# Day/night variation of elemental composition of atmospheric particulate matters in South Osaka, Japan

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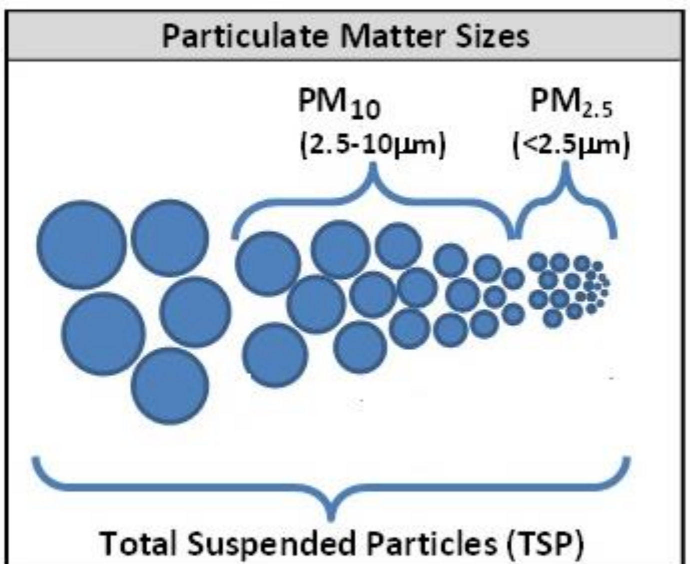
# Introduction

## Definition of Airborne Particulate Matters (PM):

*"a complex mixture of extremely small particles and liquid droplets that get into the air".*
(Environmental Protection Agency (EPA), USA)

Size: up to 160 µm - $PM_{2.5}$ and $PM_{10}$ are the most important




Chemical compositions: organic or inorganic chemical compounds (hydrocarbons, oxides (of sulfur, nitrogen), acids, and inorganic elements (Al, Na, Cl, As,……...)

# Sources of PM

Natural sources: evaporated sea spray, windborne pollen, dust, unpaved roads, fields, fires and volcanic or other geothermal eruptions.



Artificial sources: burning of fossil fuels, smokestacks, mining and construction sites, - Chemicals reactions of $SO_2$ and $NO_x$ with other materials.



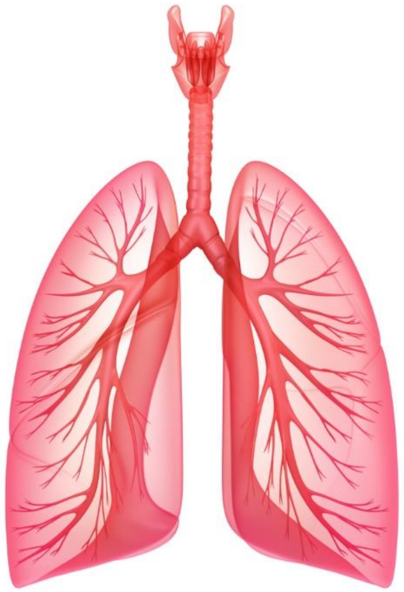
- Why PMs are important?

1. PM effects on health

2. PM effects on Environment

# Health effects of PMs

- PMs are inhalable and can enter our lungs through nose and mouth.
  - ✓Large PMs ($PM_{>10}$) are eliminated through coughing and sneezing
  - ✓Small PMs ($PM_{10}$ and $PM_{2.5}$) can penetrate the lung and may reach bloodstreams
- Exposure to PM can affect both lungs and heart and may cause a variety of problems, including:
  1. decreased lung function
  2. Asthma,
  3. Lung cancer
  4. Pneumonia
  5. Early death
  6. ………….



* In 2012, ~ 11% of deaths worldwide are the result of air pollution-related conditions.
* In Asia and Pacific region ~ 90% of the population are exposed to risky levels of air pollution.
* WHO estimated at least 300000 annually cases of early death in China due to air pollution .

# Environmental effects of PM

1. Visibility reduction - sun light scattering by PMs

2. Acidic Rains

   Acids in PM cause increasing the acidity of rain, oceans, lakes, streams - harmful to archaeological objects & plants.

$SO_2 + H_2O$ (clouds) $\longrightarrow H_2SO_4$

$NO_x + H_2O$ (clouds) $\longrightarrow HNO_3$

# Environmental effects of PM

3. Scratching/etching the surfaces of sensitive farm crops - causing damage
4. Deposition on plant leaves may reduce gas exchange and photosynthesis

# Environmental effects of PM

5. Contribute to the soiling and erosion of buildings, materials, solar panels, and paints, leading to increased cleaning and maintenance costs.

# Work objective

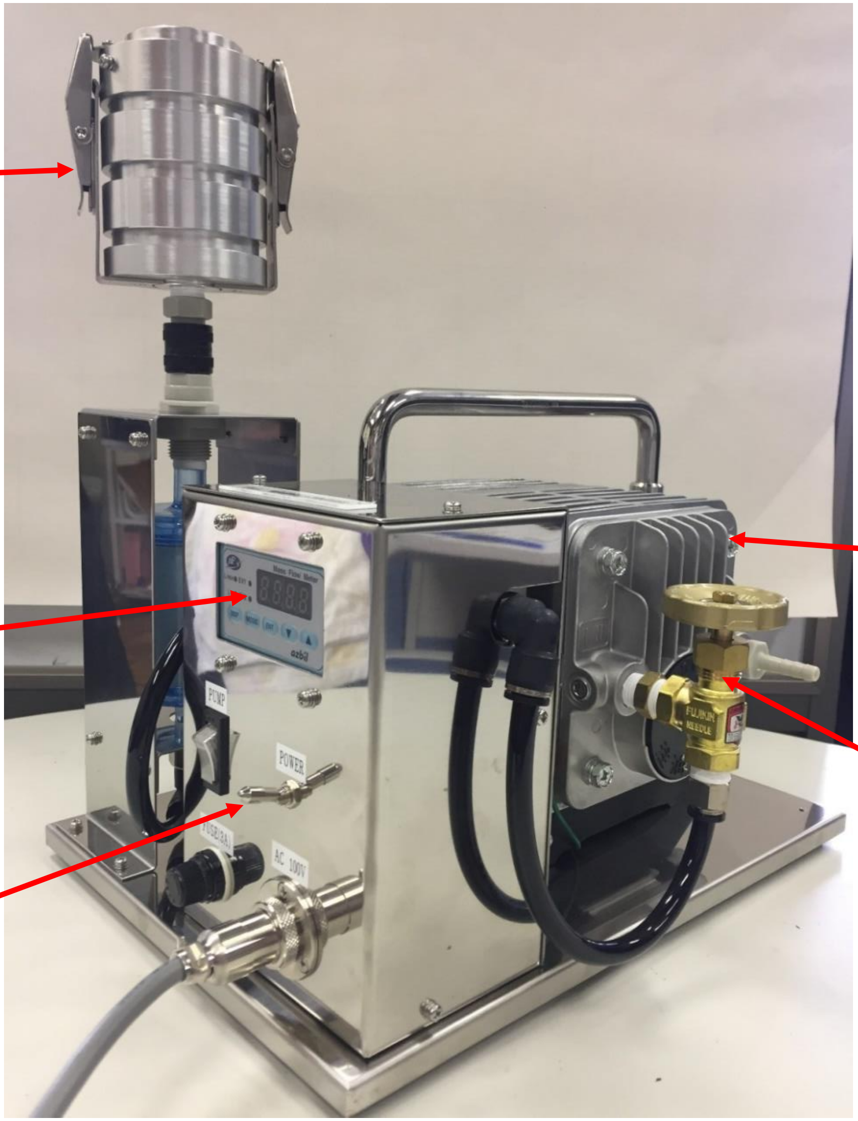
The main objective of this research is to evaluate air quality in Kumatori-cho, Osaka, Japan with respect to airborne particulates maters (PMs).

This goal can be achieved through:

1. Installation of air sampler with appropriate filters
2. Sampling of air particulates
3. Characterization of the collected samples
   a. Mass concentration ($\mu g/m^3$)
   b. Composition: elemental analysis using Neutron Activation Analysis (NAA)
3. Evaluation - comparison of the obtained data with Japanese and international standards.

# 1- Installation of air sampler (completed)

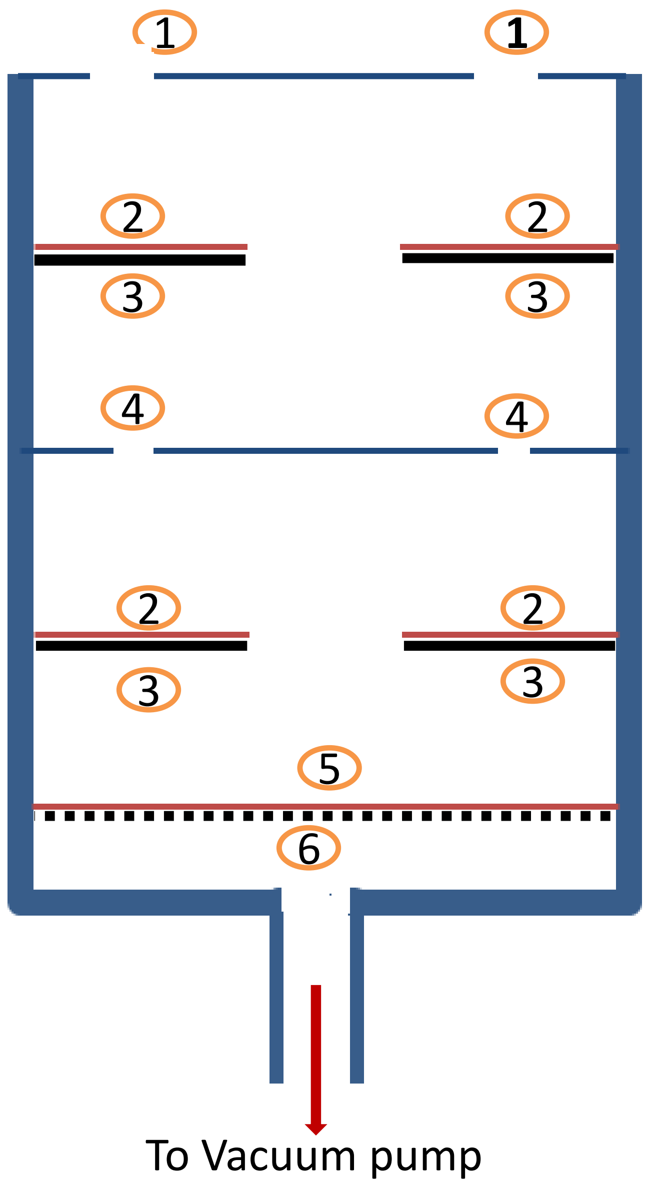
## Multi-Nozzle Cascade Impact (MCI) Sampler.



# Air sampler set-up -3rd floor of researcher building of Institute for Integrated Radiation and Nuclear Science

Timers and data logger are connected


# Filters holder




1-Wide-openings inlets

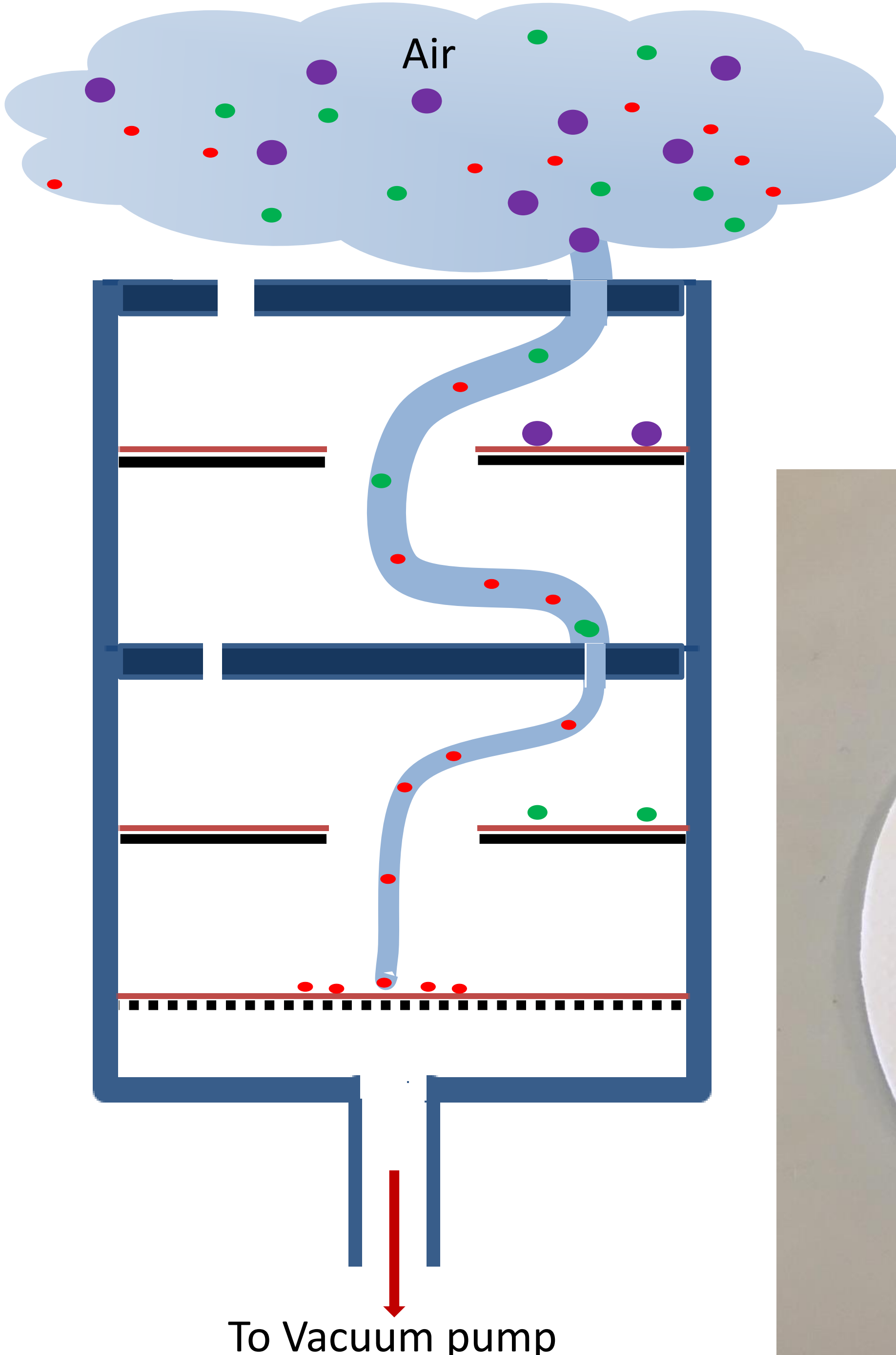
2- Doughnut-shape filters

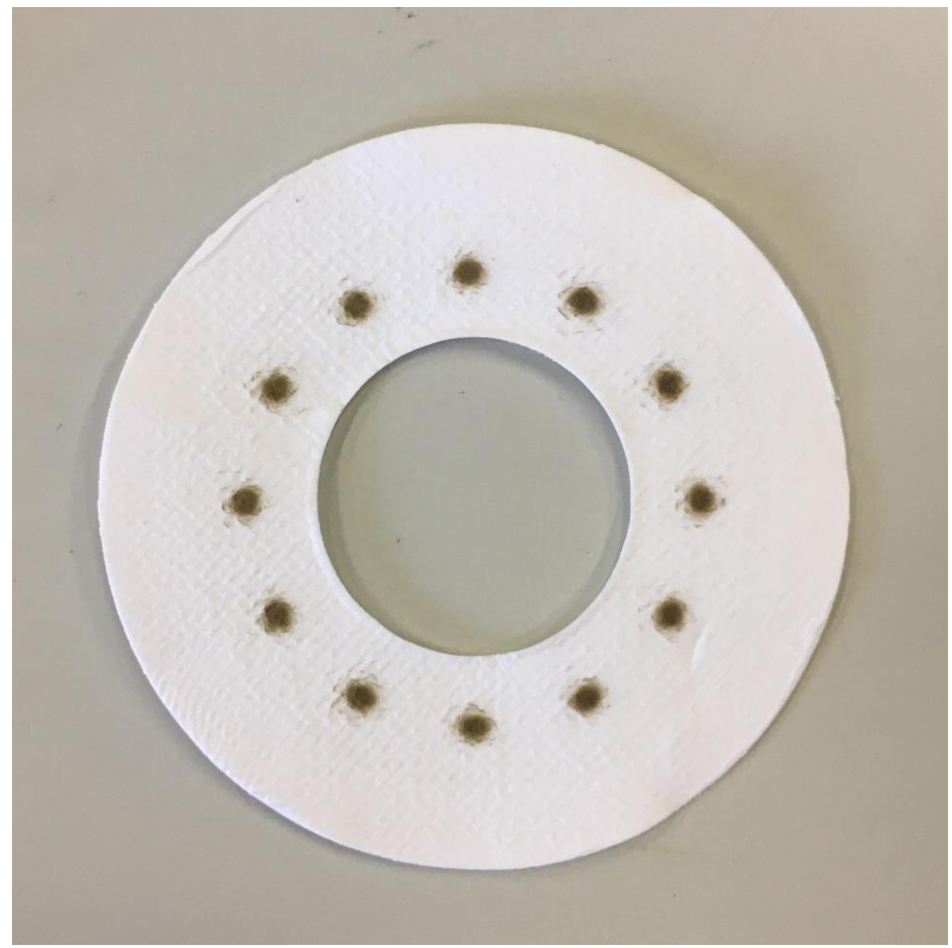
3- Filter seat

4- Narrow openings

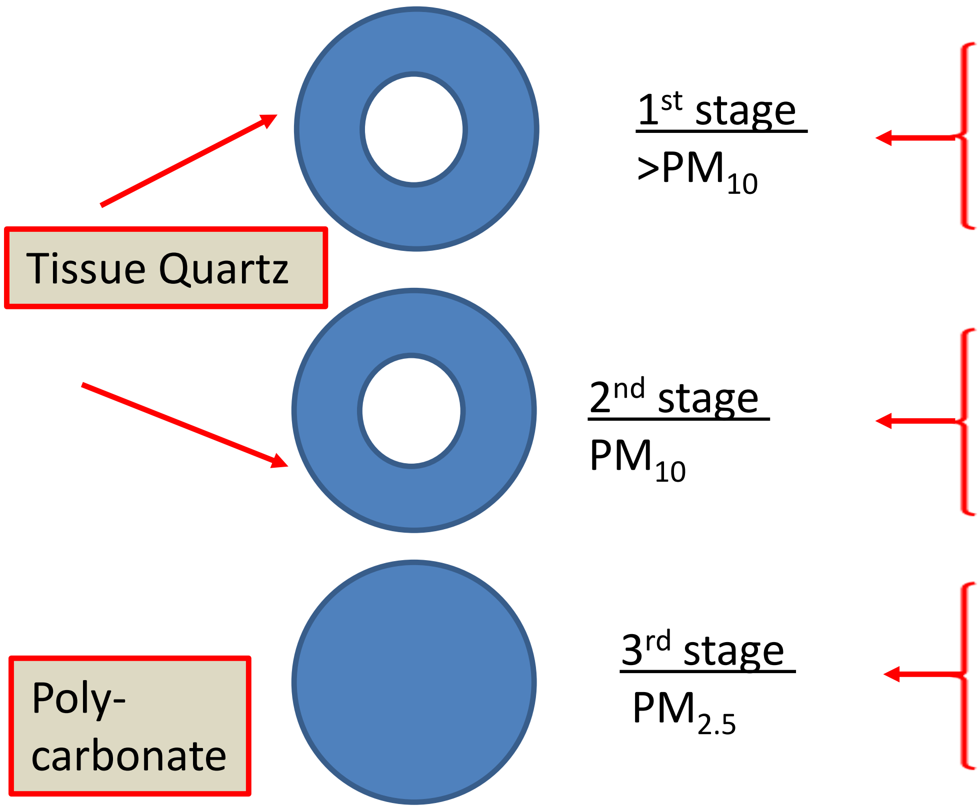
5- Backup filter

6- Plastic net


Air
To Vacuum pump



# Filter Holder

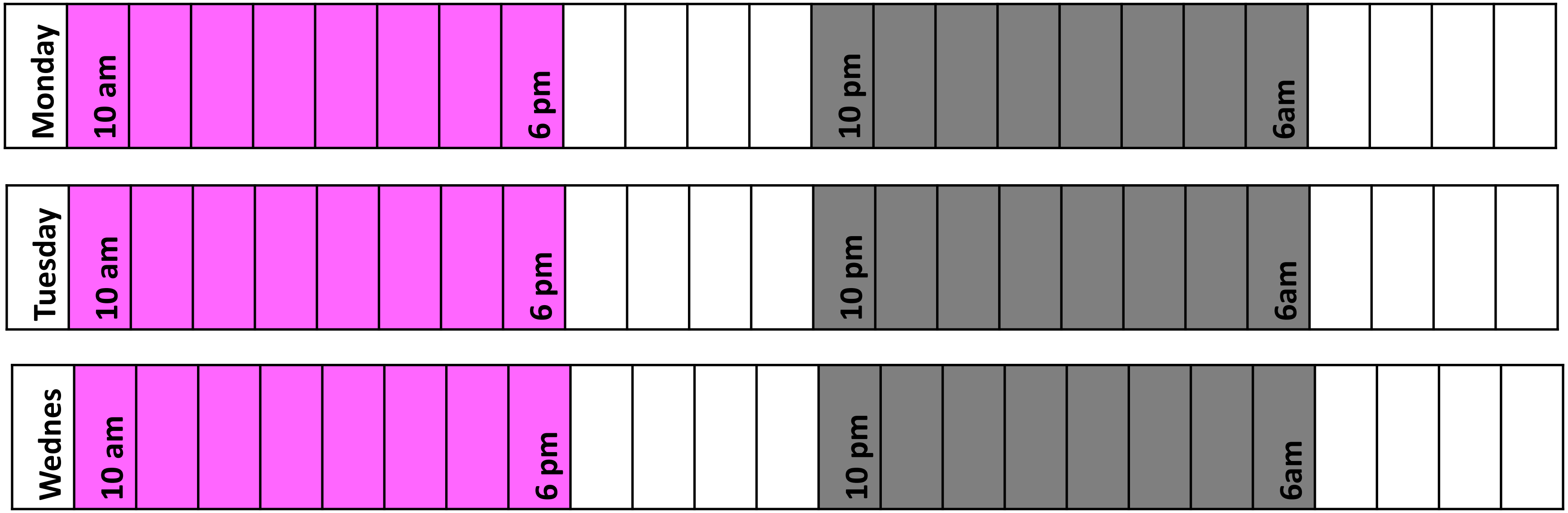



# 2- Sampling of PMs

## Day and Night collection strategy (29 May 2018 – 30 May 2019)

Day

Night



# 3- Characterization of PM

a. Mass concentration ($\mu g/m^3$)

Mass concentration =

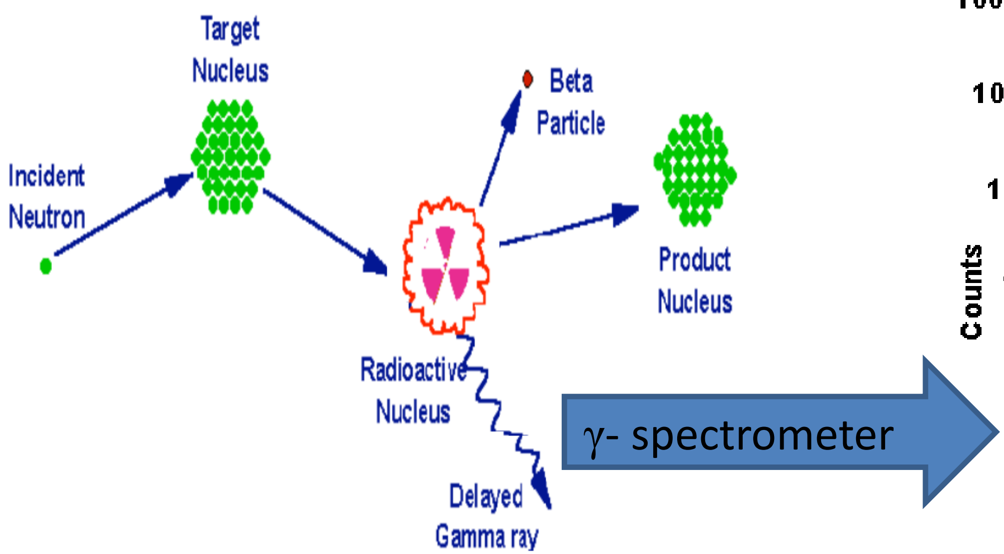
(Filter mass after collection – filter mass before collection) / air volume

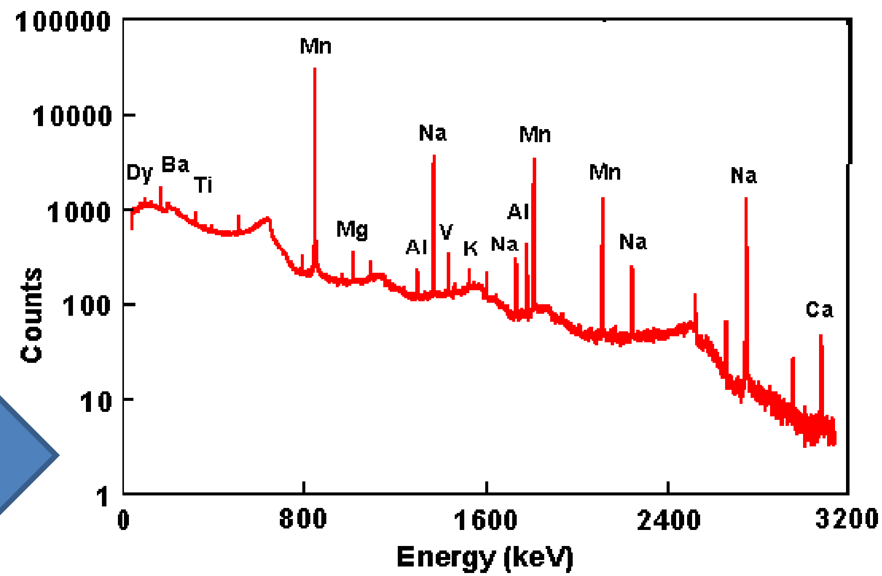
# 3- Characterization of PM

## b. Elemental Analysis using Neutron Activation Analysis (NAA)

*$K_0$*-INAA was applied for the quantitative analysis of around 24 elements.

Au was used as a comparator.

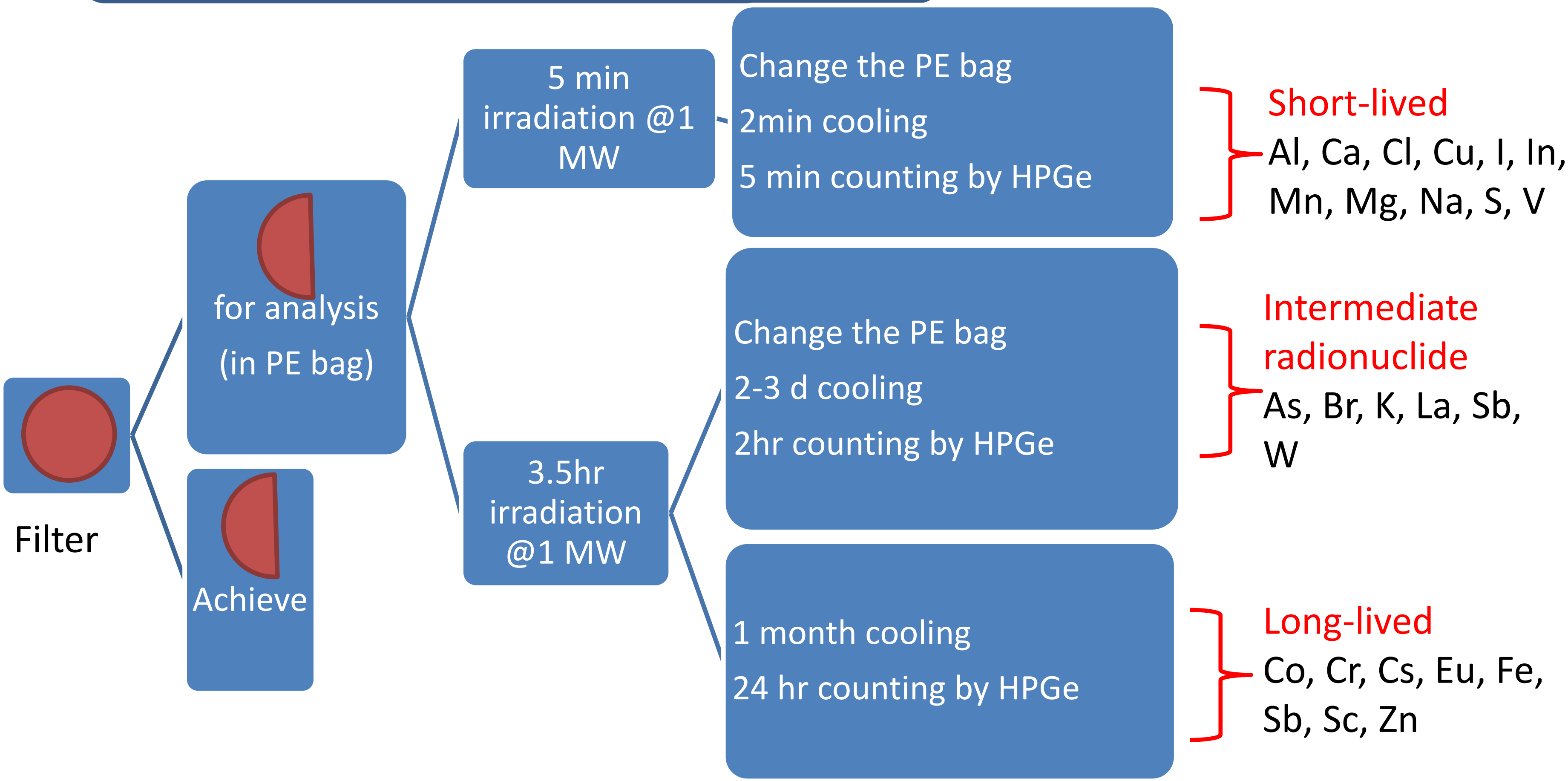



Establishment of $k_0$-method is present in my Poster

## Elemental analysis scheme:

Carried out by NAA technique

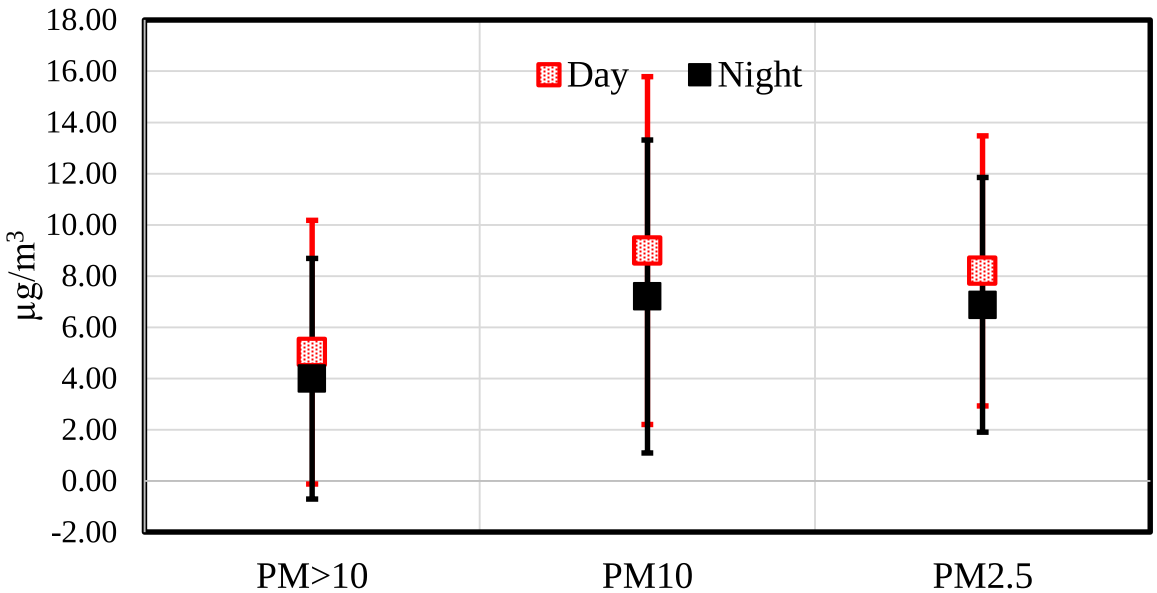



**Quality control materials:**

Apple leaves (SRM-1515, NIST), Tobacco leaves (INCT-OBTL-5, ICHTJ, Poland) and mixed standard solution (XSTC-331, SPEXCertiPrep)

# Results: 1 – mass concentration

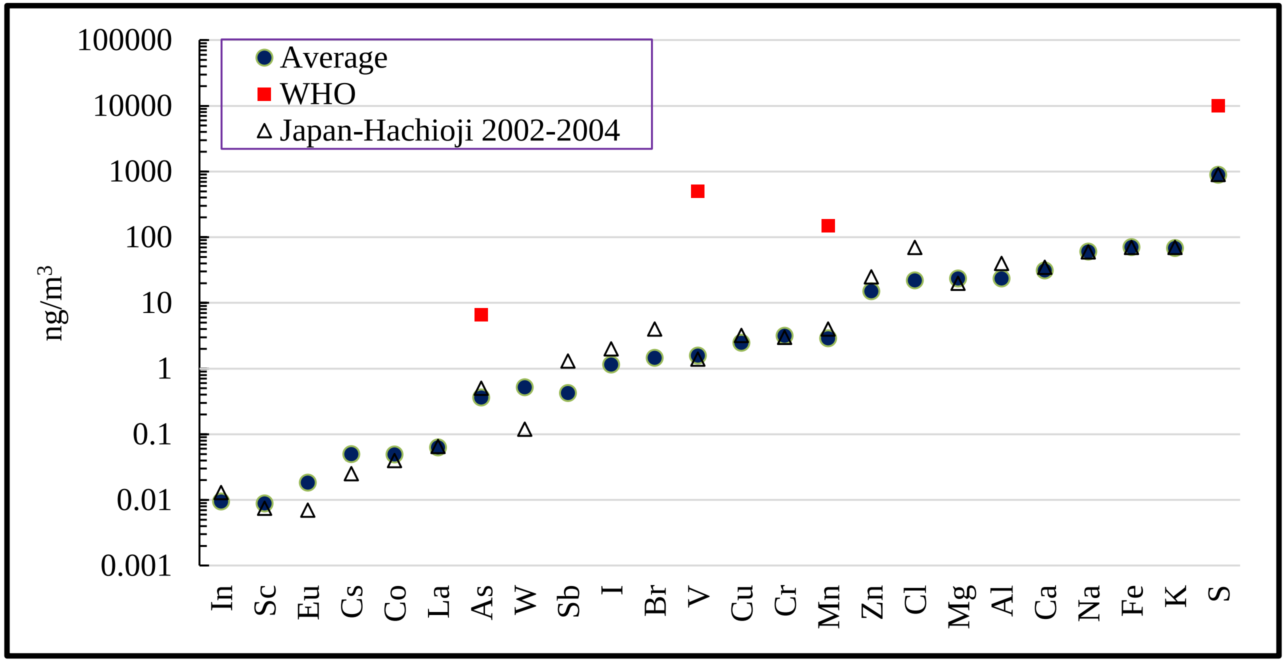
Mass concentration for PM collected from 29 May 2018 to 30 May 2019




| | Mean ± STDEV (μg/cm³) | | | WHO[1] | Japan[2] |
|---|---|---|---|---|---|
| | Average | Day | Night | | |
| $PM_{>10}$ | 4.59 ± 3.77 | 5.20 ± 5.63 | 3.99 ± 4.7 | ?? | ?? |
| $PM_{10}$ | 8.10 ± 4.92 | 9.00 ± 6.79 | 7.21 ± 6.11 | 20 | |
| $PM_{2.5}$ | 7.54 ± 4.13 | 8.20 ± 5.27 | 6.88 ± 4.97 | 10 | 15 |

[1] WHO, WHO air quality guidelines 2005.
[2] Japan Automobile Manufacturing Association , PM/$PM_{2.5}$in ambient air & related activities in Japan, 2011

# Results: 2-Elemental analysis




Average concentration levels in $PM_{2.5}$ collected from 29 May 2018 to 30 May 2019

- 24 elements
- Hazardous pollutant elements As, Mn, Cr, V, S, Sb, and W are determined


[1] Oura et al., (2007) J radioanal Nucl Chem 272:381-385

[2] WHO, Air Quality Guidelines for Europe, 2nd ed, 2000

# Results: 2-Elemental analysis

## Source of PM ?

$$Enrichement\ Factor(EF) = \frac{\left(\frac{X}{Al}\right)_{PM}}{\left(\frac{X}{Al}\right)_{crust}}$$

X and Al: concentrations of an element of interest and Al, respectively

*Interpretation:*

Natural Source: low EF (~1 for ideal case)

Anthropogenic source: high EF

1- Dust: Al, Ca, Mg, Mn, Na, K, Fe, As, V,...

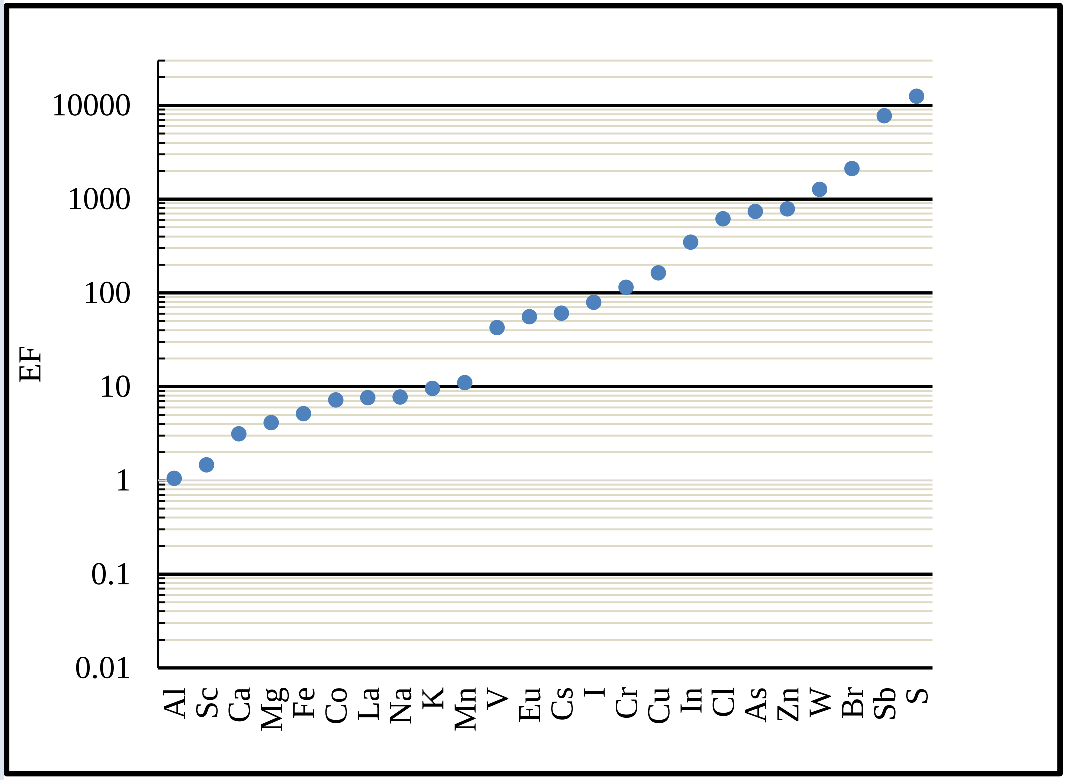
2- Industrial Processing: Al, Fe, Cu, Mn, Cr, Sb, Zn,

3- Traffic: Zn, Fe, As, Cu

4- combustion of fossil fuel: S, V, As

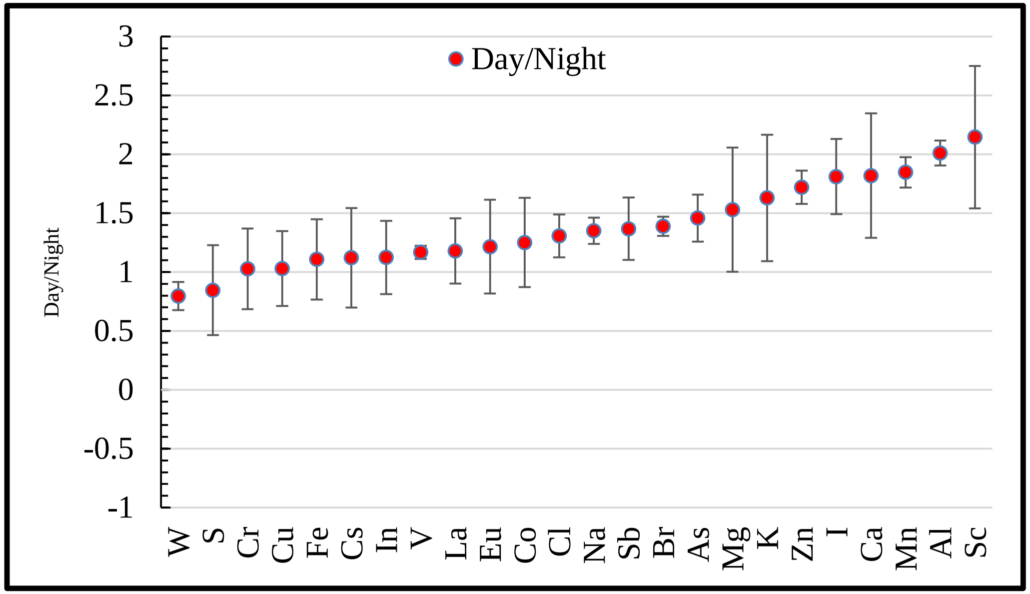
5 - Sea spray: I, Cl, Br, Na, S, ..... ).

Zhang et al., (2018) J Environ Sci, 71:119




S, Br, Cl, I, Zn, Mg, Ca, K and Na have high EFs because they have dual natural sources (i.e soil dust and sea spray

# Results: 2-Elemental analysis- Day/Night




Day/night variation of elements concentration in $PM_{2.5}$

- Higher temperature of the day-time:

  1- Stimulates the evaporation of volatile elements from the sea (I, Br, Cl).

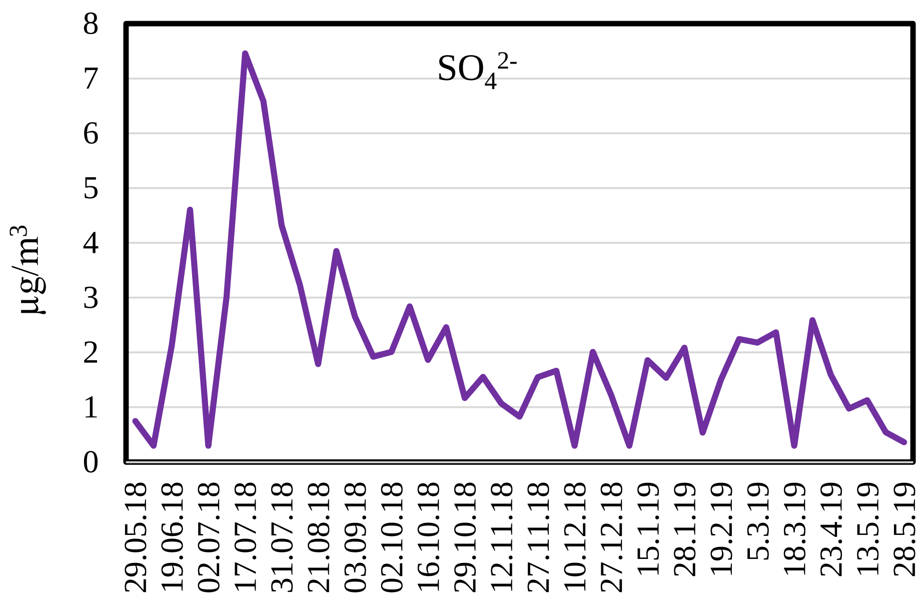
  2- Dry up the soil particulates and make it easy to be carried by air (crustal elements).

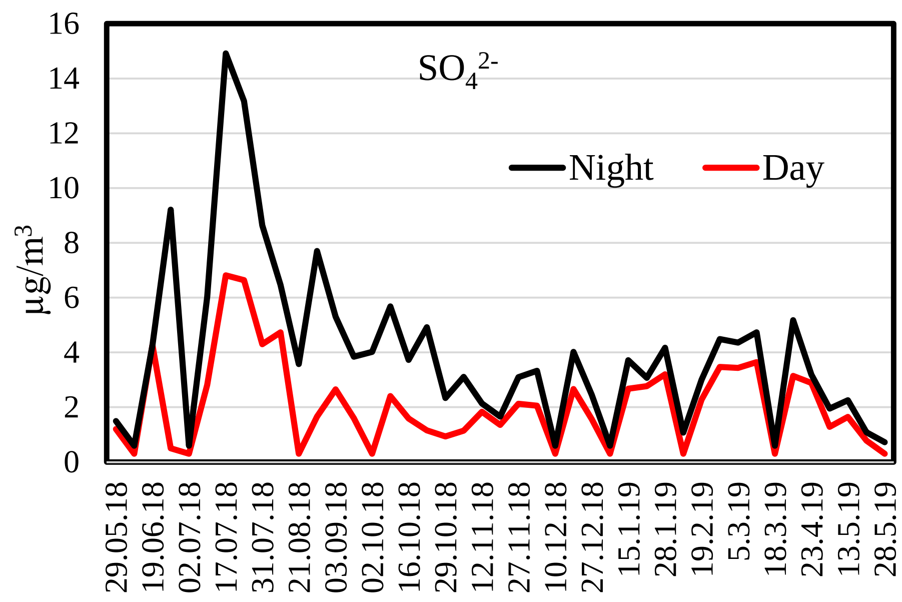
  2- Formation chemistry of PM (ex: sulphate)

# Results: 2-Elemental analysis – sulphate content

- Sulphate is a major component of PM (10-30%). (Shao et al., Atmos. Chem. Phys., 19, 6107–6123, 2019)
- It acts as indicator for $SO_2$ level
- Temperature reducer (Fasullo et al., Natural GeoSci., 11, 910–914, 2018)

Based on data obtained by NAA, sulphate ($SO_4^{2-}$) can be estimated as 25% of $PM_{2.5}$:



# Results: 2-Elemental analysis – sulphate content

Types of sulphate aerosols

1. Primary particulates
   (From soil dust and sea spray)
2. Secondary particulates
   (70% of total sulphate from oxidation of $SO_2$)
   (Hoyle et al., Atmos. Chem. Phys., 16, 1693–1712, 2016)

*730000 tons of $SO_2$ in 2005, Japan*

$SO_2 + H_2O$

↓

$HSO_3^-$, $SO_3^{2-}$

↓ $h\nu$, *Oxidant: $O_3$, $OH^-$, $O_2$, $H_2O_2$*

$H_2SO_4$ (liquid PM)

$H_2SO_4$ (liquid PM) → PM surface → Heterogeneous PM

$H_2SO_4$ (liquid PM) → $NH_3$ → $(NH_4)_2SO_4$ (PM)

Summer is more humid i.e more water is available for dissolving $SO_2$

In night times, the temperature decreases and hence the condensation increases.

Lazaridis and Koutarakis. J. Aerosol Sci 28 (1997) 107.

Japan Automobile Manufacturing Association , PM/$PM_{2.5}$in abient air & related activities in Japan, 2011

# Source Analysis - Metal correlations

## Pearson correlation coefficient, r

$$r_{x,y} = \frac{\sum_{i=n}^{n}(x_i - \bar{x}) - (y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2}\sqrt{\sum(y_i - \bar{y})^2}}$$

n is the sample size.

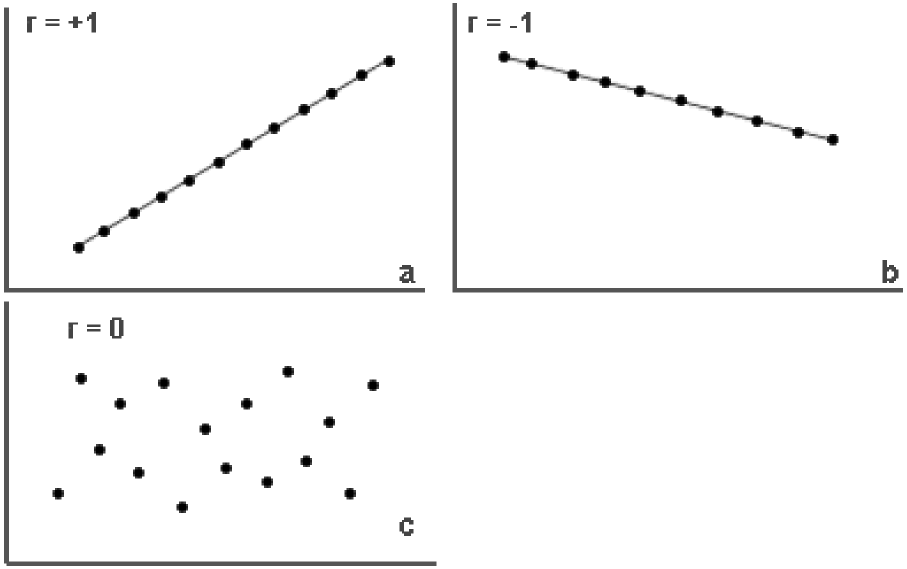
$x_i$ and $y_i$ are the individual sample points of two data set with mean values of $\bar{x}$ and $\bar{y}$

+1 ≥ r ≥ -1

+1: perfect positive linear correlation

0: No correlation

-1: Perfect negative linear correlation




In the current case, the value of "r" is interpreted as the following:

Over |0.6 | : strong correlation

| 0.4 | to |0.6| : moderate correlation

| 0.2 | to |0.4| : week correlation

Below | 0.2 | : No correlation

The "sign" determine whether correlation is positive of negative


1- Mu et al., (2018) Info Sci 435: 40-58

2- https://statistics.laerd.com/statistical-guides/pearson-correlation-coefficient-statistical-guide.php

| | Al | As | Br | Ca | Cl | Co | Cr | Cs | Cu | Eu | Fe | I | In | K | La | Mg | Mn | Na | S | Sb | Sc | V | W | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 1 | | | | | | | | | | | | | | | | | | | | | | | |
| As | 0.32 | 1 | | | | | | | | | | | | | | | | | | | | | | |
| Br | 0.48 | 0.62 | 1 | | | | | | | | | | | | | | | | | | | | | |
| Ca | 0.73 | 0.27 | 0.41 | 1 | | | | | | | | | | | | | | | | | | | | |
| Cl | 0.45 | -0.08 | 0.00 | 0.57 | 1 | | | | | | | | | | | | | | | | | | | |
| Co | 0.48 | 0.42 | 0.34 | 0.20 | -0.11 | 1 | | | | | | | | | | | | | | | | | | |
| Cr | 0.18 | 0.20 | 0.04 | 0.10 | 0.26 | 0.19 | 1 | | | | | | | | | | | | | | | | | |
| Cs | 0.14 | 0.33 | 0.30 | -0.05 | -0.07 | 0.13 | 0.09 | 1 | | | | | | | | | | | | | | | | |
| Cu | 0.37 | 0.48 | 0.35 | 0.51 | 0.08 | 0.40 | -0.01 | -0.25 | 1 | | | | | | | | | | | | | | | |
| Eu | 0.14 | -0.02 | -0.08 | -0.16 | -0.14 | 0.04 | 0.00 | 0.36 | -0.19 | 1 | | | | | | | | | | | | | | |
| Fe | 0.56 | 0.58 | 0.62 | 0.36 | -0.01 | 0.53 | 0.02 | 0.05 | 0.51 | -0.01 | 1 | | | | | | | | | | | | | |
| I | 0.60 | 0.59 | 0.73 | 0.64 | 0.13 | 0.35 | 0.12 | 0.02 | 0.60 | -0.08 | 0.66 | 1 | | | | | | | | | | | | |
| In | 0.12 | 0.62 | 0.51 | 0.16 | -0.13 | 0.30 | 0.01 | 0.41 | 0.34 | 0.00 | 0.42 | 0.47 | 1 | | | | | | | | | | | |
| K | 0.60 | 0.05 | 0.17 | 0.49 | 0.71 | 0.04 | 0.15 | 0.01 | 0.08 | -0.03 | 0.31 | 0.38 | 0.05 | 1 | | | | | | | | | | |
| La | 0.39 | 0.46 | 0.71 | 0.39 | -0.19 | 0.54 | -0.08 | 0.28 | 0.45 | -0.06 | 0.57 | 0.69 | 0.59 | 0.05 | 1 | | | | | | | | | |
| Mg | 0.77 | 0.10 | 0.43 | 0.69 | 0.49 | 0.22 | 0.11 | 0.21 | 0.28 | 0.15 | 0.29 | 0.38 | 0.00 | 0.55 | 0.28 | 1 | | | | | | | | |
| Mn | 0.57 | 0.68 | 0.59 | 0.49 | 0.26 | 0.55 | 0.17 | 0.10 | 0.64 | -0.05 | 0.69 | 0.73 | 0.54 | 0.42 | 0.52 | 0.31 | 1 | | | | | | | |
| Na | -0.18 | -0.15 | 0.08 | 0.02 | 0.00 | -0.08 | -0.17 | 0.26 | -0.11 | 0.01 | -0.20 | -0.23 | 0.00 | -0.18 | 0.06 | 0.33 | -0.30 | 1 | | | | | | |
| S | 0.12 | 0.37 | 0.53 | 0.38 | -0.20 | 0.18 | -0.27 | 0.24 | 0.33 | -0.10 | 0.29 | 0.41 | 0.57 | -0.06 | 0.64 | 0.24 | 0.19 | 0.39 | 1 | | | | | |
| Sb | 0.42 | 0.58 | 0.55 | 0.24 | 0.12 | 0.53 | 0.09 | 0.10 | 0.40 | 0.04 | 0.70 | 0.57 | 0.38 | 0.27 | 0.38 | 0.14 | 0.79 | -0.18 | 0.08 | 1 | | | | |
| Sc | 0.32 | 0.09 | 0.14 | 0.18 | 0.31 | -0.05 | 0.38 | 0.18 | -0.26 | -0.01 | -0.01 | 0.25 | -0.09 | 0.30 | -0.12 | 0.14 | 0.01 | -0.13 | -0.20 | 0.12 | 1 | | | |
| V | -0.01 | 0.29 | 0.43 | 0.20 | -0.36 | 0.22 | -0.27 | 0.36 | 0.31 | 0.04 | 0.29 | 0.34 | 0.53 | -0.20 | 0.75 | 0.11 | 0.13 | 0.34 | 0.75 | 0.11 | -0.25 | 1 | | |
| W | 0.36 | 0.31 | 0.50 | 0.30 | 0.23 | 0.13 | -0.10 | 0.12 | 0.31 | -0.06 | 0.41 | 0.45 | 0.32 | 0.31 | 0.32 | 0.30 | 0.69 | -0.08 | 0.15 | 0.56 | -0.03 | 0.10 | 1 | |
| Zn | 0.36 | 0.63 | 0.49 | 0.43 | 0.11 | 0.48 | 0.12 | -0.05 | 0.74 | -0.11 | 0.65 | 0.66 | 0.53 | 0.19 | 0.57 | 0.14 | 0.85 | -0.23 | 0.27 | 0.72 | -0.15 | 0.35 | 0.48 | 1 |

Good correlation for:-

1- Crustal elements: Al, Ca, K, Mg, Mn, Fe..

2- Sea spray elements: I, Br, Cu, S,..

3- Industrial elements: Fe, Zn, Sb, Al, Cu, Mn

4- Combustion elements: S, V, As,..

5- traffic elements: Zn, Fe, As, Cu

No correlation for Cr with all elements

Positive Matrix Factorization (EPA, USA)

# Conclusions

- $k_0$- based neutron activation analysis is a potential tool for studying the air particulate matter (PM) with respect to its powerful multi-elemental capability and accuracy
- Air quality (with respect to PM) in Kumatori-cho, Osaka meets the WHO guidelines.
- Soil dust, sea spray, industrial processing, combustion, and traffic are the potential sources of PM.
- The variation of concentration levels during day and night times are significant - in most cases - and could be attributed to the environmental conditions, the atmospheric chemistry, and formation mechanism of the particulate.
- Weather conditions (ex: temperature, precipitation, wind direction, sun hours,..) will be consider for further explanation and discussions of the obtained results.

Thank you for your kind attention

Questions?