PHD COURSE IN LIFE AND ENVIRONMENTAL SCIENCES XXXVI CYCLES

"ORGANIC AND INORGANIC CONTAMINANTS OF ATMOSPHERIC PARTICULATE MATTER"

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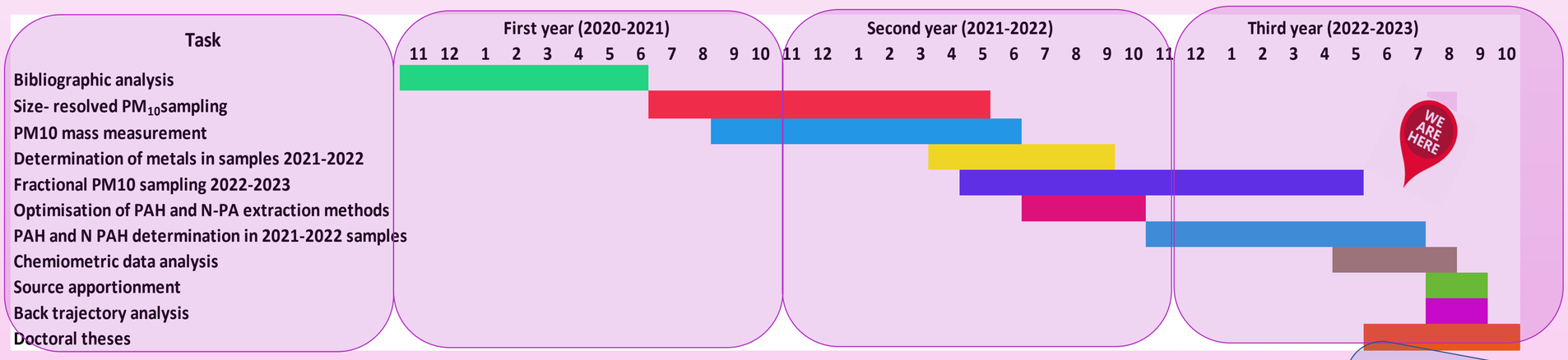
INTRODUCTION

The main objective of this PhD project is to sample, chemically characterize and study the spatiotemporal evolution of organic and inorganic pollutants in atmospheric particulate matter in the city of Ancona. In particular, the second year of the PhD project focused on: (1) the inorganic chemical characterization of the aerosol samples collected; (2) a second sampling campaign; (3) the assessment of the seasonal evolution of the aerosol's chemical composition; (4) the evaluation of the main sources of atmospheric pollutants.

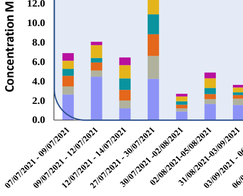


EXPERIMENTAL SECTION

First sampling campaign (July 2021 - March 2022)

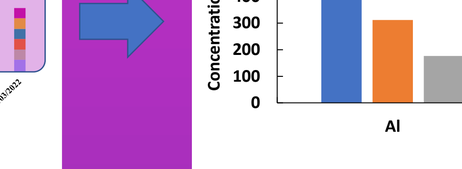
Sample treatment

Airborne samples of the first sampling campaign were subjected to microwave – assisted digestion (MARS 6) in closed PTFE vessel by adding 5 ml of HNO_3 + 1 ml of HF +1 ml of H_2O_2



Quantification of metals

Metal concentrations **(Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V)** were determined by Atomic Absorption with graphite furnace (GF-AAS), while particulate Hg was measured by the Direct Mercury Analizer (DMA)



Quality control

Field blanks were collected at the beginning and at the end of the field campaign.

Accuracy was assessed by analysing the certified reference material NIST 1648a. Results are in agreement with the certified reference values.

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Flux : 1.13 $m^3 min^{-1}$
Sampling strategy
Summer: 3 days twice a month
Rest of the year: 3 days once a month

Second sampling campaign (June 2022 - September 2022)

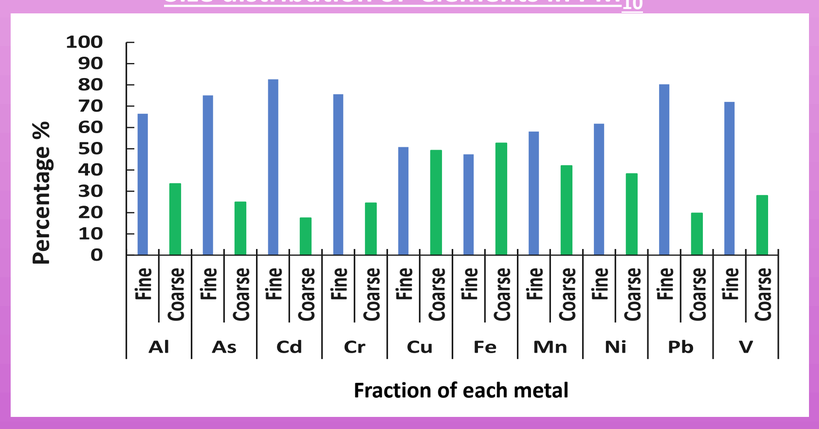
Same sampling strategy of the first campaign.
Quartz fibre filters were used for the determination of Polyciclic Aromatic Hydrocarbons (PAHs) and nitro-derivated PAH

RESULTS AND DISCUSSION

Mean concentration of metals in PM_{10}

Al = 491 ± 8 ng/m^3
Fe= 478 ± 9 ng/m^3
Mn = 5.6 ± 0.1 ng/m^3
As = 322 ± 6 pg/m^3
Cd = 56 ± 1 pg/m^3
Cr = 1.42 ± 0.03 ng/m^3
Cu = 4.36 ± 0.08 ng/m^3
Ni = 1.35 ± 0.02 ng/m^3
Pb = 1.84 ± 0.03 ng/m^3
V = 1.70 ± 0.04 ng/m^3

Size distribution of elements in PM_{10}



Fine fraction: Dp < 2.5 µm
Coarse fraction: 2.5 µm < Dp <10 µm

Al, As, Cd, Cr, Mn, Ni, Pb, V → Mainly present in the fine fraction

Cu, Fe → Almost equally distributed betwin the fine and the coarse fractions

Dlgs n. 155/2010

Metals	Annual average conc. (ng/m^3)
As	6
Cd	5
Ni	20
Pb	500

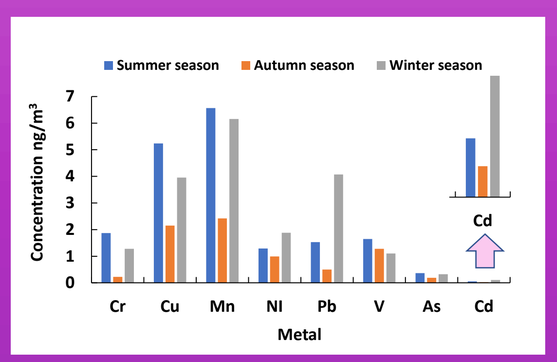
As, Ni: 10 times below legal limit

Cd: 100 times below legal limit

Pb: 250 times below legal limit

Seasonal evolution of the chemical composition of PM_{10}

Ex. Mn



- Different seasonal pattern for the studied elements
- All the studied elements showed the lowest values in Autumn, excepting V and Al
- Al, Fe, Cr, Cu, V showed a decreasing trend during the sampling period.
- Cd, Ni, Pb showed an increasing trend with winter values higher than those of summer
- Apart the usual low values in autumn, As and Mn showed similar concentration in summer and winter

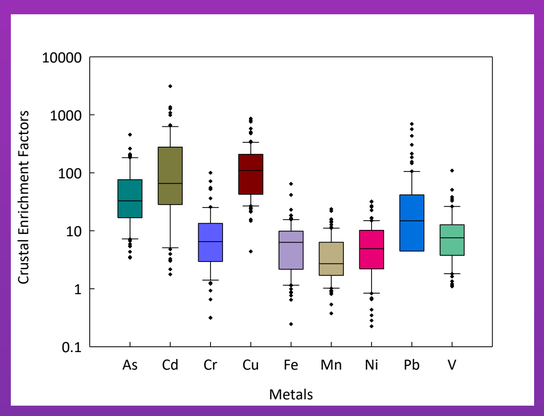
Source apportionment

Enrichment factor (EF) calculation is a first step in the source apportionment evaluation to differentiate the possible sources of elements in the atmospheric particulate matter[1].

$$EF_i = \frac{\left(C_i/C_{Al}\right)_{PM}}{\left(C_i/C_{Al}\right)_{UCC}}$$

$(C_i/C_{Al})_{PM}$ = concentration ratio of the element *i* over the reference element *Al* in the atmospheric particulate matter

$(C_i/C_{Al})_{UCC}$ = the abundance ratio of the element *i* over the reference element *Al* in the upper continental crust (UCC)[2].



EFs ≤ 10: Fe, Mn, Cr, Ni, V → GEOGENIC ORIGIN

10 < EFs < 100: As, Pb → MODERATELY ENRICHED

EFs > 100: Cd, Cu → GREATLY ENRICHED

FUTURE PERSPECTIVES

- Set up of the analytical extraction procedure for PAHs and nitro-PAHs in atmospheric aerosol
- Determination of PAHs and n-PAHs in samples collected during the second sampling campaign
- Chemometric treatment of data
- Air mass backtrajectories model to determine the sources of elements
- Source apportionment

REFERENCES

1. Zoller, W.H.; Gladney, E.S.; Duce, R.A. Atmospheric concentrations and sources of trace metals at the South Pole. Science 1974, 183, 198–201
2. Wedepohl, K. Geochim. Cosmochim. Acta 1995, 59, 1217–1232.