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APICE

Source Contribution Analysis Report (WP 4.4)

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1. Source Apportionment analysis for Particulate Matter concentrations

The contribution of the different emission sources – both anthropogenic and natural – to the Particulate Matter concentrations – has been highlighted by two different approaches: the receptor models and the Chemical Transport Models.

The two different techniques of Source Apportionment analysis, have been applied at the same time in the five cities in order to answer to these questions:

which pollutant emission mostly affects PM10 and PM2.5 concentrations?

which is the weight of the presence of the port in the studied cities in terms of PM10 and PM2.5 concentrations?

The two different Source Apportionment (SA) approaches aimed at integrating the peculiar potentialities of both techniques: by one side receptor models, more suitable to pointing out specific emission sources bind to specific markers, and, on the other side, CTMs, which extend their assessment on the formation of secondary aerosols, since they apportion the gas precursor emissions, too. Moreover, while receptor models give SA outcomes on some monitoring sites only, SA by CTMs provides outcomes on the whole studied territory with a certain resolution (spatial maps).

1.1 Source Apportionment Outcomes by Receptor Models

Receptor Models aim to re-construct the contribution of emissions from different sources of atmospheric pollutants, e.g., particulate matter (PM), based on ambient data (i.e. PM elemental and chemical composition) registered at monitoring sites. The fundamental principle of receptor modelling is that mass and species conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere. One of the main differences between models is the degree of knowledge required about the pollution sources prior to the application of receptor models. A second major difference between these different approaches is the number of observations (e.g., samples) needed to apportion sources. While Chemical Mass Balance (CMB) model assumes and needs an a-priori knowledge of the emission sources and could be used with only one sample, approaches such as Positive Matrix Factorization (PMF) need a significant number of samples (at least equal to the number of chemical species included in the model) to single out the emission sources active in a particular area and to provide statistically sound results. PMF (in Barcelona, Genoa, Thessaloniki and Venice) and CMB (in Marseille) are the two approaches adopted by the APICE Partners. Note that, even if none of these approaches can be regarded as absolute, the conclusions drawn from the inter-comparison campaign recommend using the PMF as a common approach. This work will be finalized in Marseille in early February 2013 and can not be reported here.

We report here a very synthetic summary of the results obtained in each study area.

1.2.1 Barcelona

Simultaneous sampling was carried out in two sites every four days from February 2011 to January 2012: Port of Barcelona (41°19’58”N; 2°8’27 ”E) and Palau Reial (urban background site, 41°23’15”N; 2°6’56”E). A PMF analysis was per formed on 295 cases, including simultaneous PM10 and PM2.5 measurements performed at both monitoring sites (Tab 1).

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Tab 1. Barcelona, average results.

Sources	Port: Contribution (μg/m^3) to		Palau Reial: Contribution (μg/m^3) to	
	PM10	PM2.5	PM10	PM2.5
Industrial emissions	1.8 ± 0.1	0.3 ± 0.1	0.3 ± 0.0	0.8 ± 0.1
Mineral/road dust	9.2 ± 0.5	2.1 ± 0.2	0.4 ± 0.1	3.3 ± 0.3
Ammonium sulphate	2.9 ± 0.6	7.9 ± 0.9	9.9 ± 0.9	4.8 ± 0.7
Fuel oil combustion	3.8 ± 0.3	1.1 ± 0.2	0.9 ± 0.1	2.8 ± 0.2
Vehicle exhaust emissions	6.6 ± 0.8	5.3 ± 0.5	2.9 ± 0.3	2.6 ± 0.4
Aged sea spray + nitrate	12.1 ± 1.0	9.2 ± 0.8	2.3 ± 0.4	2.0 ± 0.3
Unaccounted	0.0	0.8	1.6	1.2

The biggest differences between the port and the urban area of Barcelona were found for the mineral dust source, attributed to the influence of dust re-suspension from the new port area under construction, but also to re-suspension of road dust from the intense truck traffic around the port area. The fuel oil combustion source was also higher for the port of Barcelona, reflecting direct emissions from shipping. The contribution of the industrial emissions was also higher at the port area. This is attributed to the transport of pollutants from the industrial area in the surroundings of Barcelona. The aged sea spray+nitrate source was also higher at the port area. This source reflects aging of pollutants during transport of air masses to the monitoring site. However, the ammonium sulphate source was much higher at the urban area of Barcelona. This is attributed to the formation of secondary ammonium sulphate from SO_2 shipping.

The results show that the contribution of port emissions to PM10 and PM2.5 at the port were around 40% for both PM10 and PM2.5, being mainly attributed to mineral dust (23 and 17% for PM10 and PM2.5, respectively) and fuel oil combustion (10 and 16%, respectively). Vehicle exhaust emissions accounted for 3% in both fractions, and ammonium sulphate for 2 and 6%, respectively.

At the urban area of Barcelona the contributions from the port were 11% and 18% for PM10 and PM2.5, respectively. The influence of the port in the urban background of Barcelona is mainly attributed to fuel oil combustion (4-5%) and ammonium sulphate (6 and 12%, respectively) from the formation of secondary ammonium sulphate during transport of SO_2 emissions from the port to the urban background site.

It is important to highlight the formation of secondary aerosols in the urban area of Barcelona, from the gaseous precursors SO_2, transported from the port, and the high levels of NH_3 measured at the urban background.

1.2.2 Genoa

The monitoring campaign was organized collecting daily PM2.5 samples in three sites: two immediately outside the harbour area (Corso Firenze, 44°25'5.69"N; 8°55'38.97"E, and Multedo, 44°25'37.18"N; 8°49'49.21"E) and one in t he northern area of the city (Bolzaneto: 44°27'45.92"N; 8°54'4.40"E) about 7 km inland. The sampling started in February 2011 in Corso Firenze and in May 2011 in the other two sites and was stopped in all the sites in October 2011). A PMF analysis was performed to apportion the PM2.5 sources (Tab 2).

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Tab 2. Genoa, Average results (contribution to PM2.5 level in μg/m^3):

	Secondary sulphates	Secondary nitrates	Road traffic	Heavy oil combustion	Soil dust	local industry
Cs. Firenze	6.7 ± 0.5	1.0 ± 0.2	3.2 ± 0.3	1.9 ± 0.5	1.1 ± 0.4	-
Multedo	6.7 ± 0.4	1.1 ± 0.2	2.4 ± 0.3	1.6 ± 0.4	1.0 ± 0.2	0.7 ± 0.3
Bolzaneto	7.3 ± 0.6	1.4 ± 0.2	4.3 ± 0.6	1.5 ± 0.2	1.0 ± 0.2	-

The PM2.5 level (about 14 μg/m^3) and composition turned out to be quite uniform, with secondary components (sulphates, nitrates but organic aerosol too) very well correlated in the three sites. Road traffic gave the highest contribute to PM2.5 level in Bolzaneto located a few hundred meters from the large highway connecting Genoa to Milan. Heavy oil combustion can be attributed completely to ship emissions being any other residential source of this type negligible in the city. On average, ship emissions contributed to 10%- 15% of PM2.5 level during spring-summer 2011.

1.2.3 Marseille

The monitoring campaign in Marseille was conducted In two sites: “Cinq avenues” (43°18'18.84"N; 5°23'40.89"E, a urban background s ite where PM2.5 was collected daily from July 2011 to July 2012) and “dock east of the harbor” of Marseille (43°18'4.18"N; 5°21'48.71"E, site affected by the emissions of in dustrial zone situated in the west of Marseille; PM2.5 sampling started in November 2011 and finished in July 2012 and each filter represents a sampling period of 48 hours). EPA CMB 8.2 was used to apportion sources and estimates their relative contributions.

Tab 3. Marseille, Average results at Cinq Avenues for PM2.5 in μg/m^3 (rows order: summer, fall, winter, spring)

Biomass burning	Vehicular emissions	Vegetative detritus	Natural Gas Combustion	Shipping Main Engines	Coke production, Steel facilities
0.31 ± 0.06	6.5 ± 1.3	2.3 ± 0.5	0.01 ± 0.01	0.07 ± 0.01	0.04 ± 0.01
16 ± 3	7.0 ± 1.4	3.4 ± 0.7	0.00 ± 0.01	0.15 ± 0.03	0.08 ± 0.02
13 ± 3	8.2 ± 1.6	1.1 ± 0.2	0.03 ± 0.01	0.06 ± 0.01	0.21± 0.04
0.7 ± 0.1	6.1 ± 1.2	1.2 ± 0.2	0.01 ± 0.01	0.08 ± 0.02	0.05 ± 0.01
Unexplained organic matter (OM)	**Secondary sulfate (SO4)**	**Secondary nitrate (NO3)**	**Secondary ammonium (NH4)**	**Crustal dust**	**Sea salt**
0.38 ± 0.08	1.3 ± 0.3	0.41 ± 0.08	0.6 ± 0.1	1.8 ± 0.4	0.4 ± 0.1
0.16 ± 0.03	1.6 ± 0.3	2.2 ± 0.4	1.9 ± 0.4	1.6 ± 0.3	0.4 ± 0.1
0.28 ± 0.06	1.9 ± 0.4	2.9 ± 0.6	2.1 ± 0.4	0.7 ± 0.1	0.18 ± 0.04
1.0 ± 0.2	2.3 ± 0.5	0.75 ± 0.15	1.2 ± 0.3	1.3 ± 0.3	0.21 ± 0.04

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Tab 4. Marseille, Average results at dock east of the harbor for PM2.5 μg/m^3. (rows order: summer, fall, winter, spring)

Biomass burning	Vehicular emissions	Vegetative detritus	Natural Gas Combustion	Shipping Main Engines	Coke production, Steel facilities
0.15 ± 0.03	9.2 ± 1.8	1.3 ± 0.3	0.01 ± 0.01	0.18 ± 0.04	0.03 ± 0.01
17 ± 3	7.4 ± 1.5	0.8 ± 0.2	0.00 ± 0.01	0.10 ± 0.02	0.06 ± 0.01
7.0 ± 1.4	9.7 ± 1.9	1.2 ± 0.2	0.04 ± 0.01	0.11 ± 0.02	0.08± 0.02
1.7 ± 0.3	9.9 ± 2.0	0.9 ± 0.2	0.00 ± 0.01	0.17 ± 0.03	0.07 ± 0.01
Unexplained organic matter (OM)	**Secondary sulfate (SO4)**	**Secondary nitrate (NO3)**	**Secondary ammonium (NH4)**	**Crustal dust**	**Sea salt**
0.46 ± 0.09	1.1 ± 0.2	0.22 ± 0.04	0.75 ± 0.15	0.5 ± 0.1	0.35 ± 0.07
0.00 ± 0.01	2.8 ± 0.6	2.3 ± 0.5	1.9 ± 0.4	1.0 ± 0.2	0.4 ± 0.1
1.9 ± 0.4	2.3 ± 0.5	3.7 ± 0.7	1.9 ± 0.4	1.5 ± 0.3	1.7 ± 0.3
0.19 ± 0.04	5 ± 1	2.3 ± 0.5	1.9 ± 0.4	1.0 ± 0.2	3.0 ± 0.6

At the urban background station (Tab 3) the PM2.5 are dominated by OM. EC is also a dominant fraction. Overall composition of PM2.5 in the harbour site (Tab 4) is very similar. OM and EC represent 55% and 9% of PM2.5, respectively. Only trace elements concentrations are significantly higher in the harbour site (9% vs. 3% for the urban background site). This difference is mostly due to Ca, Na and Cl. Higher Organic markers concentrations are observed in the Urban Background station, especially levoglucosan and odd n-alkanes. Higher concentrations of Ba, Sn, Cd and Cu in the Urban site, while Na, Cl, Ca, Cs, Pb, V and Ni are more abundant in the vicinity of the harbour. During the fall and winter biomass burning (wood and green wastes) is the most abundant sources at both sites with the exception of harbour site during winter (most important source is vehicular emissions).

Harbour related activities represent only a small fraction of the PM2.5 (0.8 and 1.2% in the urban background and harbour sites, respectively).

1.2.4 Thessaloniki

Two sampling sites were selected: the City Hall at the city center (40°62'36.25"N, 22°95'38.27"E) and the Port (40°63'98.77"N, 22°91'8 3.57"E). PM2.5 daily samples were collected between 14/06/2011-22/05/2012 in selected days for a grand total of 322 samples. A PMF analysis was performed to apportion the PM2.5 sources (Tab 5).

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Tab 5. Thessaloniki, Average results (contribution to PM2.5 level in μg/m^3):

City Hall		Port	
Traffic (vehicle exhausts)	11.3 ± 0.6	**Vehicle exhausts + road dust**	16.0 ± 0.8
Industry	3.6 ± 0.2	**Industry/mineral**	14.2 ± 0.7
Marine (sea spray + ships emissions)	2.0 ± 0.1	**Sea spray**	3.0 ± 0.2
Road dust	6.1 ± 0.3	**Ship emissions**	11.3 ± 0.6
Combustion	4.4 ± 0.2	**Combustion**	5.2 ± 0.3
Secondary aerosol	11.7 ± 0.6	**Secondary aerosol**	14.1 ± 0.7
Not apportioned	8.6 ± 0.4	**Not apportioned**	8.2 ± 0.4

Two traffic-related sources are presented at the City Hall: one related to vehicle exhausts and one to road dust. These two sources are combined and presented as one source for the case of the Port. The total contribution to PM2.5 in the second case is lower. A marine-origin source with rather low PM2.5 contribution is presented at the city center. The same source is split to two different sources for the Port site: sea spray and fuel oil combustion (ships emissions), the sum of which presents stronger contribution to PM2.5 due to the proximity to the sources (about 16% of PM2.5). The combustion-related source presents seasonal variation, being more intense during the cold season, therefore it can be connected to central heating emissions. The mineral/industry source contribution is stronger at the Port site, without presenting significant seasonal variation. The secondary aerosols considerably contributes to PM2.5 at both sites (20%-25% of PM2.5).

1.2.5 Venice.

Three sampling sites were selected: Parco Bissuola (45°29'58.71"N; 12°15'40.55"E) and Malcontenta (45°29'58.71"N; 12°15'40.55"E), respect ively in the district of Mestre and in the industrial harbour area. In both the sites, PM10 daily samples were collected along the whole year 2011 and fully characterized in terms of PM10 composition. A third site, Saccafisola (45°25'42.18"N; 12°18'46.79"E), was chosen in Venic e in the area of the passenger terminal. In this case a partial chemical speciation of the PM10 samples was only performed and the source apportionment was limited to the assessment of heavy oil combustion.

A PMF analysis was performed to apportion the PM10 sources (Tab 6).

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Tab 6. Venice, Average results (contribution to PM10 level in µg/m^3):

	Bissuola Spring/Summer	Bissuola Fall/Winter	Malcontenta Spring/Summer	Malcontenta Fall/Winter	Saccafisola Spring/Summer	Saccafisola Fall/Winter
Biomass burning	5.4 ± 0.5	10 ± 1	1.1 ± 0.4	11.3 ± 1.5	-	-
Heavy oil combustion	3.7 ± 0.3	3.1 ± 0.3	6.5 ± 0.5	6.1 ± 0.5	6.1 ± 1.5	3.6 ± 0.9
Glass production	0.9 ± 0.5	1.1 ± 0.6	0.4 ± 0.2	0.8 ± 0.5	-	-
Industry (Cr)	0.6 ± 0.3	0.8 ± 0.5	1.1 ± 0.2	3.9 ± 0.5	-	-
Industry (Pb)	2.6 ± 0.5	7.3 ± 1.4	0.9 ± 0.7	1.2 ± 1.0	-	-
Road traffic	0.7 ± 0.4	1.0 ± 0.4	5.0 ± 0.5	8.3 ± 0.7	-	-
Soil dust	0.5 ± 0.1	2.1 ± 0.3	1.1 ± 0.2	2.1 ± 0.3	-	-
Secondary sulphathes	5.6 ± 0.4	6.3 ± 0.5	8.1 ± 0.9	7.8 ± 0.9	-	-
Secondary nitrates	1.0 ± 0.1	10.7 ± 0.5	1.2 ± 0.1	10.9 ± 0.5	-	-

Several industrial activities contribute to the PM10 level in the Venice area with a cumulative average weight of 10% - 20%. Heavy oil combustion is due both to ship emissions and to industrial plants: in the two inland sites (Bissuola and Malcontenta) the percentage weight of these sources does not show any seasonal trend while in Venice area (Saccafisola) a quite clear increase during the touristic season could be appreciated (in percentage terms the weight increase from about 13% to about 23% of PM10) this indicating a preponderant impact of ship emissions (large cruise ships and ferryboats).

1.2.6 Conclusions for Source Apportionment Analysis by receptor models

The long monitoring campaigns in each study area produced a quite detailed picture of PM composition and sources. Even if the results are not directly comparable since they partially depend on the position of the sampling sites, in four cities the impact of ships emissions has been detected at comparable and significant levels (between 10% -20% of the total PM) while a lower figure came out from the Marseille data set. This was the only one analysed with the CMB model and a systematic difference with the PMF approach is not surprising and would deserve a much broader discussion. The PMF approach in Marseille will be finalized at the beginning of February 2013.

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1.2 Source Apportionment Outcomes by Chemical Transport Models

Source Apportionment analysis by CTMs has been performed using the zero-out modeling technique by the groups running CHIMERE (Barcelona and Marseille) whereas for CAMx the specific PSAT tool has been applied (Genoa, Venice, Thessaloniki and once again Marseille). The zero-out method sets to zero a specific emission on the original emission inventory and measures the change in the concentration output; a complete model run is required for each source or emission sector under investigation. Particulate Source Apportionment technology (PSAT) uses reactive tracers to apportion primary PM, secondary PM and gaseous precursors to secondary PM among different source categories and source regions.

We report here a very synthetic summary of the results obtained in each study area.

1.2.1 Barcelona

Source apportionment for PM10 and PM2.5 has been evaluated by CHIMERE zero-out method for both Summer (August 2011) and Winter (December 2011) periods. The maritime contribution analysis has been calculated by the zero-out method applied on the Other Mobile Sources (SNAP 8) in which port emissions are included.

SA outcomes are here discussed for three sites: an urban site in Barcelona downtown and two sites near the Port: the World Trade Center, which can be considered as a port background site and a second site located at the very heart of the port of Barcelona.

All the three sites present exceedances of the daily PM10, both during summer and winter periods, with higher concentration both for PM10 and PM2.5 during summer than at wintertime, indicating the importance of secondary formation in PM levels in the city of Barcelona.

The highest concentrations are recorded at the site at the very heart of the port of Barcelona (Tab 7).

Tab 7. PM10 and PM2.5 concentrations recorded at 3 Barcelona monitoring sites in Summer and Winter period

Site	PM10 (µg/m^3) Summer	PM10 (µg/m^3) Winter	PM2.5 (µg/m^3) Summer	PM2.5 (µg/m^3) Winter
Barcelona downtown	40.5	24.0	19.2	14.2
World Trade Center (WTC)	52.2	40.2	24.6	22.0
Inner Port (POR)	69.4	55.2	43.2	29.4

In all the three sites, Source Apportionment outcomes for PM10 and PM2.5 are slightly different but not so much to give different ranking in the contribution analysis (Tab 8).

At summertime the most important contributors at the various sites are the following:

- urban site: on-road transport, followed by the maritime sector (included in other mobile sources);
- World Trade Center site: maritime sector, followed by on-road transport. Here, also the boundary conditions and biogenic sources have a relevant weight on PM10 and PM2.5 concentrations;
- inner port site: the maritime sector, dominates with over 50%, followed by on-road transport. Here, the external contribution is reduced from both the urban and the WTC sites, indicating the important local contribution of emissions to air quality.

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At wintertime the most important contributors at the various sites are the following:

- urban site: the contribution from outside of the domain through the boundary conditions and combustion in manufacturing industry (SNAP 3); on road traffic loses importance, as well as the maritime sector;
- World Trade Center site: the maritime sector followed by on-road transport, with the weight of combustion in manufacturing increased conversely to biogenic contributions in respect to summertime;
- inner port site: the maritime sector still dominates but with a less important weight then summertime (38%); the second contributor is the combustion in manufacturing processes.

Tab 8. SA by CHIMERE during summer (August 2011) and winter (December 2011) at 3 Barcelona sites.

PM2.5 Source Apportionment (% on total concentrations)	Urban site		World trade center		Inner port	
	summer	winter	summer	winter	summer	winter
Boundary conditions	6.3%	14.3%	8.3%	8.9%	5.5%	7.7%
Road Transport	20.5%	8.5%	18.6%	18.1%	11.7%	8.3%
Other mobile sources (including Maritime/Harbor emissions)	16.7%	4.5%	28.4%	23.2%	53.9%	38.1%
Non-industrial combustion	6.9%	3.5%	5.6%	6.5%	4.6%	3.6%
Energy production and Industries	7.4%	8.9%	7.0%	9.3%	5.8%	16.1%
Agriculture	2.5%	1.3%	2.4%	1.2%	1.4%	1.2%
Biogenic sources	5.2%	3.1%	7.2%	2.5%	4.9%	2.0%
Others	34.5%	55.9%	22.5%	30.3%	12.2%	23.0%

Focusing on the other mobile sources sector, which includes maritime emissions, the mean contribution on PM2.5 among the three sites varies between 17% at the urban sites and 54% inside the port area during summertime, whereas in winter this contribution decreases to 5% at the urban site and 38% at the port. This contribution takes into account not only the emissions from ship and vessels, but considers all the emissions coming from the SNAP 8 (other mobile sources), comprehending all on shore port activities.

Very similar results are recorded for the PM10 source apportionment (between 16% and 52% in summer and between 7% and 41% in winter). The mean contribution is rather constant throughout the year in the entire domain (approx. 7-9%), but a strong seasonality can be found at the urban site (16-17% in summer vs. 5% in winter).

The minimal contributions are lower than 1% for both summer and winter period at the scale of the APICE domain.

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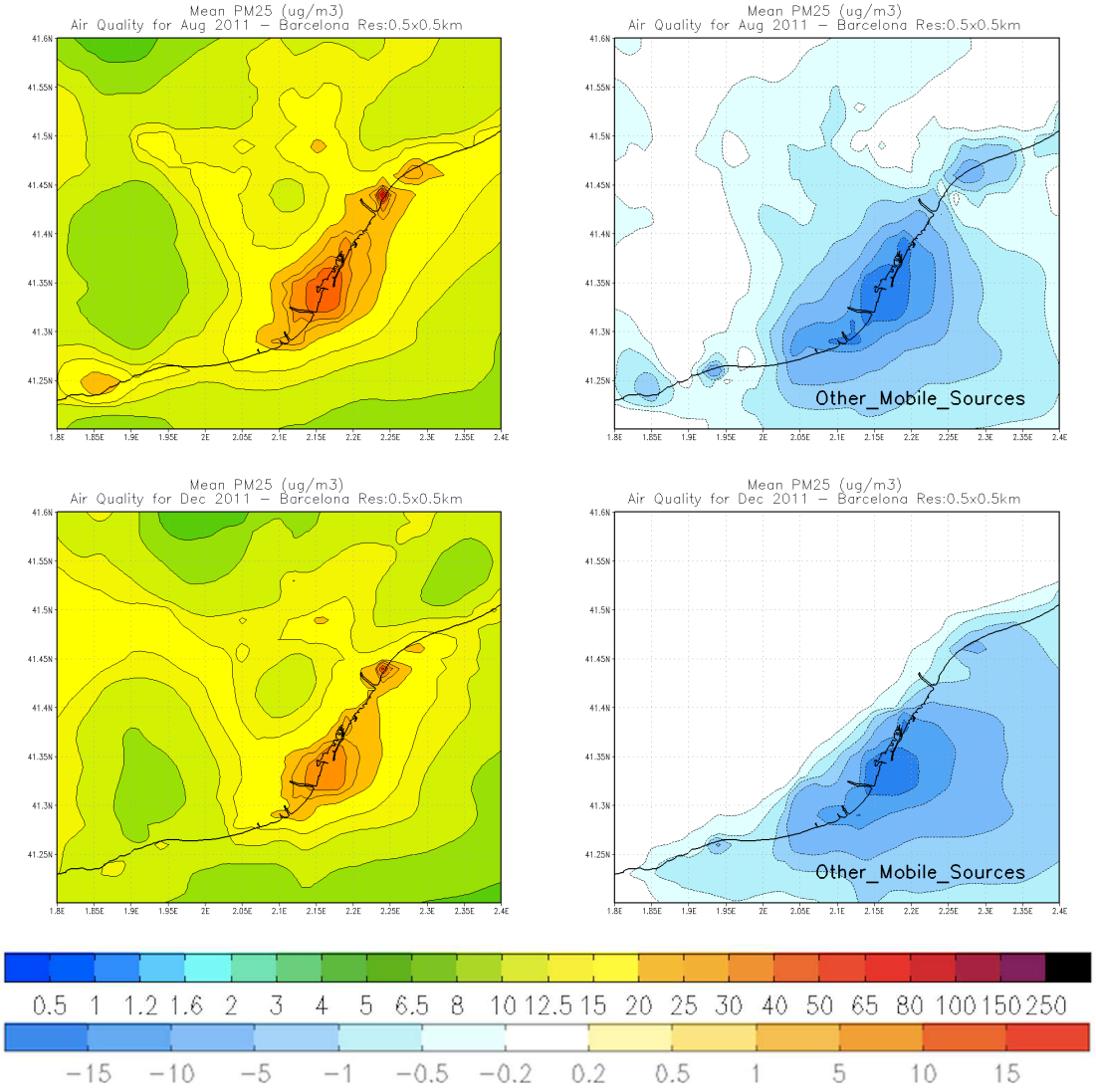
Fig 1 Monthly PM2.5 concentrations (µg m^{-3}) (left) during the summer (top) and winter (bottom) periods at the Barcelona APICE domain scale by CHIMERE model and contributions for maritime sector (right) (obtained by zero-ing out the SNAP8 sector).



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1.2.2 Marseille

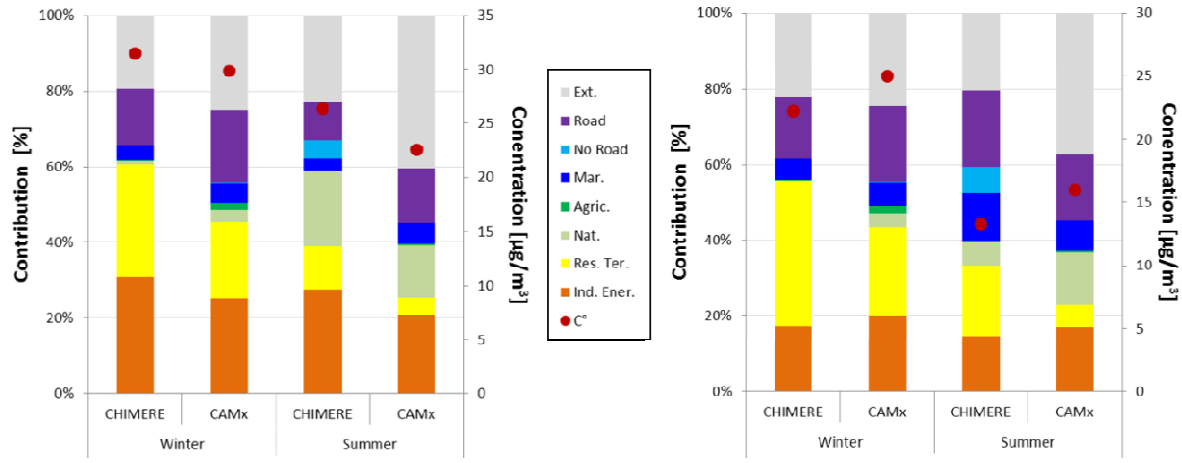
Source apportionment for PM10 and PM2.5 has been evaluated both by CHIMERE and CAMx, using zero-out modeling and tracer approach (PSAT) respectively for both winter, February 2011, and summer, August 2011 periods (Fig 2).

During the winter period, several exceedances of the daily PM10 have been monitored to the urban background station of “5 Avenues”, located downtown in Marseille. The major contributions are associated to industry-energy and residential-tertiary sectors. The road traffic significantly contributes to high PM10 and PM2.5 concentrations also.

During the summer period, PM10 and PM2.5 concentrations are lower. The industry-energy and road traffic sectors still have a major contribution to particulate matter. An additional significant contribution is issue from the natural sector. Mainly during the summer period, the external sector, representing the long-range transport, displays a large contribution to particulate matter concentrations.

Except the agriculture and the non-road and non-maritime sectors, every anthropic emission sector displays a significant contribution with different timing, spatial extent or absolute contribution. Thus, an efficient reduction of PM concentrations should involve each activity sector over large areas.

Fig 2. Concentration and relative contribution of emission sectors to the monthly PM10 (left) and PM2.5 (right) concentrations at «5 Avenues» sampling site during winter and summer periods using zero-out modeling by CHIMERE and tracer approach by CAMx with PSAT module.



SA outcomes are here discussed for two sites: an urban background site located downtown in Marseille and a second site located inside Marseille’s harbor (Tab 9). Focusing on the maritime contributions, the maximal contribution of this sector is computed during the summer period at the port site with 10% of the PM2.5 concentration. At the urban background site, the maritime contributions are lower and range between 7% and 9% of the PM2.5 concentrations. As the distance between sites is less than the spatial resolution of the model, results for urban and port sites are very similar.

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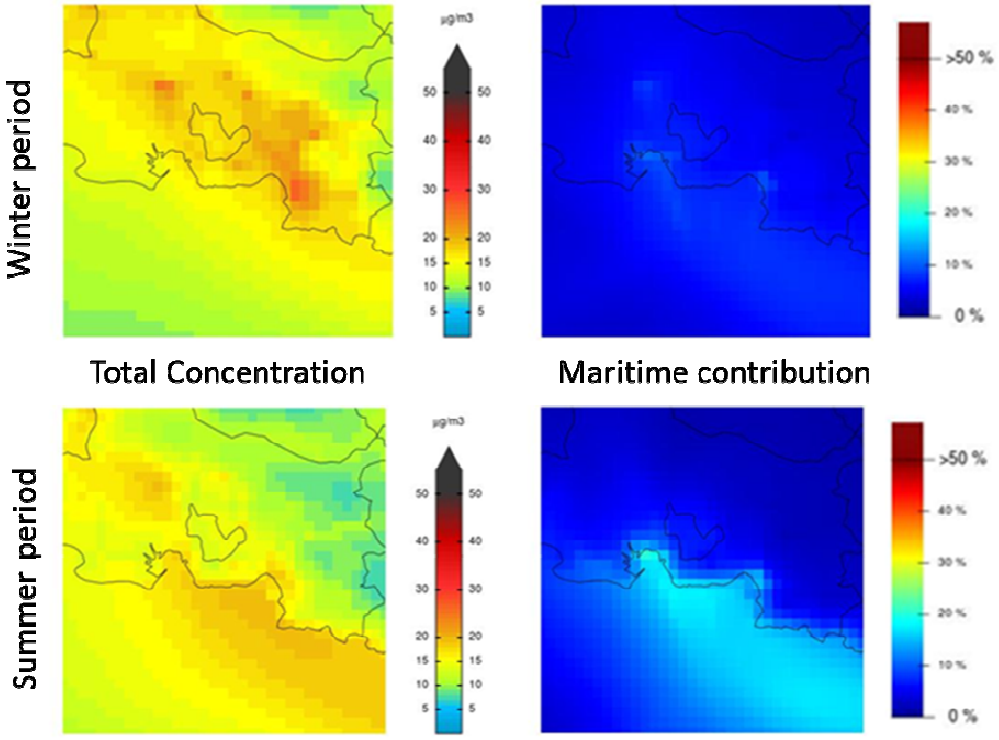
Tab 9. SA from CAMx during summer (August 2011) and winter (February 2011) at 2 Marseille sites.

PM2.5 Source Apportionment (% on total concentrations)	Urban site "5Avenues"		Inner port site	
	summer	winter	summer	winter
Boundary conditions	37%	25%	38%	26%
Road Transport	17%	20%	16%	19%
Maritime/Harbor	9%	7%	10%	7%
Other mobile sources (excluding horbour)	0%	0%	0%	0%
Residential/tertiary	5%	21%	4%	20%
Energy production and Industries	17%	21%	17%	21%
Agriculture	0%	2%	0%	2%
Biogenic sources	14%	4%	14%	4%

The application of the model over the APICE domain allows a spatial representation of source apportionment results and highlights the location of the contribution from the maritime sector (Figure 3).

The maximal contribution from the maritime sector is 11% and 20% of the total PM2.5 concentration during the winter and summer periods respectively. These maximal contributions are located inside the port area.

Fig 3 Monthly PM2.5 concentrations (left) during the winter (top) and summer (bottom) periods at the APICE domain scale by CAMx model and relative contributions for maritime sector (right).



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1.2.3 Genoa

Source apportionment for PM10 and PM2.5 have been evaluated by CAMx-PSAT for both a Summer period (June-August 2011) and a late Autumn period (15 November - 15 December 2011).
PSAT routine has been activated, allowing for a complete analysis of source impact over the whole Genoa domain. SA outcomes are here discussed for the three sites where long monitoring campaign has been performed: Corso Firenze and Multedo (costal sites) and Bolzaneto (inland), allowing to make a comparison with results obtained by receptor models analysis.
Five source categories have been considered, in view of both the main goal of APICE project (assesment of harbour impact) and the peculiar characteristic of Genoa area, in particular:

- Maritime sector
- Traffic
- Industrial sources
- Non industrial combustion plants (SNAP02 sector, in Genoa area mainly residential sources)
- Other sources (including boundary conditions)

On Tab 10 we report the contribution of above listed sources to simulated PM2.5 concentrations in the three monitoring sites.

Tab 10. SA by CAMx during summer (June-August 2011) and late-autumn (15 November – 15 December 2011) at 3 Genoa sites.

PM2.5 Source Apportionment (% on total concentrations)	Cso Firenze		Mutedo site		Bolzaneto	
	summer	fall-winter	summer	fall-winter r	summer	fall-winter
Road Transport	53%	38%	46%	32%	47%	35%
Maritime/Harbor	11%	5%	9%	4%	4%	3%
Residential/tertiary	1%	8%	2%	9%	2%	9%
Energy production and Industries	18%	19%	18%	20%	21%	20%
Others	17%	30%	25%	35%	26%	33%

The pattern obtained confirms the expected scenario for air quality in Genoa area, showing that the main pollution source in Genoa is related to road traffic, and minor contributions are given by industries and by maritime activities.
A seasonal trend can be identified in both coastal and inland sites. In fact during winter period a strong increase in the contribution of “Residential” sources is observed, which can be ascribed indeed to the presence of residential heating emissions.
Moreover in coastal sites, which lies near the harbour (almost inside when considering the spatial resolution of simulation domain) a strong reduction of maritime activities contribution is observed during winter period, when ship traffic in the harbour is lower (effect mainly related to social trend in tourism). The maritime contribution on PM2.5 concentrations varies among the three sites between 4% and 11% in summer, whereas in winter decreases to 3-5%.
Finally the comparison between coastal and inland sites is consistent with what expected, in particular considering that lower contribution of harbour activities on PM2.5 is observed for inland site.

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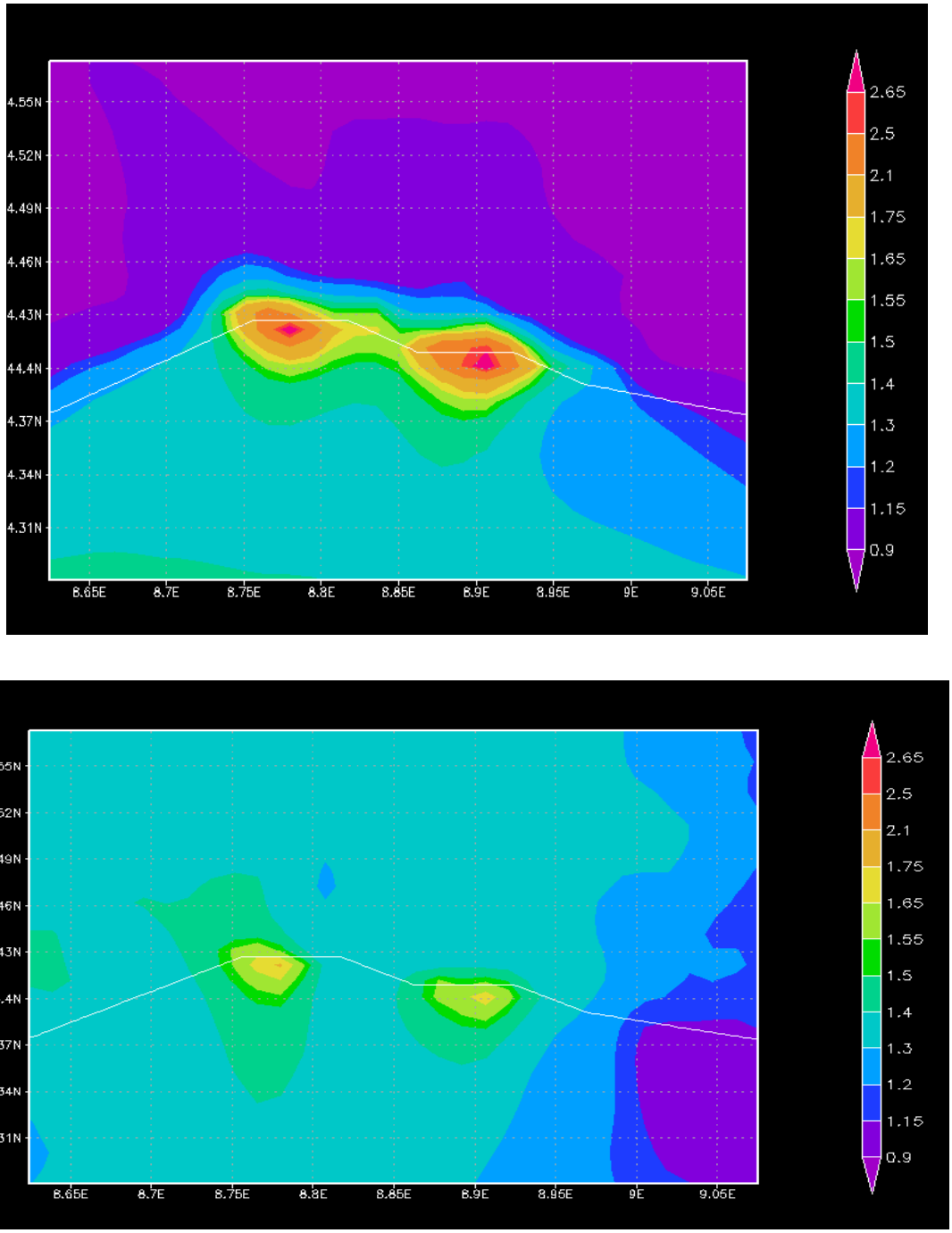
In the Fig 4 we report the concentration values of PM2.5 due to harbor activities emissions. Higher values are observed in summer period, confirming the seasonal trend observed in single receptor analysis. Also, in summer period the harbor activities impact is more evident in coastal area, where most of the Genoa urban area is located.

Fig 4. PM2.5 mean values in summer period (top) and late-autumn (bottom) in Genoa (Maritime activities sources only).



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1.2.4 Venice

Source apportionment for PM2.5 has been evaluated by CAMx-PSAT for both a Summer period (June-August 2011) and late Autumn period (15 November – 15 December 2011).
PSAT routine has been activated, allowing for a complete analysis of source impact over the Venice nested domain, which covers the urban area with an extent of 30 km and a resolution of 1 km.
PM2.5 Source Apportionment outcomes are here discussed for the three sites where the long monitoring campaign has been performed: two urban background sites, one in the Venice historical center (close to the passenger ship berths, Sacca Fisola) and one in the mainland part of the Venice Municipality (Mestre, Parco Bissuola), and one industrial site located close to Porto Marghera (industrial and commercial harbor and industrial area of Venice).
Tab 11 shows the SA for the fine airborne particulate matter (PM2.5) at the Venetian monitoring sites, expressed as % contribution to the mean concentration of the seasonal period.

Tab 11. SA by CAMx during summer (June-August 2011) and late-autumn (15 November – 15 December 2011) at 3 Venice sites.

PM2.5 Source Apportionment (% on total concentrations)	Venice		Mestre		Marghera	
	summer	fall-winter	summer	fall-winter r	summer	fall-winter
Boundary conditions	27.0%	19.0%	27.4%	17.6%	28.1%	18.1%
Road Transport	8.6%	16.8%	16.7%	20.4%	11.9%	17.5%
Maritime/Harbor	8.0%	1.8%	5.5%	0.2%	8.1%	0.9%
Central Heating	0.3%	27.0%	0.5%	32.9%	0.5%	33.0%
Industries	5.9%	7.6%	9.1%	6.4%	10.8%	6.9%
Agriculture	4.8%	8.2%	6.2%	9.1%	7.6%	8.6%
Biogenic sources	28.6%	13.4%	27.7%	10.7%	27.2%	12.3%
Leftover Sources	16.7%	6.2%	6.8%	2.6%	5.8%	2.7%

The boundary conditions, which refer to the PM amounts coming from outside the main modeling domain (256x236 km^2 covering Veneto Region and part of the neighbouring regions), play an important role on the concentration levels simulated in the Venice area, in both seasons.
In the summer period, natural sources accounts for the greatest amount of PM2.5 concentrations, followed by boundary conditions, whereas the anthropogenic source with the most relevant impact on concentrations is road transport. The maritime activities account for the 6-8% of the PM2.5 concentrations along the three monitoring sites.
During the late Autumn 2011, characterized by concentrations up to three times higher than the summer period, the wind blew from north-west and brought the emissions from the Po valley into the nested domain; in these meteorological conditions the influence of boundary conditions decreases while the relative importance of first levels diffusive emissions increases, even if road transport, wood combustion from residential heating and agriculture aren't typical emissions in Venice historical center. The maritime and harbor activities present a rather small contribution to the PM2.5 average levels during this cold scenario, mainly because the presence of the emissions of domestic heating in respect to the summer scenario. Moreover the passenger vessels traffic decrease significantly between November and March.
Fig 5 illustrates how harbor activities contribution on PM2.5 concentration is spatially distributed on the nested modeling domain, in the summer and late-autumn period. The

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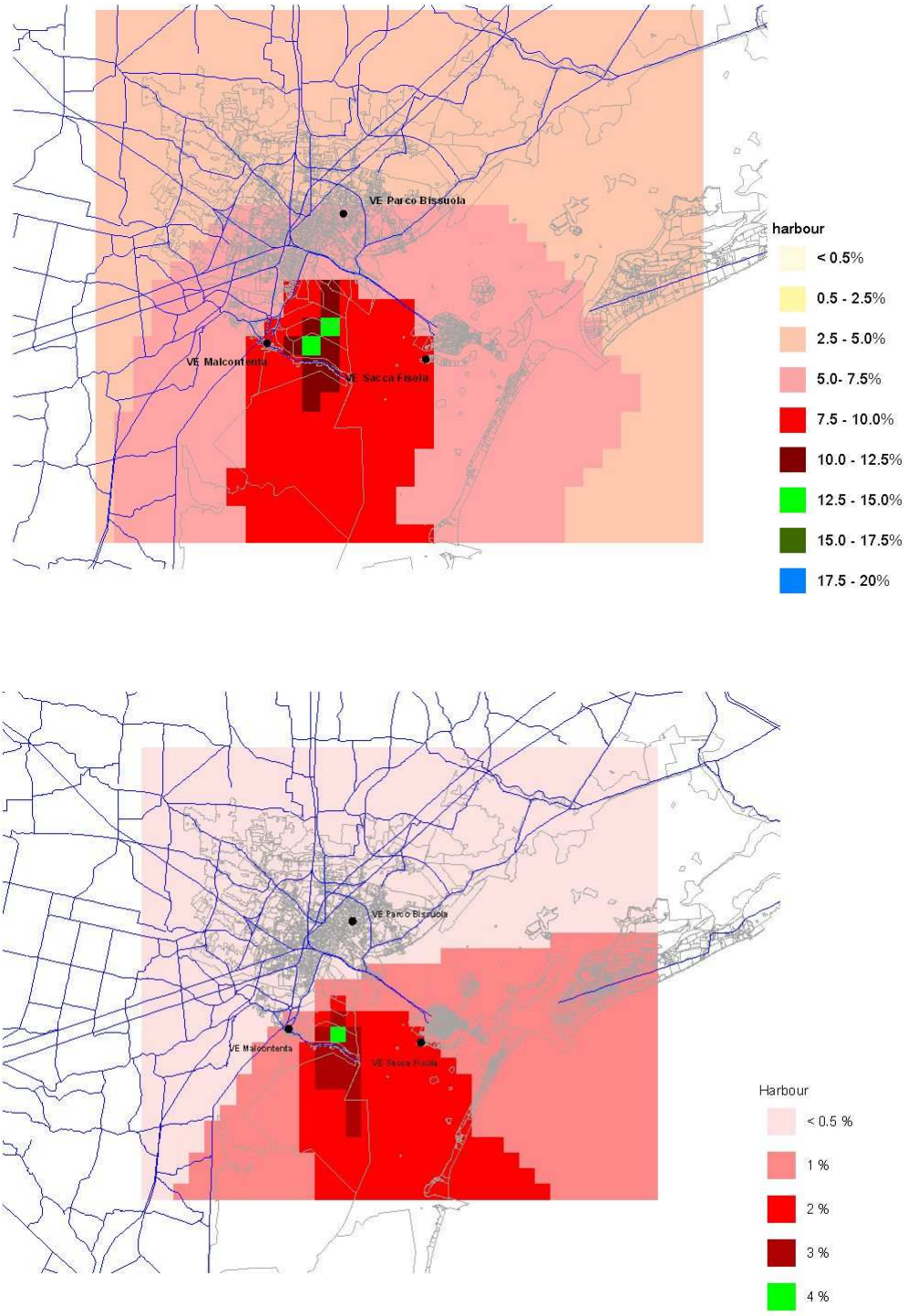
maximum contribution of harbor activities to the mean PM2.5 values is depicted in green and reaches 15% in the summer period and 4% during the cold one.

Fig 5. Spatial distribution of the % contribution of Maritime activities to the mean PM2.5 concentrations over the Venice nested domain in the summer scenario (top) and in the late-autumn scenario (bottom).



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1.2.5 Thessaloniki

Source apportionment for PM2.5 has been evaluated by CAMx-PSAT for both a Summer period (June-August 2011) and a late Autumn period (15 November – 15 December 2011).
PSAT routine has been activated, allowing for a complete analysis of source impact over the Thessaloniki domain, that covers the urban area with an extent of 120 km and a resolution of 2 km.
PM2.5 Source Apportionment outcomes are here discussed for the two sites where the long monitoring campaign has been performed: the first is in the Port area while the second is in the City Hall (Fig 6).

Fig 6. The city of Thessaloniki and the monitoring sites.

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Tab 12 presents the SA for the fine airborne particulate matter (PM2.5) at the monitoring sites. The SA analysis has revealed an important contribution of the pollution sources outside the modeling domain to the atmospheric levels of PM2.5 in Thessaloniki. However, in the results shown in Tab 12, this influence is not considered. Consequently, the results shown are indicative of the contribution of the pollution sources inside the modeling domain to the PM2.5 atmospheric pollution in Thessaloniki.

Tab 12. SA from CAMx during summer (June-August 2011) and late-autumn (15 November – 15 December 2011) at 2 Thessaloniki sites.

PM2.5 Source Apportionment (% on total concentrations)	City Hall		Port	
	summer	fall-winter	summer	fall-winter r
Road Transport	45.1	24.5	44.8	24.9
Maritime/Harbor	2.2	1.0	5.8	2.8
Central Heating	0.0	45.4	0.0	44.3
Industries	20.1	10.9	16.4	9.8
Windblown Dust	1.2	0.9	1.2	0.8
Biogenic NMVOCs	0.6	0.1	0.6	0.1
Leftover Sources	30.8	17.2	31.2	17.3

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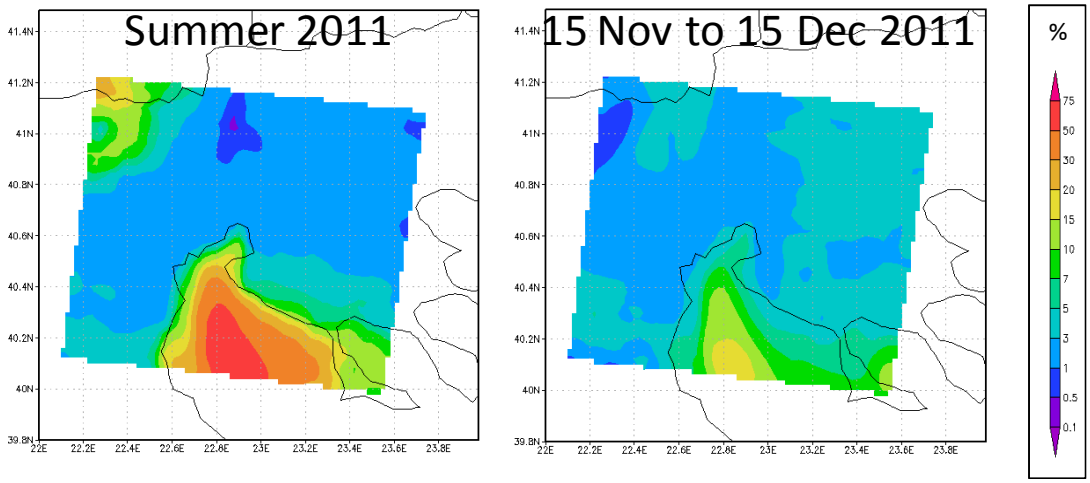
Road Transport and Central Heating have the highest contribution to PM2.5 concentrations in the Thessaloniki urban area in the summer and in the winter period examined respectively. The Maritime and Harbor activities present a rather small contribution to the PM2.5 average levels: from 6% in the port sites during summer to 1% in the urban site in the early winter period. The influence of this emission source is greater in summer compared to the winter time because of the increased ship traffic, harbor and fishing activities during summer. The influence of the Maritime and Harbor activities is smaller in the City Hall compared to the Port. The City Hall is about 5 km away from the Port and represents urban background conditions.
Fig 7 illustrates the spatial distribution of the contribution of Maritime and Harbor activities to mean PM2.5 concentration over the whole modeling domain. As expected, the CAMx results have shown that the contribution is higher over the maritime than over the coastal and continental areas of the study domain. Over the former areas, the contribution can be rather significant in the summer (more than 50%) while it is moderate in the wintertime (about 20%). In addition, the contribution is higher over the maritime areas that are more distant to the coast.

Fig 7. Spatial distribution of the % contribution of Maritime and Harbor activities to the mean PM2.5 concentrations over the Thessaloniki study domain.



1.2.6 Conclusions for Source Apportionment Outcomes by Chemical Transport Modelss

The Source Apportionment analysis by CTMs produced a quite detailed picture of the contribution of the different emission sources to PM10 and PM2.5 in each study area.
Focusing on the maritime activities impact on PM2.5 concentrations, a common feature for the five study area is an higher contribution during Summer period, when touristic ship activities are at their maximum and residential heating is at its minimum.
The maximum impact by maritime activities has been spotted always in summer: in Barcelona a contribution of 54% of harbour activities (ships and vessels and on shore harbour activities) has been calculated in the very heart of the port; a comparable contribution (~65%) is estimated in Thessaloniki over the open sea, estimation however calculated considering only the contribution of the pollution sources at local-medium scale (that is without taking into account the contribution of the emission sources outside the inner modelling domain).

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Considering only the ship and vessels emissions, in summertime a maximum value of 33% is reached in Genoa whereas in Marseille and Venice the highest values are 20% and 15% respectively.
In wintertime, the highest contributions by maritime/harbour activities become lower: 38% in Barcelona and 20% in Thessaloniki; more comparable contribution have been obtained for Genoa, Marseille and Venice: 7%, 11% and 4% respectively.
Analysing the maritime contribution over the sites of the long monitoring campaign performed in every study area, the pattern spotted is: a contribution from 2% to 17% for the urban background sites in summer that become from 0% to 7% in winter.
The contribution for the sites very exposed to harbour emissions is quite different among the study areas and strongly depends on the different exposition to the local emission within the port-city area under investigation and on the method applied to analyse the harbour contribution.

1.3 Conclusions on Source Apportionment Analysis

The first specific objective of APICE was to estimate the relative contribution of several pollution sources to air quality and to understand the similarities/differences among the port areas investigated.
This task has been carried out by the scientific group following two different techniques of Source Apportionment analysis, based respectively on receptor models and Chemical Transport Models (CTMs). The focus of these techniques was the identification of pollutant emissions that mostly affect PM10 and PM2.5 concentrations.
The two different Source Apportionment approaches aimed at integrating the peculiar potentialities of both techniques: by one side receptor models, more suitable to pointing out the bonds between specific emission sources and specific markers and, on the other side, CTMs, that extend their assessment on the formation of secondary aerosols, since they apportion the gas precursor emissions, too.
These two SA techniques have required different preparatory activities that have been implemented in parallel for each harbour area of the project. Receptor models identify, on a statistical basis, the weight of different urban sources differentiating temporal trends in concentrations; to their implementation, chemical speciation of aerosol are required to quantify the abundance of the different source tracers.
The chemical transport models, on the other hand, reconstruct the air pollutant concentrations from emissions and meteorological inputs, so they are particularly suitable for scenarios evaluation.

As input of the receptor models, during 2011, in each studied area a long air pollution monitoring campaign, with aerosol measurements and chemical speciation, has been carried out. A common feature was the choice to monitor two or more sites, in each urban area, having different exposures to emission sources. In every city, at least one site was more exposed to maritime emissions (from harbour terminals or at least from ship traffic), one site was urban background and possibly one place more exposed to surrounding industrial area.

The long monitoring campaigns in each study area produced a quite detailed picture of PM composition and sources. Even if the results are not directly comparable since they partially depend on the position of the sampling sites, in four cities the impact of ships emissions has been detected at comparable and significant levels (between 10% -20% of the total PM) while a lower figure came out from the Marseille data set. This was the only one analysed with the CMB model and a systematic difference with the PMF approach is not surprising and would deserve a much broader discussion.

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The Source Apportionment analysis by CTMs produced a quite detailed picture of the contribution of the different emission sources to the PM2.5 in each study area. As for maritime activities impact, a common feature for the five study areas is a higher contribution during the summer period, when touristic ship activities are at their maximum and residential heating is at its minimum.
The maritime contribution among the city partners is quite different, depending not only on the peculiarity of each study area (e.g.: socio-economic trends, meteorological and dispersion conditions, industrial and residential emission strength and composition), but also from the methodology applied by the partners. The higher contribution of harbour activities has been estimated in summer in Barcelona at the very heart of the port and in Thessaloniki at open sea (both over 50% of contribution), whereas in the other cities lower values have been estimated. Nevertheless at urban background sites more comparable results have been obtained with a contribution ranging from 2% to 17% in summer and 0% to 7% in winter.

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