UNIVERSITÀ DI TORINO

chimica

2023 - 2027 DIPARTIMENTO DI ECCELLENZA
Ministero dell'Università e della Ricerca

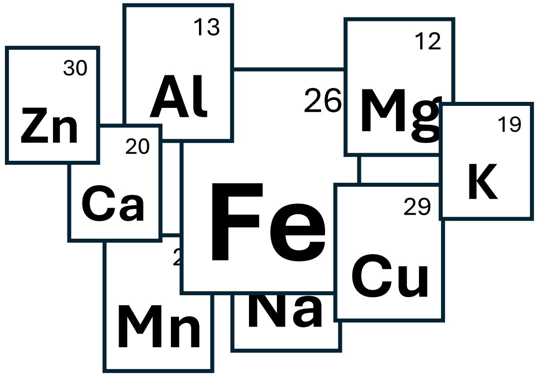
SOCIETA ITALIANA DI AEROSOL IAS ITALIAN AEROSOL SOCIETY

TORINO PM 2024

Studio della **frazione solubile** del particolato atmosferico: **composizione** e **speciazione** del PM_{10} **artico**

M. Marafante, S. Bertinetti, L. Carena, D. Fabbri, M. Malandrino, D. Vione, S. Berto

matteo.marafante@unito.it



Formate$^-$ Cl^- PO_4^{3-} Oxalate^{2-} NO_3^- SO_4^{2-} NO_2^- Malonate^{2-} Acetate$^-$ F^- Br^- NH_4^+

Studio della frazione solubile del particolato atmosferico: composizione e speciazione del PM_{10} artico

Studio della frazione solubile del particolato atmosferico: composizione e speciazione del PM_{10} artico

Zn Al Mg Ca Fe K Mn Na Cu

Formate$^-$ Cl$^-$ Oxalate^{2-} NO_3^- PO_4^{3-} SO_4^{2-} NO_2^- Malonate^{2-} Acetate$^-$ F$^-$ Br$^-$ NH_4^+

IUPAC
INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Speciation
The distribution of an element amongst defined chemical species in a system

Fe 26

Zn 30, Ca 20, Al 13, Mn, Na, Mg 12, Cu 29, K 19

Formate$^-$ Cl$^-$ Oxalate^{2-} NO_3^- PO_4^{3-} SO_4^{2-} NO_2^- Malonate^{2-} Acetate$^-$ F$^-$ Br$^-$ NH_4^+

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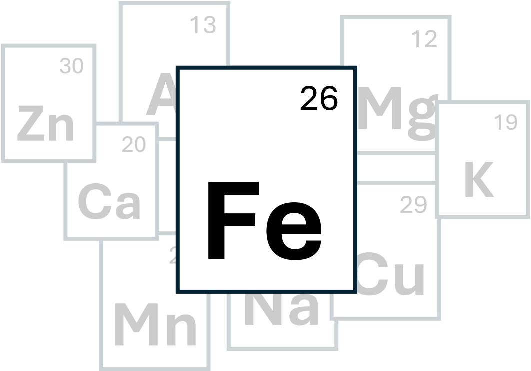

Formate$^-$ Cl$^-$
Oxalate^{2-} NO_3^- PO_4^{3-}
NO_2^- SO_4^{2-} Malonate^{2-}
Acetate$^-$ F$^-$ Br$^-$
NH_4^+

Studio della **frazione solubile** del particolato atmosferico: **composizione** e **speciazione** del PM_{10} **artico**

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Speciation
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Formate$^-$ Cl$^-$ Oxalate^{2-} NO_3^- PO_4^{3-} SO_4^{2-} NO_2^- Malonate^{2-} Acetate$^-$ F^- Br^- NH_4^+

Studio della **frazione solubile** del particolato atmosferico: **composizione** e **speciazione** del PM_{10} **artico**

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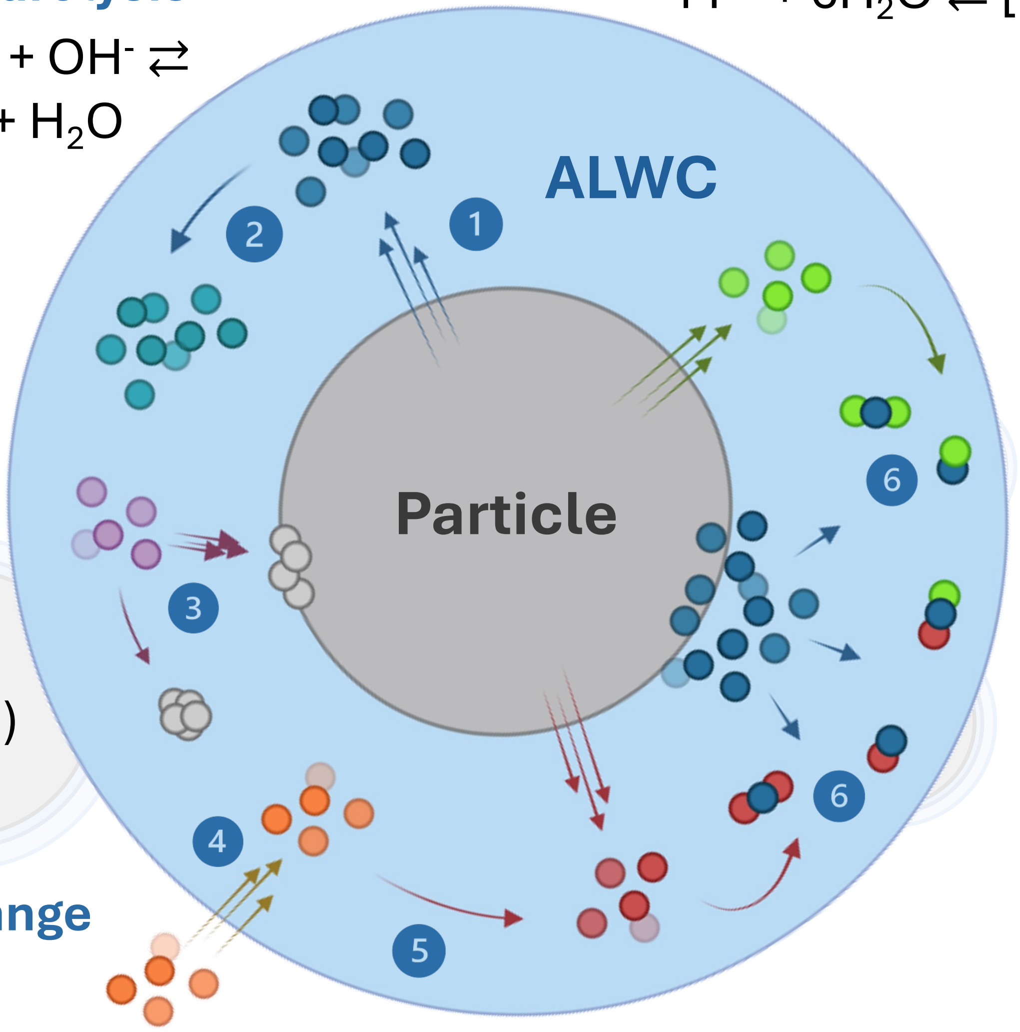
Speciation
The distribution of an element amongst defined chemical species in a system

1. Solubilization

$$M^{n+} + 6H_2O \rightleftarrows [M(H_2O)_6]^{n+}$$

2. Hydrolysis

$$[M(H_2O)_6]^{n+} + OH^- \rightleftarrows$$
$$\rightleftarrows [M(H_2O)_5(OH)]^{(n-1)+} + H_2O$$



3. Precipitation

$$[M(OH)]^{(n-1)+}\ (aq) \rightleftarrows$$
$$\rightleftarrows [M(OH)]^{(n-1)+}\ (s)$$

4. Air-Liquid exchange

$$X\ (g) \rightleftarrows X\ (aq)$$

5. Reactions

$$X \rightrightarrows Y$$

6. Complexation ML_X

$$M^{n+} + pL_1 \rightleftarrows [M(L_1)_p]^{n+}$$

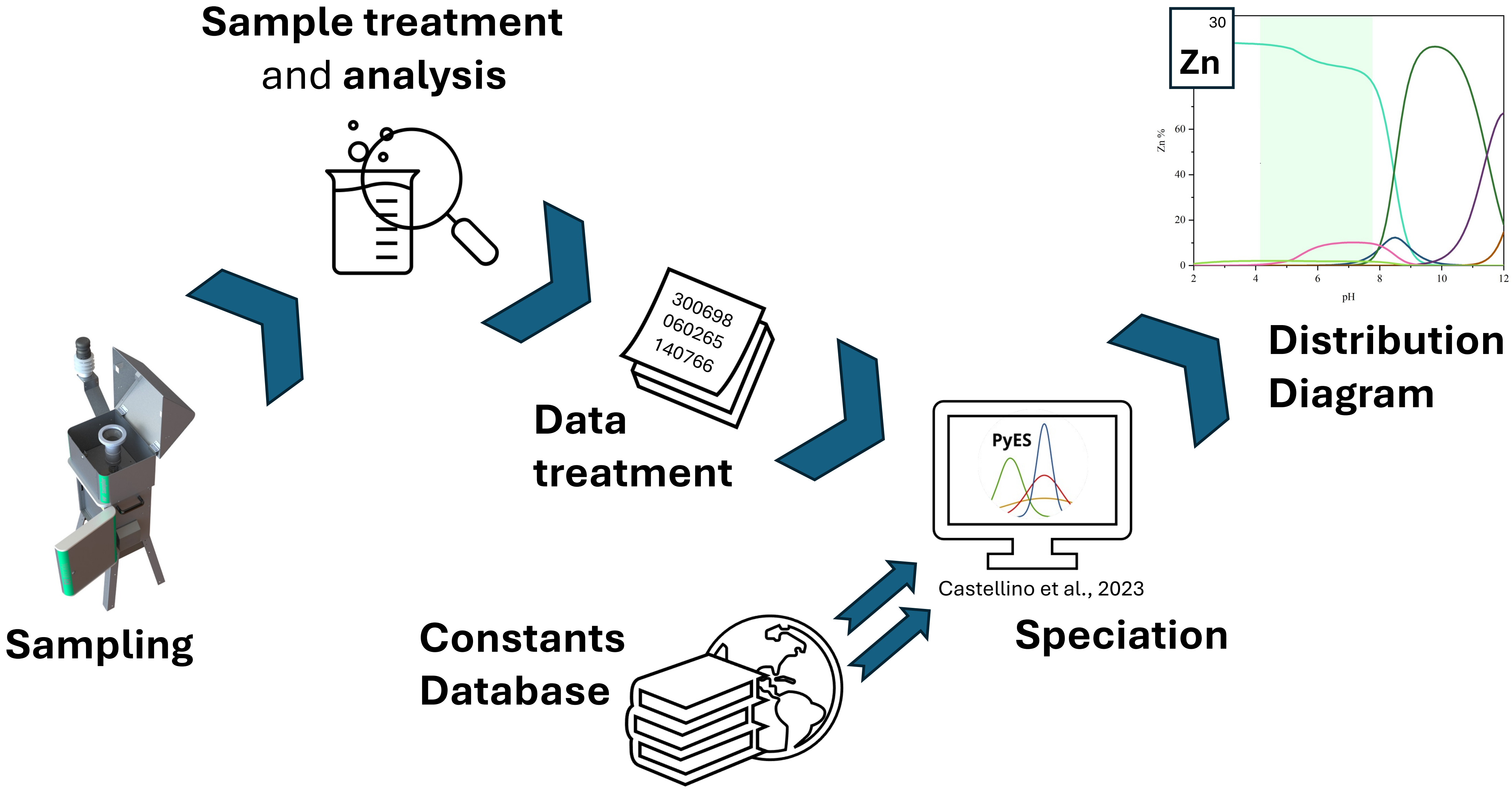
$$M^{n+} + pL_2 \rightleftarrows [M(L_2)_p]^{n+}$$

$$M^{n+} + pL_1 + qL_2 \rightleftarrows [M(L_1)_p(L_2)_q]^{n+}$$

Legend

- Free metal
- Hydrolitic species
- Ligand 1(L_1)
- Ligand 2(L_2)
- Complex ML_x
- Solid
- Gas

Workflow



Sample treatment
and analysis
300698
060265
140766
Data
treatment
Sampling
Constants
Database
PyES
Castellino et al., 2023
Speciation
30
Zn
Zn %
0
20
40
60
2
4
6
8
10
12
pH
Distribution
Diagram

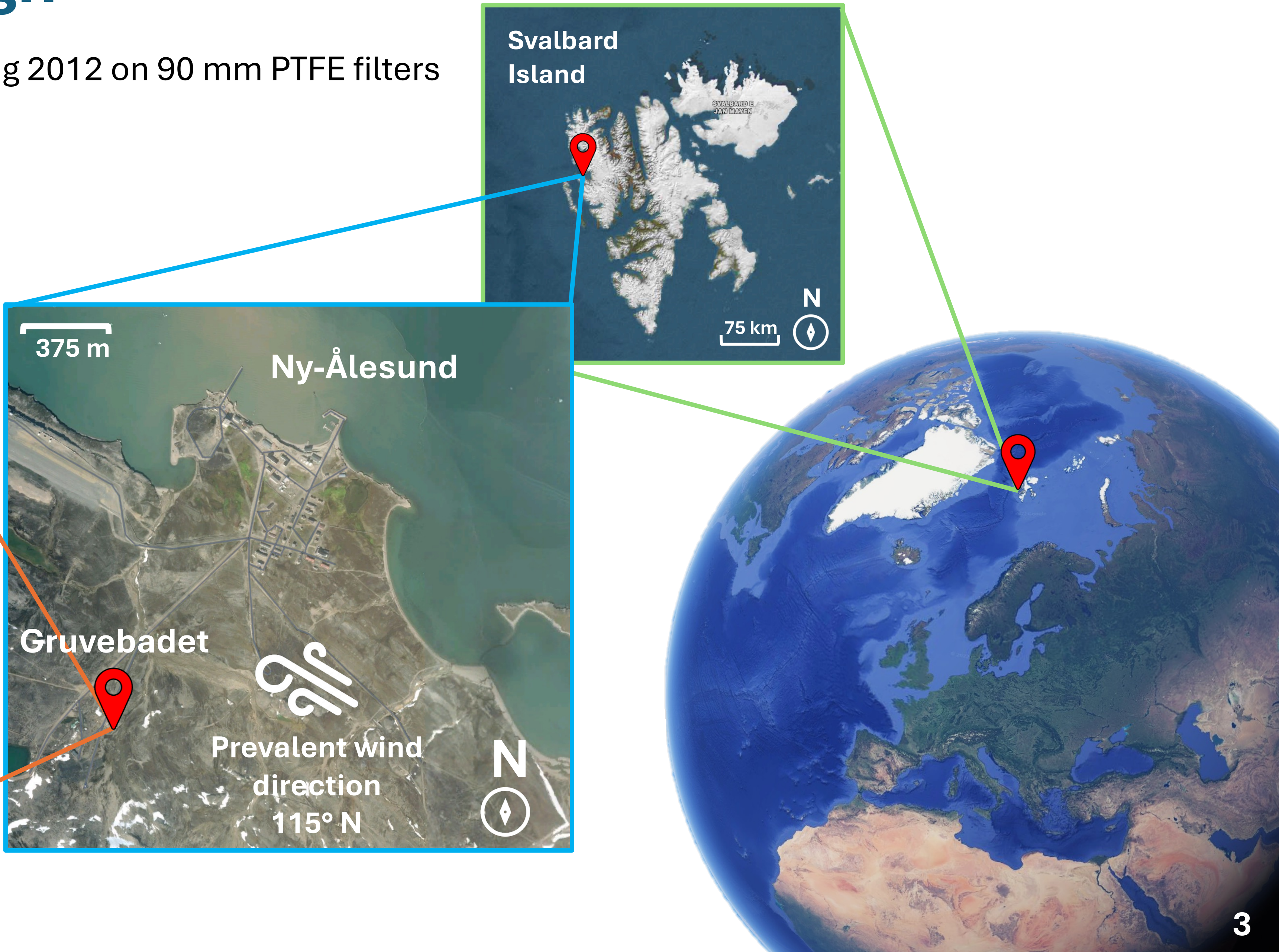
Sampling campaign

29 PM_{10} samples were collected during 2012 on 90 mm PTFE filters

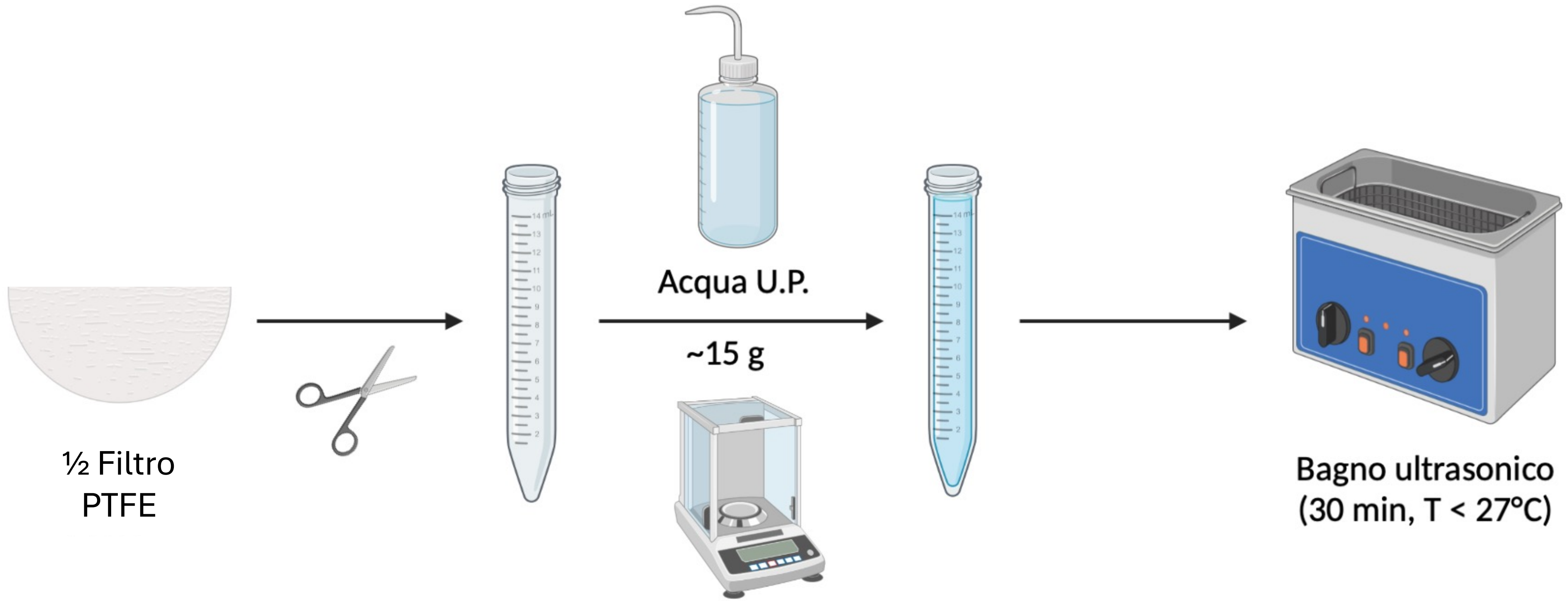
21/04/2012 ⟶ 8/09/2012

Tecora ECHO PM
High volume aerosol sampler
Sampling time ~ 4 days
Sampling flux ~ 200 l min^{-1}
Average sampling volume = 1050 m^3

Gruvebadet

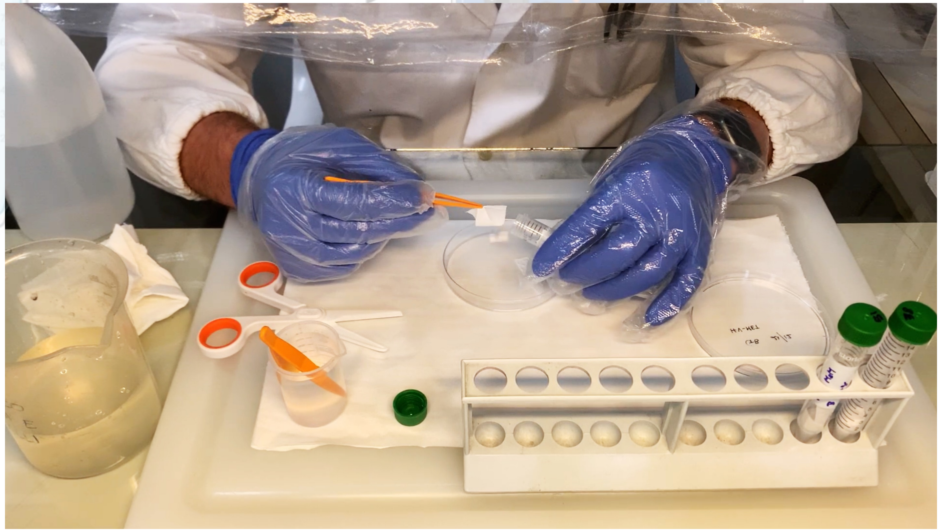


Extraction procedure



Extraction procedure

Polypropylene Tools



Clean Room

CEN/TR16269:2011 Protocol

Quantitative Analysis

~ 4 ml

pH-meter
Methrom
713
pH

~ 2 ml

IC
Dionex DX 500

~~F^-~~, Cl^-, ~~Br^-~~, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, For^-, Ac^-, Ox^{2-} Mal^{2-}

~ 8 ml

ICP-OES
Agilent 5110

Na^+, K^+, Mg^{2+}, Ca^{2+}

+

SF-ICP-MS
Thermo Fisher Element 2

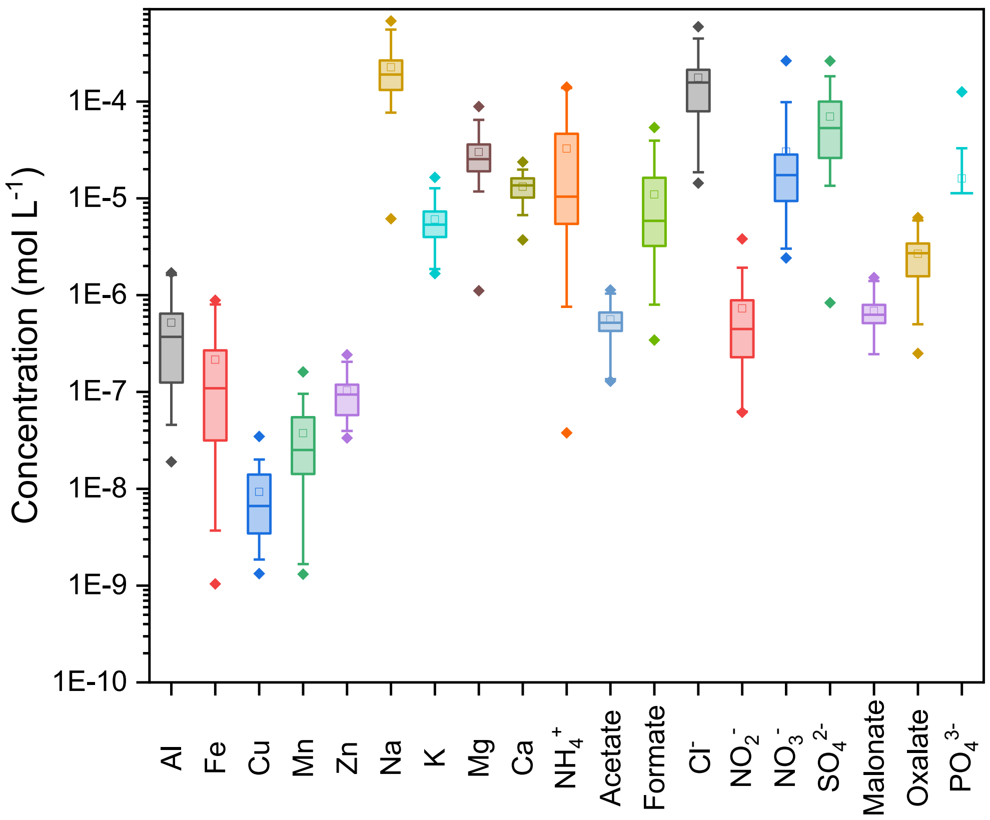
Al^{3+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}

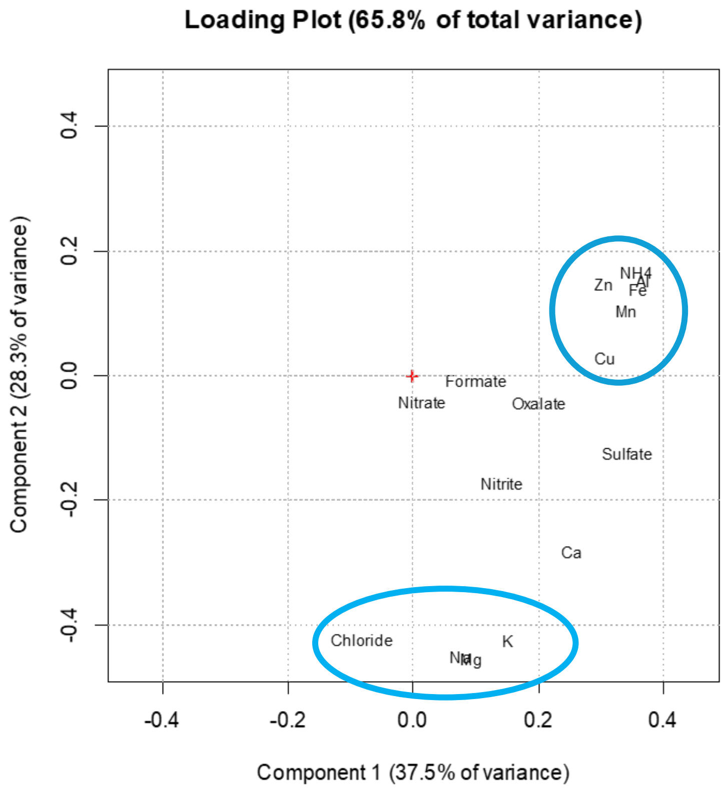
+

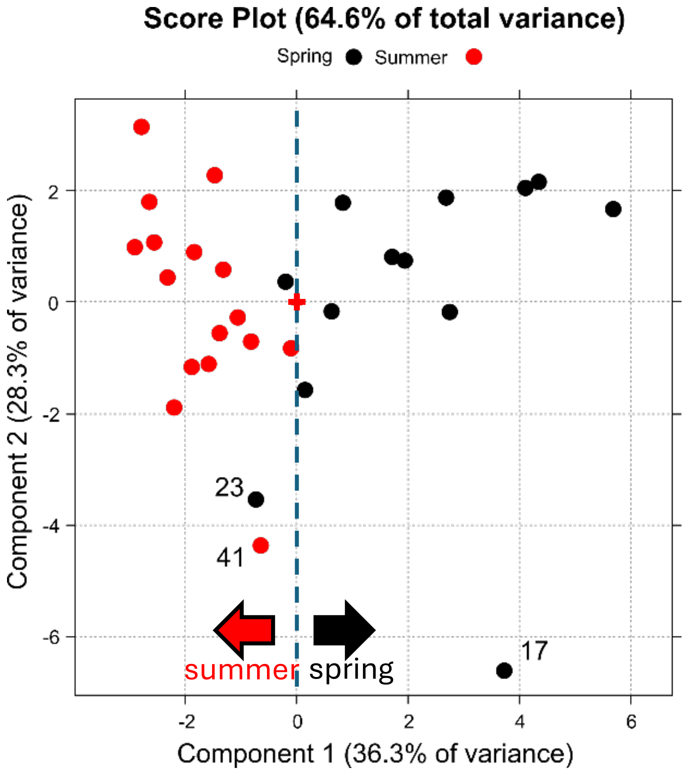
IC
Dionex DX 500

NH_4^+

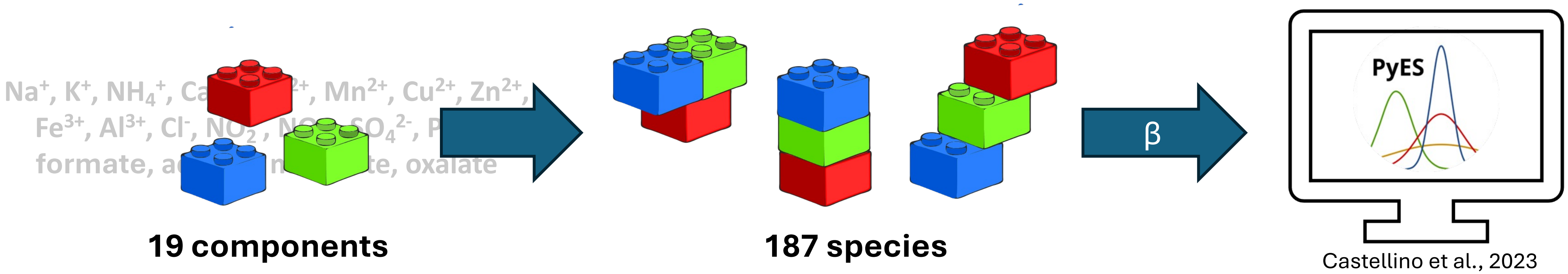
Quantitative Analysis







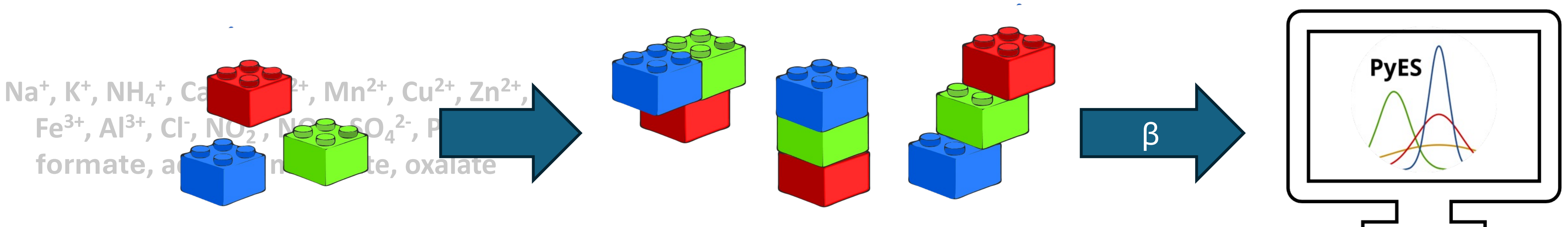
Speciation



- Different type of **thermodynamic equilibrium** have been considered

protonation equilibria	$qL^{z-} + rH^{+} \leftrightarrows [H_rL_q]^{r-qz}$	$\beta_{HL} = \frac{[H_rL_q{}^{r-qz}]}{[L^{z-}]^q[H^+]^r}$
hydrolitic species formation	$pM^{n+} + qH_2O \leftrightarrows [M_p(OH)_q]^{np-q} + qH^{+}$	$\beta_{MOH} = \frac{[M_p(OH)_q{}^{np-q}][H^+]^r}{[M^{n+}]^p}$
complexes formation	$pM^{n+} + qL^{z-} + rH^{+} \leftrightarrows [M_pL_qH_r]^{np+r-qz}$	$\beta_{MLH} = \frac{[M_pL_qH_r{}^{np+r-qz}]}{[M^{n+}]^p[L^{z-}]^q[H^+]^r}$
solids formation	$[M_p(OH)_q]^{np-q}{}_{(s)} \leftrightarrows pM^{n+} + qOH^{-}$	$K_{ps} = [M^{n+}]^p[OH^-]^q$

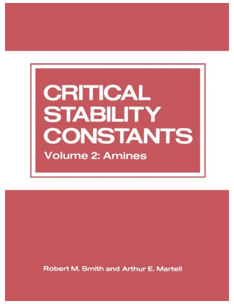
Speciation



19 components **187 species**

Castellino et al., 2023

- Different type of **thermodynamic equilibrium** have been considered
  - protonation equilibria: $For^- + H^+ \leftrightarrows HFor$ $\qquad \beta_{HL} = \frac{[H_rL_q{}^{r-qz}]}{[L^{z-}]^q[H^+]^r}$
  - hydrolitic species formation: $Fe^{3+} + 2H_2O \leftrightarrows [Fe(OH)_2]^+ + 2H^+$ $\qquad \beta_{MOH} = \frac{[M_p(OH)_q{}^{np-q}][H^+]^r}{[M^{n+}]^p}$
  - complexes formation: $Cu^{2+} + Cl^- \leftrightarrows [CuCl]^+$ $\qquad \beta_{MLH} = \frac{[M_pL_qH_r{}^{np+r-qz}]}{[M^{n+}]^p[L^{z-}]^q[H^+]^r}$
  - solids formation: $[Al(OH)_3]_{(s)} \leftrightarrows Al^{3+} + 3OH^-$ $\qquad K_{ps} = [M^{n+}]^p[OH^-]^q$



Critically Stability Constants

NIST

Critically Selected Stability Constants of Metal Complexes Database

SC-Database

$\boldsymbol{\beta_{HL}}$ $\boldsymbol{\beta_{MOH}}$ $\boldsymbol{K_{ps}}$ $\boldsymbol{\beta_{MLH}}$

$\boldsymbol{\beta_n} \longrightarrow$ Overall formation constant

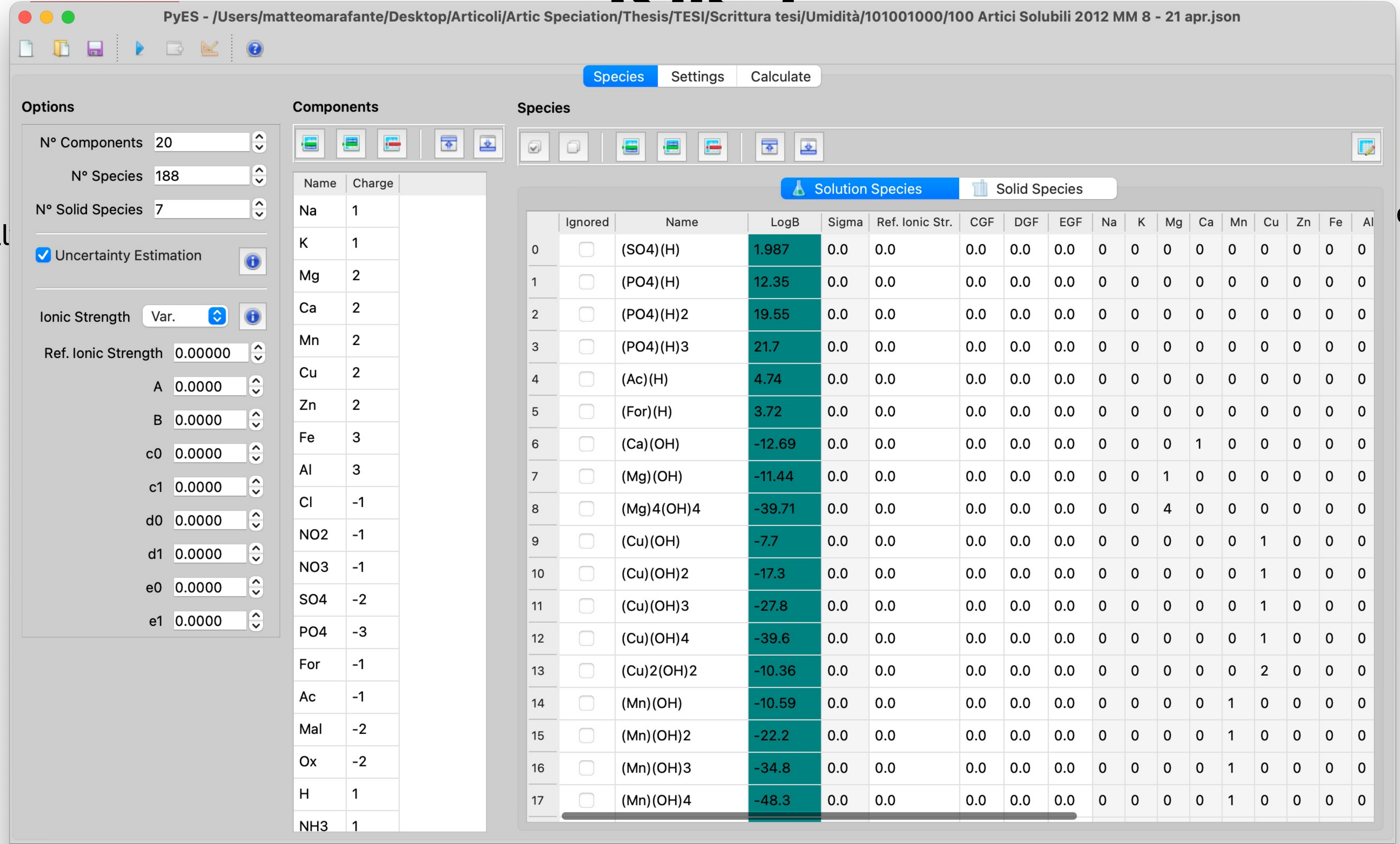
Average Ionic strength of sample < 1 mmol L^{-1}

T = 25 °C; I = 0 mol L^{-1}

Extended Debye Huckel Equation

$$logK_{eq}(I') \longrightarrow logK_{eq}(I)$$

$$logK_{eq}(I) = logK_{eq}(I') - z^{*}A\left(\frac{\sqrt{I}}{1+B\sqrt{I}} - \frac{\sqrt{I'}}{1+B\sqrt{I'}}\right) + C(I - I') + D\left((I)^{3/2} - \left((I')^{3/2}\right)\right)$$



PyES - /Users/matteomarafante/Desktop/Articoli/Artic Speciation/Thesis/TESI/Scrittura tesi/Umidità/101001000/100 Artici Solubili 2012 MM 8 - 21 apr.json

Species | Settings | Calculate

Options

N° Components	20
N° Species	188
N° Solid Species	7
Uncertainty Estimation	☑
Ionic Strength	Var.
Ref. Ionic Strength	0.00000
A	0.0000
B	0.0000
c0	0.0000
c1	0.0000
d0	0.0000
d1	0.0000
e0	0.0000
e1	0.0000

Components

Name	Charge
Na	1
K	1
Mg	2
Ca	2
Mn	2
Cu	2
Zn	2
Fe	3
Al	3
Cl	-1
NO2	-1
NO3	-1
SO4	-2
PO4	-3
For	-1
Ac	-1
Mal	-2
Ox	-2
H	1
NH3	1

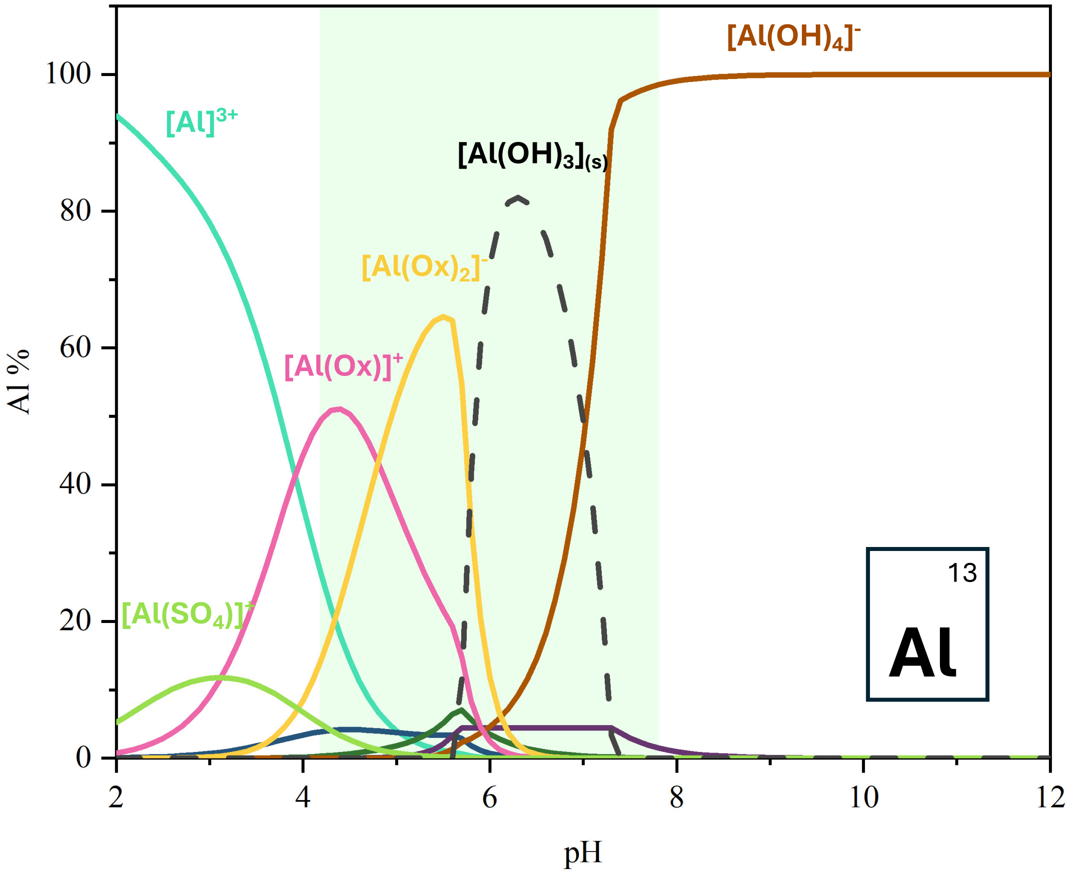
Species

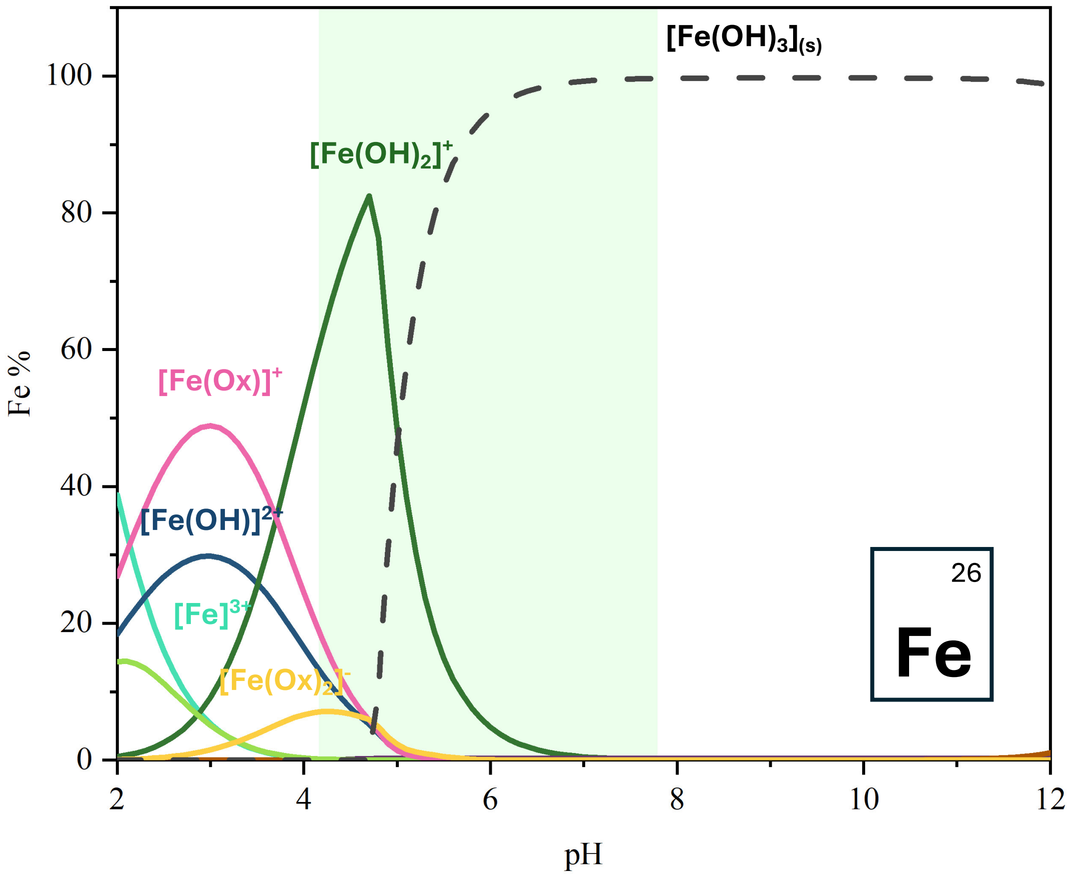
Solution Species | Solid Species

	Ignored	Name	LogB	Sigma	Ref. Ionic Str.	CGF	DGF	EGF	Na	K	Mg	Ca	Mn	Cu	Zn	Fe	Al
0	☐	(SO4)(H)	1.987	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0
1	☐	(PO4)(H)	12.35	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0
2	☐	(PO4)(H)2	19.55	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0
3	☐	(PO4)(H)3	21.7	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0
4	☐	(Ac)(H)	4.74	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0
5	☐	(For)(H)	3.72	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0
6	☐	(Ca)(OH)	-12.69	0.0	0.0	0.0	0.0	0.0	0	0	0	1	0	0	0	0	0
7	☐	(Mg)(OH)	-11.44	0.0	0.0	0.0	0.0	0.0	0	0	1	0	0	0	0	0	0
8	☐	(Mg)4(OH)4	-39.71	0.0	0.0	0.0	0.0	0.0	0	0	4	0	0	0	0	0	0
9	☐	(Cu)(OH)	-7.7	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	1	0	0	0
10	☐	(Cu)(OH)2	-17.3	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	1	0	0	0
11	☐	(Cu)(OH)3	-27.8	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	1	0	0	0
12	☐	(Cu)(OH)4	-39.6	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	1	0	0	0
13	☐	(Cu)2(OH)2	-10.36	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	2	0	0	0
14	☐	(Mn)(OH)	-10.59	0.0	0.0	0.0	0.0	0.0	0	0	0	0	1	0	0	0	0
15	☐	(Mn)(OH)2	-22.2	0.0	0.0	0.0	0.0	0.0	0	0	0	0	1	0	0	0	0
16	☐	(Mn)(OH)3	-34.8	0.0	0.0	0.0	0.0	0.0	0	0	0	0	1	0	0	0	0
17	☐	(Mn)(OH)4	-48.3	0.0	0.0	0.0	0.0	0.0	0	0	0	0	1	0	0	0	0

Criticall

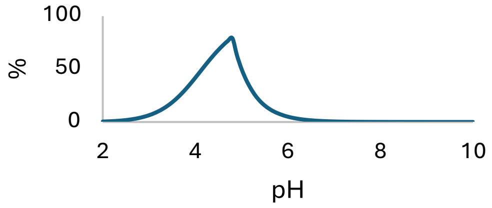
Sample 8 – 21st April



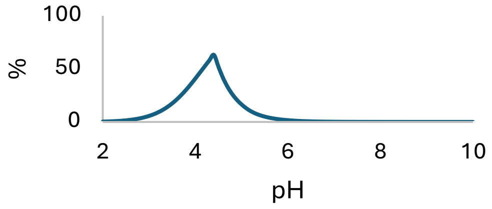


Overall

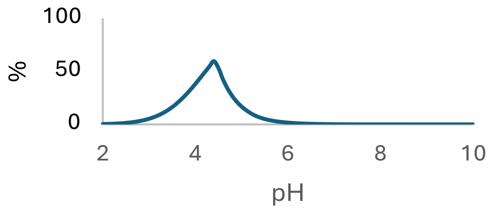
$(Fe)(OH)_2^+$ - sample #1



$(Fe)(OH)_2^+$ - sample #2



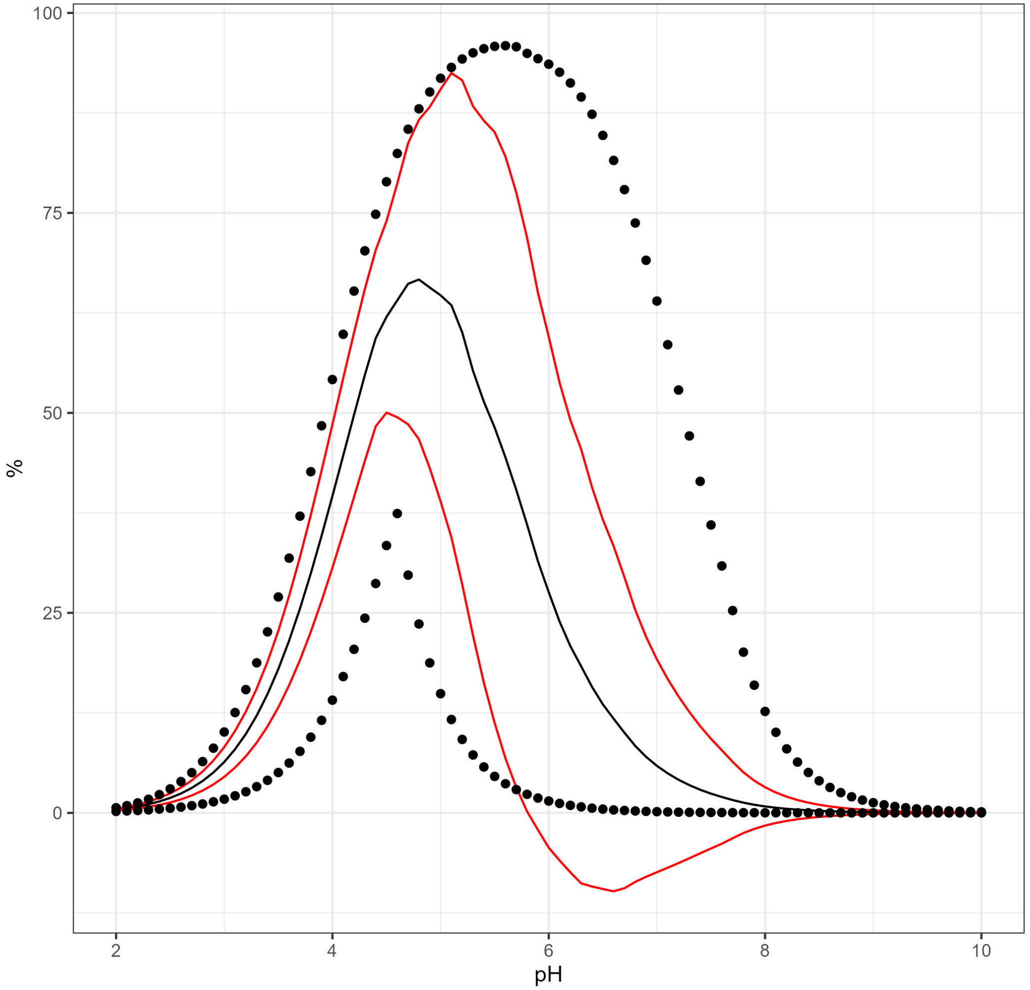
$(Fe)(OH)_2^+$ - sample #3



...

$(Fe)(OH)_2^+$ - sample #29

$Fe(OH)_2^+$



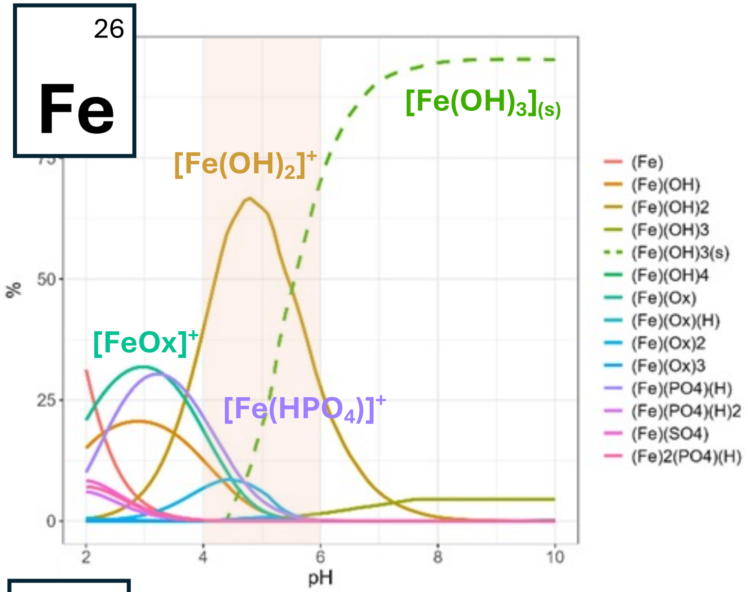
mean

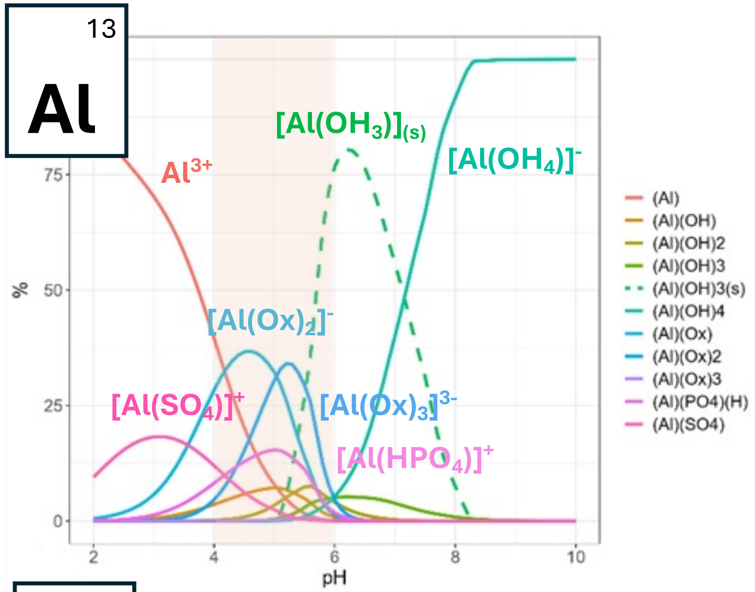
mean ± std dev

min/max

... for 75 species

The species that have formation **< 1%** were not considered





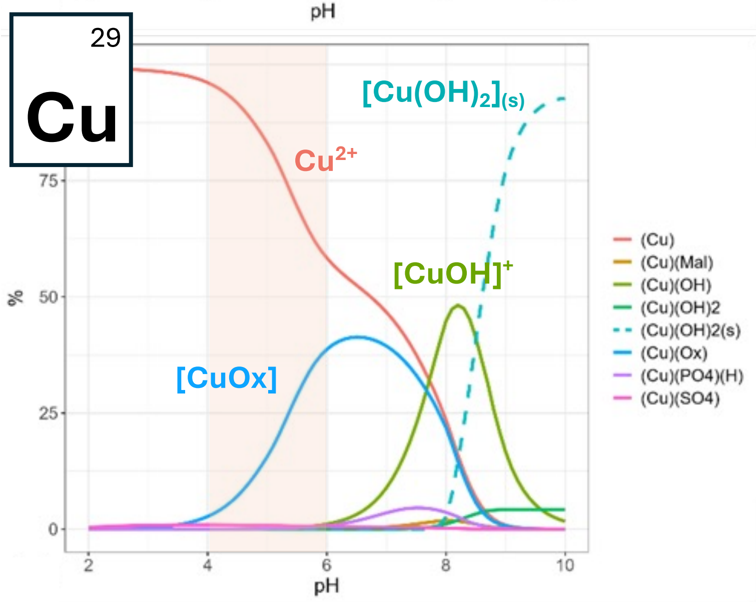
Major species (pH 4 - 6)

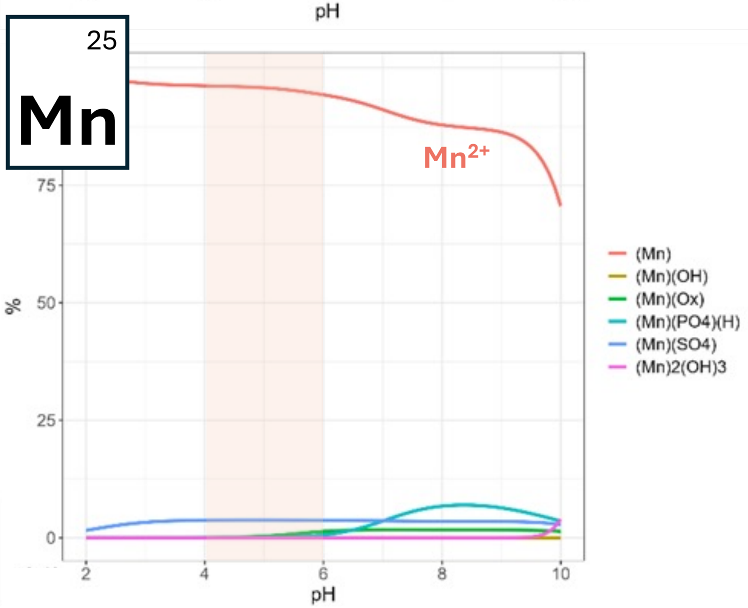
free metal (acquoions): Na^+, K^+, Mg^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}

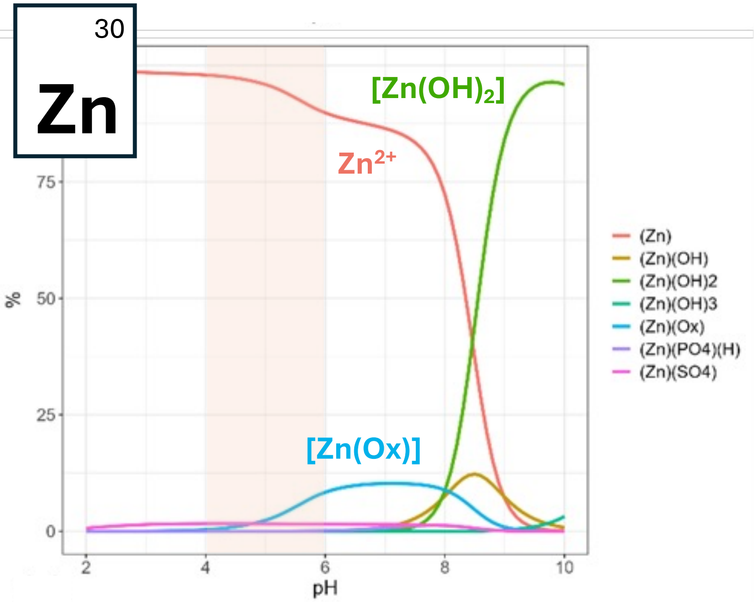
hydrolitic: $[Fe(OH)_2]^+$, $Fe(OH)_3(s)$, $Al(OH)_3(s)$

oxalate: $[FeOX]^+$, $[Fe(OX)2]^-$, $[AlOx]^+$, $[Al(Ox)_2]^-$, [CuOx]

phosphate: $[Fe(HPO_4)]^+$, $[Al(HPO_4)]^+$





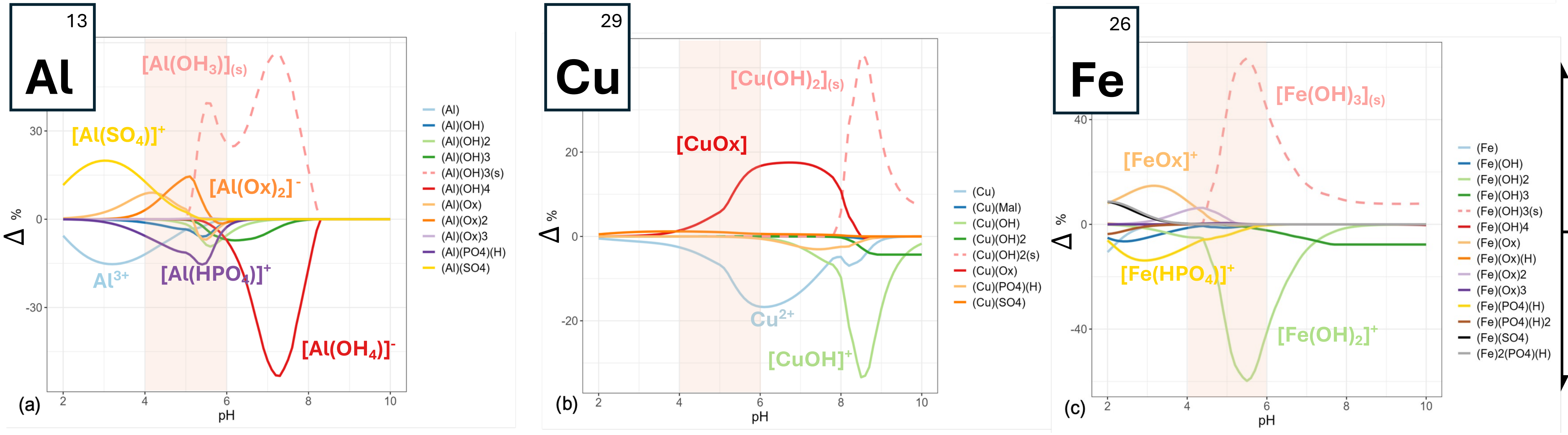


Seasonality

The atmospheric composition over the Arctic region changes significantly over the year, due to strong variability in the environmental conditions (atmospheric stability, temperature, sunlight irradiation) among the seasons. Moreover, some sources shown activity only during some period (e.g., biotic emission) or change drastically with season (e.g., anthropic emission).

Seasonality

Δ = Spring samples Speciation – Summer sample Speciation



Greater in **Spring**

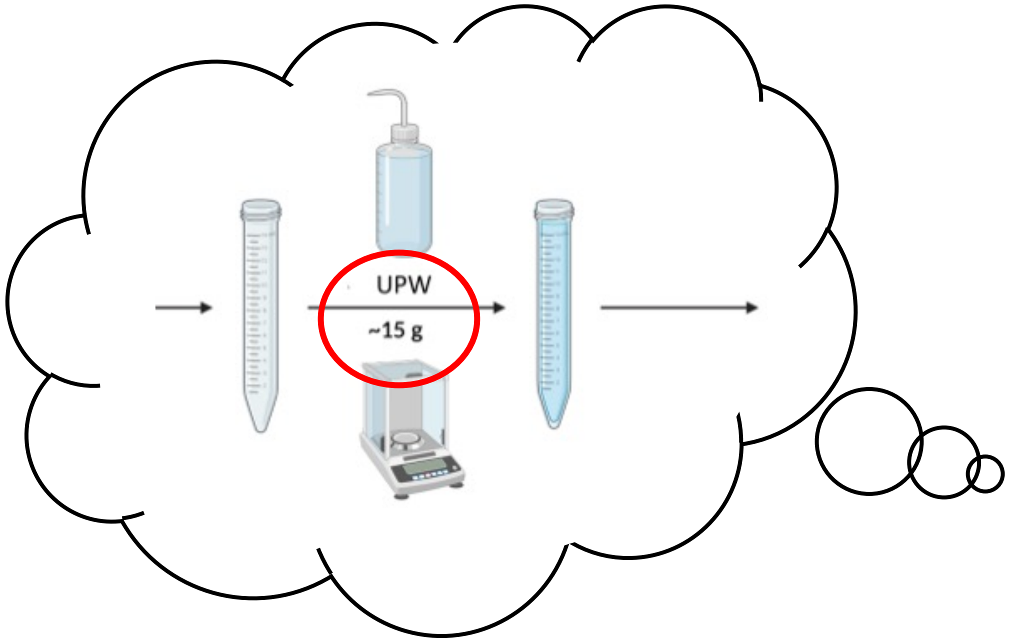
Greater in **Summer**

⬆ Spring

Sulfate, oxalate precipitation of $Al(OH)_3$, $Cu(OH)_2$, and $Fe(OH)_3$

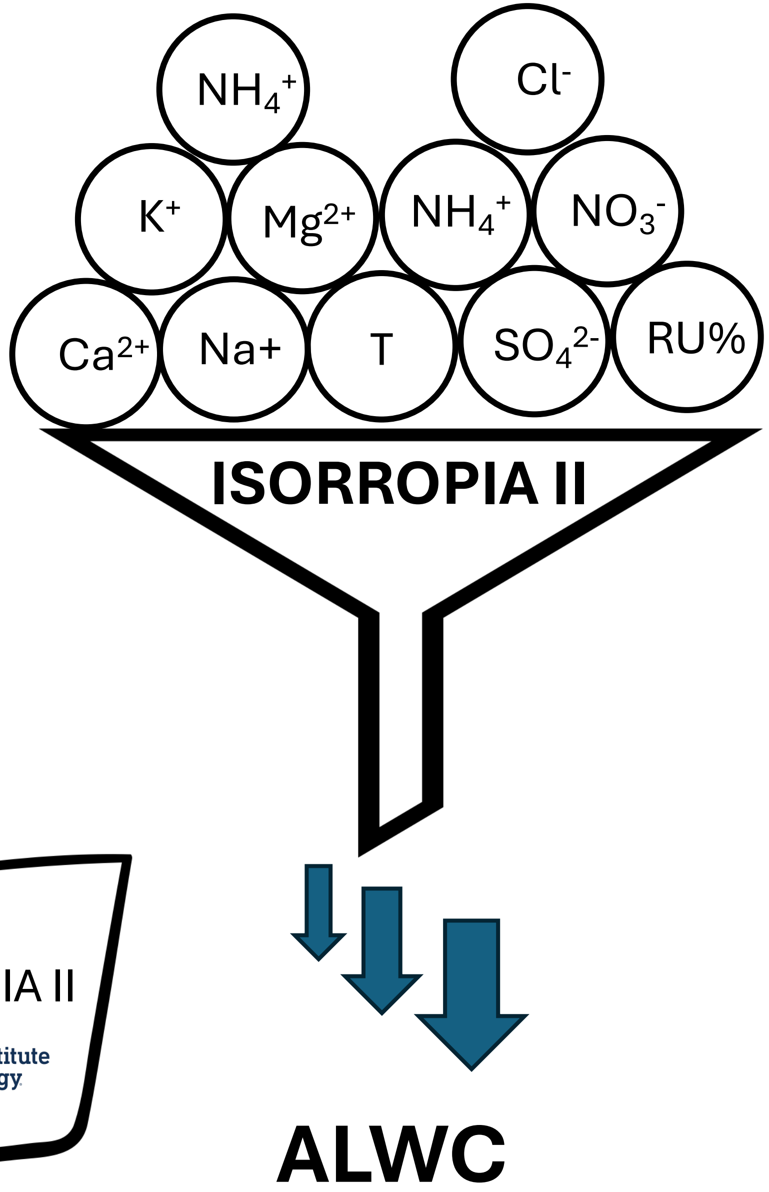
⬆ Summer

hydrolytic forms, free metals, HPO_4^{2-}

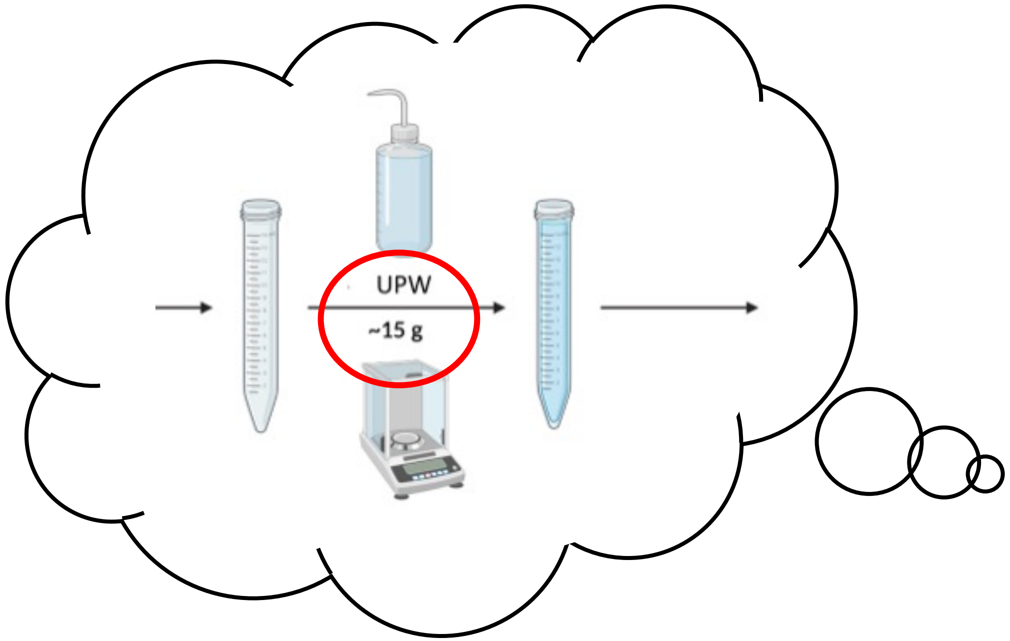


Are the 15 mL of water used for the solubilization a «realistic» volume??

Considering 1050 m^3 of air collected for each samples, they correspond about **14 mg·m^3** of Aerosol Liquid Water Content (ALWC)



Fountoukis, C., Nenes, A., 2007. ISORROPIAII: A computationally efficient thermodynamic equilibrium model for K+-Ca2+-Mg2+-NH4+-Na+-SO42--NO3--Cl--H2O aerosols. Atmos. Chem. Phys. 7, 4639–4659. https://doi.org/10.5194/acp-7-4639-2007



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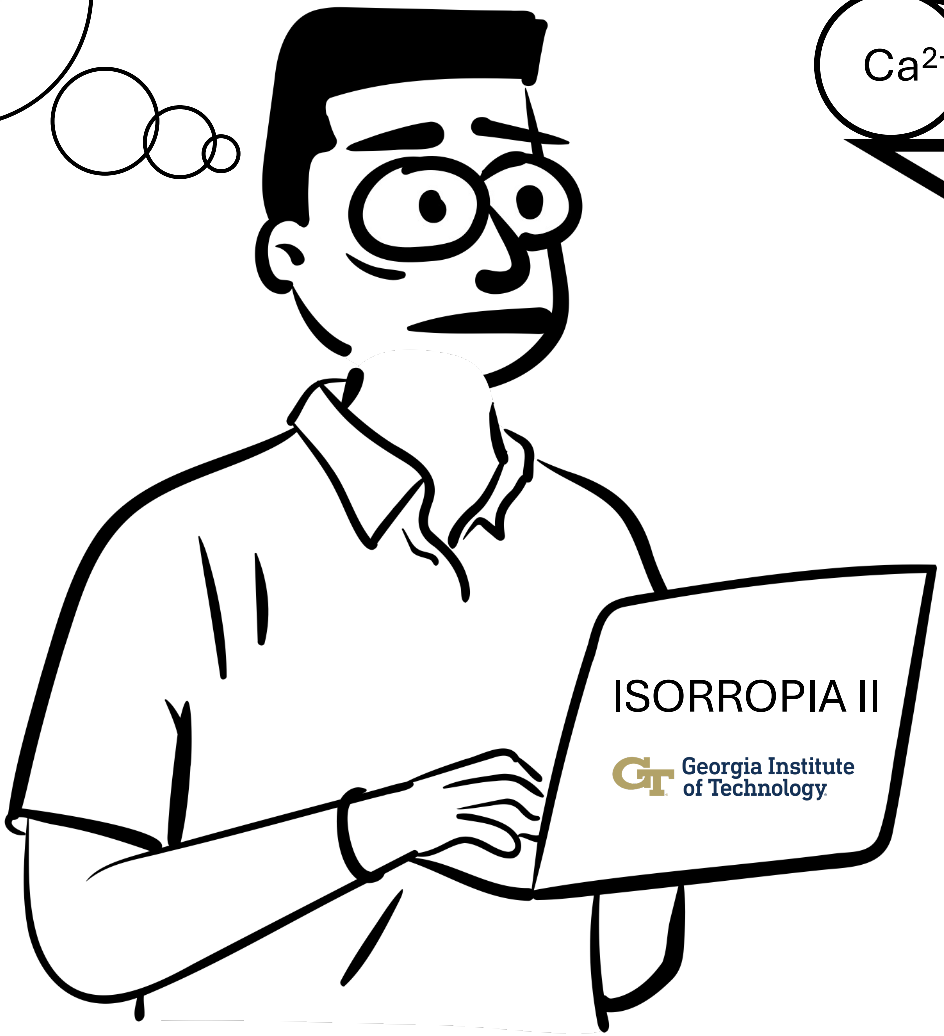
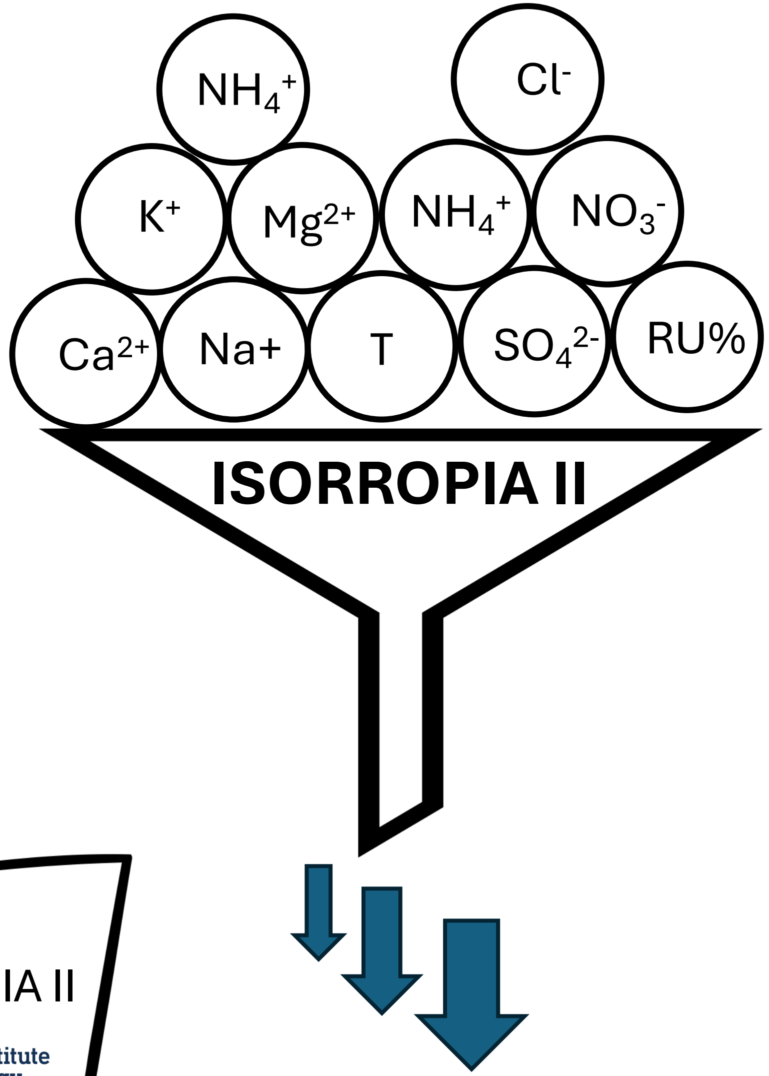
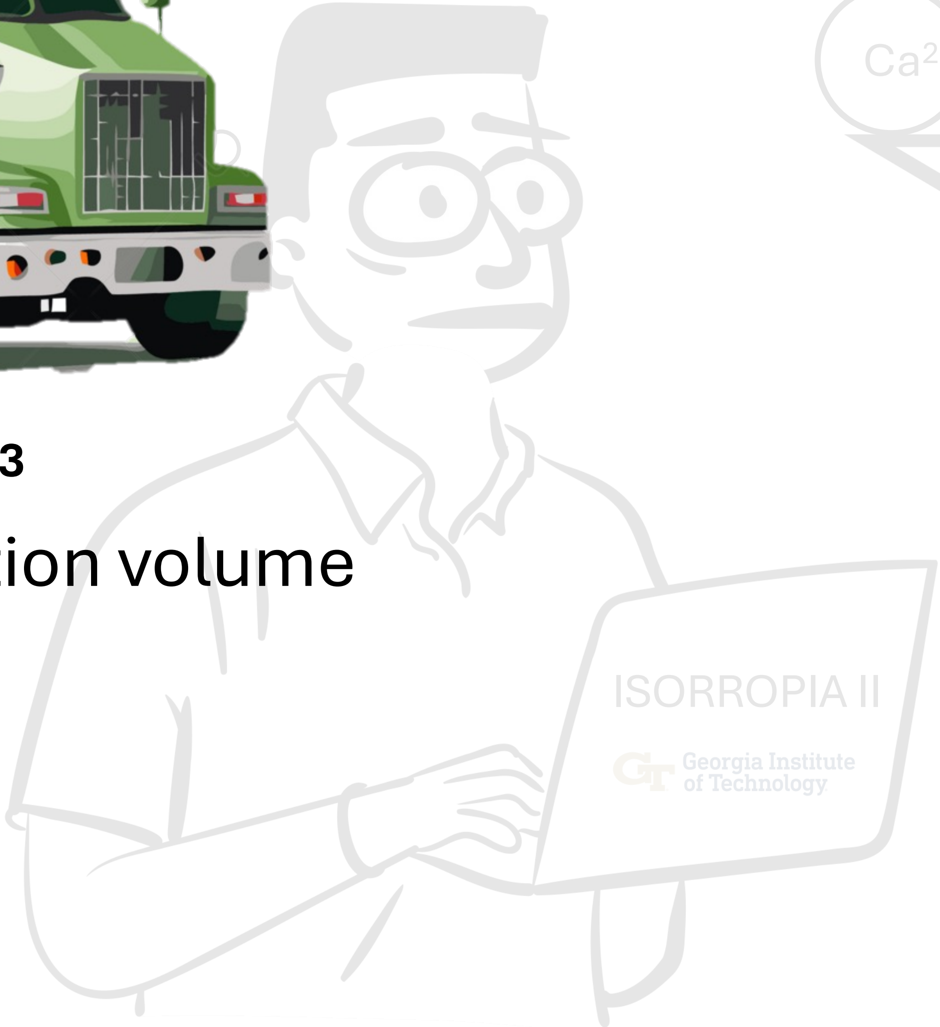




0.3 µg·m^{-3}

Fountoukis, C., Nenes, A., 2007. ISORROPIAII: A computationally efficient thermodynamic equilibrium model for K+-Ca2+-Mg2+-NH4+-Na+-SO42--NO3--Cl--H2O aerosols. Atmos. Chem. Phys. 7, 4639–4659. https://doi.org/10.5194/acp-7-4639-2007

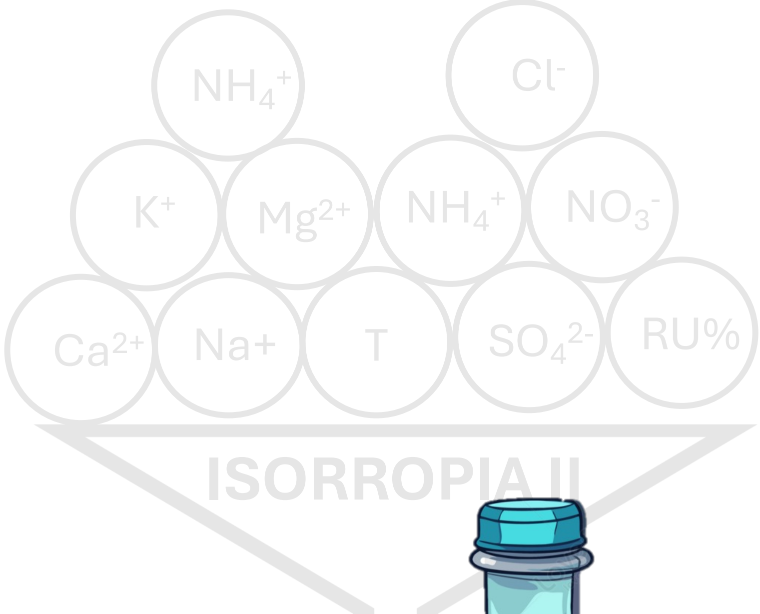


Are the 15 mL of water used for the solubilization a «realistic» volume? !

25000 dm^3

Experimental extraction volume

Considering 1050 m^3 of air collected for each samples, they correspond about **14 mg·m^3** of Aerosol Liquid Water Content (ALWC)



0.5 dm^3

0.3 µg·m^{-3}

Simulated ALWC

used for the solubilization

25000 dm^3

a «realistic» volume?

correspond about 14

of Aerosol Wa

(AWLC)

0.5 dm

ted AWLC

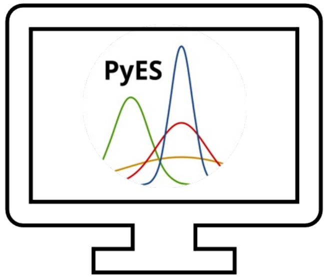
Diluition correction

Components concentrations

x10^4

pH < 4

Average I = 1.9 mol·L^{-1}



Na^+, K^+ and Mg^{2+}

increment of the interaction with Cl^- and SO_4^{2-}

Ca^{2+}

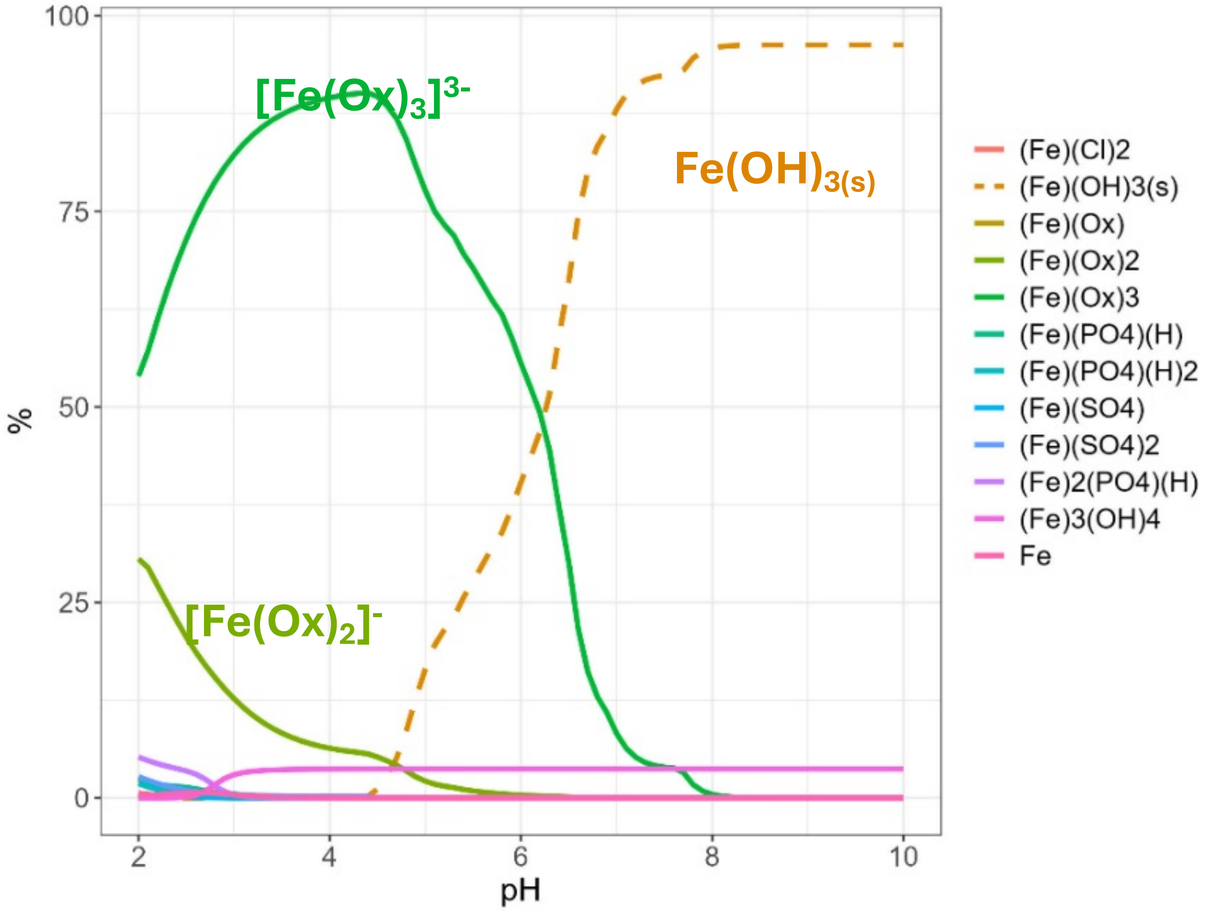
occurs as the solid $CaSO_4$ over the entire pH range;

Al^{3+}, Cu^{2+}, and Fe^{3+}

increment in the interaction with the oxalate;

Fe-oxalate

complexes compete with $Fe(OH)_3$(s) at pH 5-6

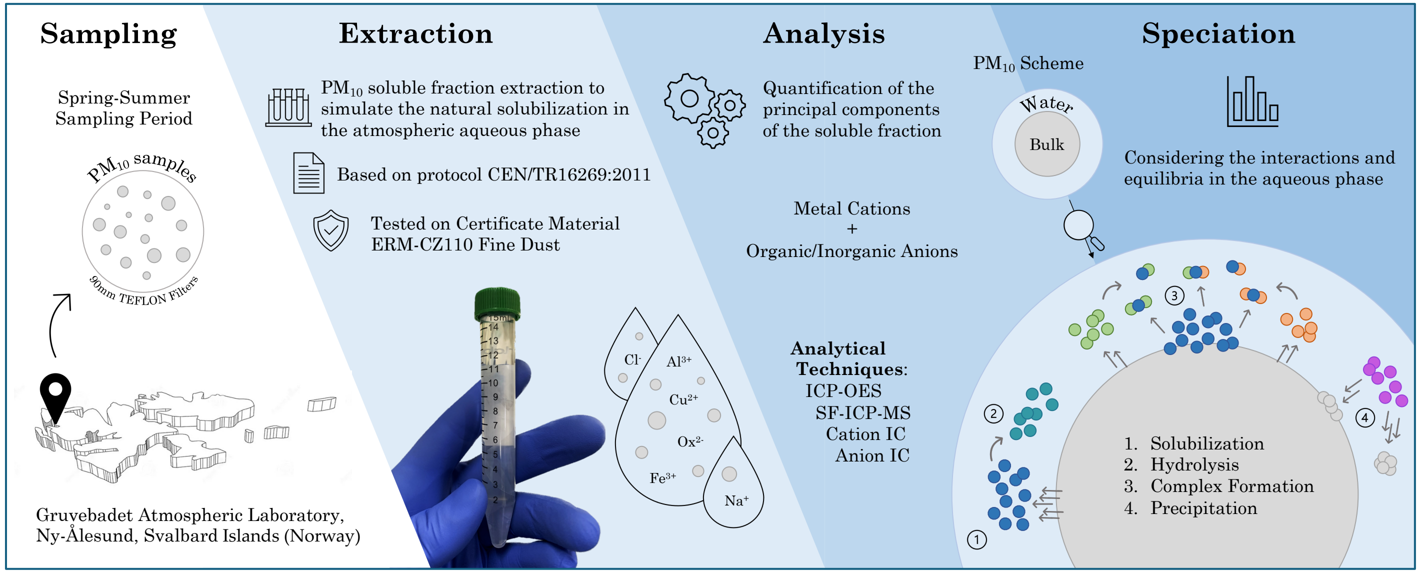


The concentration of the investigated metals reflects their **origin**: those associated with the marine source (Na, K, Mg, and Ca) reach higher concentrations. The other components, associated with crustal and anthropogenic sources, often have lower concentrations but show seasonal variability

The higher metals' concentration in the spring samples promotes the formation of species with sulfate and oxalate and the precipitation of hydrolytic species, while soluble hydrolytic species are enhanced in summer

The speciation models suggest an important role of **oxalate** as ligand for stabilizing Al^{3+}, Fe^{3+}, and Cu^{2+} in solution, especially in high concentrate solutions

preliminary results that are useful to define the main species that could be formed in solution



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RESEARCH PAPER

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Chemical characterization and speciation of the soluble fraction of Arctic PM_{10}

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Abstract
The chemical composition of the soluble fraction of atmospheric particulate matter (PM) and how these components can combine with each other to form different species affect the chemistry of the aqueous phase dispersed in the atmosphere: raindrops, clouds, fog, and ice particles. The study was focused on the analysis of the soluble fraction of Arctic PM_{10} samples collected at Ny-Ålesund (Svalbard Islands, Norwegian Arctic) during the year 2012. The concentration values of Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, formate, acetate, malonate, and

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Thank you !!!

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