

Emissions of nanosilver and its behavior in wastewater treatment plants

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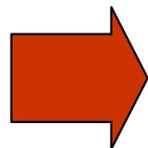
Nanosilver

What we know?

- Silver species (AgCl , Ag^0 , etc.) used for antimicrobial control are regulated by European Biocidal Product Directive (BPD)
- Free silver ions (Ag^+) control microbes
- Main nano species in use is silver chloride (>90% AgCl)

What we do not know?

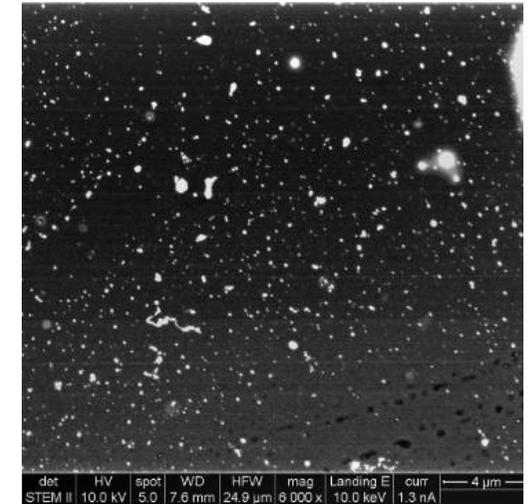
- Amounts of market volumes and relevance
- Emissions to soil and water
- Behavior in the wastewater treatment plant (WWTP)



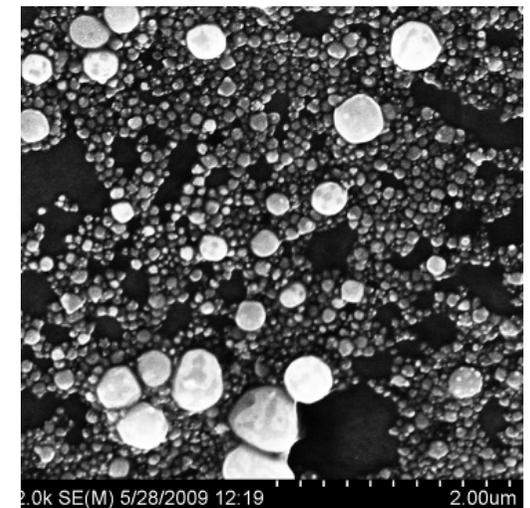
Risk to humans and the environment uncertain

Studies on Emission and Fate

1. Emission by an industrial laundry
2. Influence on nitrification in activated sludge (four silver products investigated)
3. Mass balance in wastewater treatment plant (WWTP: pilot-plant and municipal treatment plant)

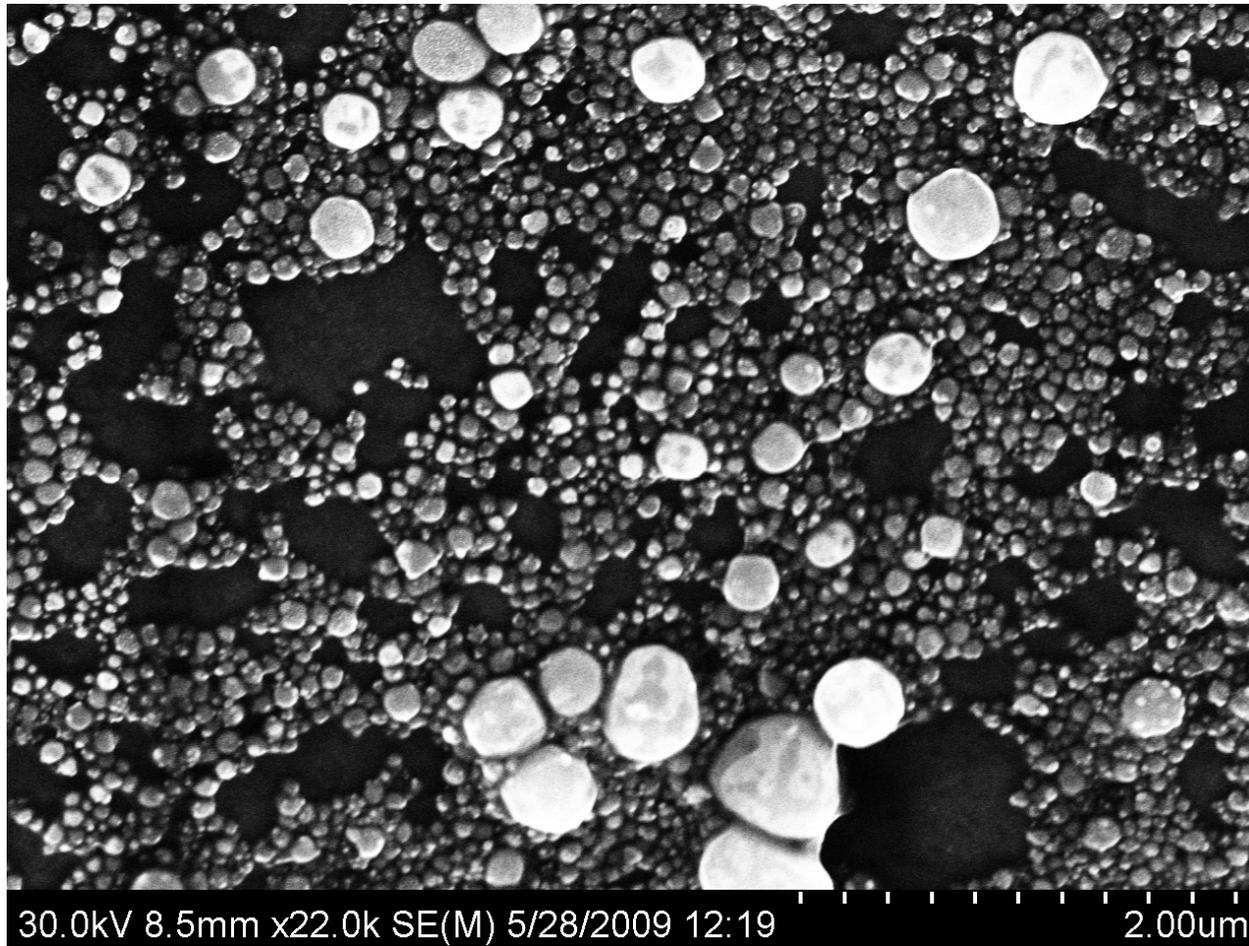


Silver Products		Size (nm)	Product
Silver nitrate	AgNO ₃	-	-
Colloidal Nanosilver A	nAg-A	5-50	AgPure WS10
Colloidal Nanosilver B	nAg-B	5-50	SmartSilver Pro
Particulate Silver Chloride	AgCl	20-500	iSys AG
Microcomposite-Silver	Micro	5-50	HeiQ AGS-20

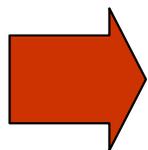
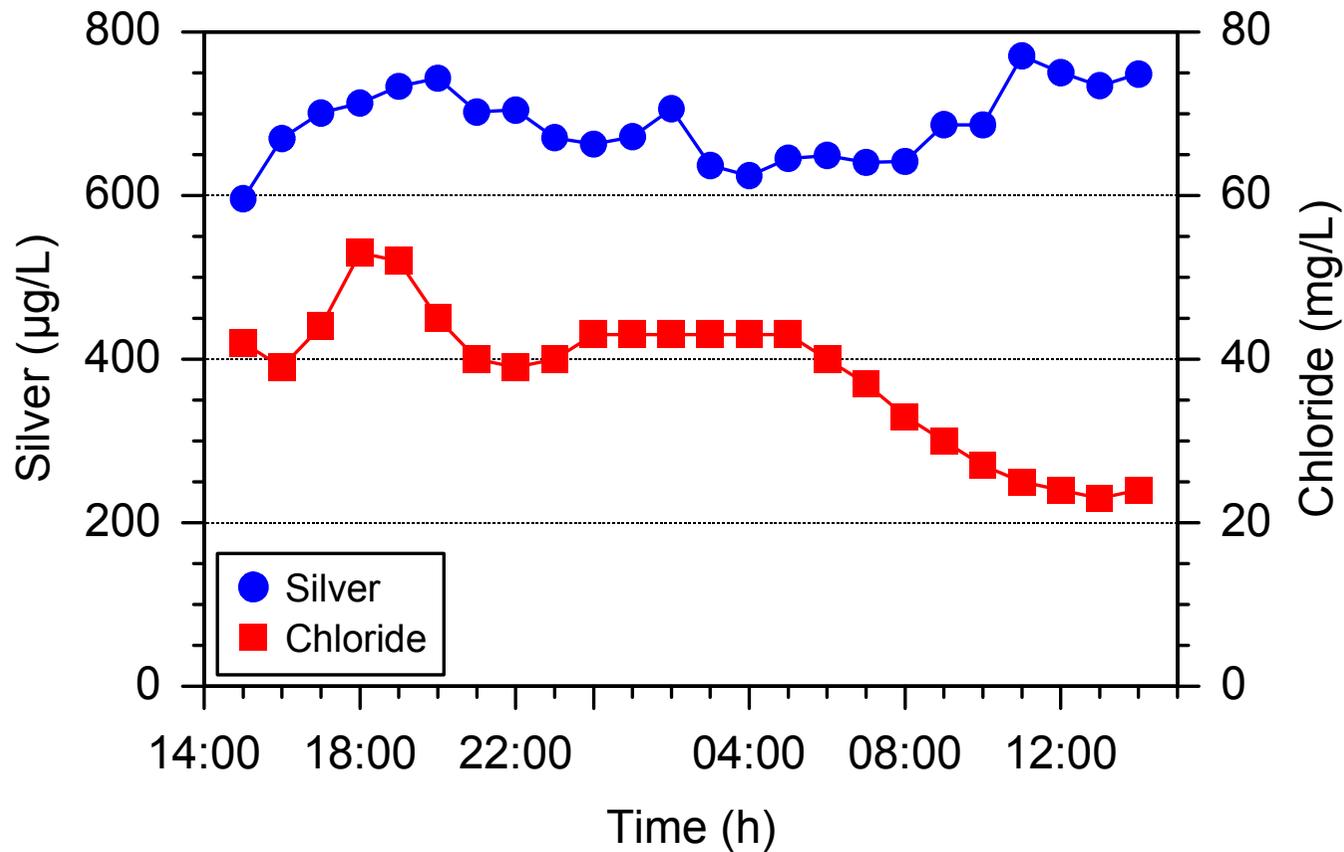


1. Emission from Laundry

AgCl additive used for cotton

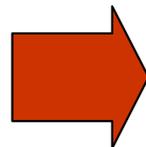
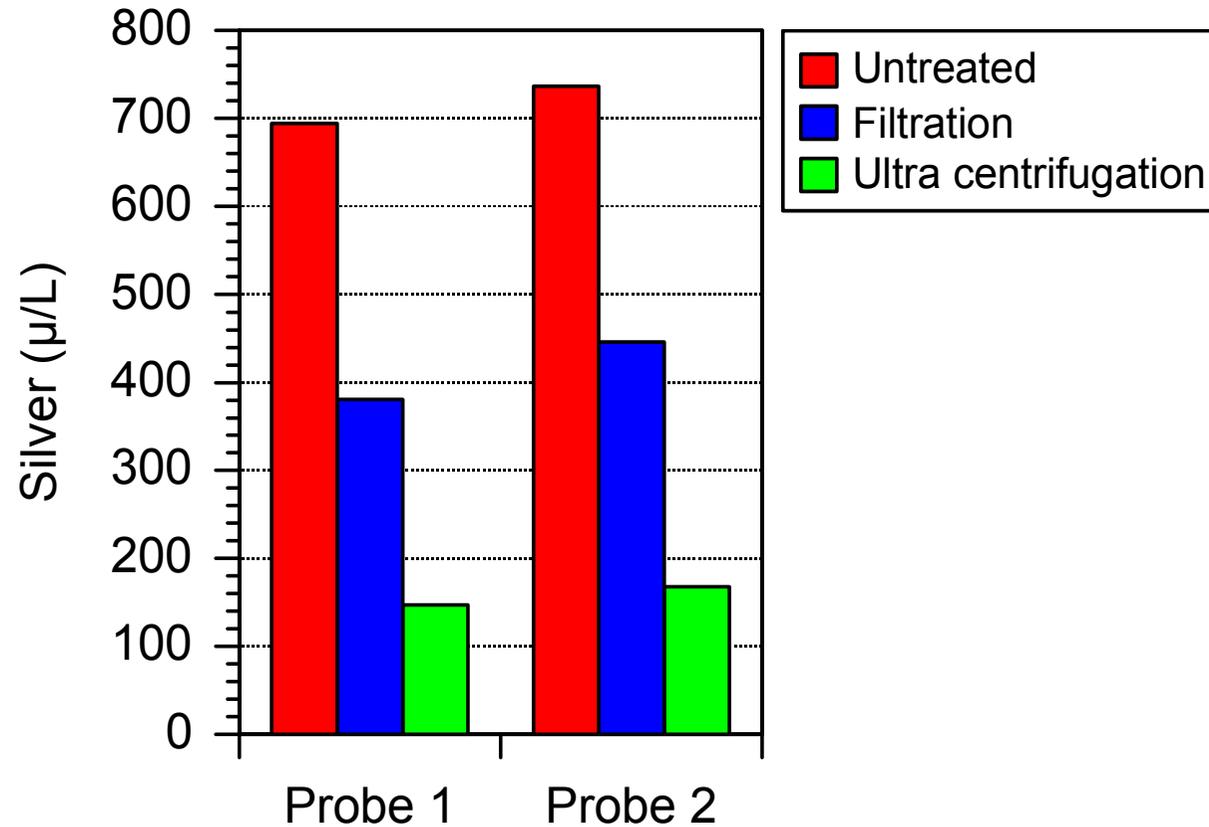


Discharge of Nanosilver



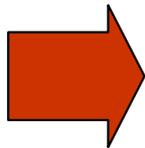
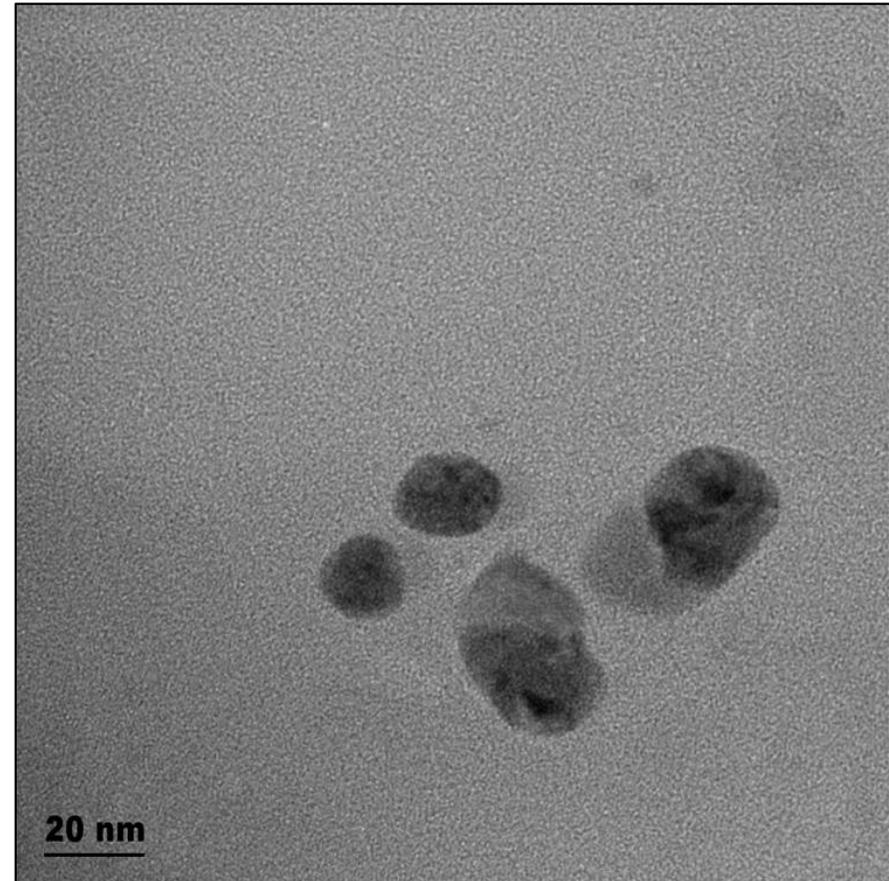
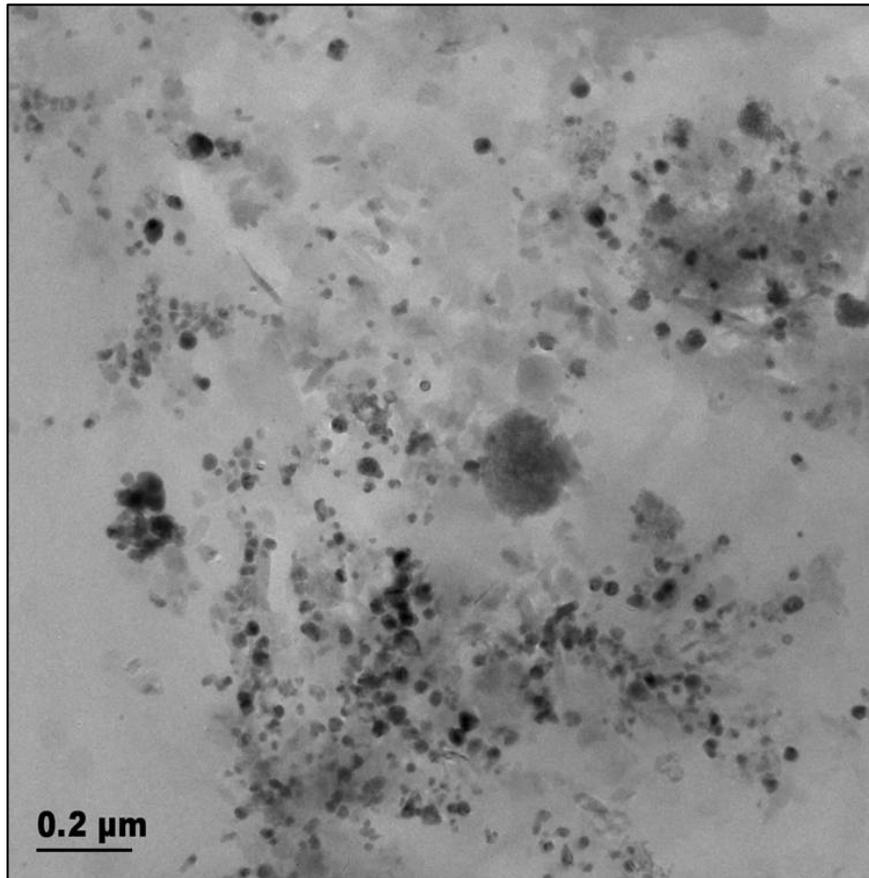
- Annual load 20-30 kg/a in discharge
- Predicted silver concentration in WWTP 10-20 mg/kg TS

Sample Preparation



- Filtration (0.45 µm): 40% elimination
- Ultra centrifugation: 40% Elimination

Detection of Nanosilver by SEM-EDX

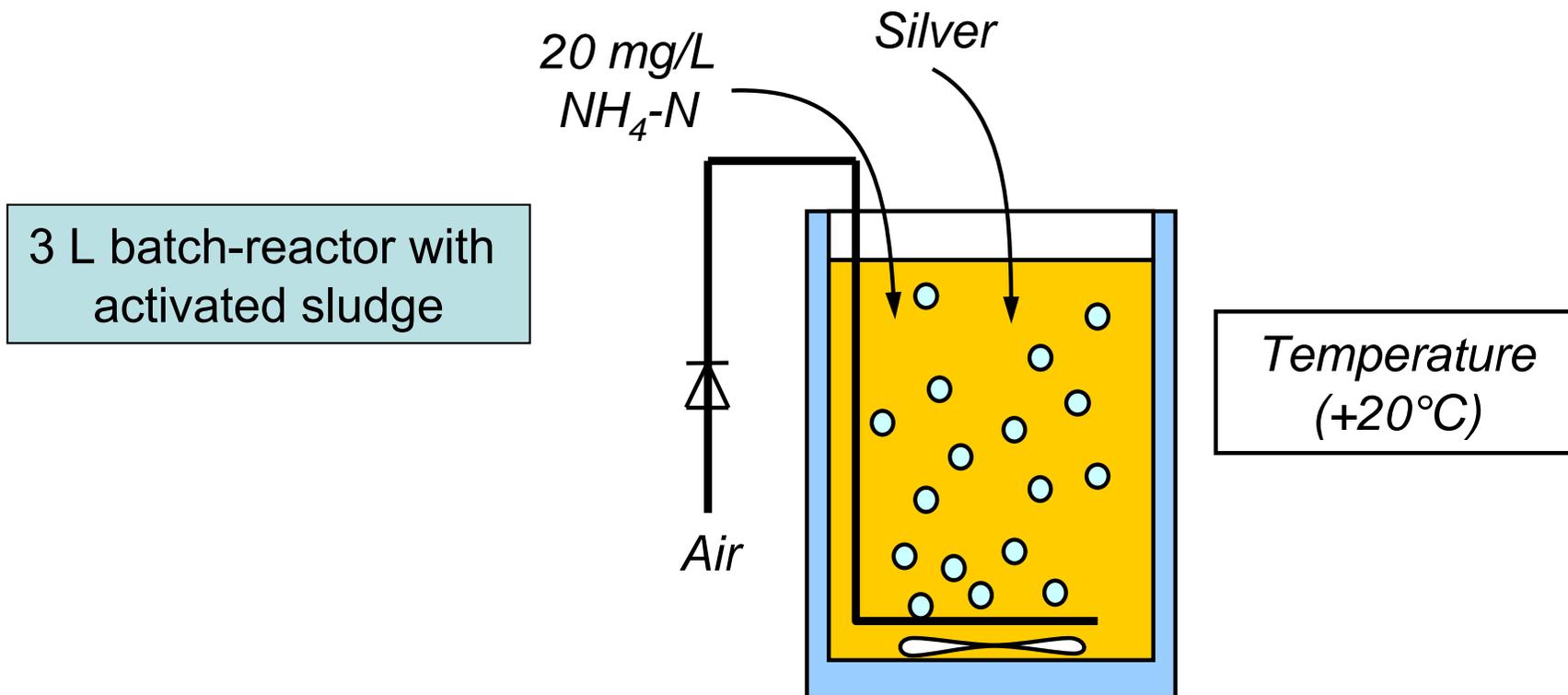


Ag often associated with sulfur signal (no chloride)

2. Influence on Nitrification in Activated Sludge

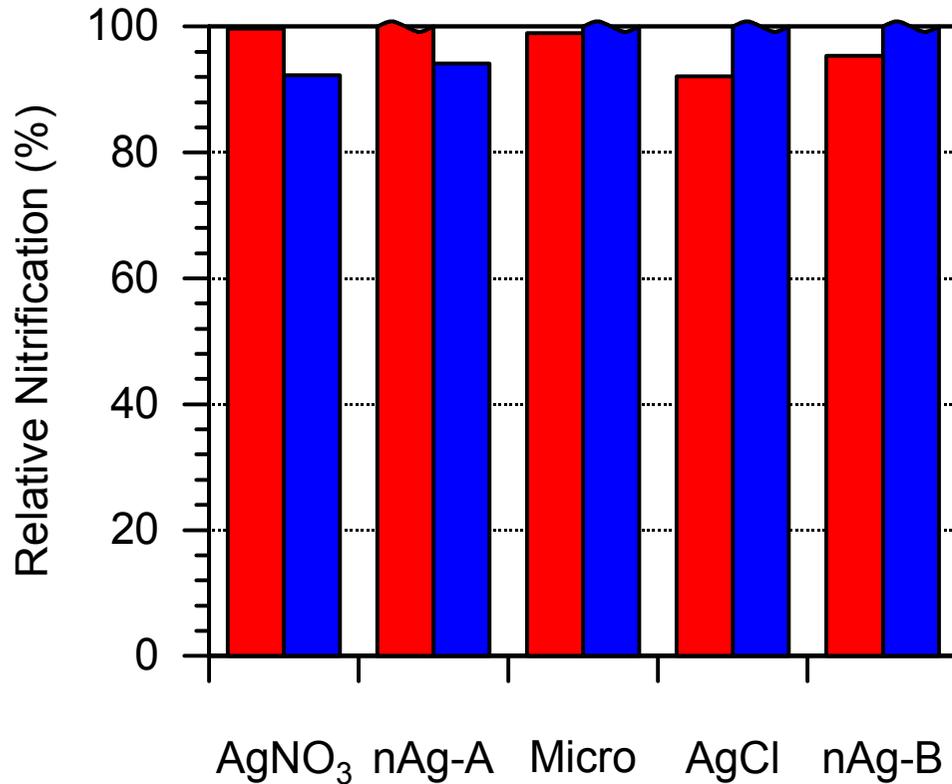
Nitrification in real activated sludge

- Addition of 5 Silver products (1, 100 mg/L)
- Exposure 2 hours and 6 days
- Ammonium degradation compared with reference reactor

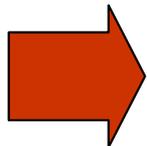
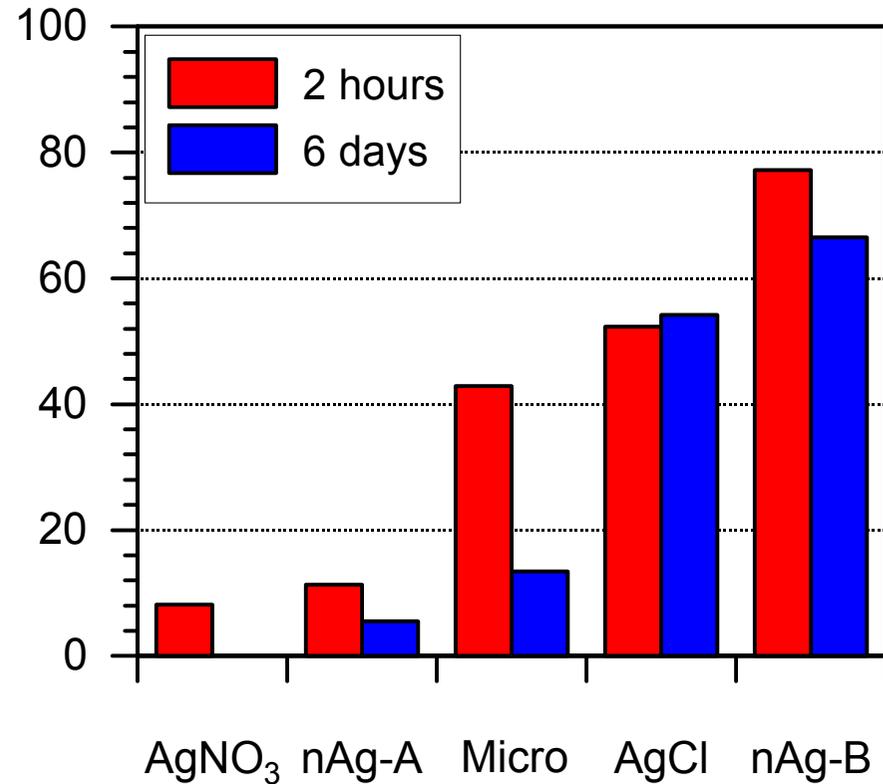


Inhibition Test Results

Addition of 1 mg/L Ag
(250 mg Ag/kg dry matter)



Addition of 100 mg/L Ag
(25,000 mg Ag/kg dry matter)

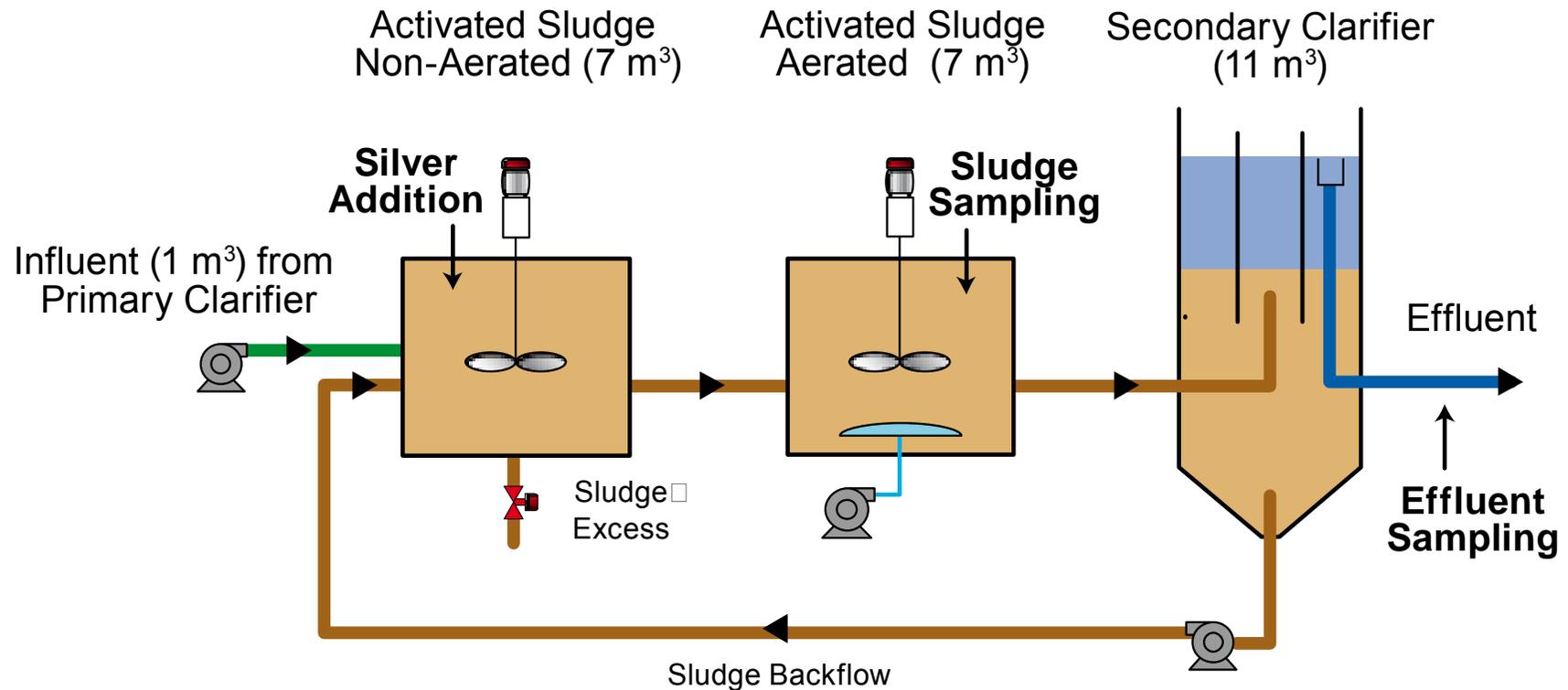


Nanosilver has no impact on nitrification under realistic conditions (real wastewater sludge, concentrations)

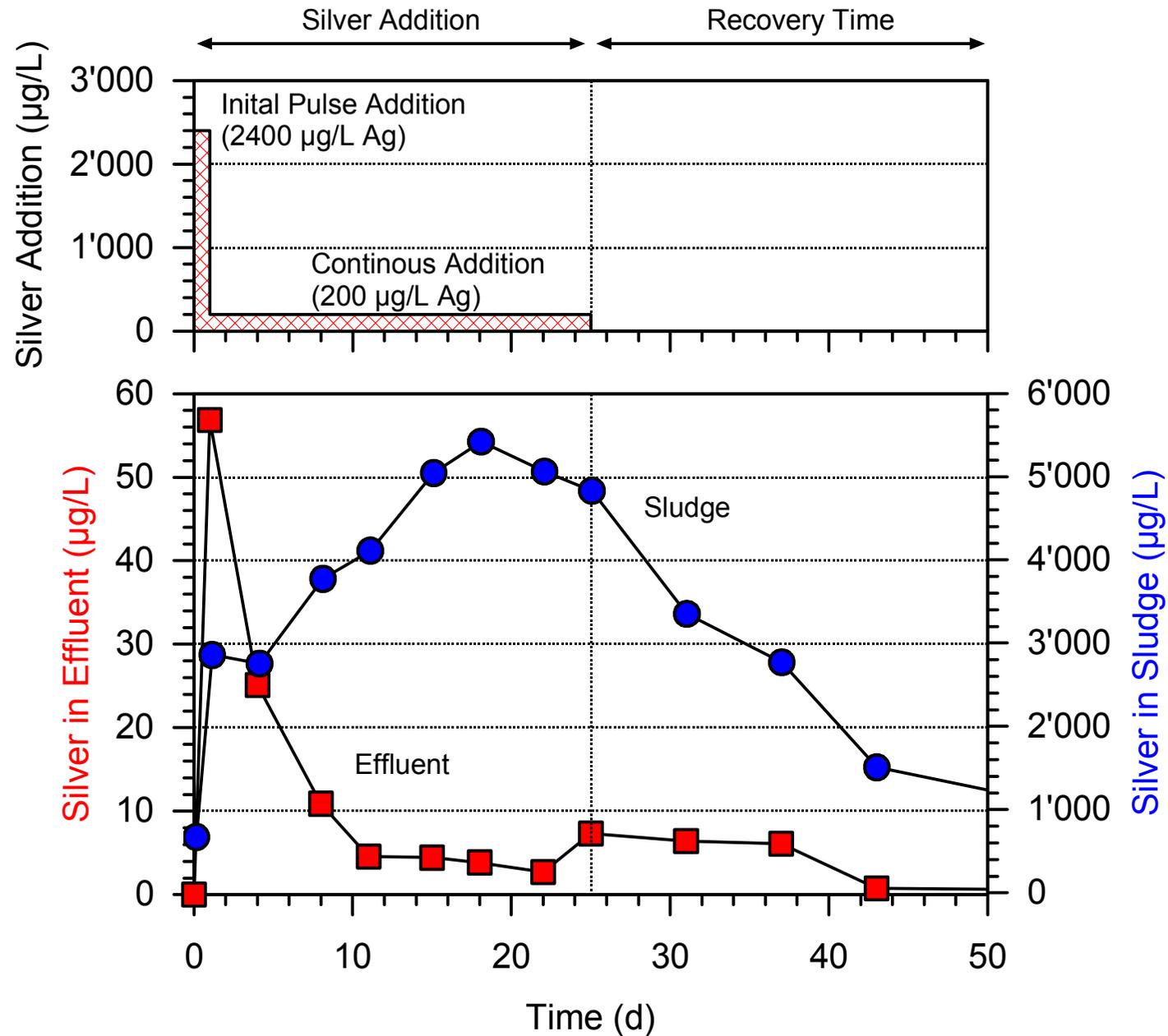
3. Mass Balance in WWTP

Pilot-Plant (70 equivalent inhabitants)

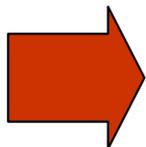
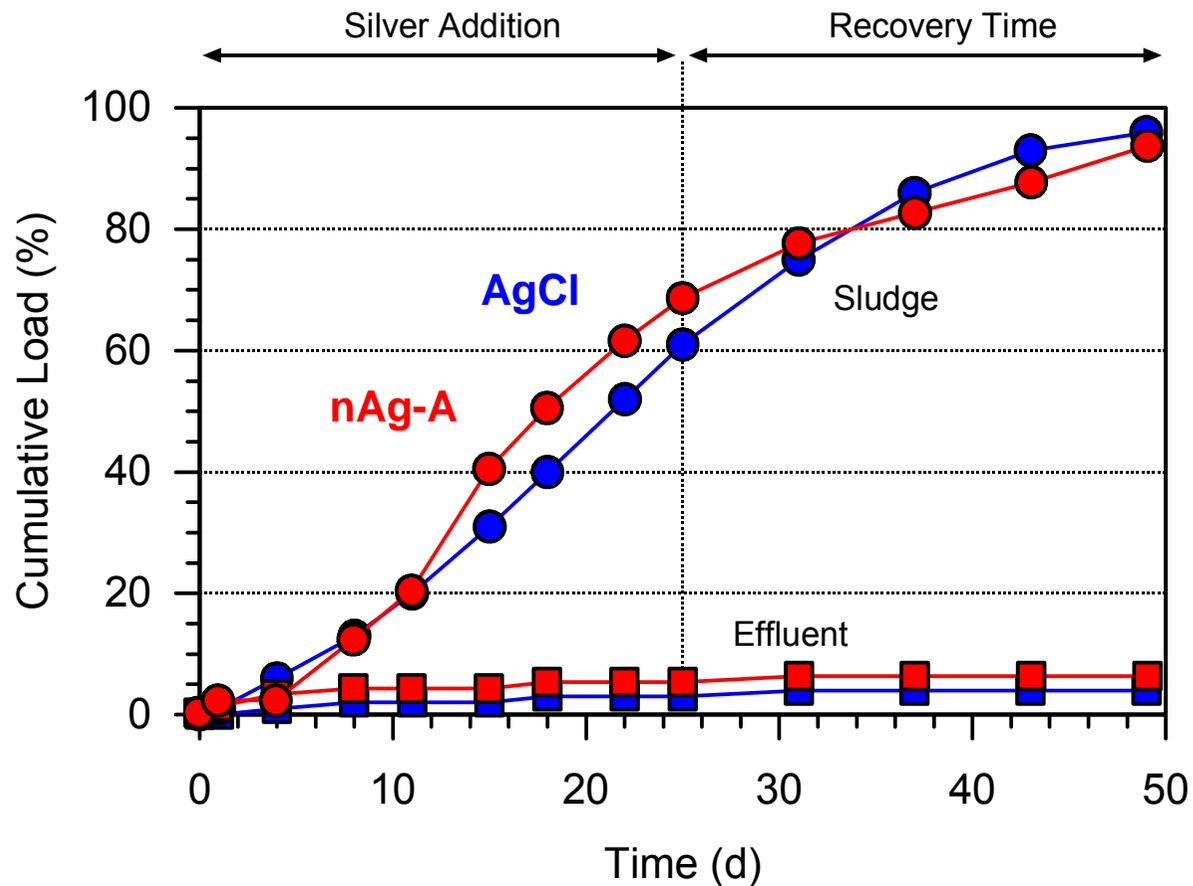
- Influent: 1 m³/h wastewater, directly from combined sewer
- Activated sludge: 12 days age , 3 g/L dry matter
- Silver addition (nAg-A, AgCl): 25 days continuously



Silver Concentration (AgCl)



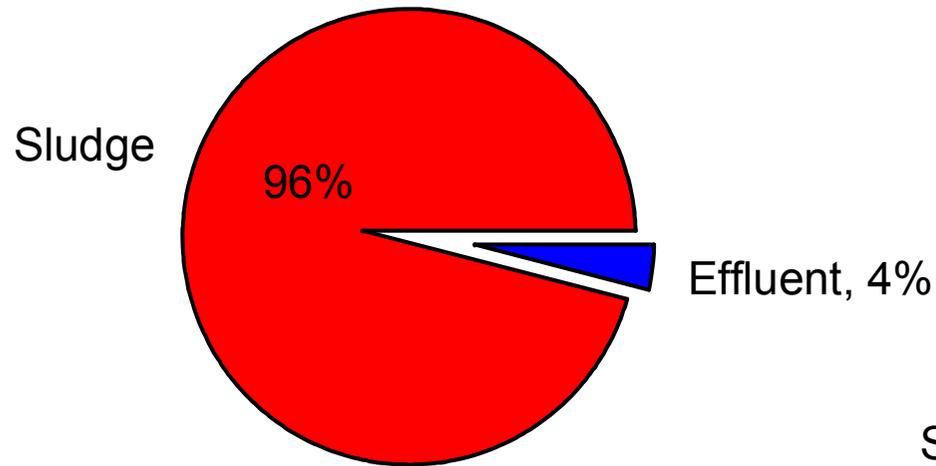
Cumulative Silver Load



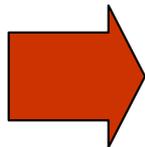
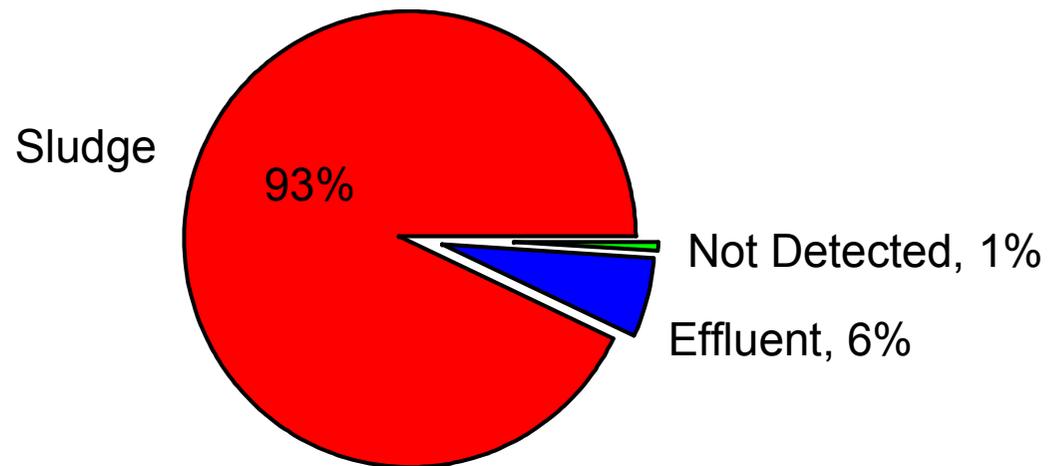
Efficient elimination of nanosilver in WWTP

Nanosilver Mass Balance

Addition of AgCl



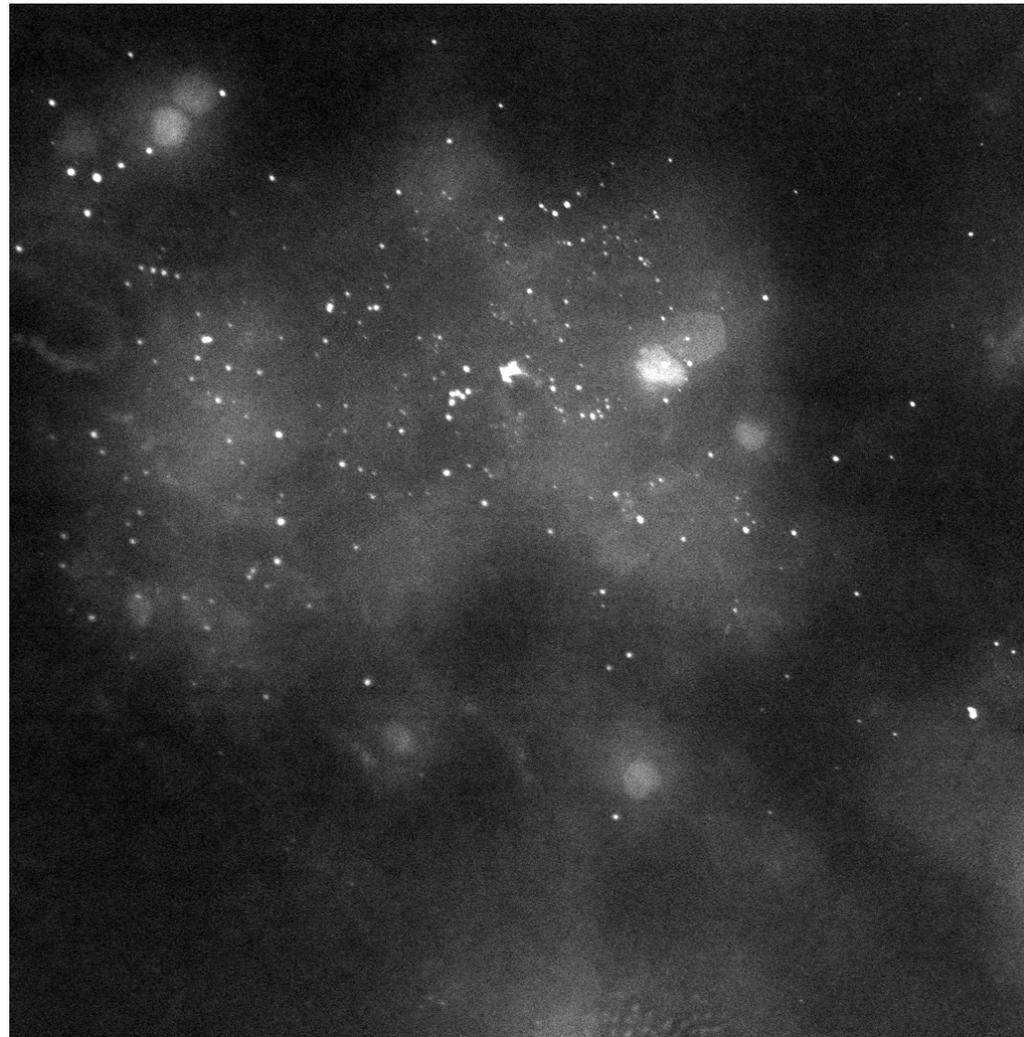
Addition of nAg-A



Correlation between mass flow of nanosilver and suspended solids (dry matter)

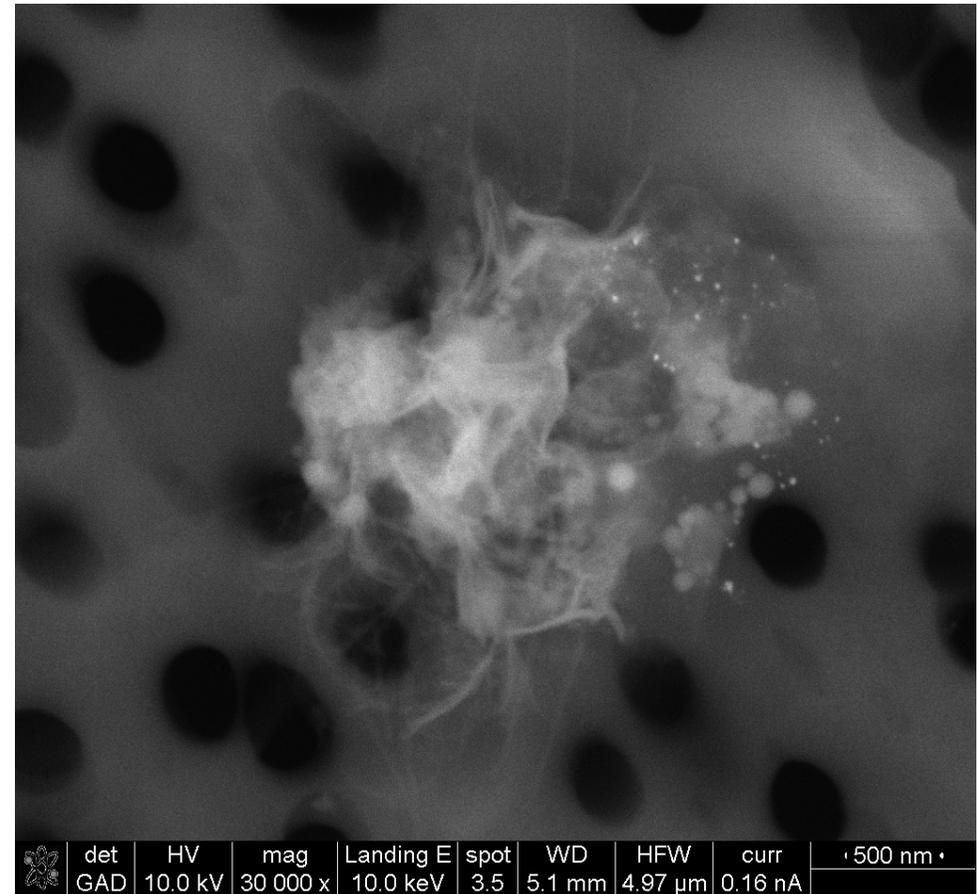
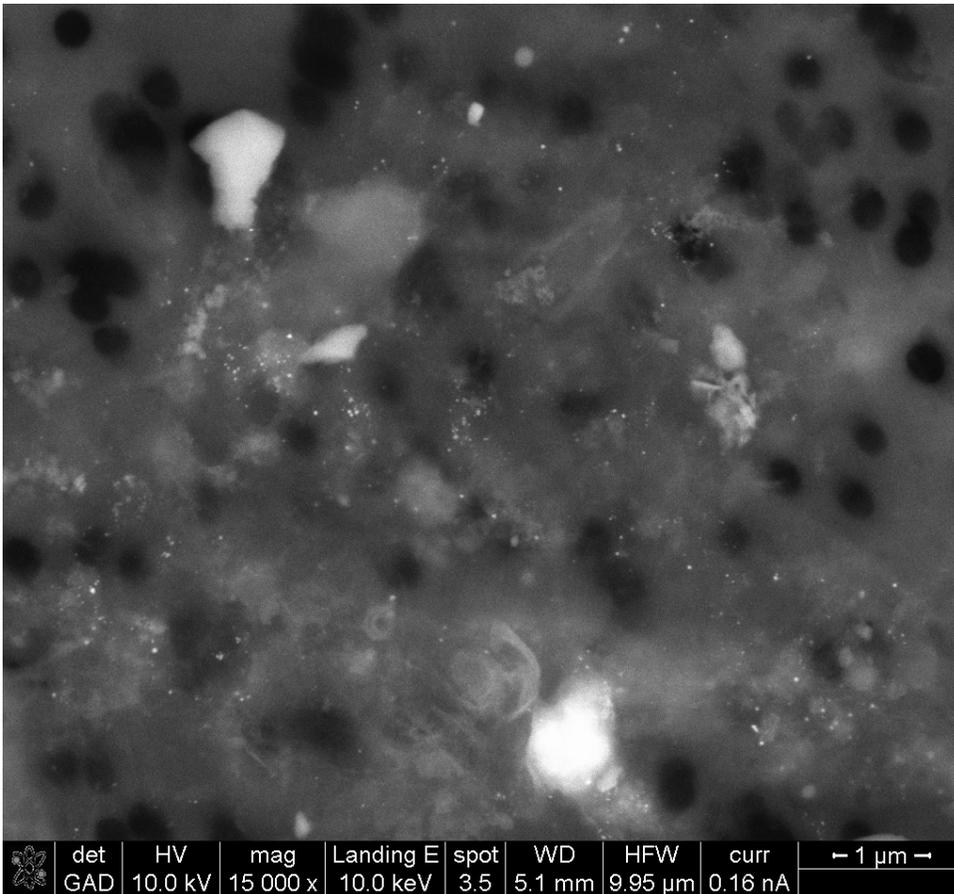
Aerated Sludge

nAg-A in sludge flocs

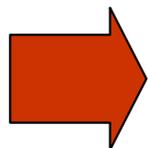
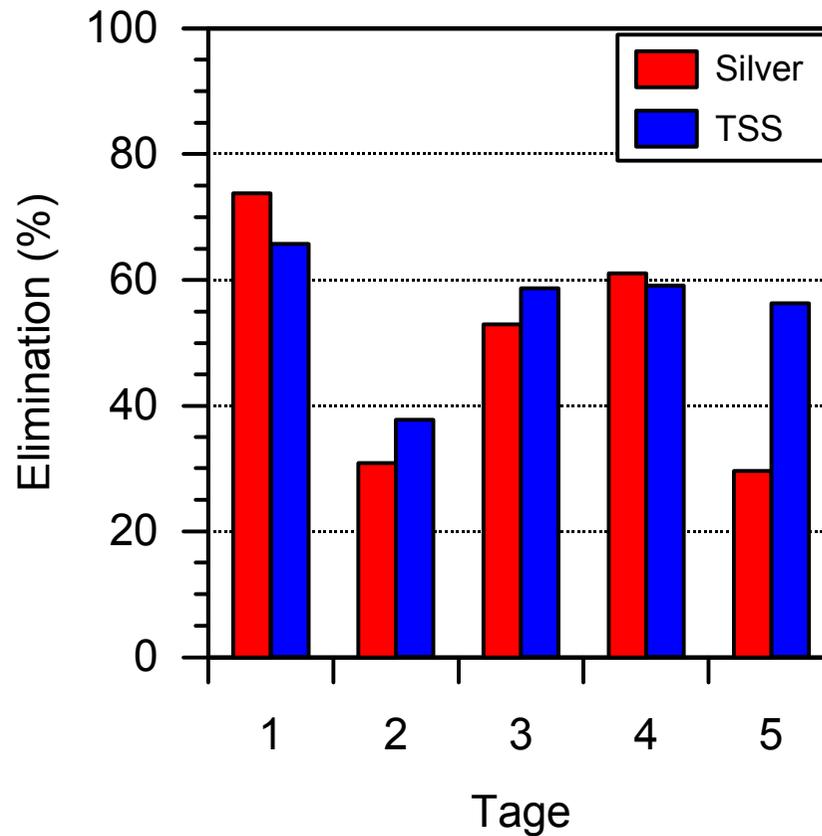


Effluent

nAg-A in sludge flocs



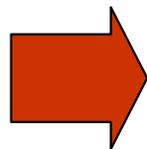
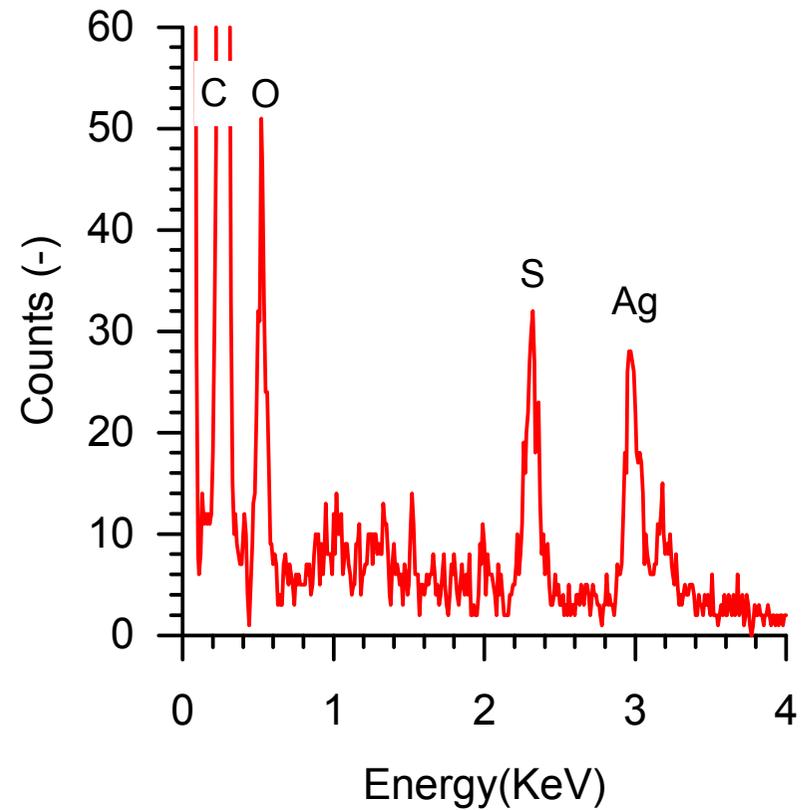
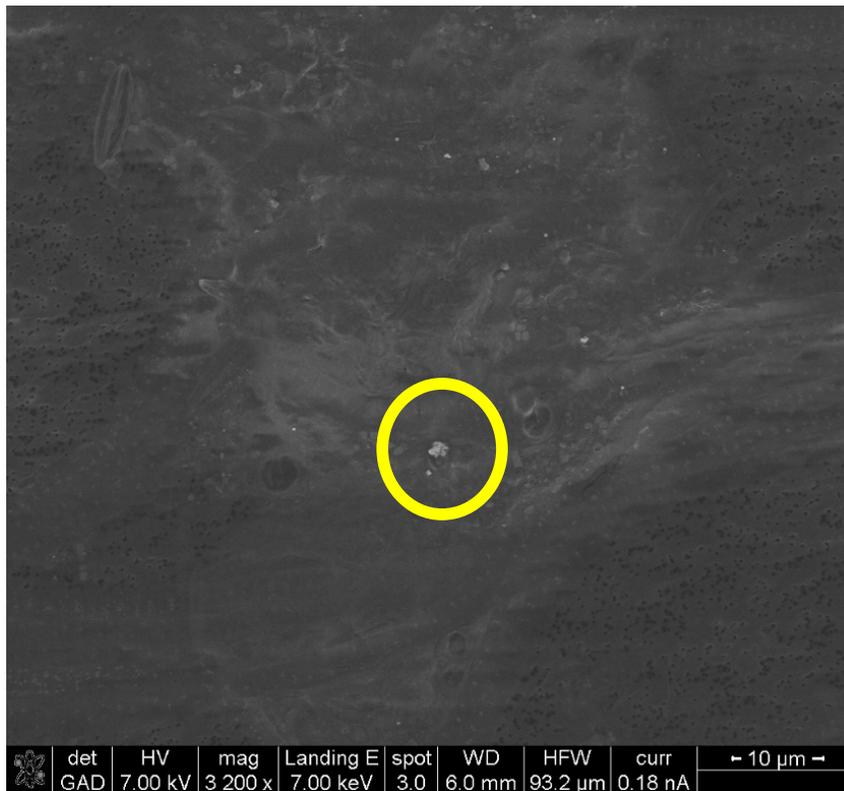
Tertiary Treatment (Filtration)



Efficient elimination of nanosilver in WWTP

Effluent

EDX of silver particles (after addition of AgCl)

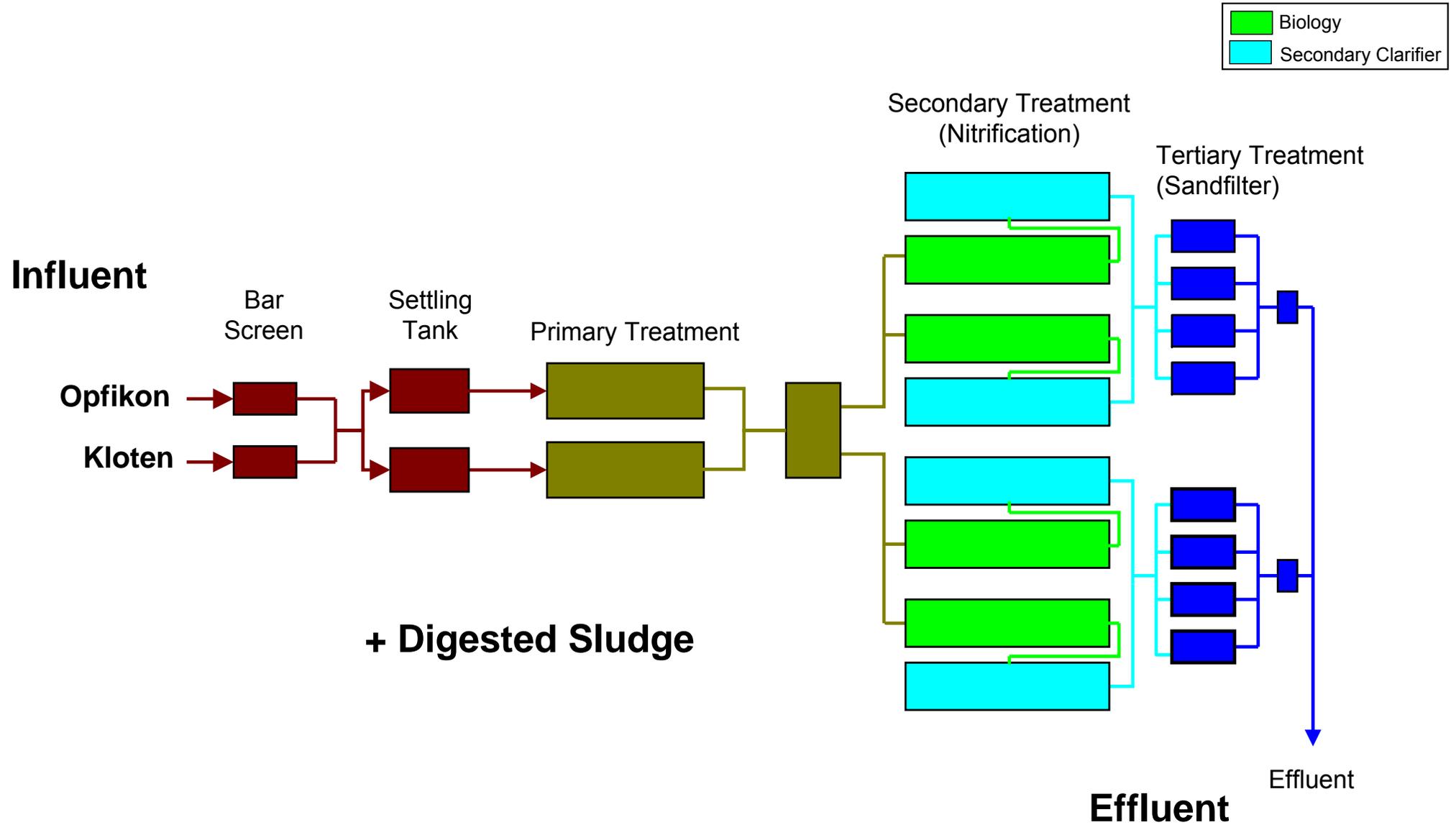


Nanosilver is present as silver sulfide

Mass Flow in Real WWTP (70,000 E.I.)



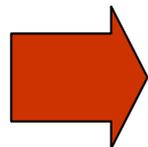
Sampling in WWTP



Occurrence of Silver in WWTP

Sample ¹	Silver	Influent		Effluent (µg/L)	Sludge
		Opfikon*	Kloten**		
1	Ag (µg/L)	14.0	1.9	0.54	870
				6%	94%
2	Ag (µg/L)	18.4	1.6	0.19	860
				2%	98%
3	Ag (µg/L)	12.3	5.3	0.08	740
				1%	99%
4	Ag (µg/L)	12.3	2.5	0.07	580
				1%	99%

¹ Sampling under conditions of dry weather flow



Excellent elimination of nanosilver confirmed

* Worst-case situation: nanosilver from industrial laundry

** Corresponding to background concentration

Conclusions

Nanosilver Emission

- Small amounts release into aquatic systems (paints, finishing)
- Release as micrometer composites or attached to larger particles

Nanosilver in wastewater

- Low influent concentrations (under worst-case conditions)
- No effect on nitrification
- Excellent elimination in WWTP (95-99%; CH micropollutants: >80%)
- Attached to sludge flocs (filtration possible)
- Rapid transformation to insoluble silver sulfide
- Annual emission per capita 4-40 mg/a Ag

General remark

- Lab conditions give limited insight to environmental behavior
- Which applications in contact with water really exists?

Acknowledgements

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**Thank you for your
attention!**

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