PHD COURSE IN LIFE AND ENVIRONMENTAL SCIENCES

Report Form for PhD student annual evaluation (XXXVI and XXXVII cycles)

Name of PhD student: FALGIANI ANNAMARIA

Title of PhD research: ORGANIC AND INORGANIC CONTAMINANTS IN THEATMOSPHERIC PARTICULATE MATTER

Name of PhD supervisor: PROF.SSA ILLUMINATI SILVIA
Research lab name: Analytical Chemistry for environment and Food

Cycle:
 X -XXXVI
[ ] XXXVII

PhD Curriculum::
[ ] Marine biology and ecology
[ ] Biomolecular Sciences
X Civil and environmental protection

DISVA instrumentation labs/infrastructure eventually involved in the project:
[ ] Actea Mobile Laboratory
[ ] Advanced Instrumentation lab
[ ] Aquarium
[ ] MassSpec lab
[ ] MaSBiC
[ ] Simulation/informatics lab
X Other. Please, indicate: Clean room

ABSTRACT (1000 characters, including spaces):
The main goal of the present PhD project is to sample, chemically characterize and study the spatial-temporal evolution of organic and inorganic pollutants in the atmospheric particulate matter over the city of Ancona, a highly polluted area of the Marche Region. The harbour of Ancona has recently become a crucial step in the MSC cruises along the Adriatic Sea, adding an additional source of atmospheric pollution, especially concentrated during summer. In order to evaluate the air quality in this area, samples of size-segregated PM_{10} were collected by a six-stage high-volume cascade impactor with size classes between 10 µm and 0.49 µm. A sampling strategy of 3 days was adopted since July 2021 for the determination of the mass concentration of particulate matter and the chemical characterization of the size-segregated atmospheric aerosol, in terms of inorganic (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, Zn) and organic (PAH and Nitro-PAH) pollutants.

Part 1. Scientific case of the PhD Research (2 to 3 pages, including figures)

BACKGROUND

Studying atmospheric aerosols is of great concern in environmental research. Aerosol effects on climate, Earth radiative balance (directly by absorbing or scattering sunlight radiation[1] and, indirectly, by acting as cloud condensation nuclei or modifying cloud radiative properties and cloud lifetimes[2], biogeochemical cycles and public health have been widely recognized.

The city of Ancona is an important junction for the distribution of goods and the transfer of passengers at European level. The Ancona district is also dotted by several industries, mainly located along the Esino Valley. Several pollution sources affected this area, such as the big oil refinery at Falconara Marittima, the A14 or "Adriatic Highway", the international airport, and and, more recently, the MSC cruises stops during their journey along the Adriatic Sea.

SCIENTIFIC AIMS

The main goal of the present PhD project is to sample, chemically characterize and study the spatial-temporal evolution of organic and inorganic pollutants in the atmospheric particulate matter over the city of Ancona. In particular, the second year of the PhD project focuses on: 1) the collection of different size-segregated fractions of PM_{10} in the city of Ancona; (2) the inorganic chemical characterization of the aerosol samples collected; (3) the assessment of the seasonal evolution of the aerosol chemical composition; (4) the evaluation of the main sources of atmospheric pollutants with particular attention to the impact of maritime traffic.

WORKPLAN AND RESEARCH ACTIVITIES

From July 2021 samples of atmospheric particulate matter have been collected in Ancona, within the campus of the Università Politecnica delle Marche. has been used. Six PM_{10} fractions (10 -7.2µm; 7.2-3.0 µm; 3.0-1.5µm; 1.5-0.95µm; 0.95-0.49 µm; <0.49 µm) have been collected by a Teflon-coated high-volume PM_{10} sampler. The flow rate of the sampler is 1.13 m^3 min^{-1} (±10%). A sampling strategy of 3-day exposure time of the filters was adopted. Samples were collected twice a month during the summer and once a month during the rest of the year. In this second year of my PhD project, the first sampling campaign for the year 2021-2022 was completed, all analyses for the determination of atmospheric particulate concentrations were carried out, and the seasonal evolution and the mass size distribution were evaluated. In addition, chemical analyses are proceeding for the determination of the organic and inorganic pollutants.

WP 1. Objective.

The size-segregated aerosol mass concentration and its evolution during summer is studied in the city of Ancona.

Methods. During the 2nd year of my PhD project, I continue the determination of the size-segregated aerosol mass concentration and its evolution in relation to different emission sources. The aerosol mass collected on the filters was determined by a differential weighing procedure as reported in my previous first-year report. The data were processed with an inversion methodology for continuous aerosol mass size distribution and the results reported in the differential form $\Delta m/\Delta lnD$ (wherer Δm = mass concentration for each stage; $\Delta logDp$= difference of logarithms of stage size boundaries).

Expected/Obtained Results. The results of samples collected from July 2021 to March 2022 are reported in Fig 1. The average mass concentration of the total PM_{10} given as sum of the mass concentration of particulate matter in each fraction is 16 ± 1.4 µg m^{-3}. These values are in good agreement with those measured by the fixed stations belonging to the Air Quality Survey Network of the Marche Environmental Protection Agency (ARPA-MARCHE) and are below the legal limit for PM_{10} (Fig. 1). The size-resolved mass fractions showed a bimodal distribution with a fine mode FM (<2.5µm) and a coarse mode CM (2.5-10µm). FM accounted for ~55% of the total PM_{10} and increases during the summer week-ends, when an intense maritime traffic occurred in the harbor of Ancona. FM also increases during winter season probably due to domestic heating. CM accounts for ~40% of the total PM_{10}. Its concentration remained almost constant during the autumn/winter season. A slighlty increase can be observed at the end of January 2022.
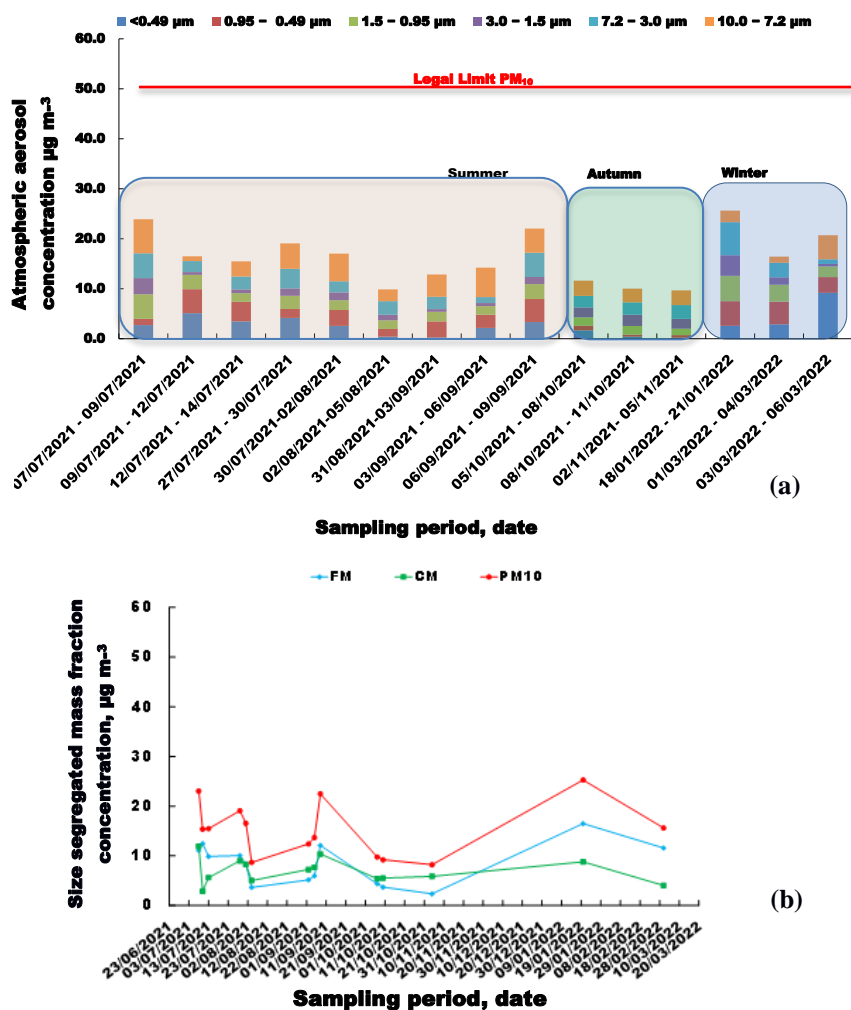
Fig.1 Size- segregate aerosol concentration (a) and the seasonal evolution of the two PM10 modes (b) (fine and coarse fractions) during the year 2021-2022.

WP 2. Objective. The chemical characterization of aerosol in the second year of my PhD project has been evaluated with particular focus on the trace metal content, because of their potentialities to be used as tracers of different emission sources[3,4].

Methods. An aliquot (1/8) of each original filter was subjected to a two-step microwave (MW) digestion procedure after the previous addition of 5 mL ultrapure HNO_3, 1 mL ultrapure H_2O_2 and 1 mL ultrapure HF. Trace metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn) were determined in the MW digested solutions by Atomic Absorption Spectrometer (GF-AAS), equipped with a graphite furnace (GTA120 Graphite Tube Atomizer) and a Zeeman-effect background corrector. Another aliquot (1/64) of each original filter was directly analyzed for particulate mercury (PHg) determination by using a Direct Mercury Analyzer.

Expected/Obtained Results. In the present report, preliminary results on the atmospheric concentration of Co, Cr, Mn, Ni, Se, V and Hg are reported in Fig. 2. Average atmospheric concentrations of the studied metals during July 2021 are here reported as mean ± SD: Co 0.50 ±0.08 ng m³; Cr 1.71 ±0.83 ng/m³; Mn 9.3 ± 4.5 ng/m³; Ni 0.82 ± 0.10 ng/m³; Se 1.19 ± 0.24 ng/m³; V 2.77 ± 0.69 ng/m³. All the metals, with the exception of Se and Ni, seemed to increase during weekend with mean concentrations about 15 % higher than the other days. Mn and V showed a continuous increasing trend, passing from 6.9 ng/m³ and 2.0 ng/m³ to 16 ng/m³ and 3.7 ng/m³, respectively.
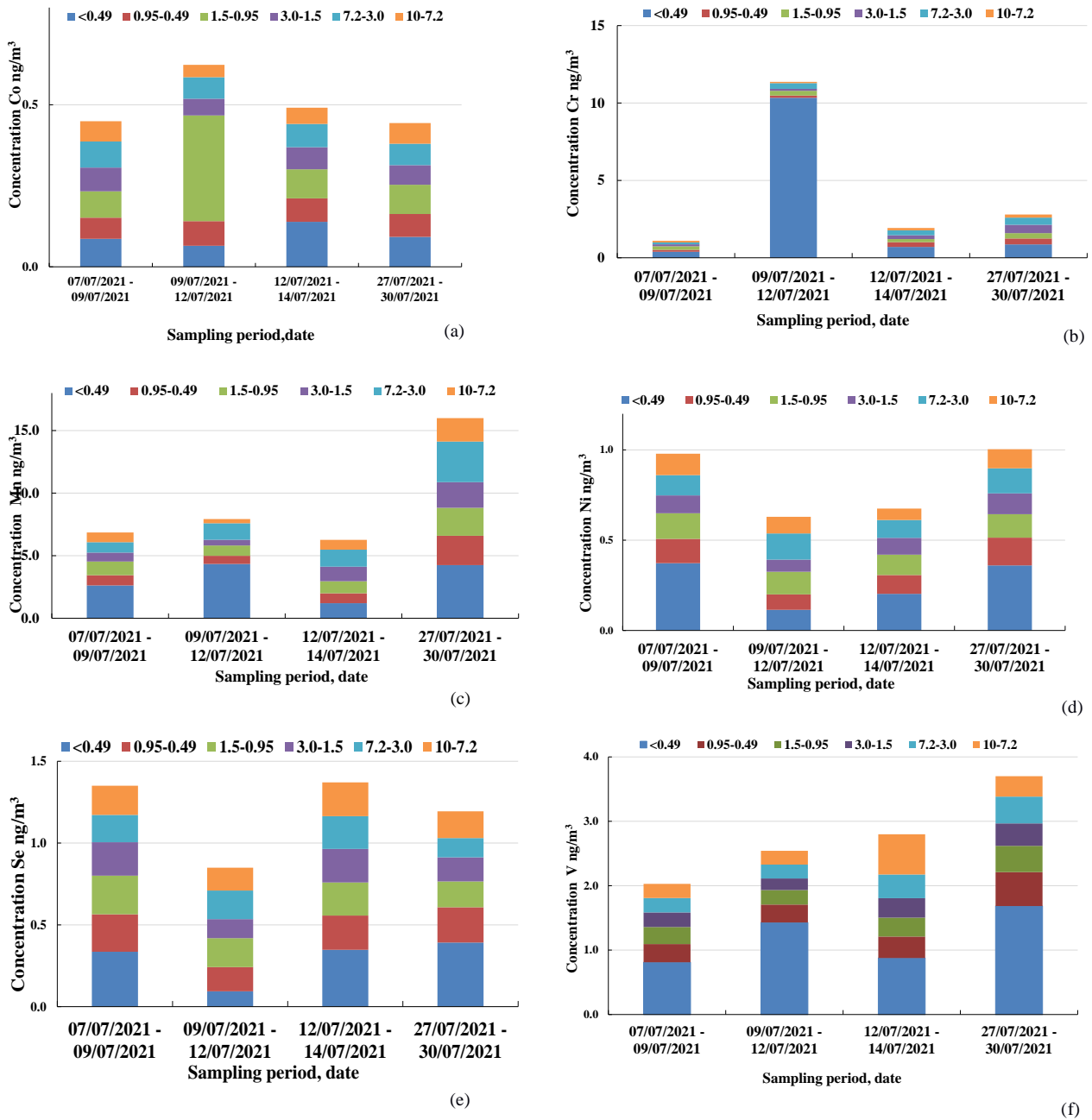
Fig. 3. Summer evolution of size-segregated concentration of Co (a), Cr (b), Ni (c), Mn (d), Se (e), and V (f) in the atmospheric aerosol over Ancona.

By assuming the size distribution of the PM over Ancona in two fractions, I compute the relative percentages of each metal in the fine mode (<2.5µm) and in the coarse mode CM (2.5-10 µm): Co, FM 62.5% and CM 37.5%; Cr, FM 58.6% and CM 41.4%; Mn, FM 59.7% and CM 40.3%; Ni, FM 62% and CM 38%; Se, FM 57.6% and 42.4%; V, FM 67% and CM 33%. The contribution of each metal studied in July 2021 shows a higher concentration in the fine fraction than in the coarse one, with V showing the highest percentage in the fine fraction (70% FM vs. 30%CM).

Fig. 3 shows the evolution of the size-resolved atmospheric concentrations of PHg in the city of Ancona. For this metal, results from July 2021 to July 2022 are available. PHg showed high concentrations during summer 2021, then it decreased in autumn and increased again during winter and spring seasons. During summer 2022, PHg concentrations are lower than those recorded in summer 2021, with values comparable to those of spring season.
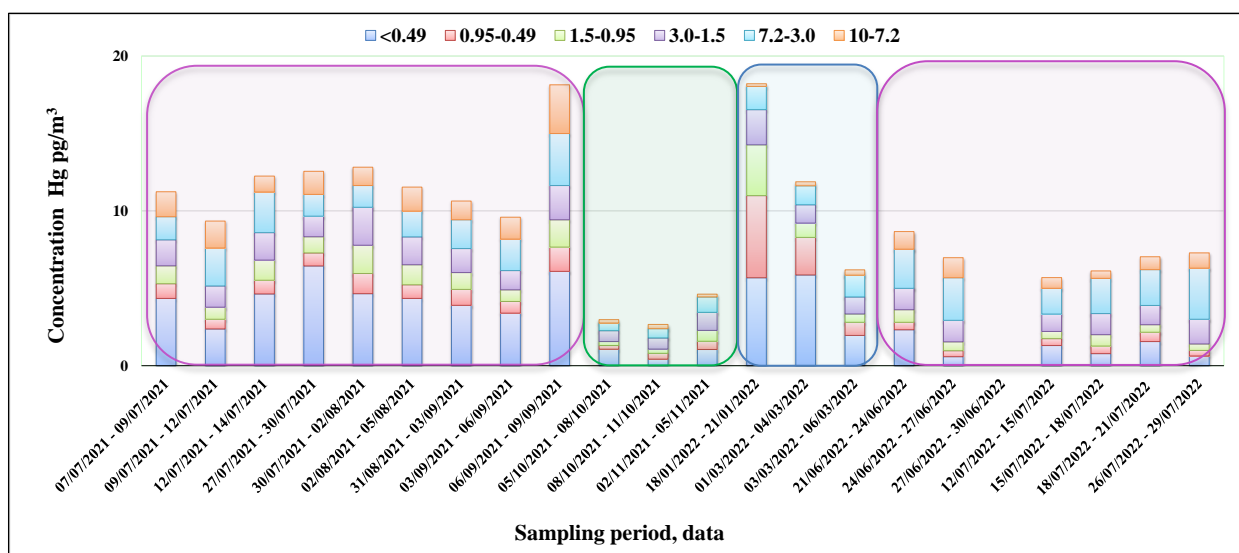
Fig. 3 Seasonal evolution of size-segregated particulate Hg in atmospheric aerosol over Ancona.

Future perspectives.

From June 2022, a second sampling campaign of atmospheric aerosol was carried out to study the concentration and the seasonal evolution of organic pollutants (PAH and nitro-PAH), as well as the inorganic chemical composition.

The third year of the PhD project will focus on:

- Determination of metals in sample 2021-2022
- Development of analytical extraction methods for PAHs and N-PAHs and determination in 2021-2022 samples
- Analysis of air back trajectories to determine the sources of atmospheric particulate matter
- Chemiometric data analysis

REFERENCES

1 Charlson, R.J., Schwartz, S.E., Hales, J.M., Cess, R.D., Coakley Jr., J.A., Hansen, J.E., Hofmann, D.J., 1992. Climate forcing by anthropogenic aerosols. Science 255, 423-430.
2 Albrecht, B.A., 1989. Aerosols, cloud microphysics, and fractional cloudiness. Science 245, 1227-1230.
3 Wolff, E.W.; Barbante, C.; Becagli, S.; Bigler, M.; Boutron, C.F.; Castellano, E.; de Angelis, M.; Federer, U.; Fischer, H.; Fundel, F.; et al. Changes in environment over the last 800,000 years from chemical analysis of the EPICA Dome C ice core. Quat. Sci. Rev. 2010, 29, 285–295,
4 Weller, R.; Wöltjen, J.; Piel, C.; Resenberg, R.; Wagenbach, D.; König-Langlo, G.; Kriews, M. Seasonal variability of crustal and marine trace elements in the aerosol at Neumayer station, Antarctica. Tellus, Ser. B Chem. Phys. Meteorol. 2008, 60 B, 742–752.

Part 2. PhD student information on the overall year activity (courses/seminars/schools, mobility periods, participation to conferences)

List of attended courses/seminars/schools

1. 09.12.2021 "Emissioni inquinanti gassose di origine industriale" RSE- (Ricerca Sistema Energetico)
2. 10.12.2021 "Emissioni inquinanti gassose di origine industriale" RSE- (Ricerca Sistema Energetico)
3. 16.12.2021 "Emissioni inquinanti gassose di origine industriale" RSE- (Ricerca Sistema Energetico)

4. 17.12.2021"Emissioni inquinanti gassose di origine industriale" RSE- (Ricerca Sistema Energetico)
5. 18.01.2022 Evento formativo "Sicurezza Informatica" – ARPAM
6. 12.05.2022 Corso di formazione "MUD, registri e formulari: il controllo sulla tracciabilità dei rifiuti" SAFA (Scuola Alta Formazione Ambientale)
7. 18-19-20.05.2022 PM2022 – IAS (Società Italiana di Aerosol)
8. 13.09.2022 "La figura del Pubblico Ufficiale e dell'Ufficiale di Polizia Giudiziaria nell'ambito dell'espletamento di attività di accertamento di illeciti ambientali" – Avv. Bertuzzi- ARPAM
9. 20.09.202 "le procedure negli illeciti ambientali – Avv. Bertuzzi-ARPAM
10. 27.09.2022 "Le procedure di accertamento degli illeciti ambientali: illeciti amministrativi" -A. Bertuzzi – ARPAM
11. 03.10.2022 – "Emissioni odorigene" - SRE (Scuola odori)
12. 04.10.2022 "Le procedure di accertamento degli illeciti penali" - Avv. Bertuzzi – ARPAM

13. 04.10.2022 – "Emissioni odorigene" - SRE (Scuola odori)
14. 13.10.2022 – "Emissioni odorigene" - SRE (Scuola odori)

List of conferences/workshops attended and of contributions eventually presented

1 15.12.2021 Docenza: "Il regolamento CE n. 1272.2008 -CLP – Master regolatorio M-Squared
2. 14.01.2022 "Particolato atmosferico, composizione inorganica ed organica: dal campionamento all'analisi" - Seminario UNIVPM
3. Annamaria Falgiani*, Flavio Vagnoni, Sébastien Bau, Matteo Fanelli, Federico Girolametti, Giada Giglione, Behixhe Ajdini, Cristina Truzzi, Anna Annibaldi, Silvia Illuminati. Seasonal evolution of atmospheric aerosol in the city of Ancona". X Convegno Nazionale sul Particolato Atmosferico 2022, Bologna 18-20 Maggio 2022. "Oral presentation by A. Falgiani.
4. 16.07.2022 Docenza: ""Il regolamento CE n. 1272.2008 -CLP – Master regolatorio M-Squared

Part 3. PhD student information on publications

List of publications on international journals

[*Example of format* Nava, G., Carducci, F., Itri, R., Yoneda, J.S., Bellini, T., Mariani, P. "Quadruplex

List of publications on conference proceedings

C1. None.

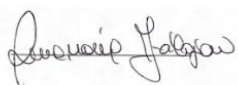### *List of other publications (books, book chapters, patents)*

B1. None.

[13.10.2022]

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