Variability of fine and coarse aerosol over the Western Mediterranean Basin during the Minerva 2015 research cruise campaign

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1. The research cruise campaign

The Mediterranean Sea is surrounded by an area densely populated with a high level of industrialization, which is contributing to air pollution from anthropogenic sources in addition to already present natural sources like Saharan dust, emissions from active volcanoes and wildfires.[1]

The Institute of Atmospheric Pollution of the National Research Council (CNR-IIA) is conducting periodic measurements campaigns to understand processes and influences of various sources on the Mediterranean Basin, focusing, among others, on the Particulate Matter (PM) air pollution.[2]

The 2015 cruise campaign was conducted during the summer (26th of June to 13th of July), in the Western Mediterranean, starting from Sicily (Palermo); the route and the anchorage sites are shown in **Fig. 1**. Except for Cagliari, MA2 and B. Bonifacio, in which the anchorages were made in daytime, in all other cases, the anchorages were made at night.

2. Fine and Coarse Particulate

Measurements of *fine* ($PM_{2.5}$) and *coarse* ($PM_{2.5-10}$) were made with a sampling time of 24 hours on 47øMm Teflon filters, by using two High Volume Skypost (PM-HV). Filters were conditioned and weighted before and after sampling, the *particulate concentration* was thus obtained *gravimetrically*.

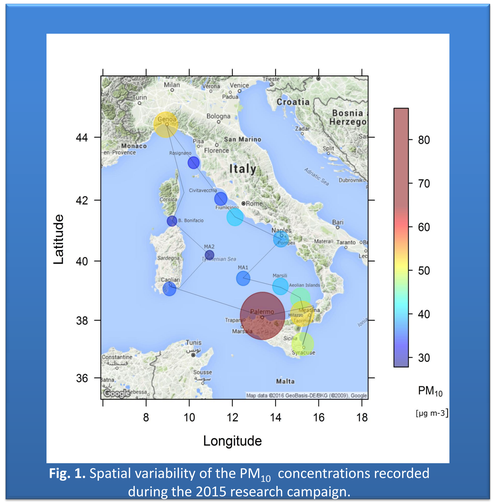


Fig. 1. Spatial variability of the PM_{10} concentrations recorded during the 2015 research campaign.

PM_{10} ($PM_{2.5}$ + $PM_{2.5-10}$) concentrations are shown in **Fig. 1** from which it is possible to deduce that the larger concentrations (higher than the limit value of Italian Legislation, D. Lgs. 155/2010, equal to 50 µg m^{-3}) were sampled in the South of Italy and, as an exception in the North, in the Gulf of Genoa; both these areas are densely industrialized.

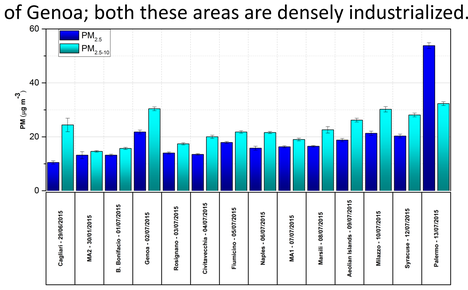


Fig. 2. Concentrations of $PM_{2.5}$ and $PM_{2.5-10}$ recorded during the route.

Measurements of $PM_{2.5}$ and $PM_{2.5-10}$, shown in **Fig. 2**, indicate a predominance of the coarser component during all the cruise, except for Palermo, where the fine particulate reached a value of 53.8 ± 1.1 µg m^{-3}.

$PM_{2.5}$ Elements

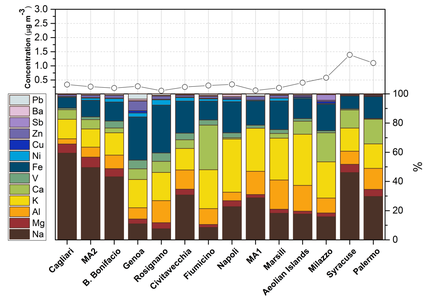


Fig. 3a. Sum of major and trace element concentrations detected in $PM_{2.5}$ (upper) and contribution of each element at the various sites (lower) (only elements with contribution >1% were reported).

A significative contribution of Fe, Zn and Pb was releaved in Genoa; the presence of Ba was releaved in Naples and an important contribution of Sb was observed near Milazzo.

3. Elements Concentrations

Teflon filters were digested with a mixture of HNO_3/H_2O_2 in an microwaves digestion system and then analyzed by *ICP-MS* for the determination of the *major and trace elements concentrations*.[3]

The sum of the elements concentration we analysed in $PM_{2.5}$ size fraction (**Fig. 3a**, upper) was lower than that we found for $PM_{2.5-10}$ (**Fig. 3b**, lower); we detected 0.8-6.8% and 3.1-8.9%, as elemental mass concentration, over the total mass concentration of $PM_{2.5}$ and $PM_{2.5-10}$, respectively.

$PM_{2.5-10}$ Elements

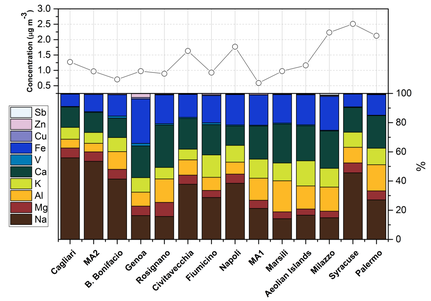


Fig. 3b. Sum of major and trace element concentrations detected in $PM_{2.5-10}$ (upper) and contribution of each element at the various sites (lower) (only elements with contribution >1% were reported).

The presence of Fe and Zn was releaved in Genoa and a little but important contribution of Sb was observed near Milazzo.

A receptor model, the *Positive Matrix Factorization (PMF),* was applied to identify the principal PM contributing factors. The optimum number of factors, evaluated with Q-value, was 6. Thanks to the concentration of factors in each species (**Fig. 4a** and **Fig. 4b**), markers of possible sources were identified, establishing the nature of each factor.

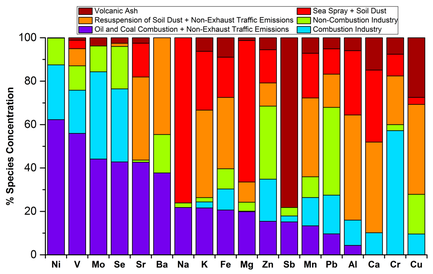


Fig. 4a. Contributions of factors in $PM_{2.5}$ species.

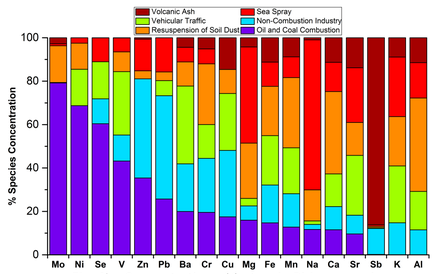


Fig. 4b. Concentration of factors in $PM_{2.5-10}$ species.

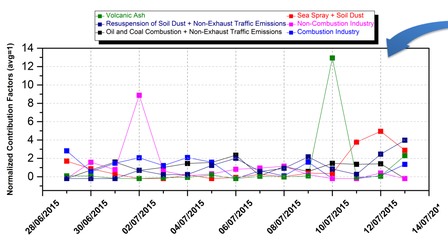


Fig. 5a. Temporal variability of normalized contribution factors identified for $PM_{2.5}$ size fraction.

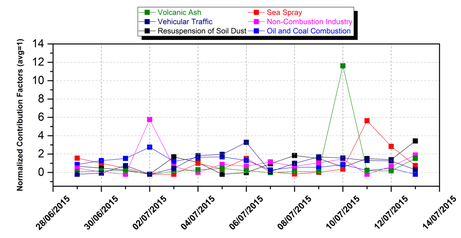
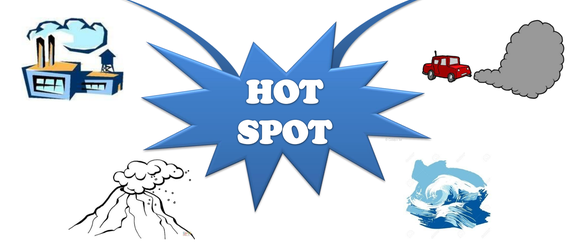


Fig. 5b. Temporal variability of normalized contribution factors identified for $PM_{2.5-10}$ size fraction.



Two important hot-spots were identified (**Fig. 5a**): on the 2nd of July, a peak of non-combustion industry in **Genoa** was detected and, on 10th of July, a peak of volcanic ash passing near **Vulcano** and staying in Milazzo was recorded. The last days (11th, 12th, 13th) an increase of sea spray and soil dust, due the rougher sea, was observed.

Three hot-spots were identified (**Fig. 5b**): on the 2nd of July, factors of non-combustion industry, and of oil and coal combustion showed a peak in **Genoa**; on the 6th of July, there was an increase of vehicular traffic factors in **Naples**; on 10th of July, a peak of volcanic ash near **Vulcano** and staying in Milazzo was recorded. Finally, on 11th of July, a peak of sea spray was aslo observed.

4. Conclusions

During the Minerva 2015 Research Campaign particulate measurements were conducted. The particulate coarser fraction ($PM_{2.5-10}$) was higher than finer component ($PM_{2.5}$). In 3 sites over 14, the particulate (PM_{10}) was higher than limit value of 50 µg m^{-3}. The major and trace elements were releaved using ICP-MS, and then the mainly influencing species at various sites were identified. Principal contributing factors were also determined with PMF and various hot-spots were highlighted, both of anthopogenic origins, like industry for Genoa or vehicular traffic for Naples, and natural sources, like volcanic ashes or sea spray. Further chemical analysis on particulate matter, like organic matter and ionic species, will allow us to better indentify the main PM contributing factors in the Mediterranean Basin.

References

1. **Bencardino, M., Sprovieri, F.** Cofone, F., and **Pirrone, N.** (2011) Variability of Atmospheric Aerosol and Ozone Concentrations at Marine, Urban, and High-Altitude Monitoring Stations in Southern Italy during the 2007 Summer Saharan Dust Outbreaks and Wildfire Episodes. Journal of the Air & Waste Management Association, 61, 952-967.
2. **Bencardino, M., Pirrone, N., Sprovieri, F.** (2014) Aerosol and ozone observations during six cruise campaigns across the Mediterranean basin: temporal, spatial, and seasonal variability. Environmental Science and Pollution Research, 21, Issue 6, 4044-4062.
3. **Sprovieri, F., Bencardino, M.**, Cofone, F., and **Pirrone, N.** (2011) Chemical Composition of Aerosol Size Fractions at a Coastal Site in Southwestern Italy: Seasonal Variability and Transport Influence. Journal of the Air & Waste Management Association, 61, 941-951.