METROLOGY AT NANOSCALE

Characterisation of size distribution and chemical composition of nanoparticles in the emissions and ambient air around waste incineration plants

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Introduction

Introduction : context

Atmospheric emissions of nanoparticles from incineration plants

Context:

- Nanoparticles
  - a nanoparticle is a particle which has a range in size between 1 to 100 nanometers (3 dimensions)
  - bigger particles can also be composed of nanostructures
  - they can be intentional of non-intentional (by products)
- Intentional nanoparticles
  - more and more widely used due to their properties and performances which can be applied in many industrial sectors.
  - can be associated to risks to human health and the environment that need to be assessed and controlled.
  - growingly used everyday products, may end up in wastes and be encountered in waste treatment sectors such as waste incineration
- Municipal solid and hazardous waste incineration plants :
  - likely to emit nanoparticle substances in the atmosphere, by direct transfer of intentional nanoparticle substances from waste to emission or by formation of nanoparticle substances due to thermal transformation of material during combustion (Nanofluegas, 2014).
  - Regulation : ELV Total suspended particles (TSP) 10 mg/m^3_0
  - Descrease in mass emission does not mean decrease of the contribution of the smallest particles to the emissions

Introduction : objectives

Atmospheric emissions of nanoparticles from incinerators

Objectives:

- Identification at the source of the chemical species, the morphology and quantification of the flux of species emitted in the atmosphere as nanoparticles (intentional or non-intentional)

- Search for the species idenitified (tracer) in the environment in the ambiant air close to the sources

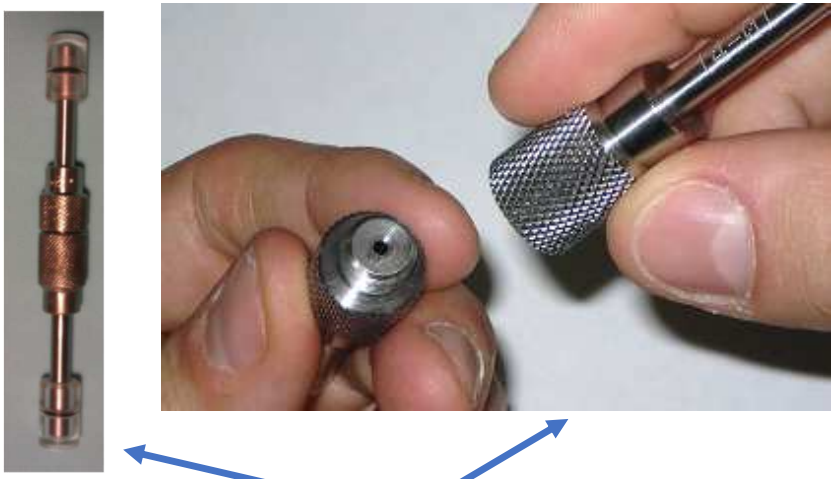
Material and methods

Material and methods

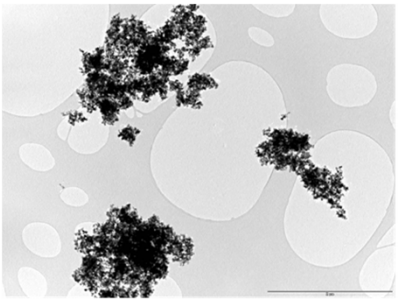
Mini particle sampler (MPS) combined to transmission electron microscopy (TEM)

First attempt of use of the Mini particle sampler (MPS) combined to transmission electron microscopy (TEM) as a common detection method in the emissions of and in the ambient around an industrial site

- Qualitative approach to identify (elemental composition) and characterize (size, morphology) nanostructure from unknown samples
  - 0,5 nm to 10 µm size range, size resolution 0,5 nm
  - Energy dispersive X-ray analysis (EDX) analysis of target particles in the grid to evaluate the relative contribution of elements
  - Designed for ambient air and indoor applications but adapted for the first time here to characterize atmospheric emissions (proof of concept)

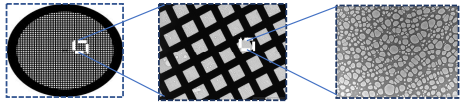


MPS sampler equipped with TEM grids,

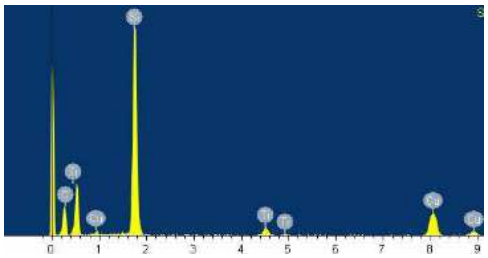


Exemple of TEM observation

TEM grids



Exemple of EDX analysis

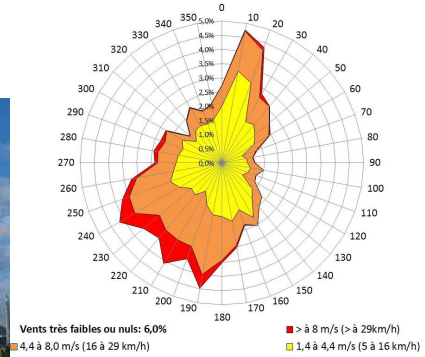


Material and methods

Ambiant air measurements in the vicinity of industrial sites

Impact distances and position of sampling points in the ambient air around sites determined using :

- the ADMS 5.2 Gaussian model of emissions dispersion
- combined to a weather monitoring station



2 types of sampling points characterized according to their position against site and prevailing winds:

- sampling points positioned upwind the site: non exposed to emissions
- sampling points positioned downwind the site : exposed to emissions

Limits of the approach

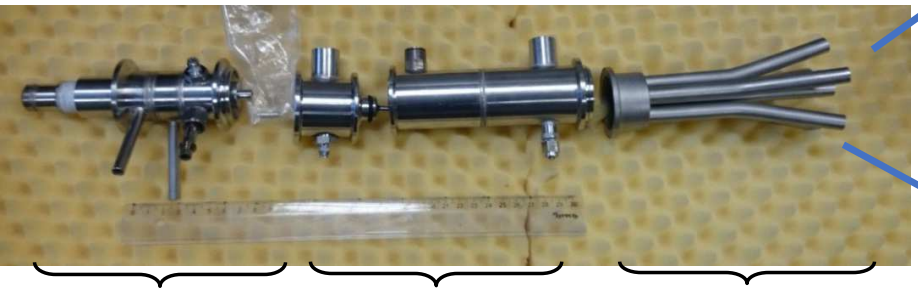
- Qualitative information on size, morphology and semi-quantitative information on elemental composition
- Exploratory : Short term mobile samples taken (from a few minutes to an hour),
  - different from recommendations made in terms of strategy to be used for the monitoring of regulated pollutants in the ambient air in the vicinity of classified facilities for the protection of the environment (ICPE)
  - lack of temporal and spatial representativeness

Material and methods

Atmospheric emissions measurement methods

Measurement techniques :

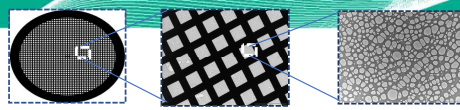
FPS Dekati 2-steps dilutor : conditioning of the flue gas and aerosol/ Dilution ratio controlled using CO_2 as tracer gas



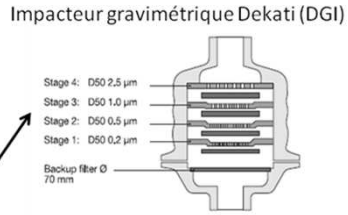
1st stage of dilution: perforated tube

2nd stage of dilution nozzle and ejector

Flow repartition device



MPS sampler equipped with TEM grids, used in a configuration adapted to emissions measurements (first attempt/proof of concept) ions

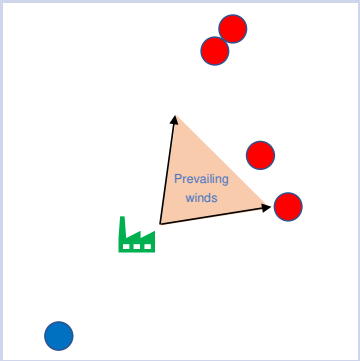
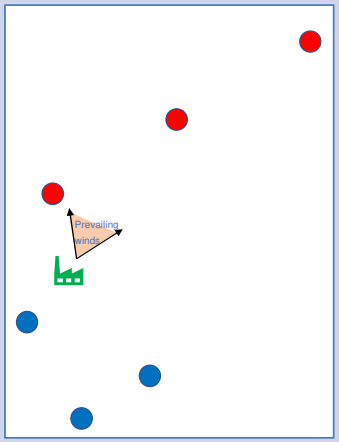
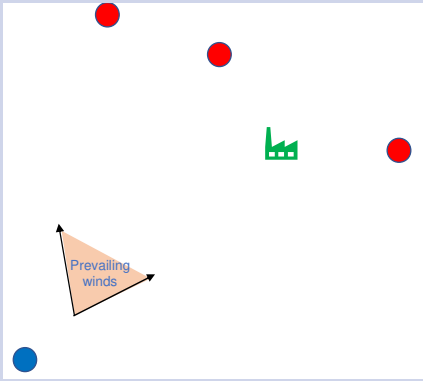


DGI Dekati Impactor : mass (weighing scale resolution 1 µg) and chemical analysis (analysis of metals using ICP/OES : NF-EN-11885 standard) in the range 200 nm - 2.5 µm

Dekati Electric Low Pression Impactor (ELPI) online measurement of the concentration in number and size distribution between 7 nm and 2.5 µm

Material and methods

Sampling sites

Site	A	B	C
Incinerator type	municipal solid waste incineration plant	hazardous waste incineration plant	municipal solid waste incineration plant
Process/ Fume treatment devices	-2 chimneys, -dry flue gas treatment process, ESP combined to PTFE filter	-2 incineration lines, -line 1 : dry flue gas treatment process, -line 2: wet flue gas treatment (scrubber)	-2 chimneys -wet flue gas treatment: ESP+ scrubber
Localisation of ambient air sampling points (impact distances between 400 m and 1000 m) prevailing winds upwind sampling point downwind sampling point			
Measurement campaigns	Emissions and ambient air	Ambient air	Ambient air

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Results

Results : atmospheric emission measurements

Quality insurance

LOQ

Manual impaction Limit of Quantification (LOQ)					
Mass (mg/filter)	Cr (µg/filter)	Fe (µg/filter)	Ni (µg/filter)	Cu (µg/filter)	Zn (µg/filter)
1	0,13	0,5	0,13	0,13	0,13

Site blanks

Parameter	Site blanks (mg/filter)
PM0.2	< LOD= LOQ/3
0.2 µm<D<0.5 µm	< LOD= LOQ/3
0.5 µm<D<1 µm	< LOD= LOQ/3
1 µm <D<2.5 µm	< LOD= LOQ/3

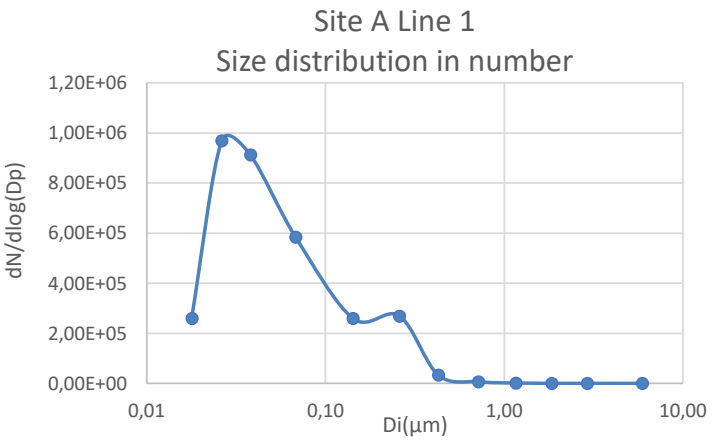
		PM2.5	PM1	PM0.5	PM0.2	Average Ratio Sample/Blank
Cu	L1 Concentration (µg/m$^3_0$)	1,32	1,18	1	0,66	
	L2 Concentration (µg/m$^3_0$)	0,78	0,73	0,5	0,27	
	Blank (µg/m$^3_0$)	0,27	0,22	0,16	0,11	4,3
Cr	L1 Concentration (µg/m$^3_0$)	21,27	19,03	13,83	4,27	
	L2 Concentration (µg/m$^3_0$)	16,87	6,74	1,86	1,24	
	Blanc (µg/m$^3_0$)	3,38	2,55	1,73	0,9	4,6
Ni	L1 Concentration (µg/m$^3_0$)	18,58	15,45	10,02	2,09	
	L2 Concentration (µg/m$^3_0$)	11,86	11,5	8,51	2,36	
	Blanc (µg/m$^3_0$)	0,23	0,18	0,14	0,09	58,0
Fe	L1 Concentration (µg/m$^3_0$)	94,61	82,79	59,79	27,81	
	L2 Concentration (µg/m$^3_0$)	89,2	84,61	60,97	20,09	
	Blanc (µg/m$^3_0$)	9,23	8,21	7,18	6,16	8,1
Zn	L1 Concentration (µg/m$^3_0$)	13,38	11,39	9,11	6,63	
	L2 Concentration (µg/m$^3_0$)	7,4	6,31	4,04	2,93	
	Blanc (µg/m$^3_0$)	0,73	0,69	0,64	0,59	11,4

Results atmospheric emission measurements

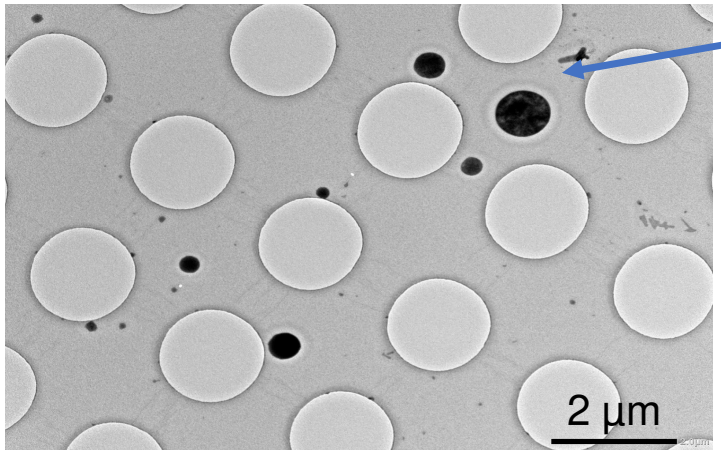
Site A: Results in number/size, morphology and elemental composition

Number/size distribution (ELPI measurement) :

- Total number comprised between 2,85 E5 and 7,35 E5 #/cm^3 $O_{2\ ref}$ (in agreement with data from the litterature (Kumar et al, 2013))
- 2 modes observed:
  - the main one <100 nm
  - a second one around 300 nm

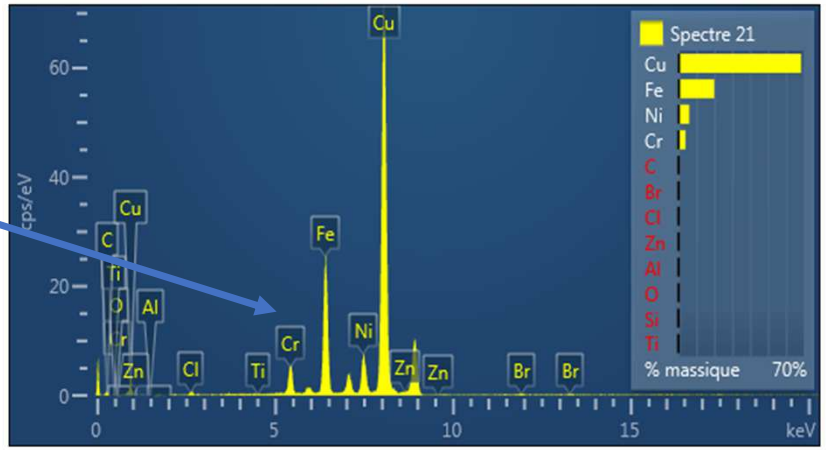


Morphology and elemental composition



mainly spherical metallic particles in the range of size between 50 and 500 nm

Elemental composition dominated by iron, nickel and chromium. Contribution of copper artefact currently observed because the grids are made of copper



Results atmospheric emission measurements

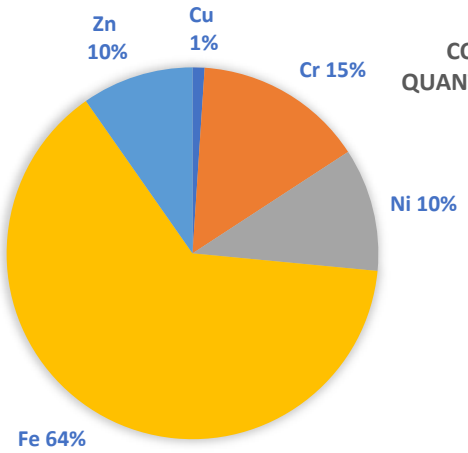
Site A: Results in concentration : mass and chemical species

DGI PM2.5 : 0,3 mg/m$^3_0$

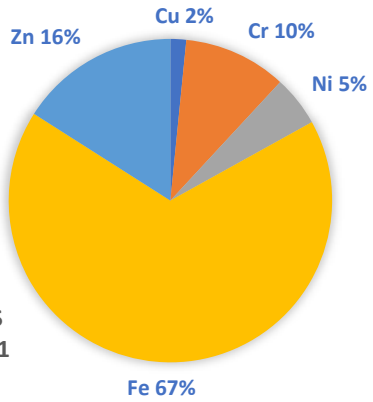
- coherent with ELV TSP <10 mg/m$^3_0$, in agreement with periodic control TSP 0,1 mg/m$^3_0$
- mainly PM0.2

Quantification of species identified by TEM/EDX (Cr, Cu, Ni, Fe et Zn) by analysis of DGI filters using

- PM2.5: sum of Cr, Cu, Ni, Fe et Zn represents about 65% of the aerosol collected
- Fe main specie found, between 63 and 83% of the metals quantified
- Good agreement with EDX analyisis
- Zn and to a lesser degree Fe preferentially present in size below 200 nm

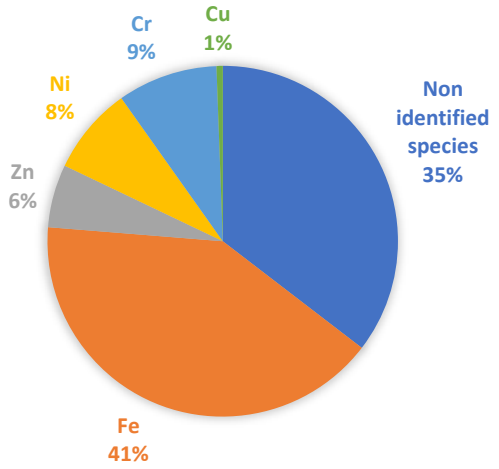


PM0.5
CONTRIBUTION OF METALS
QUANTIFIED TO SUM OF METALS L1



PM0.2 CONTRIBUTION OF METALS
QUANTIFIED TO SUM OF METALS L1

CONTRIBUTION OF METALS TO PM2.5 PARTICLES
COLLECTED USING THE DGI IMPACTOR L1

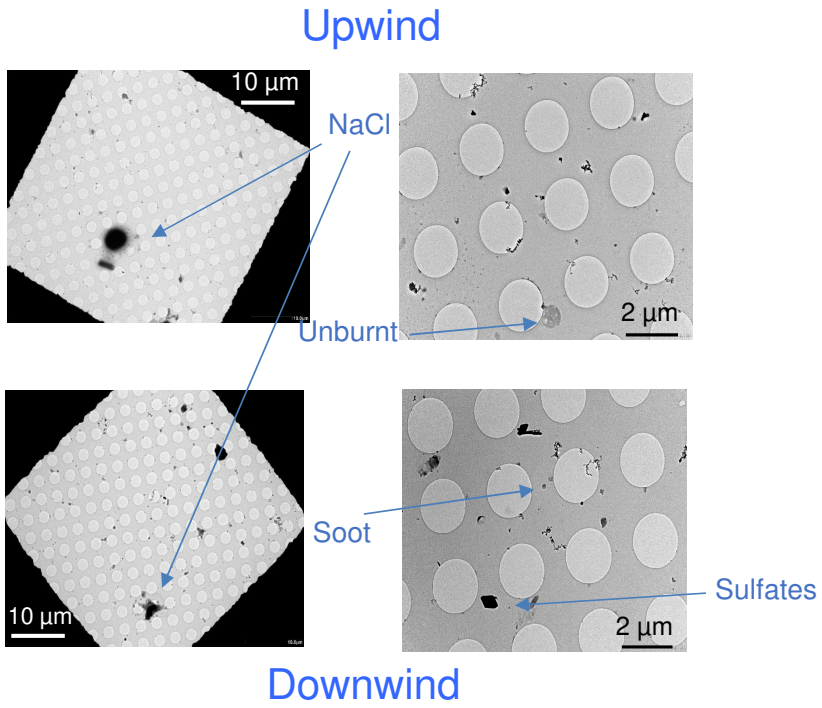


Results: ambiant air measurements

Observation of samples (MPS/TEM)

Site A:

- None of the samples taken in the ambient air exhibited the presence of metallic spherical nanoparticles.
- No difference was observed between upwind and downwind sampling points
- Species observed : soot, NaCl, ubiquitous in ambient air samples



Sites B and C: same observations made

Conclusions and perspectives

Conclusions and perspectives

First attempt of use of the Mini particle sampler (MPS) combined to transmission electron microscopy (TEM) as a common detection method in the emissions of and in the ambient around an industrial site

Adaptation of MPS to characterization of emissions using dilution, proof of concept conclusive:

Results :

- Extremely low levels of nanoparticles substances emitted by the municipal solid waste incineration plant prior to dispersion
- Aerosol found in the ambient air did not show a profile specific of the site studied and no difference was observed between upwind and downwind sampling points around the sites.

Perspectives:

- Combined use of these two approaches interesting but ambient air measurement method, qualitative and exploratory approach that would require evolution to compensate lack of spatial and temporal representativeness: increase of sampling duration ?
- Preliminary results, more trials necessary to confirm observation and study other type of sources : focus on the characterization of the emissions of a hazardous waste incineration plant?

Thank you for your attention

Acknowledgements

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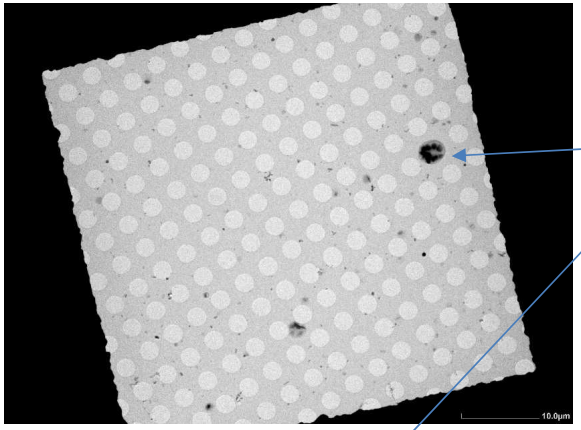
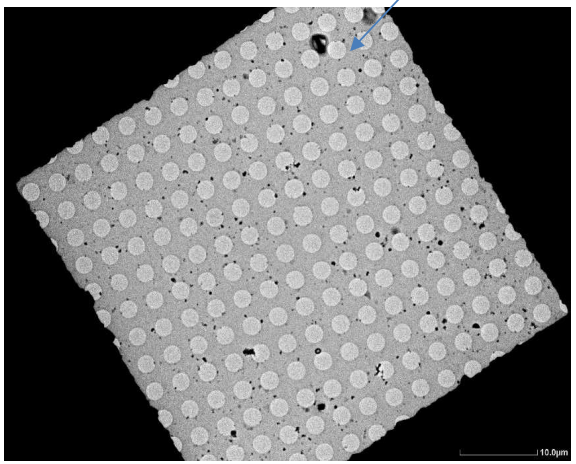
Results ambiant air measurements

SITE B observation of results (MPS/TEM)

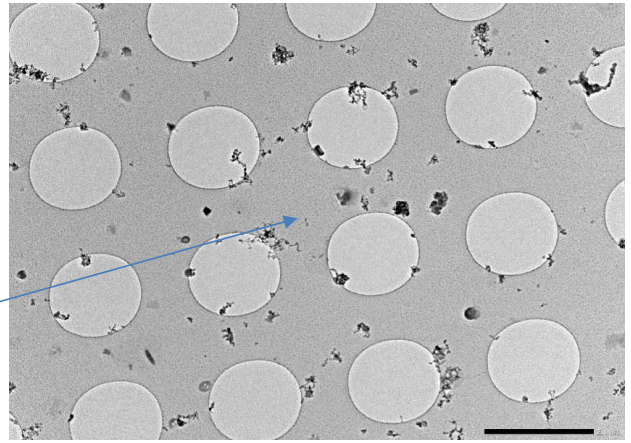




NaCl

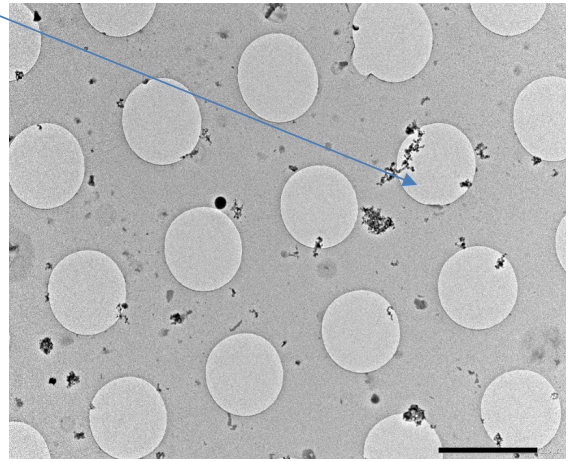
Soot

Upwind



2 µm

Downwind

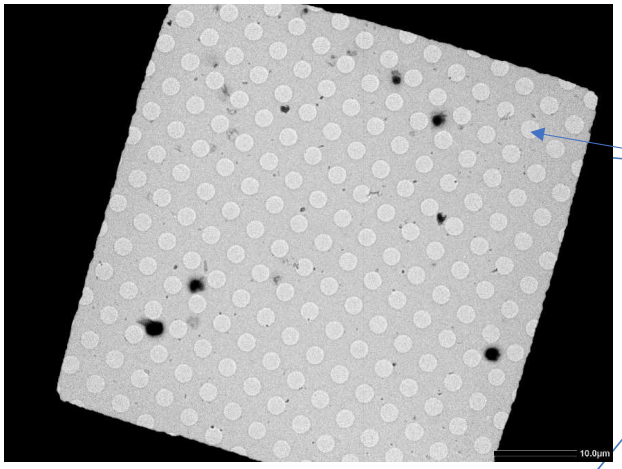


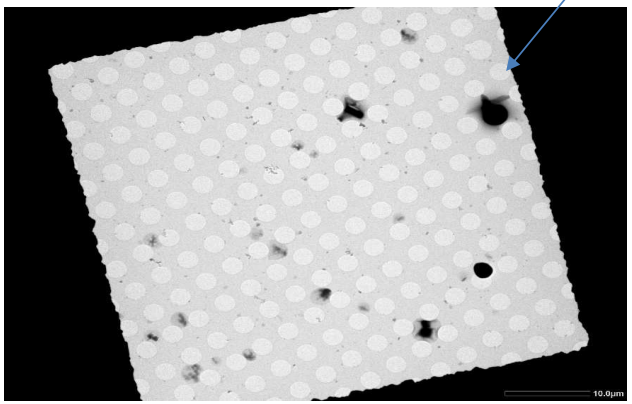
2 µm

No difference observed between samples collected upwind and downwind of the industrial site B

Results ambiant air measurements

SITE C observation of results (MPS/TEM)





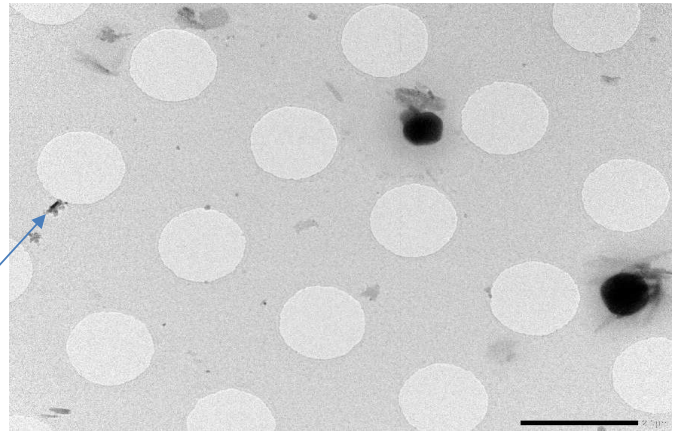
Upwind

NaCl

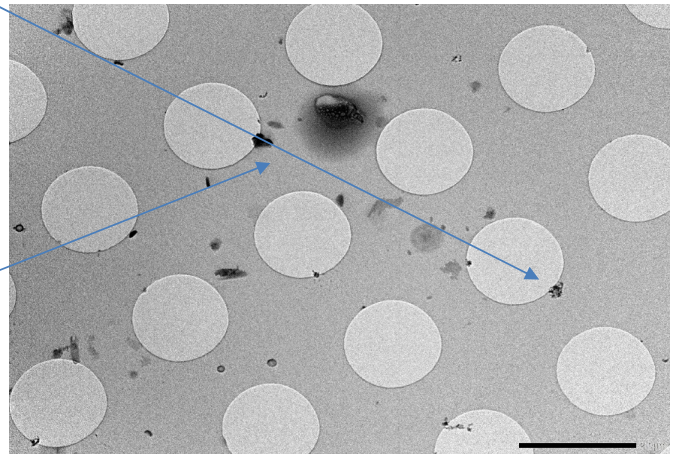
Soot

Downwind

NaCl



2 µm



2 µm

No difference observed between samples collected upwind and downwind of the industrial site C

Results: discussion

Emissions measurements

- Adaptation of MPS to characterization of emissions using dilution, proof of concept conclusive:
  - Set-up and matrix conditions delivered to the MPS are adapted
  - Good agreement between results from MPS observation/ EDX determination and traditional approaches in terms of size distribution and chemical analysis
- Aerosol characteristics
  - distribution in numbers centered below 100 nm and 300 nm
  - mainly spherical metallic particles in the range of size between 50 and 500 nanometers
  - Extremely low levels of concentrations prior to dispersion

Ambient air measurements

- Aerosol found in the ambient air did not show a profile specific of the site studied and no difference was observed between upwind and downwind sampling points around the sites.

Suitability of the two approaches?

- Synergy: A Good knowledge of the source can explain trends observed in the environment: extremely low emissions, absence of signature in the environment
- but an increase of sampling duration in the ambient air is necessary improve time representativeness.