Consiglio Nazionale delle Ricerche

Istituto di Scienze dell'Atmosfera e del Clima

Methodological study for chemical-physical characterization of $PM_{2.5}$ samples by means of ATR-FTIR spectroscopy

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XII Convegno
sul Particolato Atmosferico

NAPOLI PM 2026

IAS – Società Italiana di Aerosol
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Method:

- Optimization of ATR-FTIR spectra acquisition;
- Choice of automated data set management system;
- Optimization of data processing;
- Multivariate statistical analysis (PCA and cluster analysis).

Aim of ATR-FTIR analysis:

- Collect solid and accurate information on functional groups of $PM_{2.5}$;
- Achieve a comprehensive chemical characterization;
- Identify of the main sources of particulate matter emissions;
- Identify the primary and secondary sources;
- Study the spatial and seasonal variability.

Measurement campaigns in the framework of TOX-IN-AIR project

2024

JANUARY

S	M	T	W	T	F	S
	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31			

FEBRUARY

S	M	T	W	T	F	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29		

MARCH

S	M	T	W	T	F	S
					1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28	29	30
31						

APRIL

S	M	T	W	T	F	S
	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30				

MAY

S	M	T	W	T	F	S
			1	2	3	4
5	6	7	8	9	10	11
12	13	14	15	16	17	18
19	20	21	22	23	24	25
26	27	28	29	30	31	

JUNE

S	M	T	W	T	F	S
						1
2	3	4	5	6	7	8
9	10	11	12	13	14	15
16	17	18	19	20	21	22
23	24	25	26	27	28	29
30						

JULY

S	M	T	W	T	F	S
	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31			

AUGUST

S	M	T	W	T	F	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29	30	31

SEPTEMBER

S	M	T	W	T	F	S
1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	18	20	21
22	23	24	25	26	27	28
29	30					

OCTOBER

S	M	T	W	T	F	S
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30	31		

NOVEMBER

S	M	T	W	T	F	S
					1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28	29	30

DECEMBER

S	M	T	W	T	F	S
1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	19	20	21
22	23	24	25	26	27	28
29	30	31				

Measurement campaigns in the framework of TOX-IN-AIR project

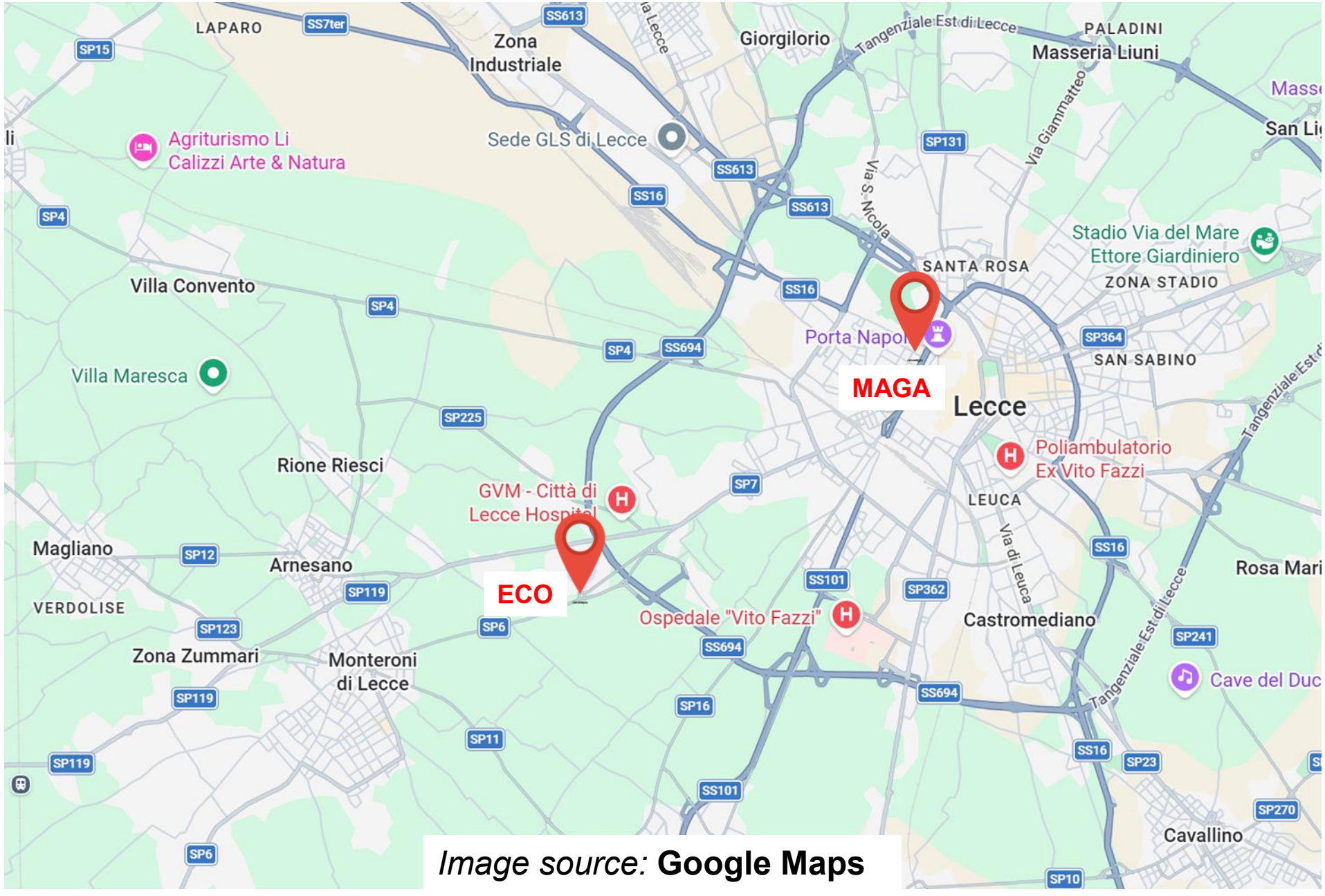
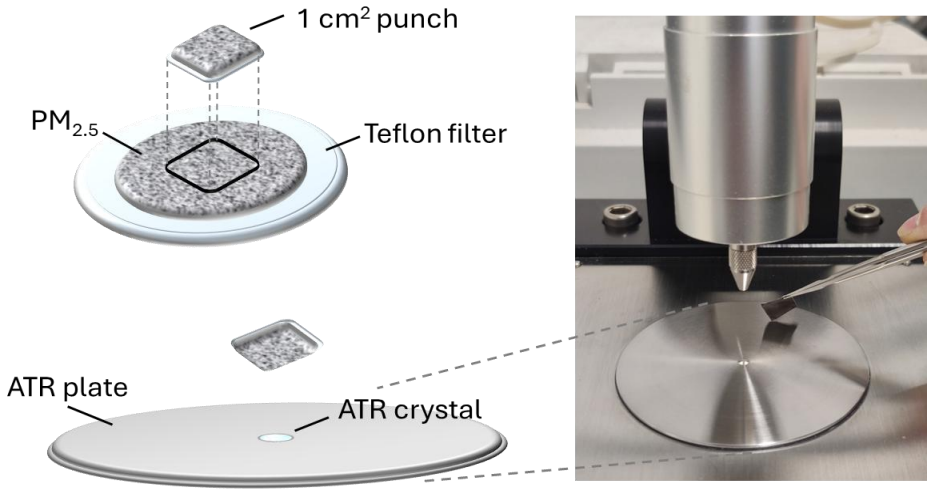
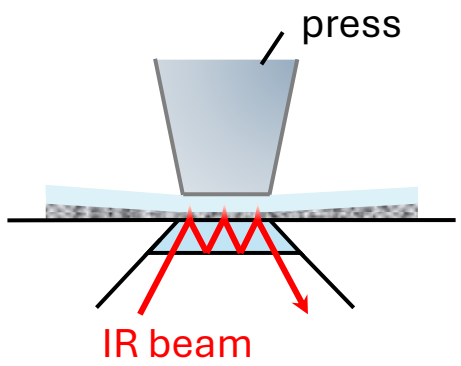


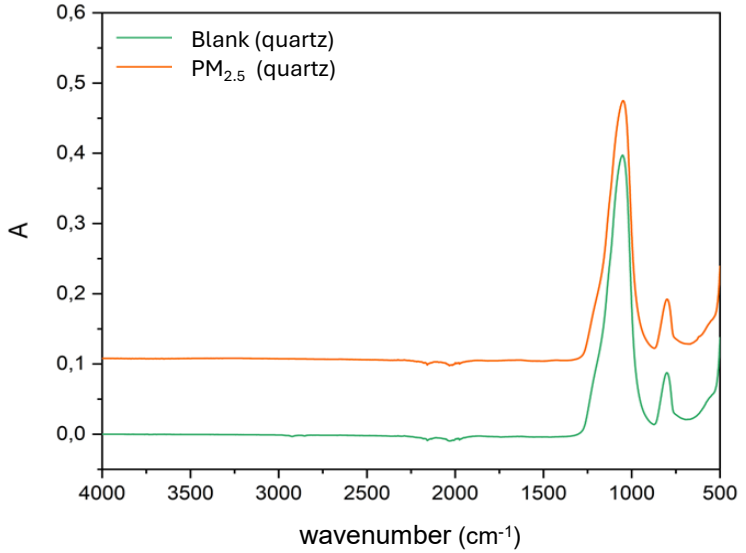
Image source: **Google Maps**

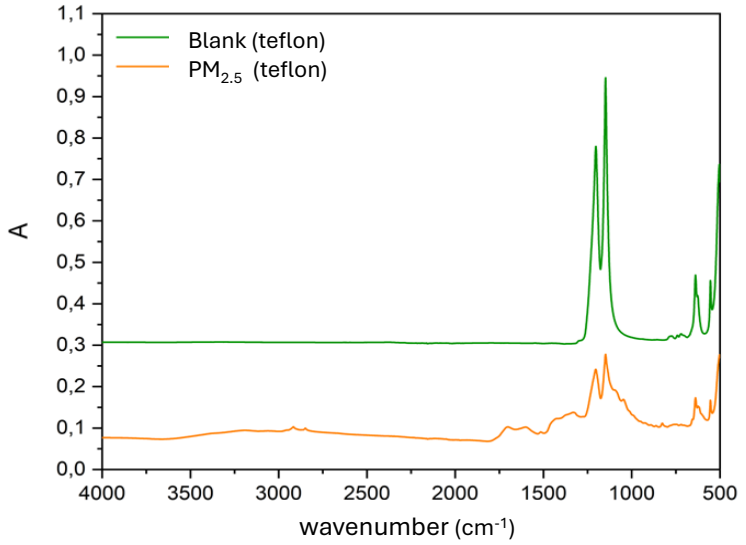
Attenuated Total Reflectance (ATR)-Fourier Transform Infrared (FTIR) Spectroscopy



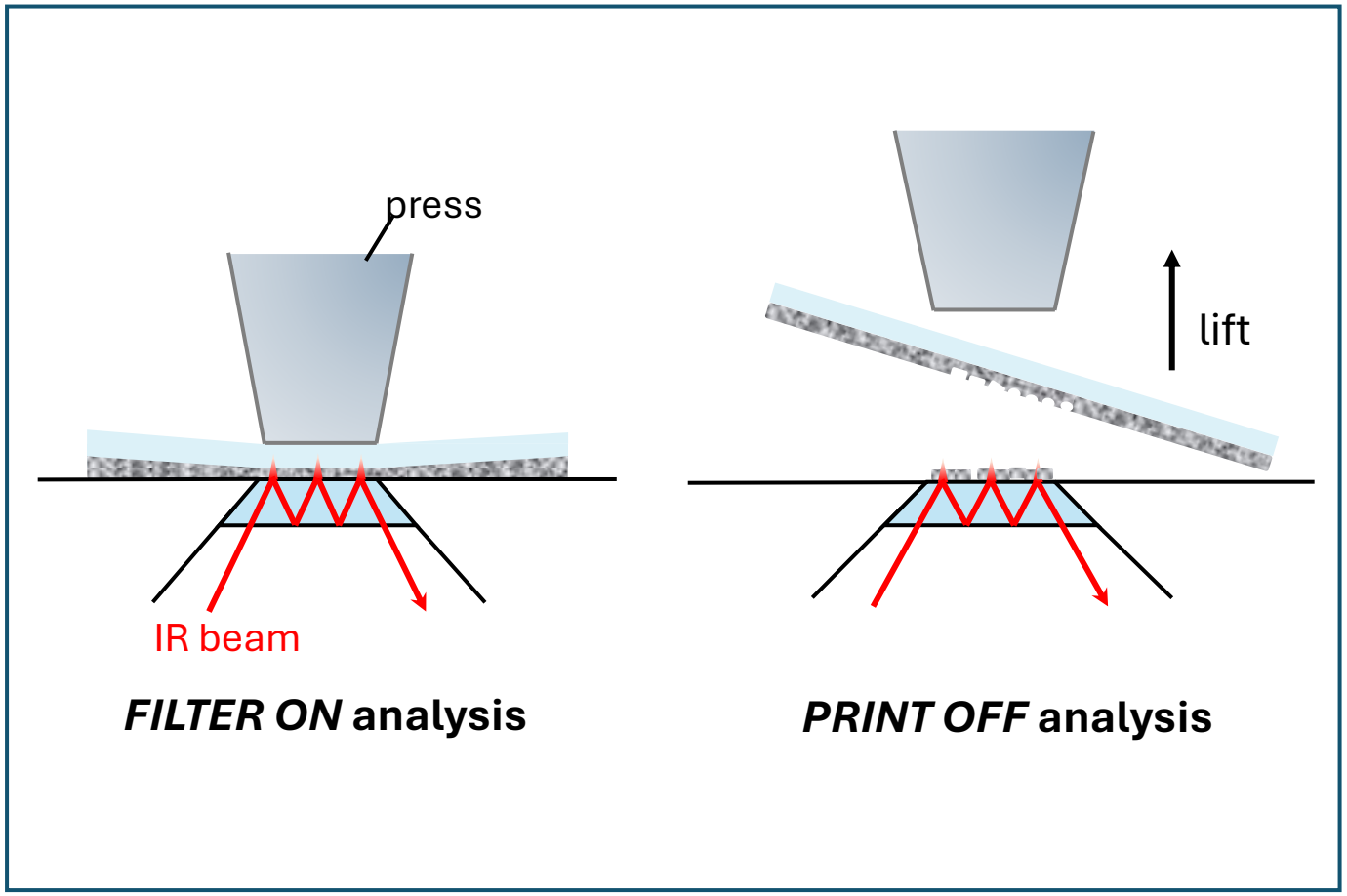


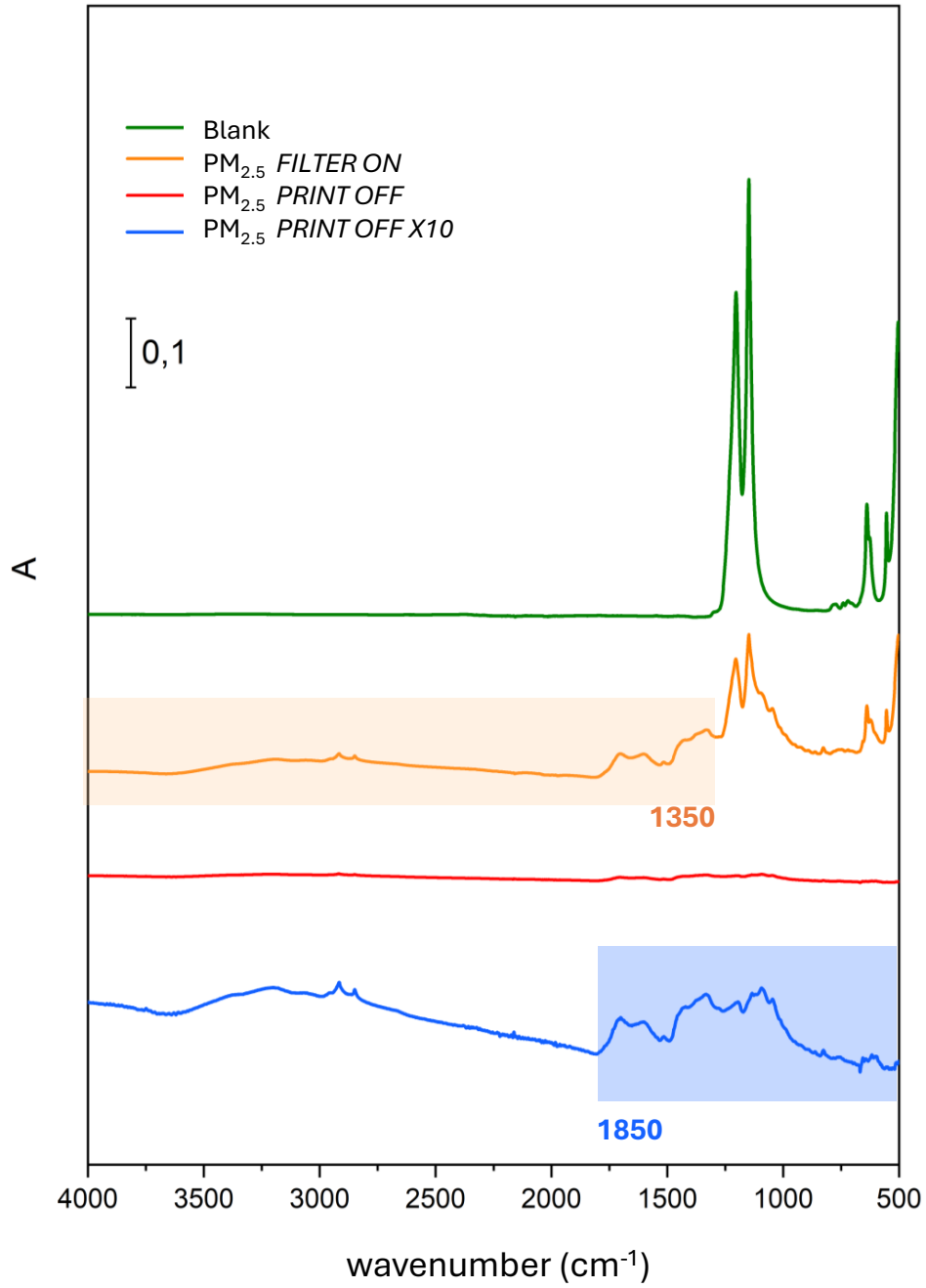
Selection of suitable substrate

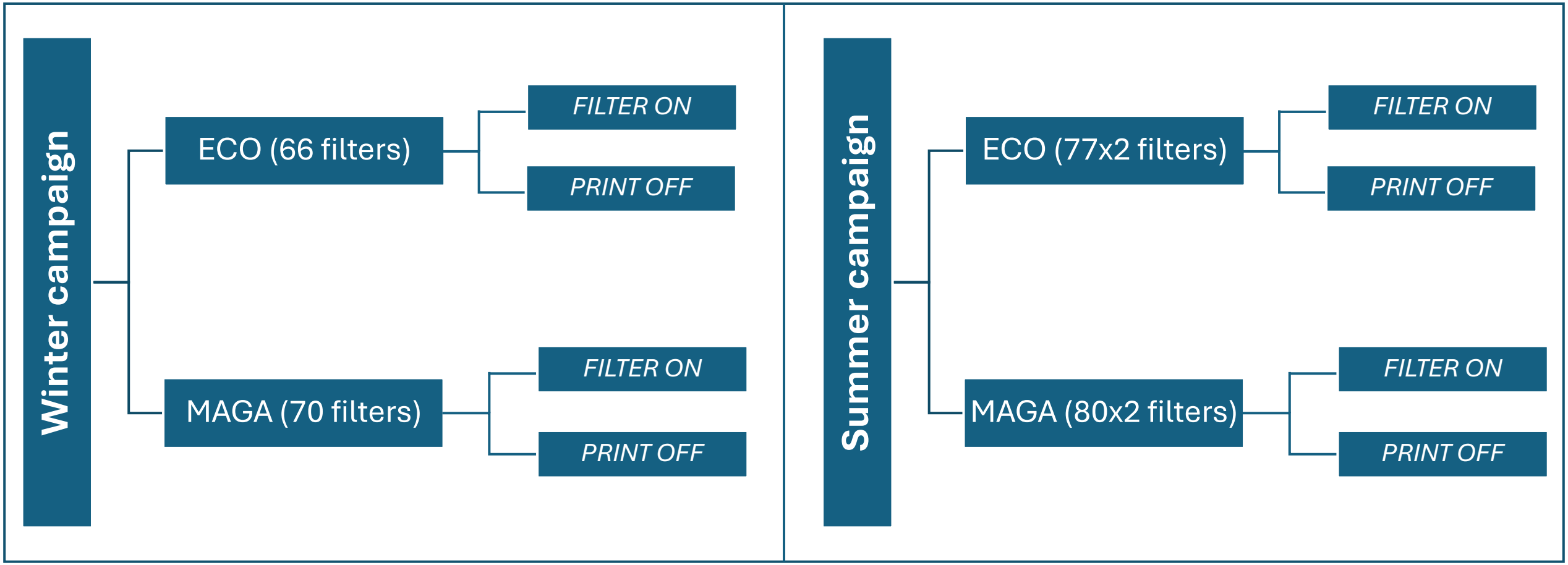




Spectra acquisition mode



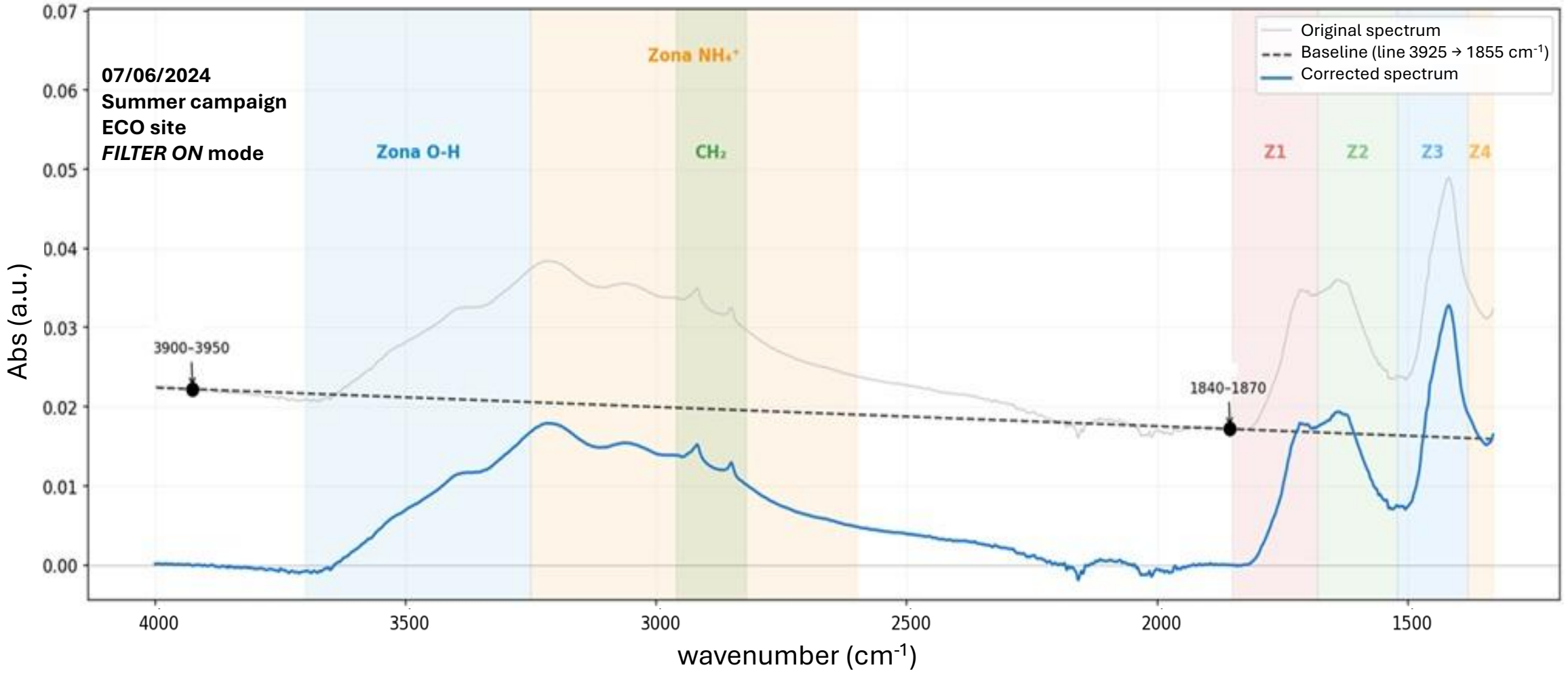




Total number of ATR- FTIR spectra acquired = 586

→ very large data set

Pre-processing of *FILTER ON* spectra and selection of spectral regions



- NH_4^+ (2600–3250 cm^{-1})
- O-H (3250–3700 cm^{-1})
- CH_2 (2820–2960 cm^{-1})
- Z1 (1680–1850 cm^{-1})
- Z2 (1520–1680 cm^{-1})
- Z3 (1380–1520 cm^{-1})
- Z4 (1330–1380 cm^{-1})

Spectral structure and definition of variables (*FILTER ON* mode)

Variable	Numerator	Denominator	Meaning
NH_4^+/OH	Zone NH_4^+ (2600–3250 cm^{-1})	Zone O-H (3250–3700 cm^{-1})	N-H vs O-H structural
OH/bb	Zone O-H (3250–3700 cm^{-1})	OH-NH broadband total	Structural O-H
NH_4^+/bb	Zone NH_4^+ (2600–3250 cm^{-1})	OH-NH broadband total	Fraction N-H
CH_2a/bb	CH_2 stretc. asym. (2918 cm^{-1})	OH-NH broadband total	Organic aliphatic compounds
CH_2s/bb	CH_2 stretc. sym (2850 cm^{-1})	OH-NH broadband total	Organic aliphatic compounds
CH_2s/CH_2a	CH_2 stretc. sym (2850 cm^{-1})	CH_2 stretc. asym (2918 cm^{-1})	Aliphatic chain
Z2/Z1	Z2 (COO^-)	Z1 (C=O)	Acid-base balance
Z4/Z3	Z4 (NO_3^-)	Z3 (NH_4^++ COO^-)	NO_3^- relative
Z1_2/bb	Z1+Z2	OH-NH broadband total	C=O + COO^-
Z3_4/bb	Z3+Z4	OH-NH broadband total	NH_4^+/NO_3^-

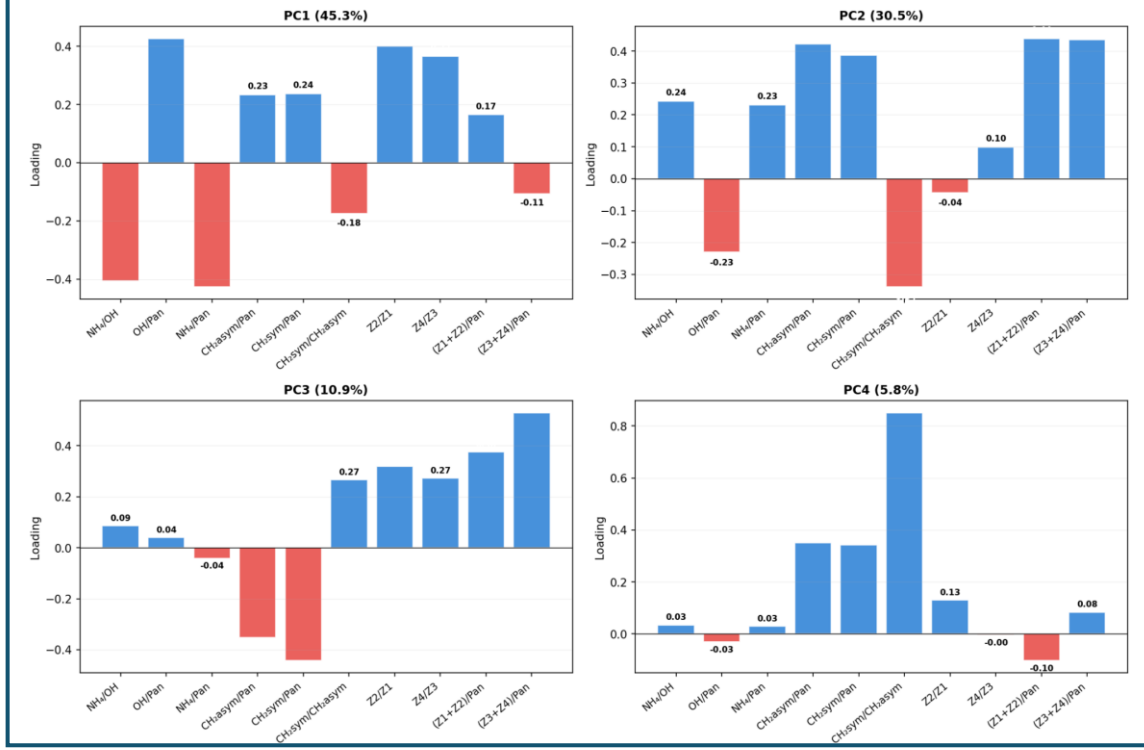
Spectral structure and definition of variables (*PRINT OFF* mode)

Variable	Numerator	Denominator	Meaning
Z2/Z1	Z2	Z1	COO^-/C=O acid-basic balance
Z3/Z1	Z3	Z1	NH_4^+/NO_3^-/COO^- vs C=O
Z4/Z3	Z4	Z3	band ~1207 relative to Z3
Z5/Z3	Z5	Z3	SO_4^{2-}/Si-O relative to NH_4^+/NO_3^-
Z6/Z5	Z6	Z5	bending/stretching SO_4^{2-}
Z5/Z1	Z5	Z1	SO_4^{2-}/Si-O relative to C=O
Z6/Z1	Z6	Z1	SO_4^{2-} bending relative to C=O
Z1_2/tot	Z1+Z2	Z1+Z2+Z3+Z4+Z5+Z6	Carbonyl/carboxyl moiety
Z3/tot	Z3	tot	NH_4^+/NO_3^-/COO^- moiety
Z5_6/tot	Z5+Z6	tot	SO_4^{2-}/Si-O total moiety

Principal Component Analysis (PCA)

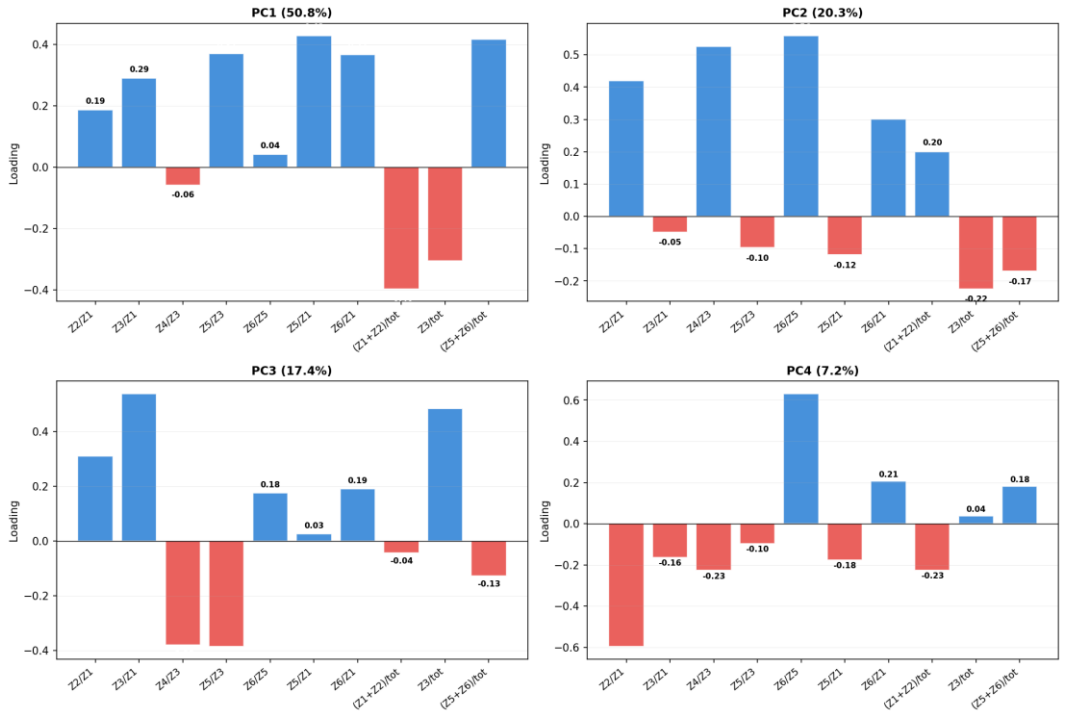
FILTER ON

PC	Explaining variance	Cumulative variance
PC1	45.3%	45.3%
PC2	30.5%	75.8%
PC3	10.9%	86.7%
PC4	5.8%	92.5%



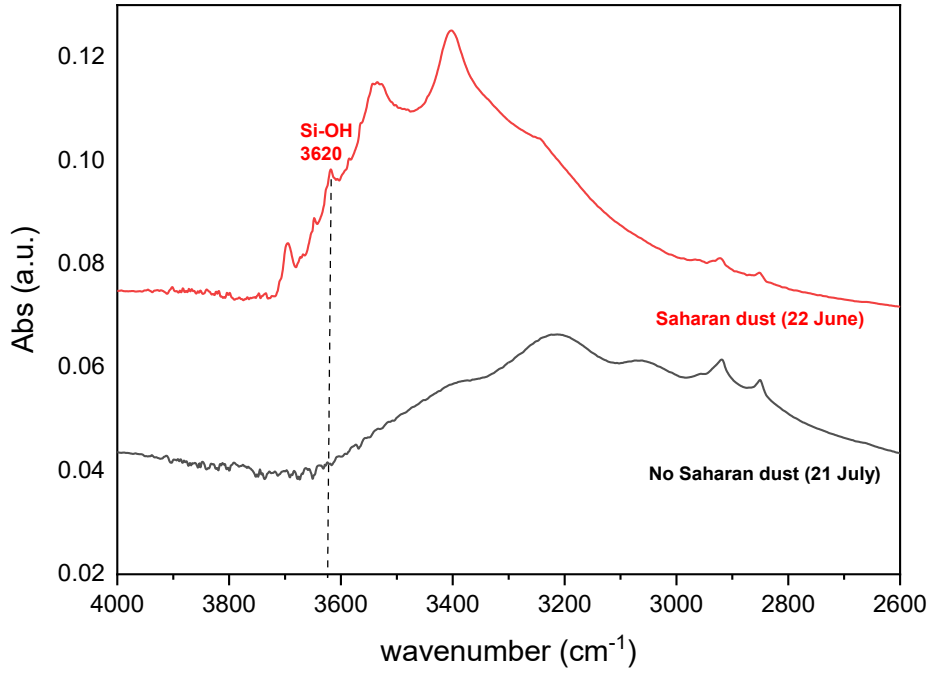
PRINT OFF

PC	Explaining variance	Cumulative variance
PC1	50.8%	50.8%
PC2	20.3%	71.1%
PC3	17.4%	88.5%
PC4	7.2%	95.7%



Cluster analysis: chemical characterization and change over time

	June	July	August
$COO^-/C=O$	↑	↓	↓
NO_3^-	significant contribution	↓	↓
NH_4^+	significant contribution	↑	↑
SO_4^{2-}	significant contribution	significant contribution	significant contribution
organic compounds	aliphatic compouds	aromatic compounds	aromatic compounds
OH	11 events	1 event	1 event



Limitations of the method:

- Two variables in the *FILTER ON* samples were found to be redundant;
- CH_2s/CH_2a is numerically unstable for samples with very weak C-H signals;
- Some samples in *PRINT OFF* mode with very low signals (total area < 0.5 a.u.) are unreliable for quantitative ratio analysis.

Potential of the method:

- Correlation between the carbonyl/carboxylate and NH_4^+/NO_3^- signals compatible with a common origin due to secondary photochemical oxidation processes;
- Correlation between organic carbonyl and sulfate moiety due to secondary aerosol;
- Identification of the main sources of particulate matter emissions (primary and secondary).

Goals and future prospects:

Study and variability comparison between the two sites (ECO and MAGA) and seasonal (winter and summer) by means of ATR-FTIR spectroscopic technique.

UNIVERSITÀ DEL SALENTO
L'Ateneo tra i due mari

CNR ISAC

UNIVERSITÀ DEGLI STUDI DI BARI ALDO MORO

TOX in air

XII Convegno
sul Particolato Atmosferico

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