pirene and the other PAHs, called "PAH profile", is relatively stable in the air of the different cities, the B(a)P concentration is used as an index of the carcinogenic potential of the total PAHs.

The greater dangerousness seems to be the prerogative of those compounds whose molecular structure is characterized by a number of aromatic rings between 3 and 7. Other PAHs are probable or possible carcinogens for humans (group 2). Benzo(a)Pirene, as well as being carcinogenic, is believed to cause genetic mutations, infertility and developmental disorders. For this reason, the current legislation has set a target value for this compound.

Reference level

The legislation defines reference levels only for Benzo (a) Pirene as shown in the following table:

	Reference	Parameter	Limit value
B(a)P	Target value	Annual mean of daily average values on particulate PM10	1 ng/m^3

Measurement method

The Italian reference standard for air quality is the Legislative Decree 155/2010 which is the implementation of the European Union Directive 2008/50/EC: it provides as reference method for the measurement of Benzo(a)Pirene the technical standard UNI EN 15549: 2008 "Air quality. Normalized method for measuring Benzo(a)Pyrene concentration in ambient air ".

Measurement principle: HPLC chromatography.

Mode of operation: PAHs are determined on the PM10 sample by chemical treatment and analytical determination (HPLC chromatography for PAHs)

Results

On the particulate samples collected, in addition to Benzo(a)Pirene, a further 8 PAHs were determined as standardized:

- Fluoranthene
- Pyrene
- Benz(a)Anthracene
- Crysene
- Benzo(b)Fluoranthene
- Benzo(k)Fluoranthene
- DiBenz(a,h) Anthracene
- Benzo(g,h,i)Perylene

The focus was on B(a)P as, as previously mentioned, it is the only PAH regulated by current Italian and European legislation, being indicative of the carcinogenic potential of total PAHs.

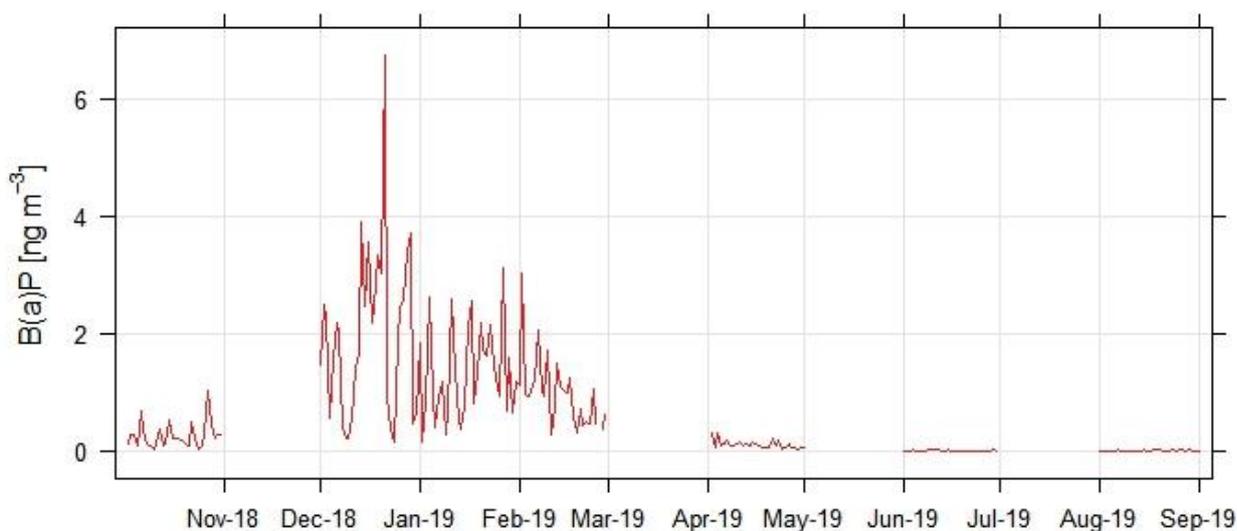The figure below show the trends of B(a)P concentrations:

Fig. 23 – Trend of daily mean B(a) concentrations

The tables below show the periods during which the measurement campaign was conducted and the relative average B(a)P concentration values by period and a comparison between the measured values in the BBCLEAN campaign (2018/2019) and in 2017 campaign:

period	Average B(a)P [ng/m3] BBCLEAN campaign 2019	Average B(a)P [ng/m3] ARPA VDA campaign 2017
Campaign	**0,66**	**0,89**
October	0,25	0,43
December	1,97	2,99
January	1,31	-
February	1,00	1,76
April	0,11	0,18
June	0.005	0,00
August	0,005	0,03

The average annual value is 0.66 ng/m^3, lower than that recorded in 2017, below the target value (1 ng/m^3).

The highest concentration values were recorded during the cold months (December -January-February), both due to the weather conditions and the increased emission load. The highest value was recorded on 21/12/2018 with a value of 6.47 ng/m^3.

The lowest values measured in the winter months of 2019 compared to 2017 are due to meteorological conditions that were particularly favorable to dispersion and to the lower emission of pollutants. In fact, winter 2018/2019 was milder than the average of previous winters. These

conditions have presumably led to use the heating systems less with particular reference to the wood-burning ones which are frequently used as complementary heating systems.

We wanted to evaluate the correlation between the measured concentrations of B(a)P and the levoglucosan, in order to verify its origin in terms of emissive source.
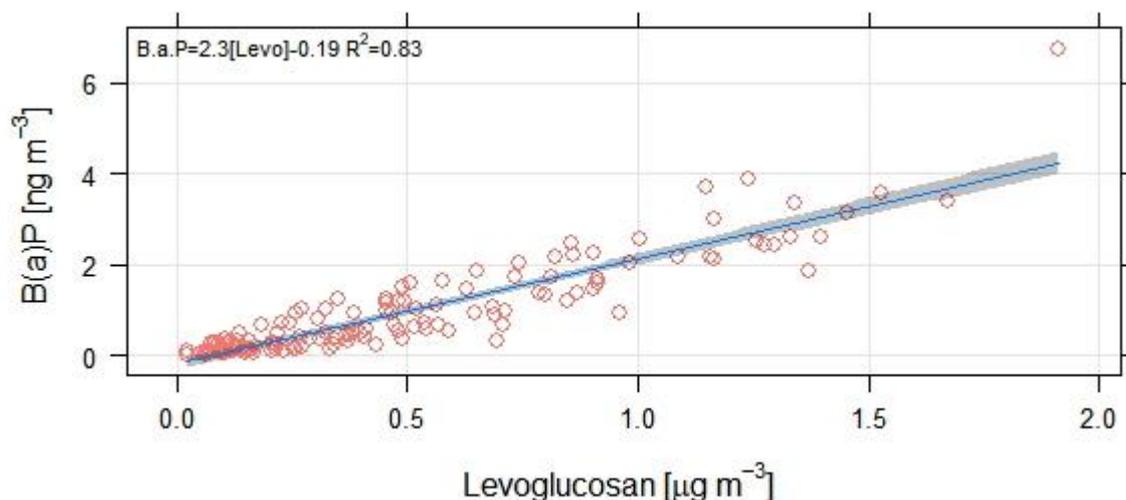

Fig. 24 – Correlation between daily concentrations of levoglucosan and B(a)P . The grey zone represents the estimated 95% confidence intervals of the fit.

Fig. 24 shows a very good correlation (R^2 = 0.83) between the two variables, which leads to being able to state with sufficient certainty that B(a)P is mostly emitted by the combustion of wood biomass.

Even for many of the PAHs analyzed a good correlation with levoglucosan was found; in particular for B(b)Fluoranthene and B(k)Fluoranthene similar correlation coefficients (R^2 = 0.83) while R^2 were found to be slightly lower for the other compounds, confirming that these PAHs derive predominantly from biomass burning appliances.

	B(a)P	B(a)Antr	Cris	B(b)Fluor	B(k)Fluor	DB(ah)Antr	B(ghi)Per
Levoglucosan	0,83	0,78	0,78	0.83	0.83	0.79	0.77

Finally, the correlation between the B(a)P and the BC and its two components (BCbb and BCff) was investigated.

For comparison, the following figures show the correlation between B(a)P and BCbb and between B(a)P and BCff.
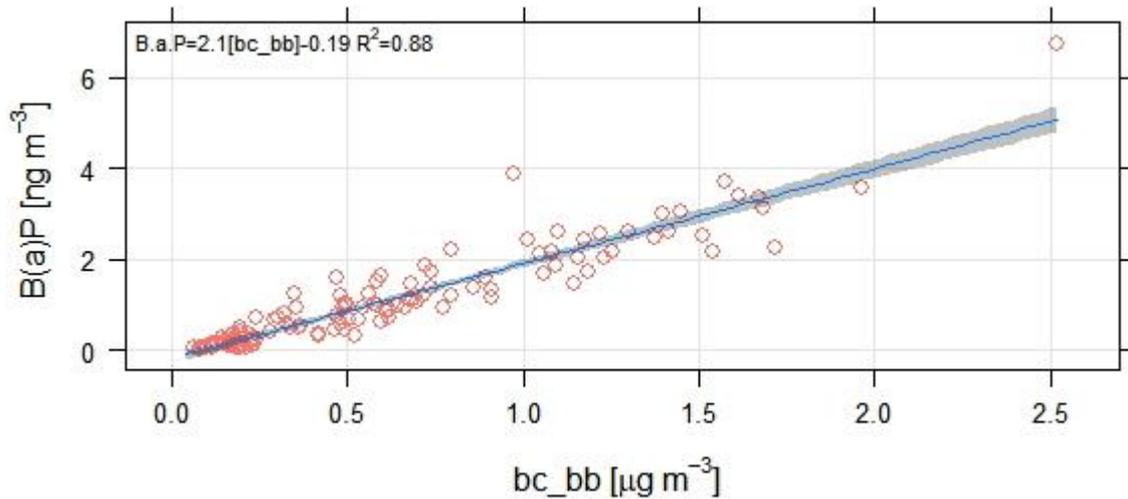
Fig. 25 – Correlation between daily concentrations of black carbon from biomass (BCbb) and B(a)P. The grey zone represents the estimated 95% confidence intervals of the fit.
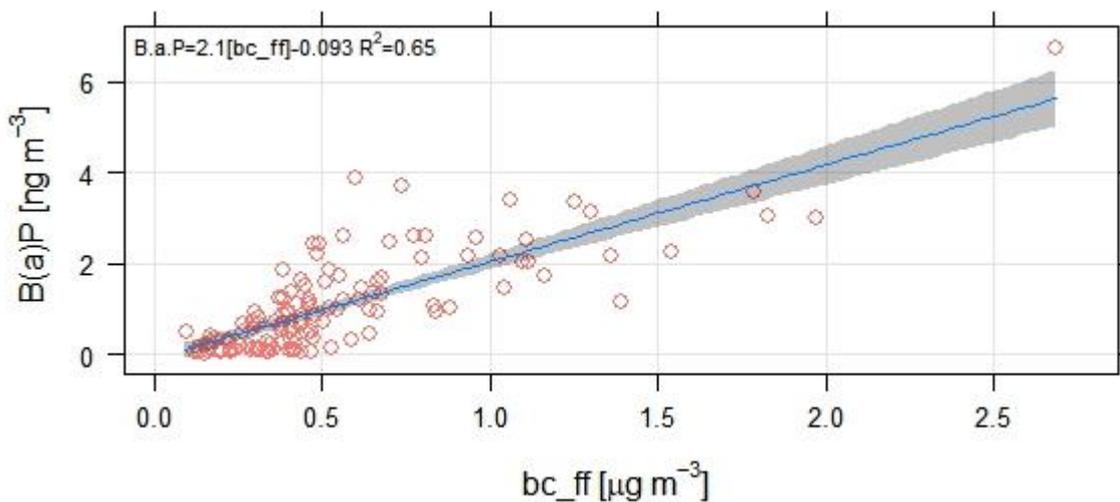

Fig. 26– Correlation between the daily concentrations of black carbon from fossil fuel (BCff) and of B (a) P The grey zone represents the estimated 95% confidence intervals of the fit.

It is evident that B(a)P strongly correlates (R^2 = 0,88) with the component of BC from biomass burning, while it correlates less with the fossil fuel component (R^2 = 0,65). A less marked linearity (with values of R^2 close to 0.60) is obtained between the concentrations of B(a)P and nitrogen oxides (NOx and NO2), which are, typically considered as road traffic tracers.

It can be deduced, therefore, that the combustion of biomass in this site is the primary source of B(a)P, while hydrocarbon combustion (road traffic and heating with fossil fuels) have a lower contribution to the measured concentrations.

- **Ions (Anions/Cations)**

Water-soluble inorganic ions, such as NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^- and Cl^- are significant components of atmospheric particles, which varies depending upon the particle source and the seasonality.

The evaluation of the ionic component (chlorides, phosphates, fluorides, nitrates, sulphates, ammonium, sodium, calcium, potassium, magnesium) is determined in Ionic Chromatography (IC) and allows the estimation of the contribution of the inorganic secondary component of the particulate, therefore less correlated to the strictly local sources. In particular, nitrates are indicative of combustion sources (traffic and heating) and reach the highest concentrations in winter as low temperatures favor condensation. Sulphates, on the other hand, although their formation is favored in the summer season, due to intense solar radiation, maintain an almost constant contribution throughout the year. In the atmosphere, nitrates, sulfates and ammonium bind to the particulate in the form of salts, or as ammonium nitrate and ammonium sulfate.

Potassium (K) is another well-known marker of biomass burning. During agricultural activities, nitrogen, phosphorus and potassium are supplemented in the soil with fertilization purposes.

In the absence of other important sources, such as soil dust, sea salt, water soluble K can be another satisfactory biomass marker.

Reference level

The European and national legislations do not provide any reference value for these ions, as it is not harmful to human health or to ecosystems.

Measurement method

Ion chromatography (AQUION/ICS-1000 modules) was employed for determining the concentration of water soluble anions and cations (Cl^-, NO_3^- , SO_4^{2-}, Na^+, NH_4^+ , K^+, Mg^+, Ca^{2+}), based on the CEN/TR 16269:2011 guideline.
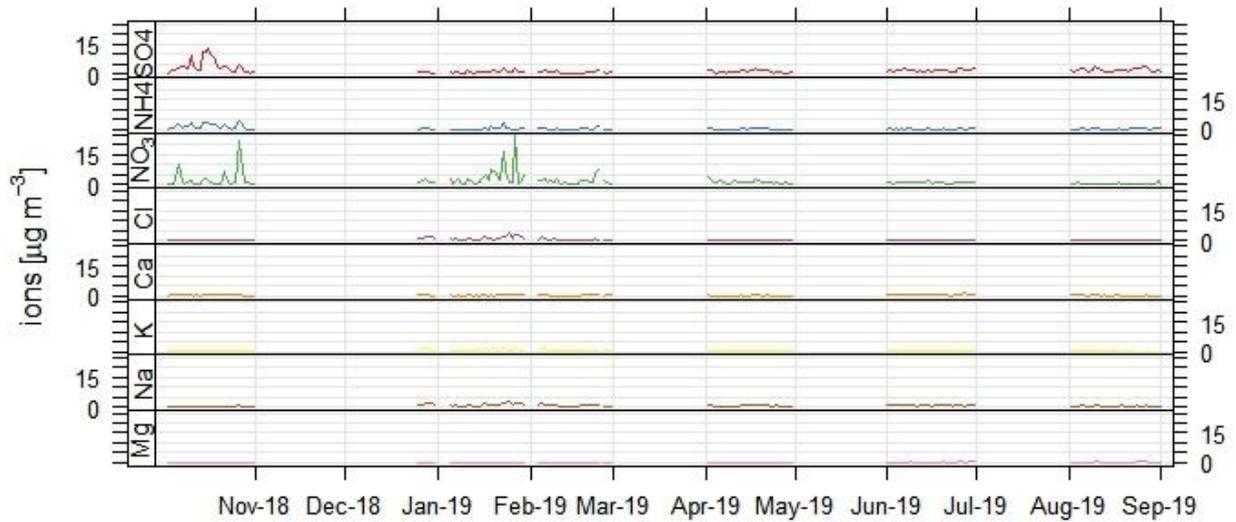
Results

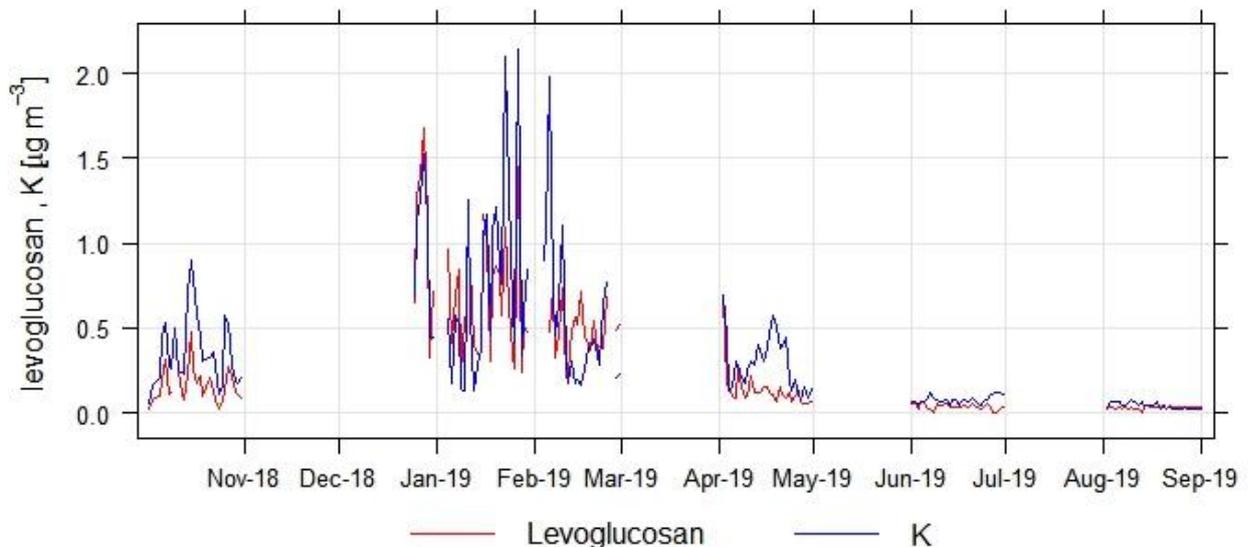*Fig 27 – Trends of daily average concentrations of ions*

Fig 28 – Trends of daily average concentrations of levoglucosan and potassium (K)

A no significant correlation between soluble K and levoglucosan concentrations was found. This poor correlation (R^2= 0,65 over the whole period and R^2= 0,47 for the winter months) may be attributed to the presence of K in dust, which is also a component of particulate matter.

The ionic component with the other determined pollutants will allow to estimate the source apportionment of ambient particles PM10 by Positive matrix factorization (PMF) in order to confirm the results obtained by this study.

4.3.4 Estimation of wood burning contribution to PM10

Given the purpose of the BBCLEAN project and in particular the monitoring study in the pilot area, discussed in this report, it was decided to test some simple methods to estimate the sources of particulate and in particular the contribution of wood combustion to the formation of particulate matter (later called PMbb).
The following methods have been applied:

1. Estimation of the PMbb obtained thanks to the levoglucosan measurements on filter
2. Estimation of the PMbb deriving from the measurements with the AE33 aethalometer

The first approach is based on the quantification of the mass deriving from the combustion of biomass on the basis of the levoglucosan measurements sampled on filters.
The studies based on its measurement first focus on determining the OC concentrations associated with biomass combustion (OCbb) using a multiplicative factor (f) as follows:

$$OC_{bb} = f \; x \; levoglucosan,$$

where f corresponds to the ratio $(OC/levoglucosan)_{biomass}$ considered as representative of the source or source mixture studied. It should be noted that OCbb is calculated here rather than OMbb (organic matter from biomass burning) because conventional filter measurement methodologies do not allow the direct analysis of OM.
The values of f reported in literature, and determined by emission measurements or empirically from data obtained in ambient air, vary almost an order of magnitude and are generally between 3 and 15. As mentioned previously, these differences are explained primarily by the great diversity of chemical composition of the particles emitted as a function of the combustion parameters. The choice of a value of 7, previously used by Puxbaum et al. (2007) for different European background sites, makes it possible to fix an intermediate value between 3 and 15. Nevertheless, in order to limit the risks of overestimation, some authors (Favez et al., 2019) proposed to set an upper bound also based on the measurements of OC (total) and considering that the value of f cannot be greater than the average of the 3 lowest daily ratios (OCtotal / levoglucosan) for each case study. In this way, OCbb remains logically lower than OCtotal. Specifically, starting from the results of the measurements, the average of the 3 lowest OCtot / levoglucosan quotients for the pilot area was equal to 5.

The concentration of PMbb can then be estimated by successive application of 2 new multiplicative factors, making it possible to convert OCbb into OMbb then OMbb in PMbb (by integrating the elemental carbon contribution from biomass combustion). Based on literature data, these factors have been chosen here as respectively equal to 1.6 and 1.1, so that:

PMbb = f x levoglucosan x 1,6 x 1,1

The choice of values of 1.6 and 1.1 again limit the risks of overestimation of PMbb concentrations, even if for aerosols emitted by biomass burning appliances the OMbb/OCbb ratio can reach and exceed the value of 2.

The second method is instead based on the measurements performed with the AE33 aethalometer and on the different parameters deriving from these measurements.
A first approach was to evaluate the distinct two fractions of Carbon (BC) that can be linked to the combustion of biomass (BCbb) and to the combustion of hydrocarbons (BCff). These fractions can be used to estimate, through a multiplicative factor, the PM10 concentrations related to the two emissive sources:

PMff = a x BCff
PMbb = b x BCbb

where PMff and PMbb represent the concentration in mass of particles deriving respectively from the combustion of hydrocarbons and from the combustion of biomass. In addition to BC, PMbb and PMff consist mainly of primary organic aerosols. The coefficients a and b derive (i) from the scientific literature on fossil combustion and (ii) from previous studies; reference was made, in particular, to studies conducted by INERIS and LCSQA (Laboratoire Centrale de Surveillance de la Qualité de l'air).

A further investigation of data collected at the Saint-Marcel site tested an alternative methodology for estimating the organic matter deriving from the combustion of biomass starting from the AE33 measurements.
Some authors, Favez et al, 2019, studied the correspondence between the estimates deriving from the analysis of levoglucosan and those obtainable starting from the measurements with the AE33 in the N-UV (near UV) (particle absorption measurements at 370nm). In fact, the latter are influenced not only by Black Carbon, but also by organic compounds with a structure similar to PAHs (BrC, brown carbon).
Since the absorption in the infrared (measurements around the wavelength of 900nm) is influenced only by the Black Carbon, it is possible to determine the absorption fraction, in the near UV due to both Black Carbon and BrC, according to the following formulas:

$b_{abs}BrC_{UV} = b_{abs}total_{UV} - b_{abs}BC_{UV}$
$b_{abs}BC_{IR} = a \times \lambda_{IR}^{-1}$
$b_{abs}BC_{UV} = a \times \lambda_{UV}^{-1}$

$\rightarrow b_{abs}BC_{(UV)} = b_{abs}BC_{(IR)} \times (\lambda_{UV} / \lambda_{IR})^{-1} = b_{abs}BC_{(IR)} \times (\lambda_{IR} / \lambda_{UV})$

$b_{abs}BC_{(IR)} = b_{abs}tot_{(IR)}$

$b_{abs}tot_{(\lambda)} = MAC_{(\lambda)} \times BCi$

where:

$b_{abs}tot$, $b_{abs}BC$ and $b_{abs}BrC$ are the total absorption coefficient of BC and BrC, respectively,

λ represents the wavelength considered,

IR and UV represent the wavelengths respectively in the near infrared and in the near ultraviolet,

$MAC(\lambda)$ represents the default mass absorption cross section used by AE33 aethalometer,

BCi represents the measurement provided by the AE33 for each of the 7 wavelengths.

The MAC values used by the AE33 software are 18.47 at 370 nm (BC1) and 7.19 at 950 nm (BC7). From the previous system of equations we obtain the following relation:

$B_{abs}BrC_{(370nm)} = (18,47 \times BC1) - ((7,19 \times BC7) \times (950 / 370))$

$B_{abs}BrC_{(370nm)} \approx 18,5 \times (BC1 - BC7)$

The comparison between these two approaches would tend to show a better linearity between the estimates made starting from filter measurements (levoglucosan) and BrC optical absorption measurements ($b_{abs}BrC370nm$), compared to those with the BCbb.
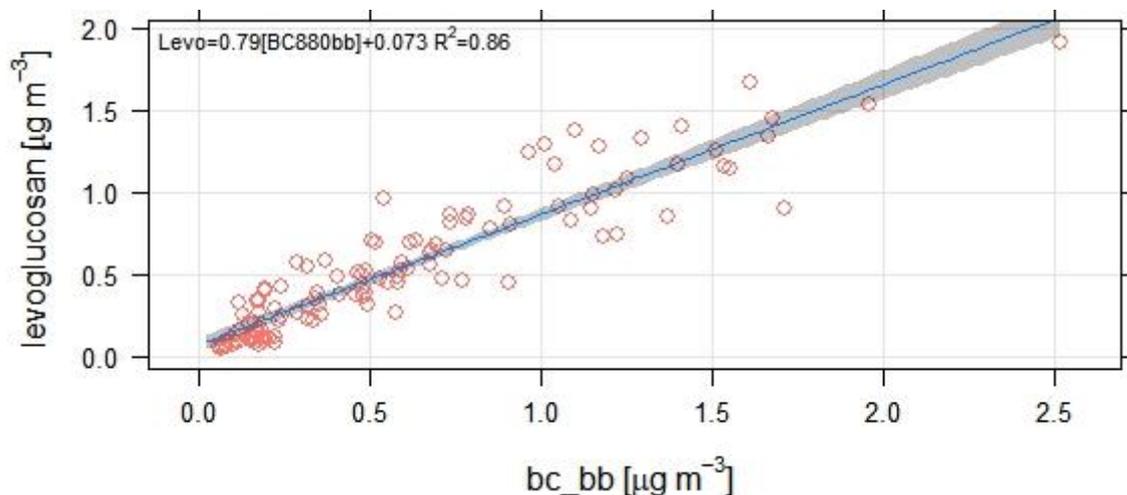

Fig. 29 - Correlation between the concentrations of levoglucosan and the BCbb parameter deriving from the AE33 measurements; The grey zone represents the estimated 95% confidence intervals of the fit.
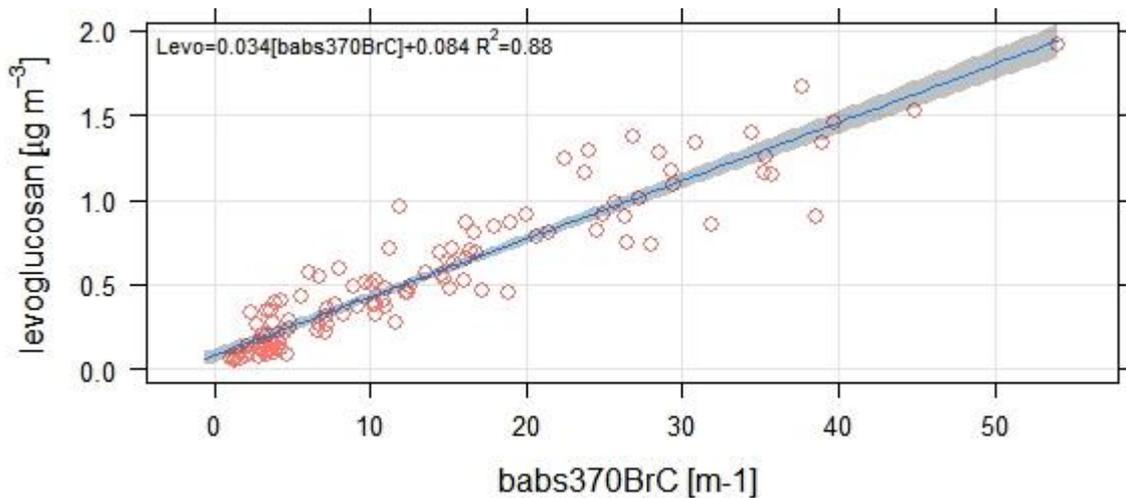
Fig 30 - Correlation between the concentrations of levoglucosan on a filter and the babs370BrC parameter deriving from the AE33 measurements; The grey zone represents the estimated 95% confidence intervals of the fit.

Therefore, for the alternative method that considers the BrC, there would be a weaker dispersion (R^2 = 0.88) of the values of the multiplicative factor b which allows to calculate PMbb from b_{abs}BrC370nm as follows:

$$PMbb = b \times b_{abs}BrC_{(370nm)}$$

Considering the slope (m=0.034) of the correlation line in Fig. 31 and the multiplicative coefficients mentioned above to obtain the PMbb from the concentrations of levoglucosan on a filter, we obtain a multiplicative factor b equal to:

$$b = 0,034 \times 5 \times 1,6 \times 1,1 = 0,3$$

This result is in line and very similar to what is shown in the elaborations reported in the LCSQA study and in the related technical notes. These studies report a value of 0.31 which derives from the measurements taken in winter on 8 urban sites in France. No references were found to other similar studies, especially for rural or semi-rural sites in the Alpine context comparable to the Aosta Valley pilot area, but considering that the studied source is unique and well defined, excluding the inevitable differences between different types of sites and emissions due to biomass combustion (depending on the type of appliance or plant, the type of wood burnt, …), it can be concluded with some confidence that the results on the Saint-Marcel site confirm what was found in the studies cited.

Applying this multiplicative coefficient b to the daily average value of babs370BrC we can obtain an estimation of the contribution in absolute and percentage terms of biomass combustion to the

measured PM10 concentrations, even in the absence of levoglucosan measurements on PM10 samples.

The following graphs show the trend of the estimated PM10bb compared to the measured PM10 and the trend of the percentage contribution.
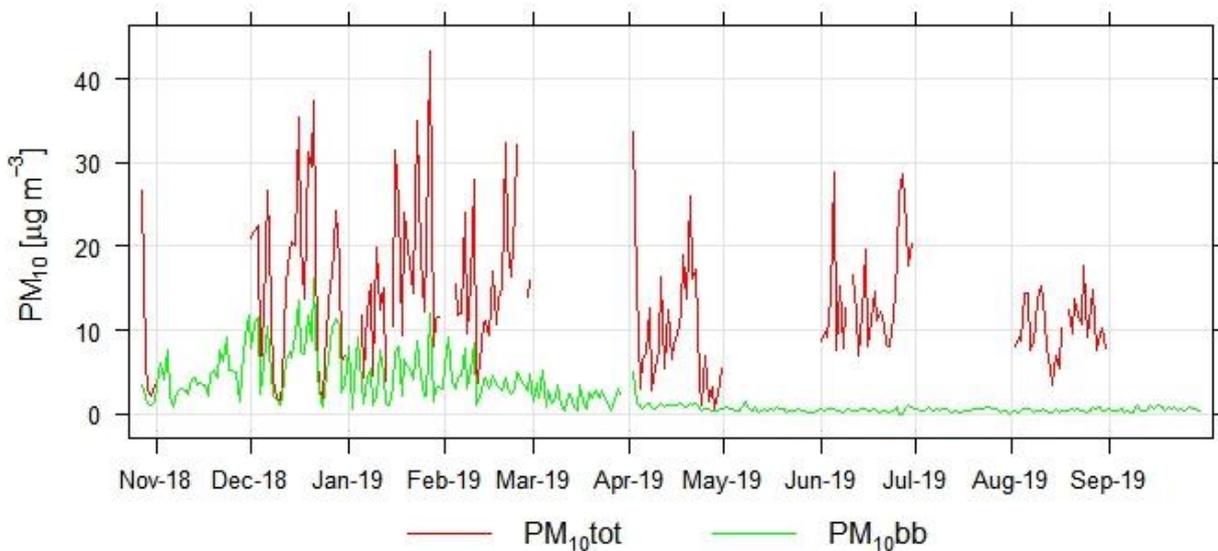

Fig. 31 - Trend of measured PM10 daily concentrations and estimated PMbb daily concentrations

Fig. 32 - Trend of estimated biomass burning percentage contribution to daily PM10 mass concentrations

Probably this source apportionment approach tends to overestimate biomass burning contribution on lower levels of PM10.

Estimated biomass burning contribution to PM10 varied between 0% and 92% , with higher values in cold months, in particular in December (presenting an average value of 49%) and negligible contributions in the warm season, where also levoglucosan and benzo(a)pyrene measured concentrations were very low.

The high values of late April are probably overestimated and due to the very low levels of the detected PM10 (PM10 < 5 µg/m^3)

period	Average PM10bb (%)
campaign	**22**
October	36
December	49
January	27
February	27
April	16
June	3
August	4

Conclusions

The Alpine area is characterized by an increasing use of wood biomass for domestic heating during the last years. The main impact is on air pollution affected by increasing PM10 and PAH concentrations.

The aim of the present study was to investigate the PM10 speciation in order to estimate the biomass burning contribution to total emissions.

A pilot rural area was selected in the Aosta Valley: the Municipality of Saint Marcel, where a monitoring station equipped with an aethalometer, PM10 samplers and a NOx analyser, has been set up.

The monitoring system allowed to have the following data:

- equivalent BC mass concentration
- NOx concentrations
- PM10 concentration
- PM10 chemical speciation (EC/OC, levoglucosan, PAHs, water soluble inorganic ions).ù

Correlations concerning these parameters and particularly between BC vs levoglucosan have been studied and the amount of PM due to biomass burning to total PM10 (PMbb) has been calculated.

PMbb in Saint Marcel [µg/m3] = 0.3 x $b_{abs}BrC_{(370nm)}$

where $b_{abs}BrC_{(370nm)}$ = 18,5 x (BC1 - BC7) and BC1 and BC7 are the output of the aethalometer.

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