

Detection of engineered nanoparticles (ENP) in the environment: Analytical challenges

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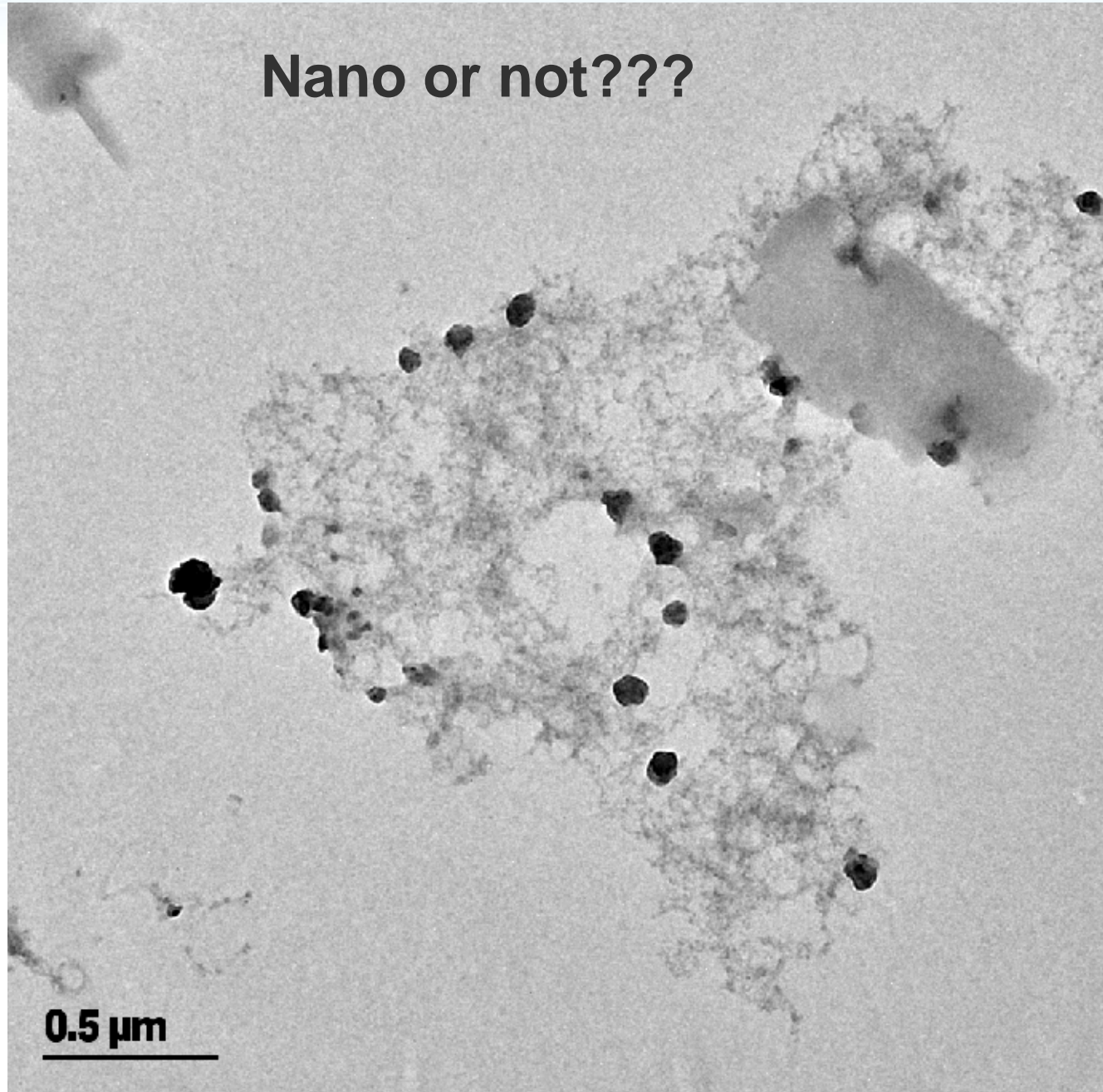
Swiss Light Source (SLS), Microscopy Centers of ETH (EMEZ) and Empa

Methods to characterize ENP

Method	Size (nm)				PSD capability	Shape ^A capability	Agglomeration state capability ^B	Concentr. range	Surface Chemistry / Charge / Area	Structure / Crystallinity	Single part./ population	Dynamics capability ^C	Level of perturbation
	1	10	100	1000									
AFM	●	●	●	●				ppb – ppm			sp		medium
BET	●	●	●	●				powder			pp		high
Centrifugation	●	●	●	●				det. dep.			pp		low
Dialysis	●	●	●	●				det. dep.			pp		low
DLS	●	●	●	●				ppm			pp		minimum
Electrophor.	●	●	●	●				ppm			pp		minimum
EELS/EDX	●	●	●	●				ppm in sp			sp		high
ESEM	●	●	●	●				ppb – ppm			sp		medium
Filtration	●	●	●	●				det dep			pp		low-medium
Flow FFF	●	●	●	●				UV: ppm,			pp		low
Sed FFF	●	●	●	●				ICPMS: ppb			pp		low
HDC	●	●	●	●				det. dep.			pp		low
ICP-MS	●	●	●	●				ppt – ppb			pp		N/A
LIBD	●	●	●	●				ppt			sp		minimum
NTA	●	●	●	●				ppb-ppm			sp		minimum
SEC	●	●	●	●				det dep			pp		medium
SEM	●	●	●	●				ppb – ppm			sp		high
SLS	●	●	●	●				ppm			pp		minimum
SAED	●	●	●	●							sp		high
Spectrometry	●	●	●	●				ppb – ppm			pp		minimum
TEM	●	●	●	●				ppb – ppm			sp		high
Turbidimetry	●	●	●	●				ppb – ppm			pp		minimum
Ultrafiltration	●	●	●	●				det. dep.			pp		medium
XPS	●	●	●	●				powder			pp		
XRD	●	●	●	●				powder			pp		high

Hasselöf and Kaegi 2008

Nano or not???

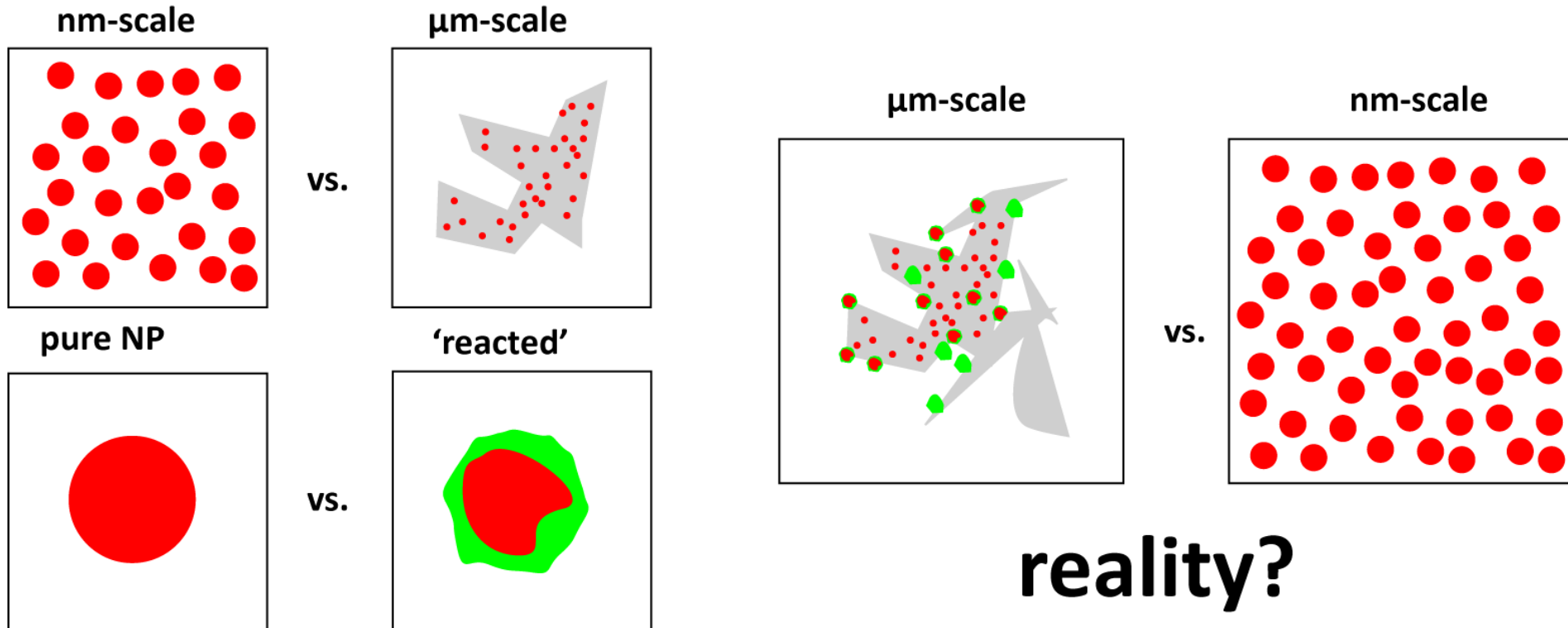


Laboratory vs. environment

release
(LCA, are the NP released as individual NP or as 'composite' particles?)

transport

exposure & hazard
that what forms of NP are we exposed and is there a hazard



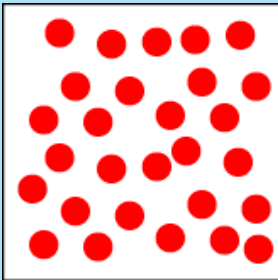
Lab scale experiments are based on 'the red dot system', **risk assessments** are based on lab experiments, and **decisions** are made based on risk assessments. Is this a reasonable approach for NP?

Analytical challenges

- **discriminate** between natural 'NP' (colloids) and ENP.
- **detect** ENP in complex colloids.

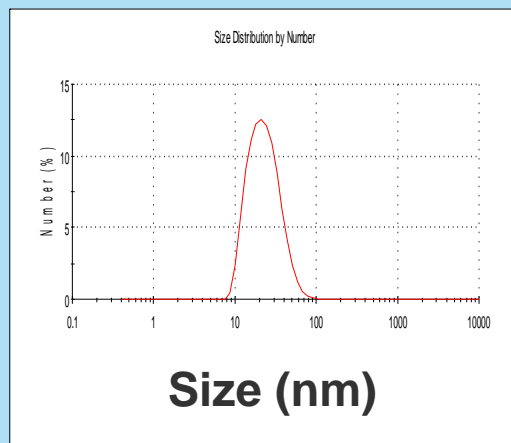
(Ag-NP)

Laboratory



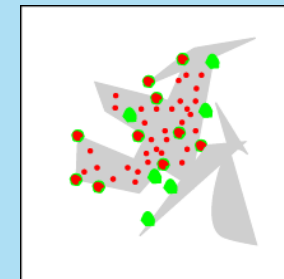
DLS (dynamic lightscattering)

ICPMS



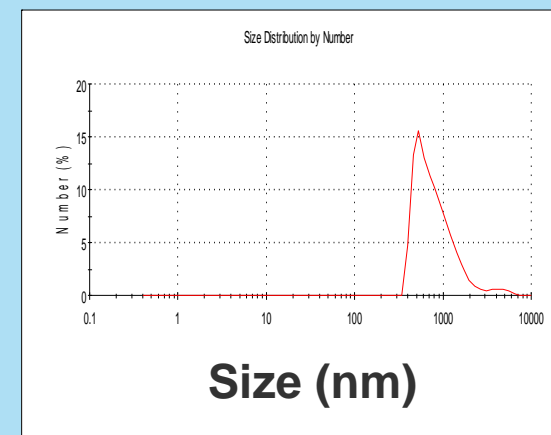
250 ppm Ag

Environment



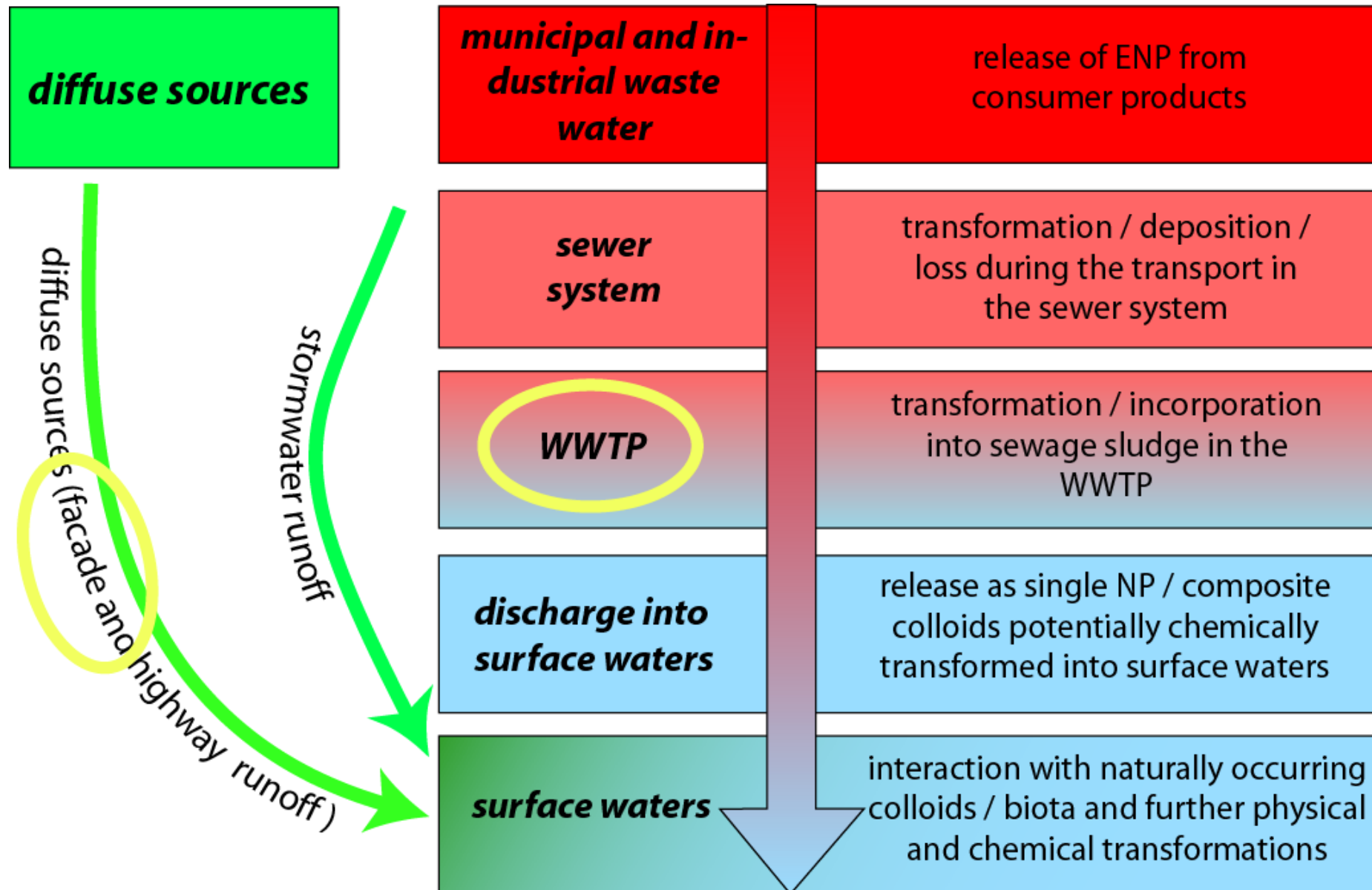
DLS

ICPMS



10 ppb Ag

ENP in the urban watercycle

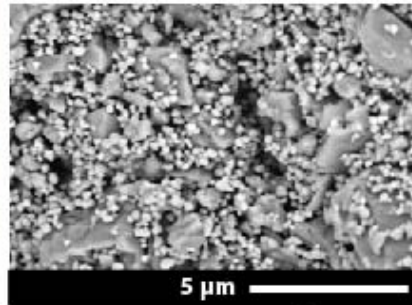


Runoff from facades I: TEM and ICP-MS

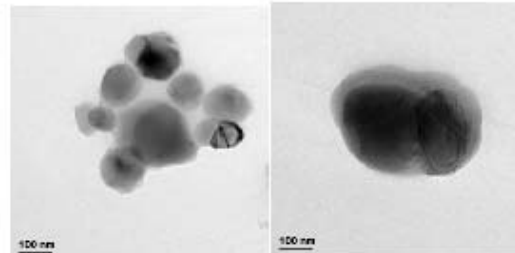
Kaegi et al., *Env. Poll.* 156, 233



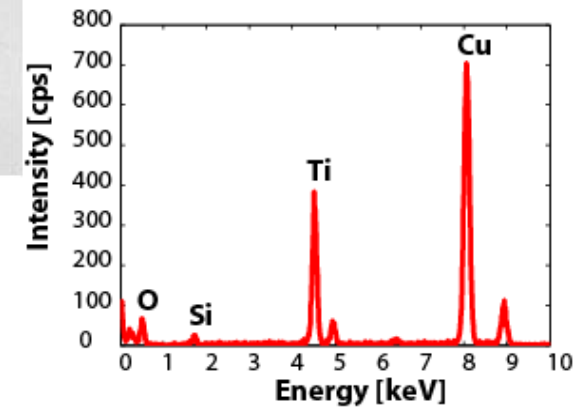
New facade (1.3 m²)



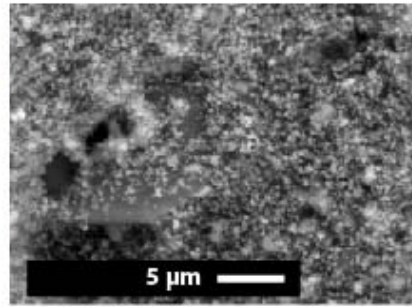
SEM(BSE) image of the new facade



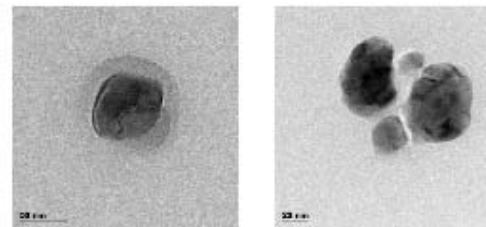
TEM-images of the facade runoff (new facade)



Building facade (painted with the same product as the new facade)



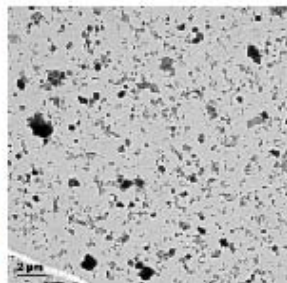
SEM(BSE) image of the new facade



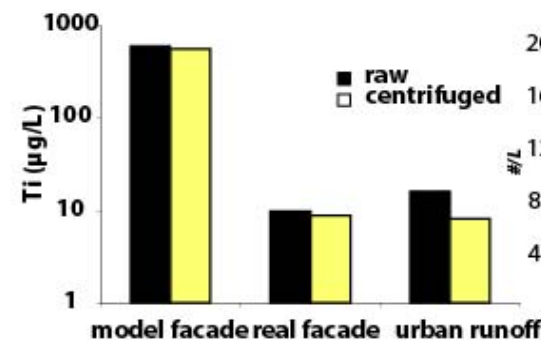
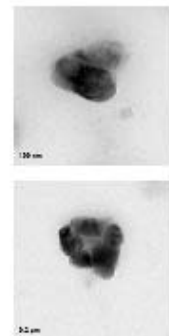
TEM-images of the facade runoff (aged facade)



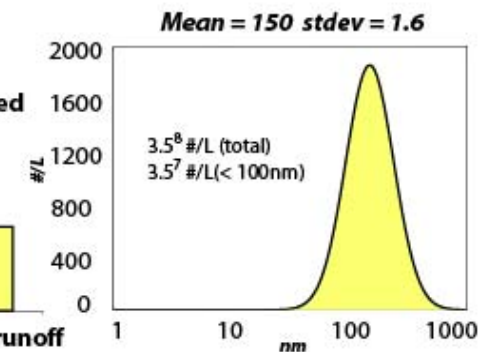
Discharge of the runoff into the urban creek



TEM-images of the runoff



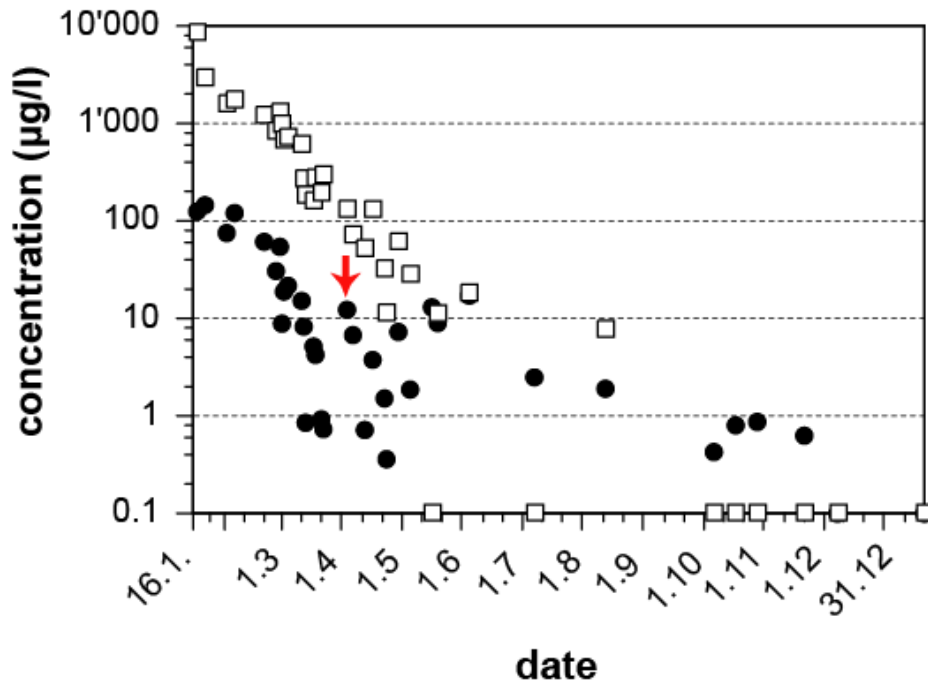
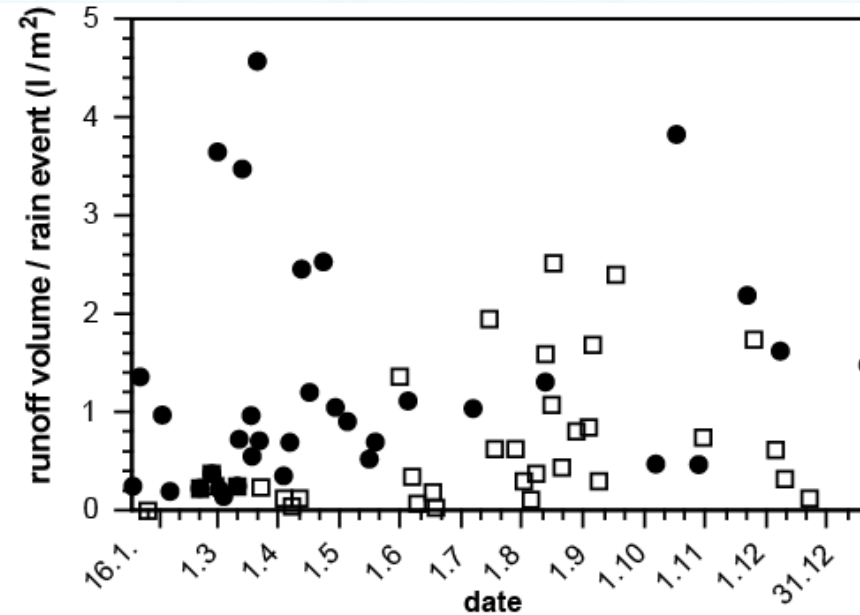
Ti concentrations in the raw and in the centrifuged samples (ICP-MS)



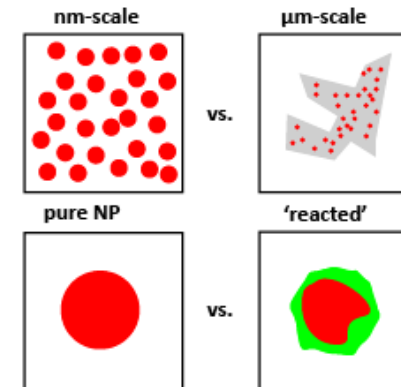
Modeled log-normal distribution of the TiO₂ particles in the runoff.

Runoff from facades II: (more) TEM and ICP-MS

Kaegi et al (2010), Env. Pol., 158,(9), 2900-2905



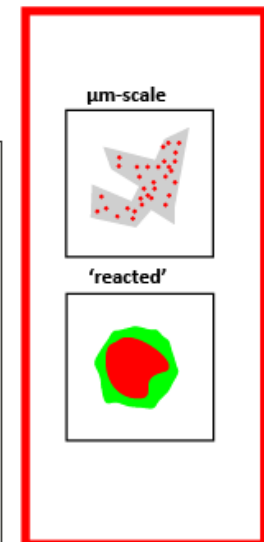
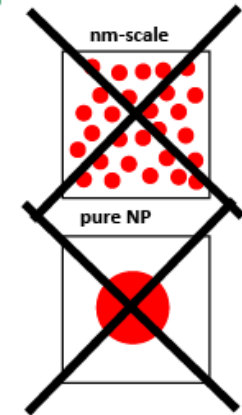
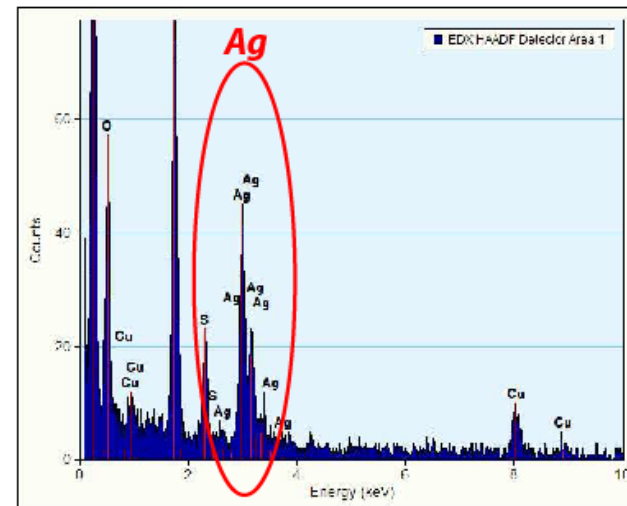
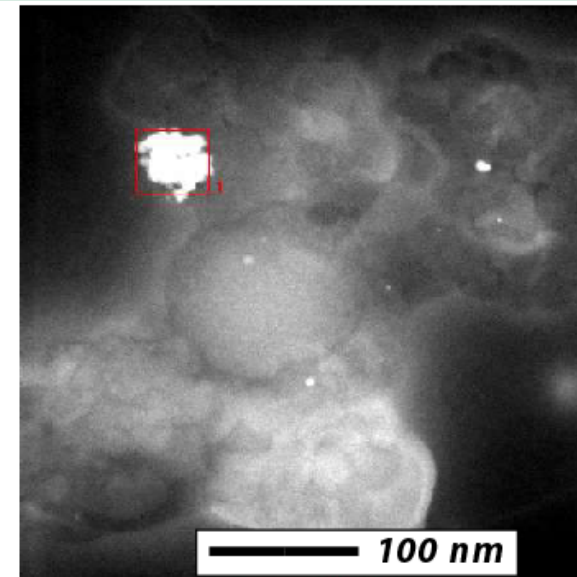
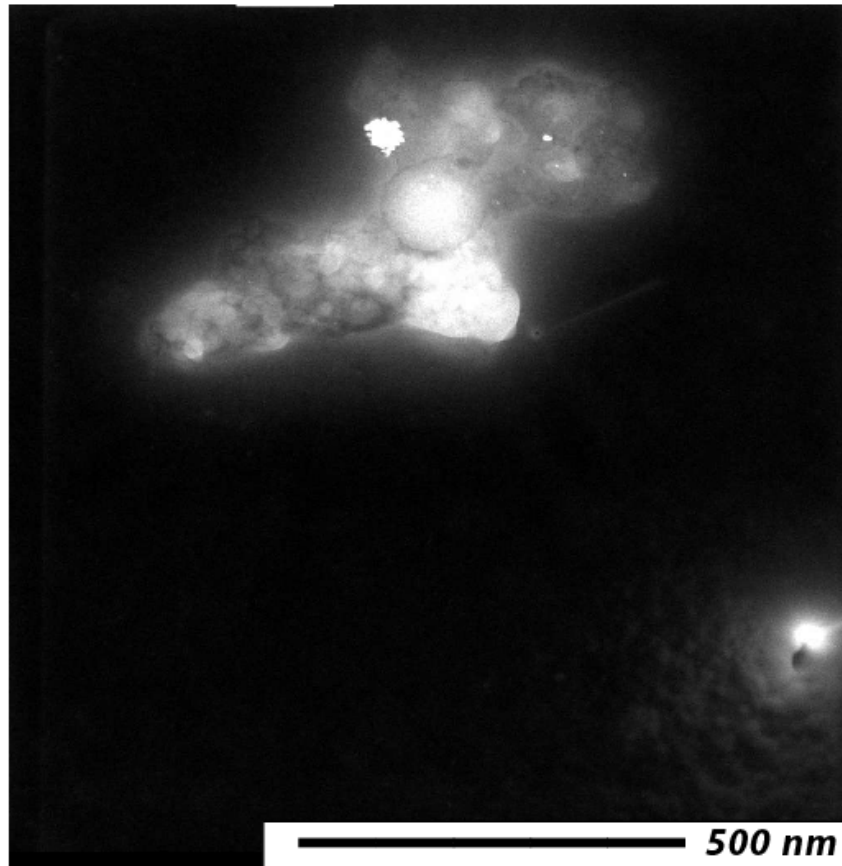
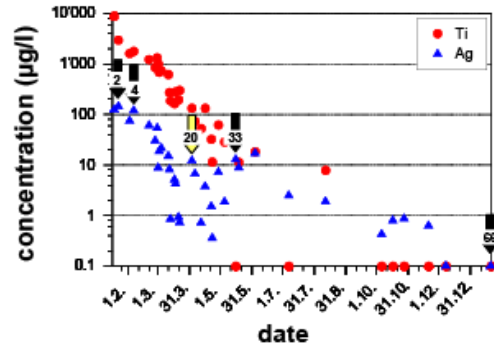
A strong leaching of the Ag-NP was observed during the initial runoff events with a maximum concentration of 145 µg/l Ag. After a period of one year, more than **30%** of the Ag-NP were released to the environment.



Ag-NP in composite colloids

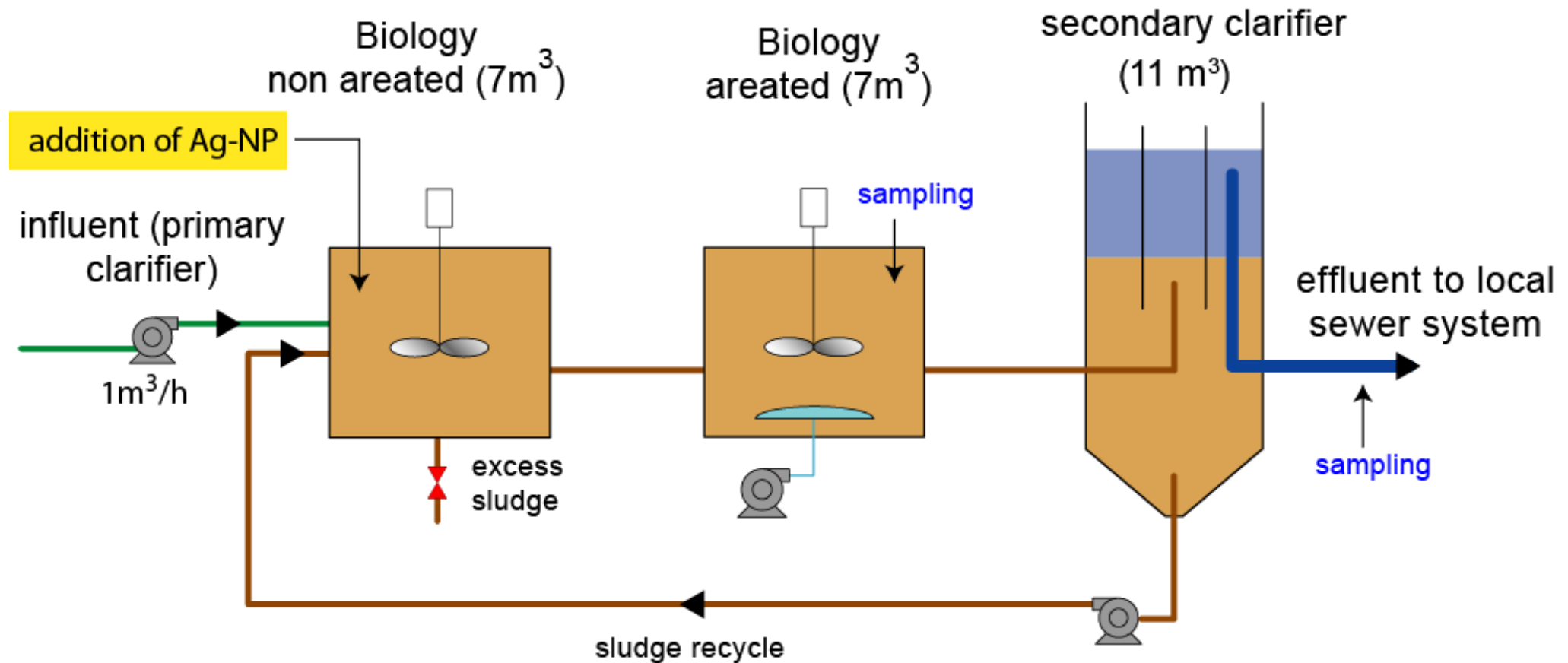
Ag-NP released from facades: Runoff event 20

Ag concentration: 12 µg/L; runoff: 0.35 L/m²

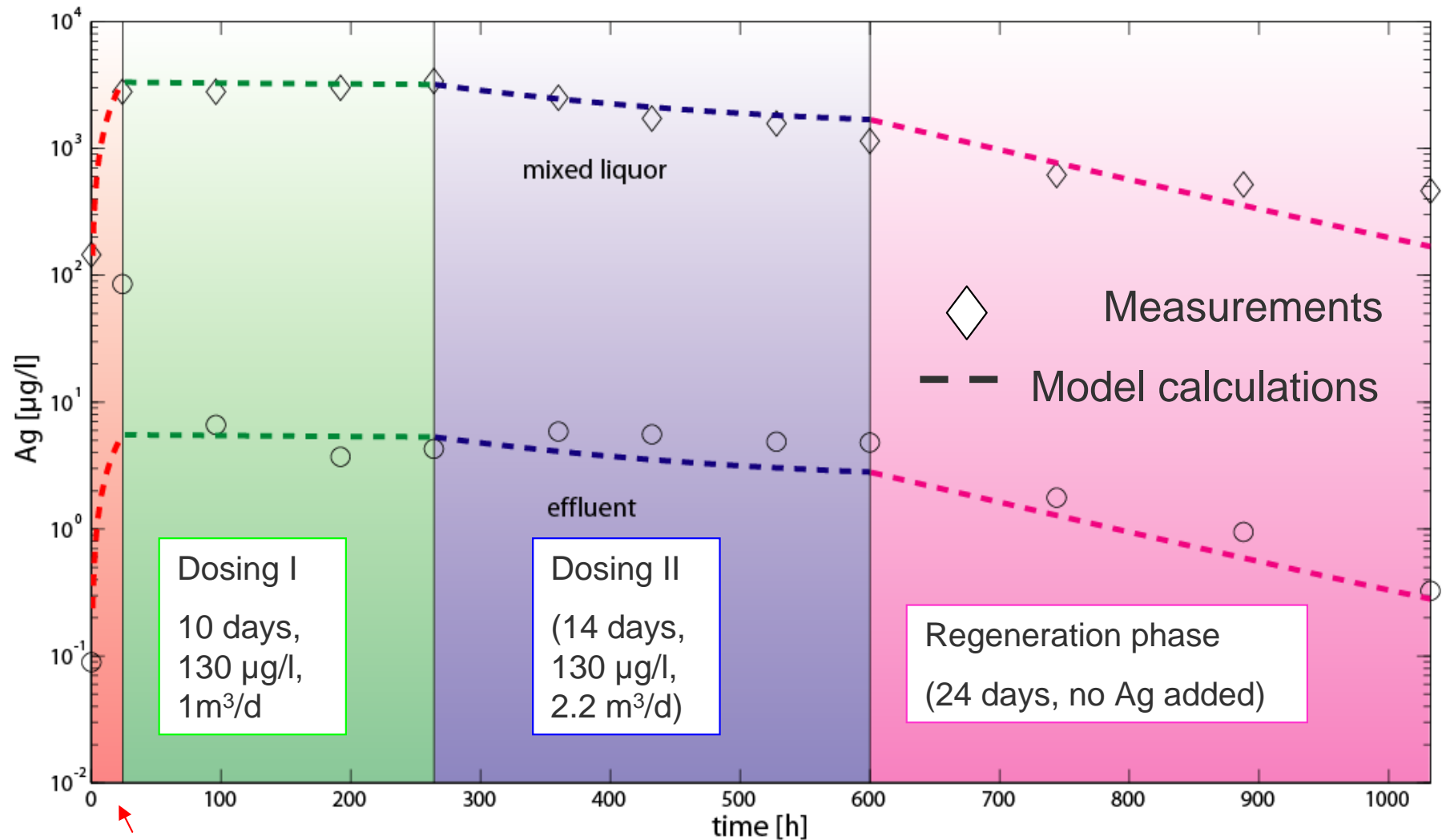


Wastewater treatment: TEM, ICP-MS and XAS, and some common sense

Experimental setup I

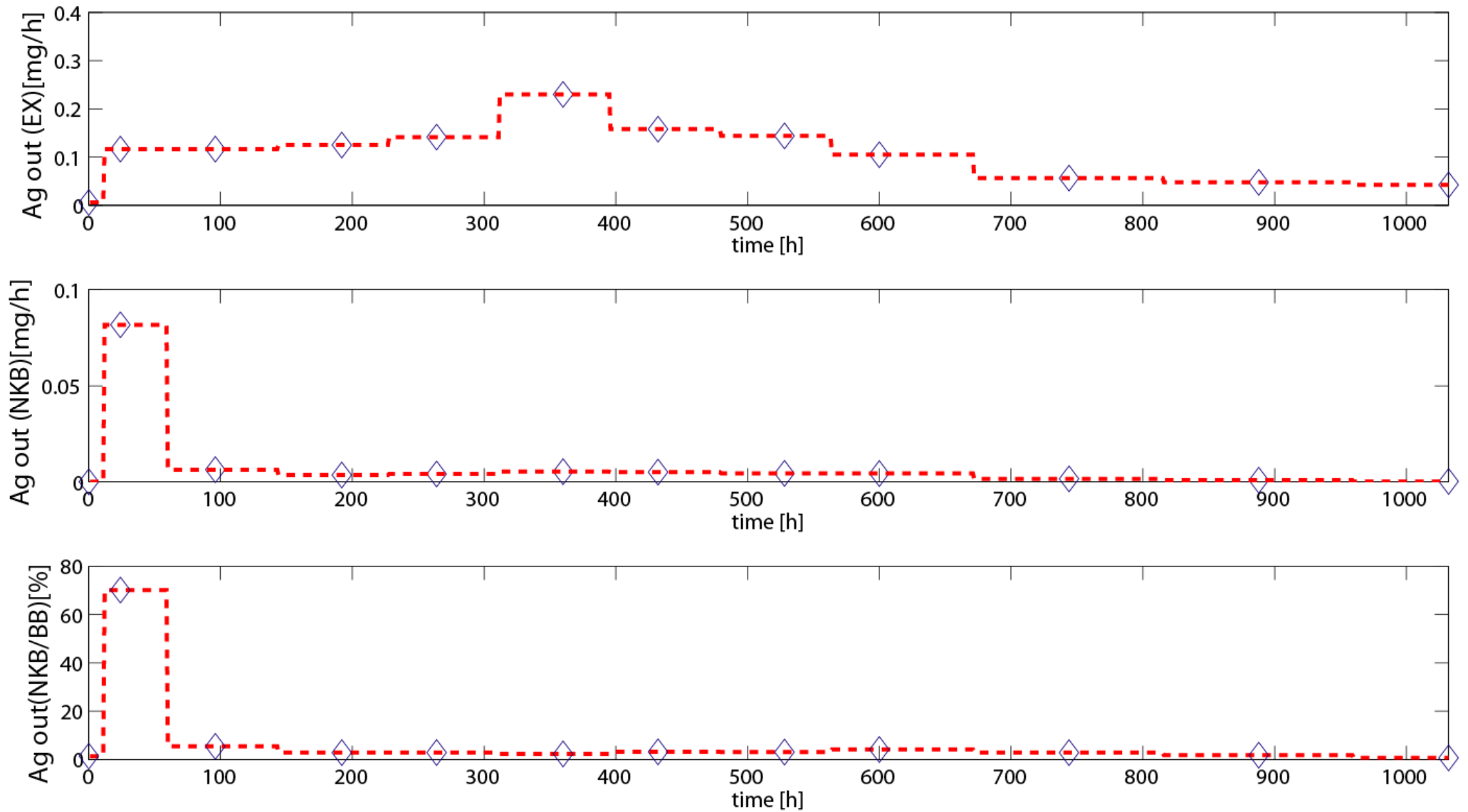


Experimental setup II and model calculations



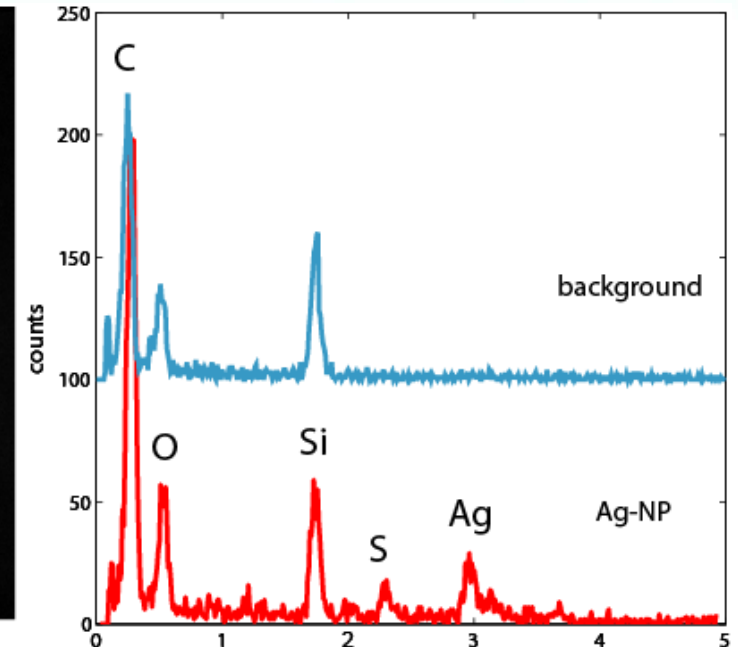
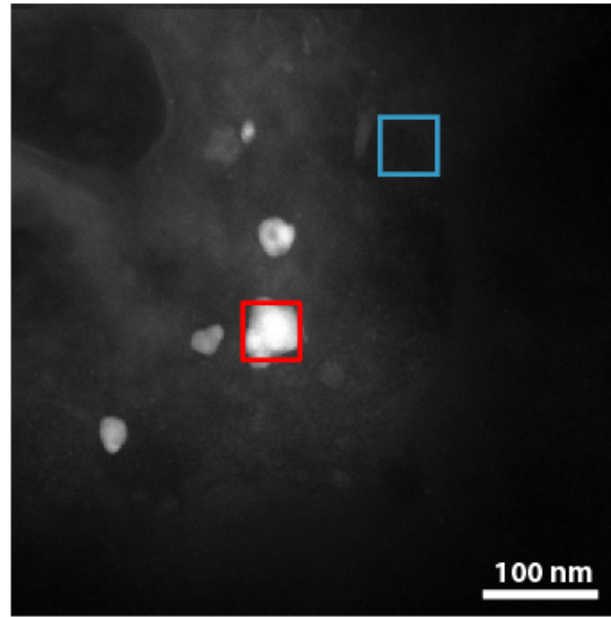
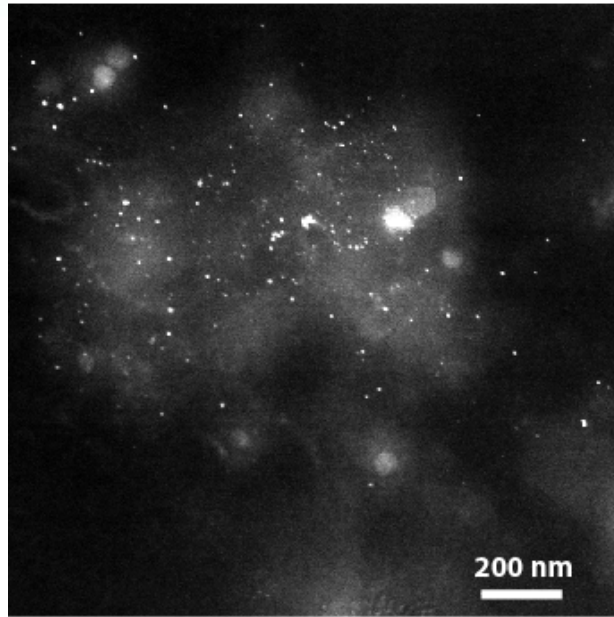
Initial spike (1 day, 2400 µg/l)

Mass flux of Ag

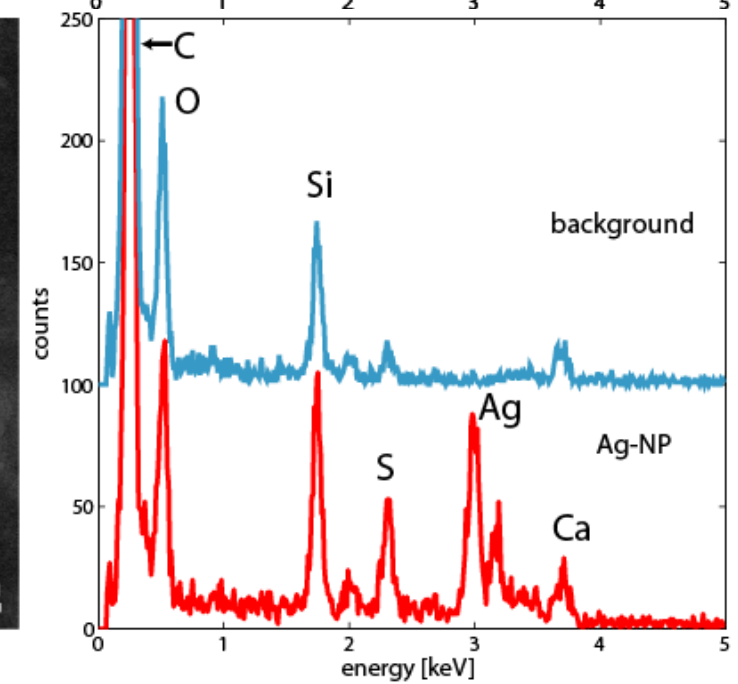
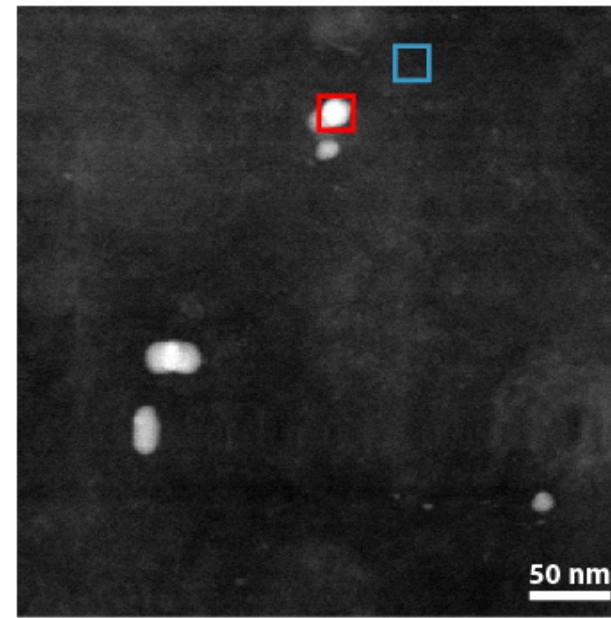
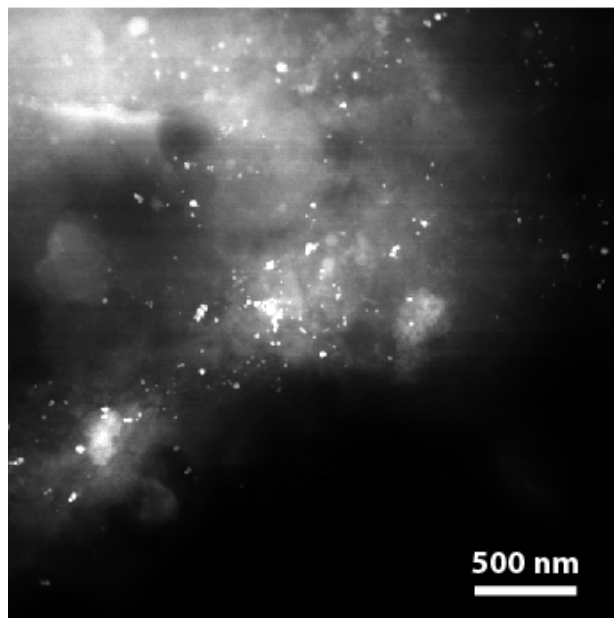


TEM: HAADF and EDX

Aerated tank

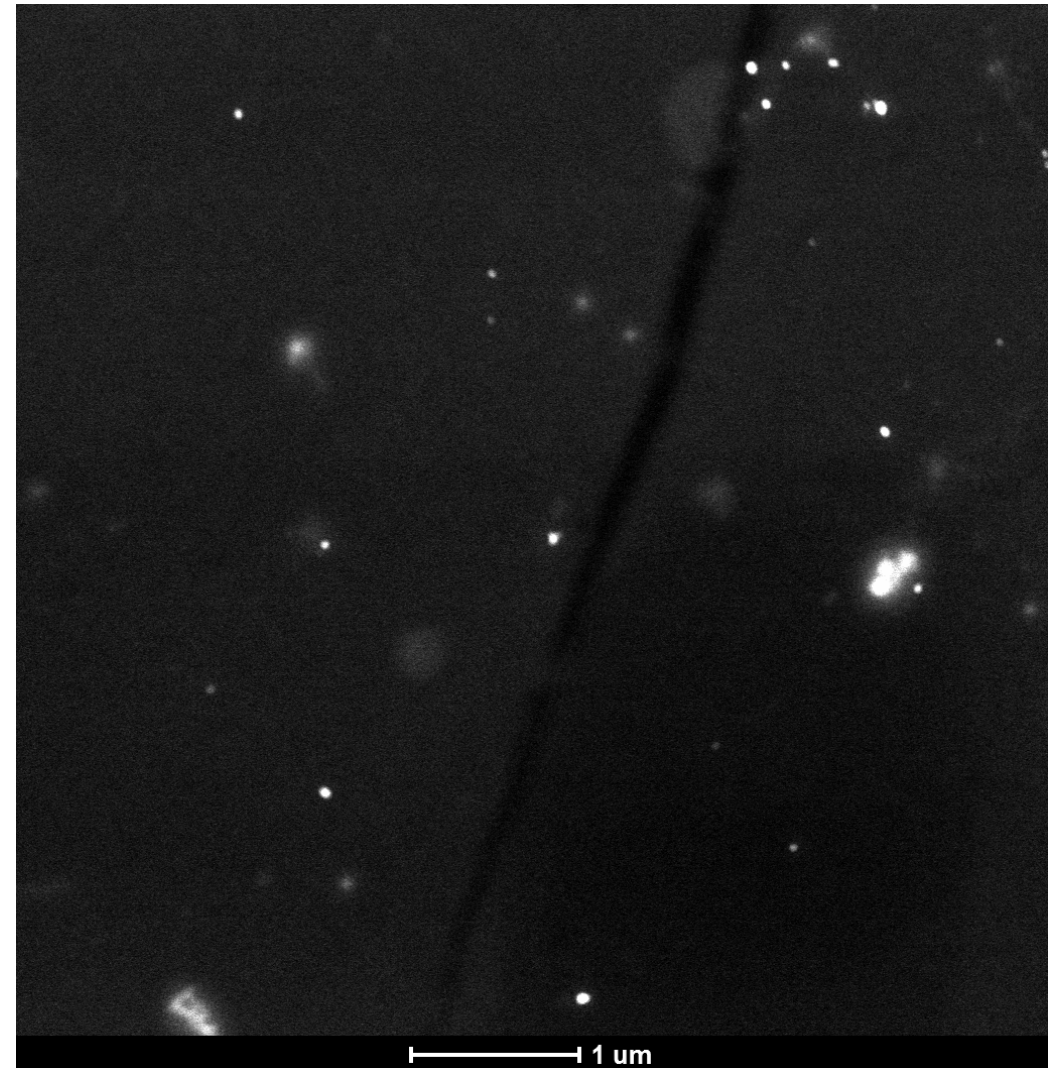
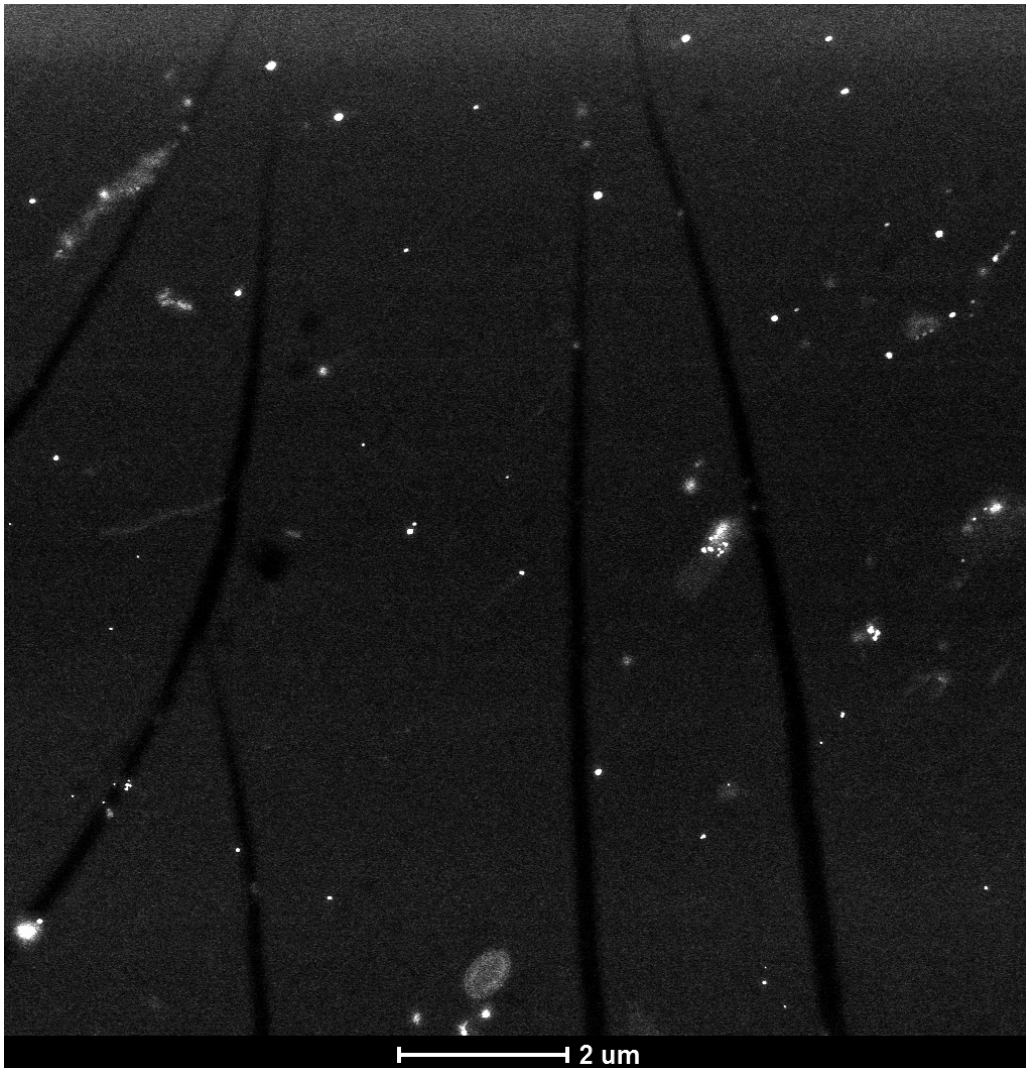


Secondary clarifier

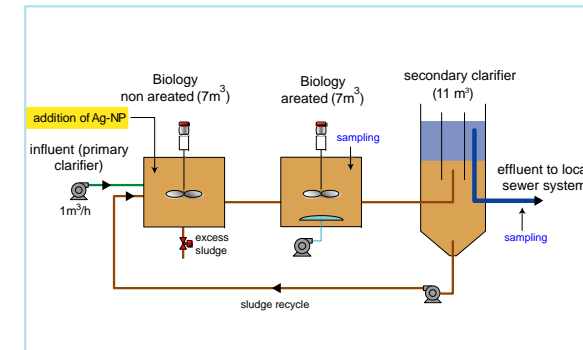
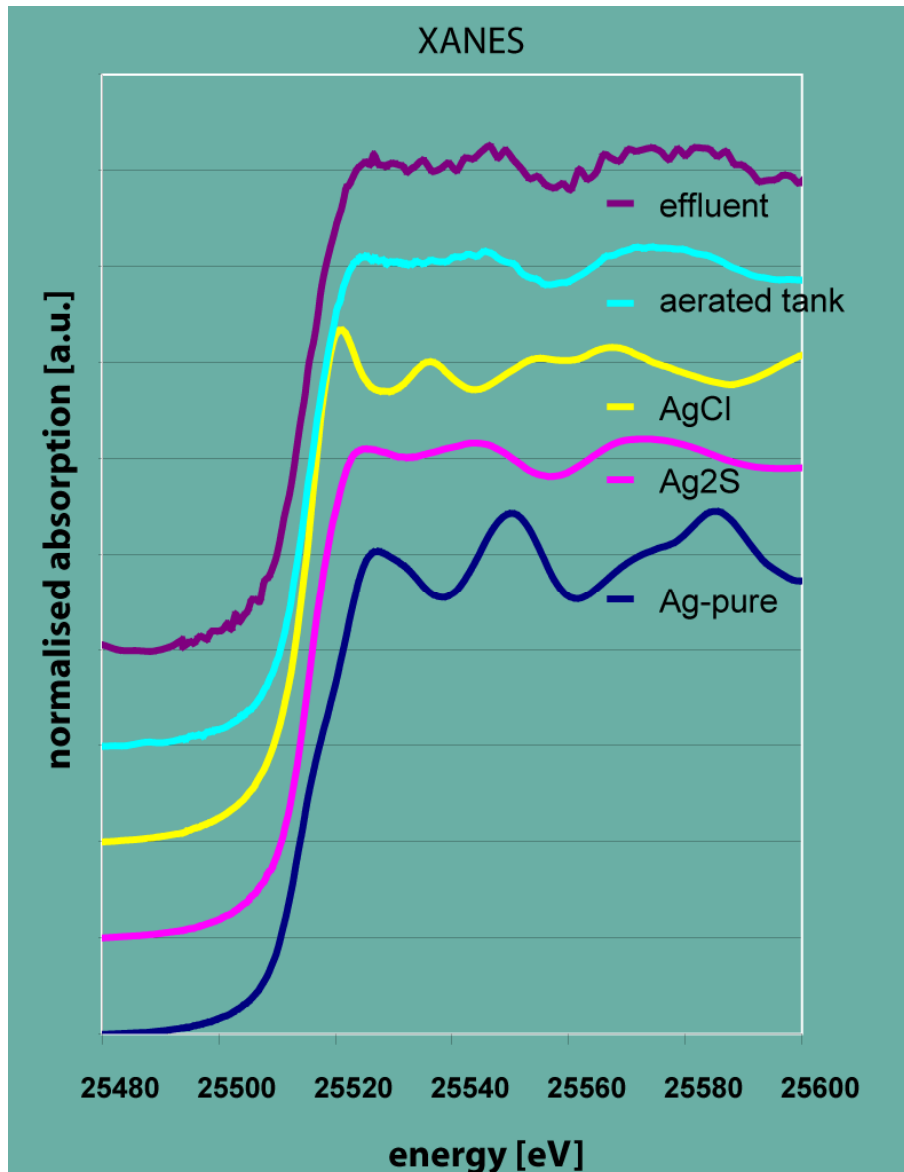


TEM: HAADF

Secondary califier after the initial dosage



Speciation of Ag: XANES



XAS performed on bulk samples allows determining the speciation of the Ag. For that purpose, measured spectra are combined with spectra from reference materials (linear combination fitting)

LCF XANES

	Ag-pure	Ag ₂ S	Sum	R-value
Pilot - ARA				
aerated tank	2%	98%	100%	0.00007
effluent	15%	87%	101%	0.00050

Conclusions

