Silver Particles in Wastewater Treatment Plants

Michael Burkhardt, Ralf Kägi et al.

Berlin, 8th/9th January 2012

HSR
HOCHSCHULE FÜR TECHNIK
RAPPERSWIL
FHO Fachhochschule Ostschweiz

eawag
aquatic research

Outline of Presentation

1. **Objectives**
2. Nitrification Process
3. Pilot Scale WWTP
4. Full Scale WWTP
5. Conclusions

Who cares on Silver Release and Pathways to Water?

Release
(Emission)

Façade

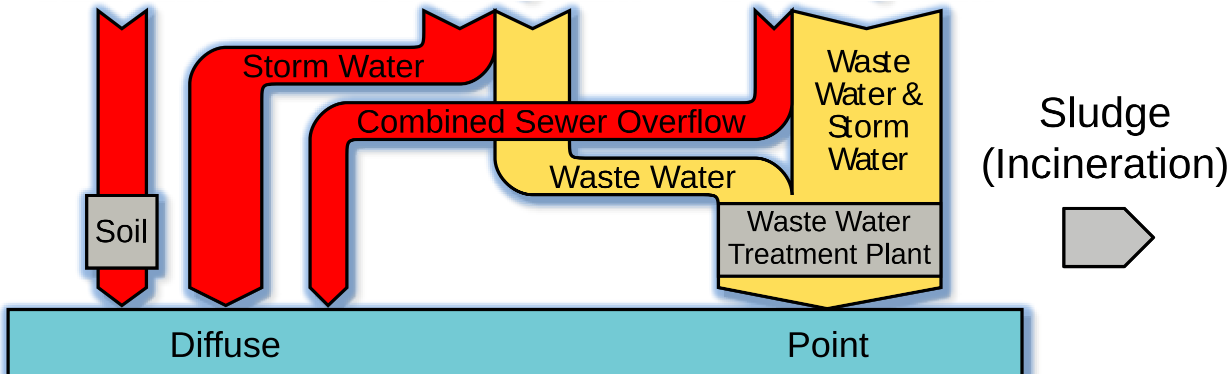
Laundry

Pathways

Stormwater Infiltration

Separated Sewer System

Combined Sewer System

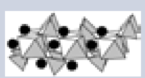
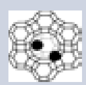
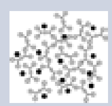
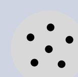
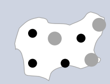
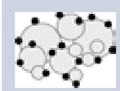
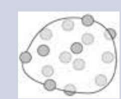
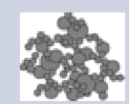


Receiving Waters

Silver may enter and affect receiving waters by point sources

Who cares on Products and Amounts - What's “nanosilver”?*

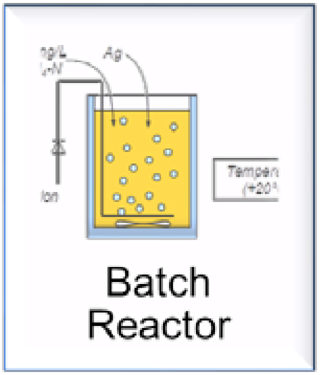
- In Europe <50 t/a particulate silver in use, <4 t/a Ag for textiles (90% AgCl)
- 30% of all nano-projects dealing with “nanosilver” (Maynard 2006)

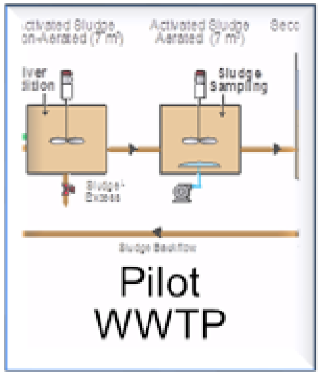
	Silver Ion Exchange				Silver Salt		Metallic Silver	
Silver Form	Silver Zirconium Phosphate	Silver Zeolithe	Silver Glass	Silver Polymer	Microcomposite Silver Chloride	Silver Chloride	Metallic Microcomposite Silver	Metallic Nanosilver
Size (nm)	Ion	Ion	Ion	Ion	20 - 500	20 - 500	5 - 25	5 - 25
Matrix	Exchange Resin	Alumo Silicate	Phosphate Glass	Polymer	Titanium Dioxide, Zeolithe	-	Amorphous Silicate	-
Size (nm)	>1000	>1000	>1000	>1000	>1000	-	>1000	-
Struktur								
Dosage Form	granular	granular	liquid	liquid	granular	liquid	liquid, granular	liquid

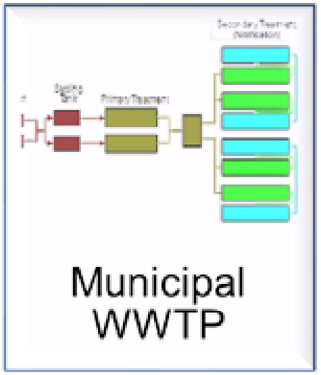
* Burkhardt et al. (2011): Entsorgung nanosilberhaltiger Abfälle in der Textilindustrie - Massenflüsse und Behandlungsverfahren. Forschungsbericht, Rapperswil, Schweiz.

Goal of the Study: Behavior of Silver in Wastewater

- Influence on nitrification in activated sludge
  (silver chloride, metallic nanosilver, metallic microcomposite silver)
- Mass balance in a pilot WWTP with 70 equivalent inhabitants
  (silver chloride, metallic nanosilver)
- Mass balance in a full-scale WWTP with 60'000 equivalent inhabitants
  (including silver discharge by laundry)







Test conditions represent “real world” (composition matrix) and analytical methods are state-of-the-art for environmental samples

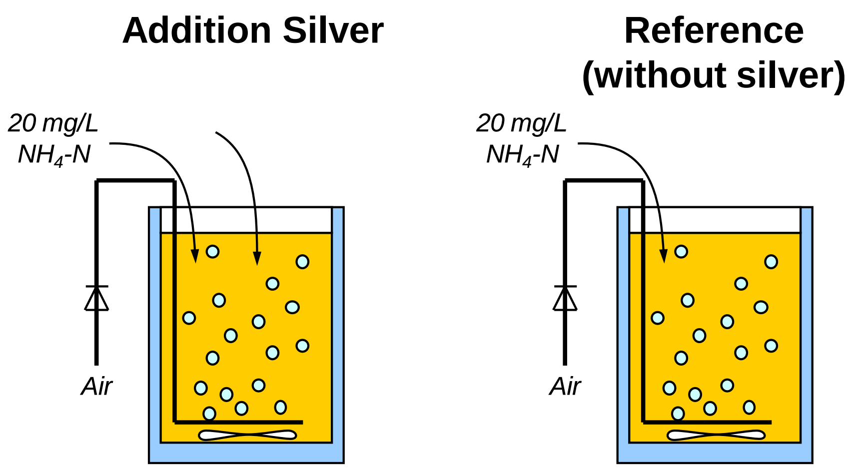
Outline of Presentation

1. Objectives
2. **Nitrification Process**
3. Pilot Scale WWTP
4. Full Scale WWTP
5. Conclusions

Nitrification Inhibition Test with Real Activated Sludge

Aerated batch reactors operated with 3 L activated sludge

- Addition of four silver products
  - 1 mg/L Silver, corresponding to 250 mg Silver / Dry Matter
  - 100 mg/L Silver, corresponding to 25’000 mg Silver / Dry Matter
- Exposure time to silver 2 hours and 6 days
- Addition of ammonium and oxidation within 2 hours measured
- Reactors without silver for each product as reference



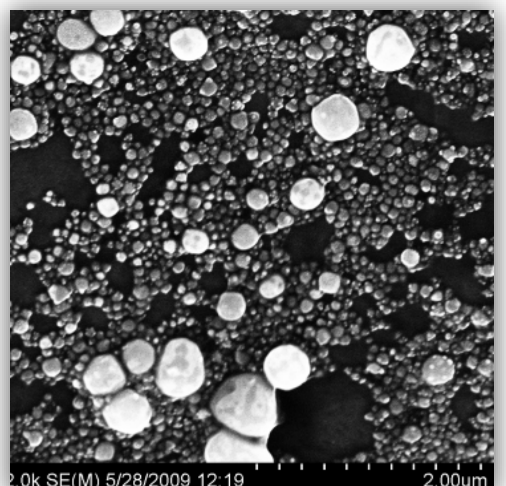
3 L Batch reactors, Temperature +20°C

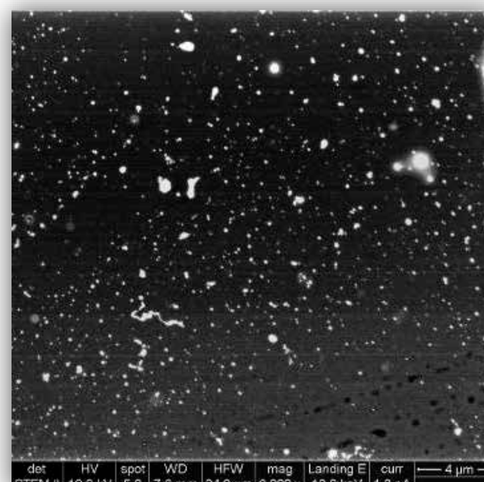
Tested Silver Forms (Market Products)

Silver Forms		Product
Silver nitrate (Reference)	$AgNO_3$	-
Silver Chloride	AgCl	iSys AG
Metallic Nanosilver A	nAg-A	AgPure WS10 *
Metallic Nanosilver B	nAg-B	SmartSilver Pro
Metallic Microcomposite Silver	Micro	HeiQ AGS-20

** Similar to JRC NM-300 K*

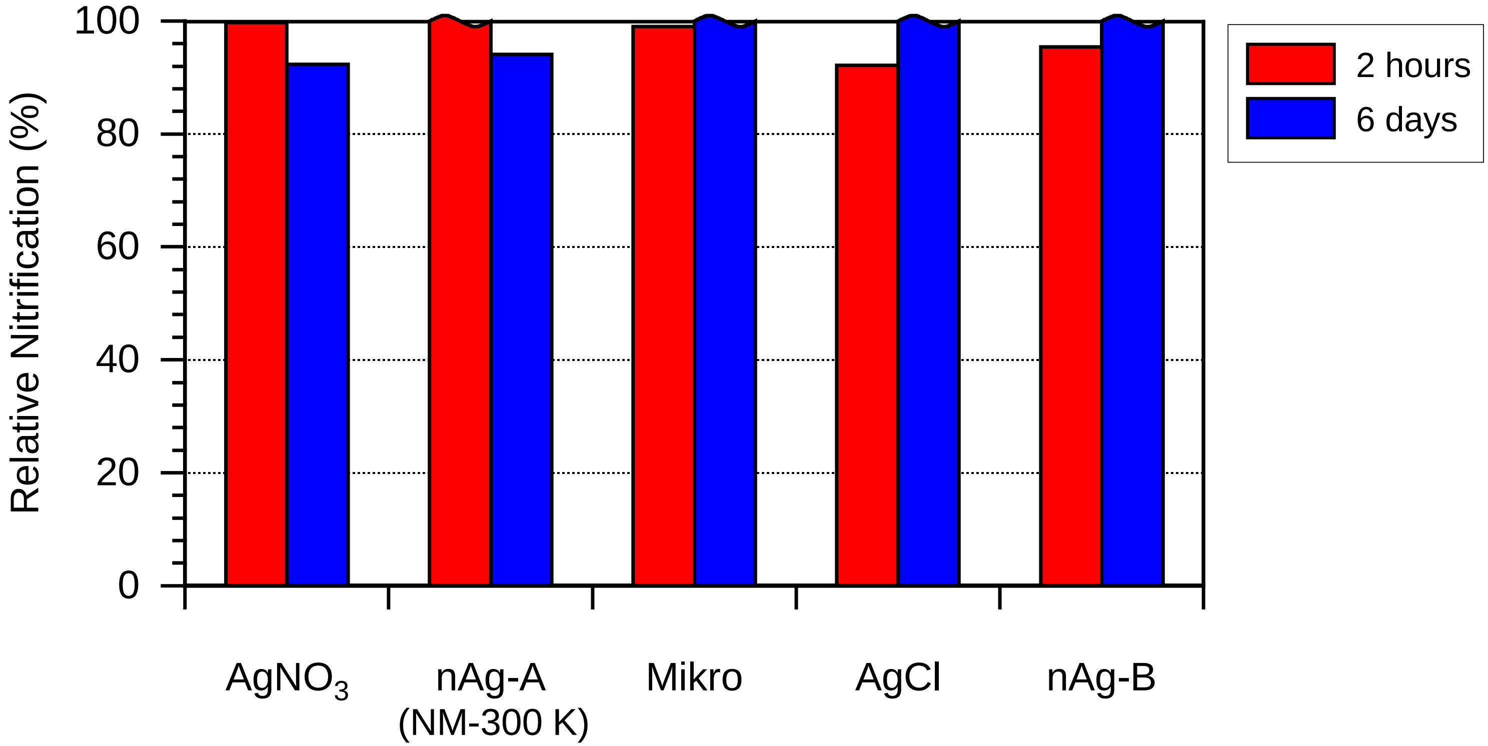
Silver Chloride (iSysAG)





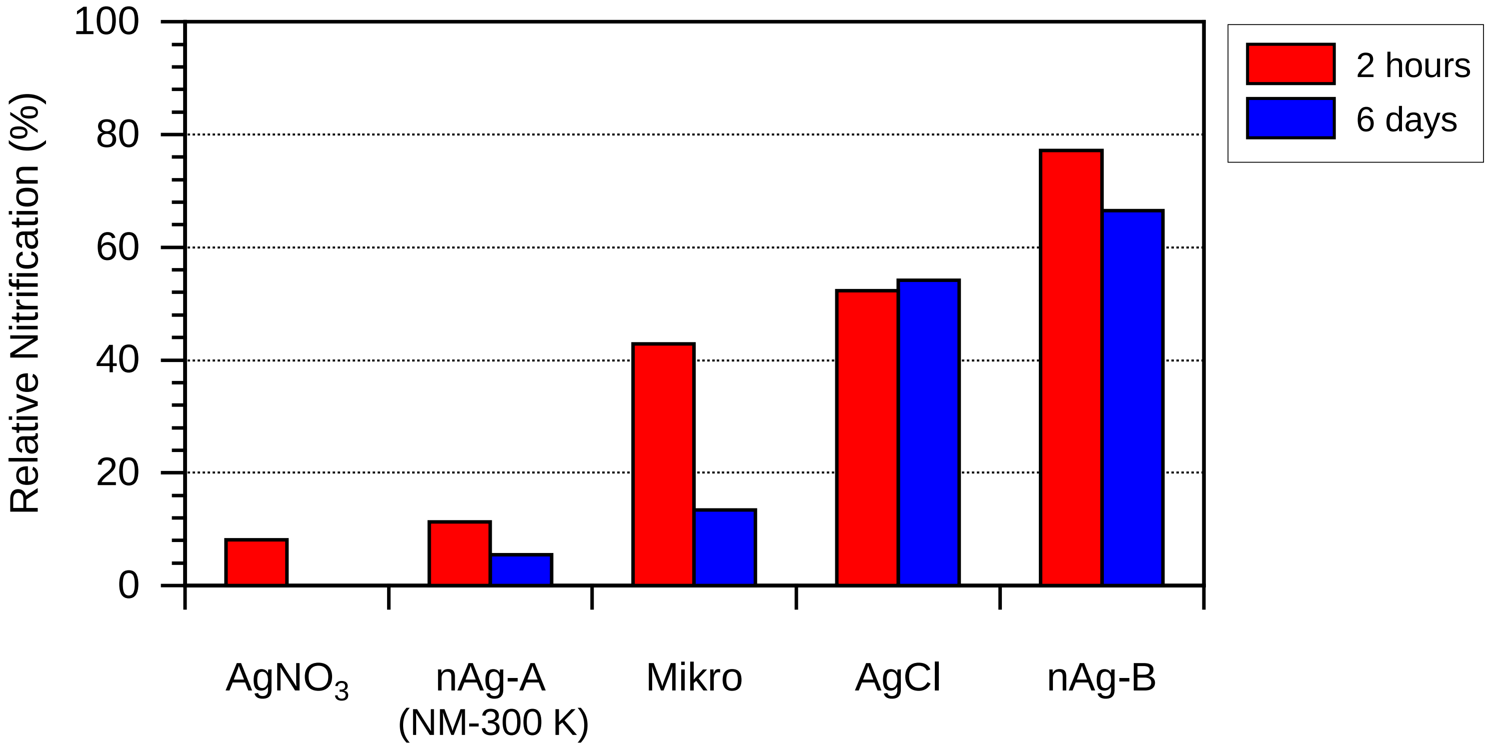
Metallic Nanosilver A (NM-300 K)

Nitrification Results of 1 mg/L Silver Addition



Concentration of 250 mg Ag /kg DM represents "worst-case" (even higher than by discharge of photochemistry in the past)

Nitrification Results of 100 mg/L Silver Addition



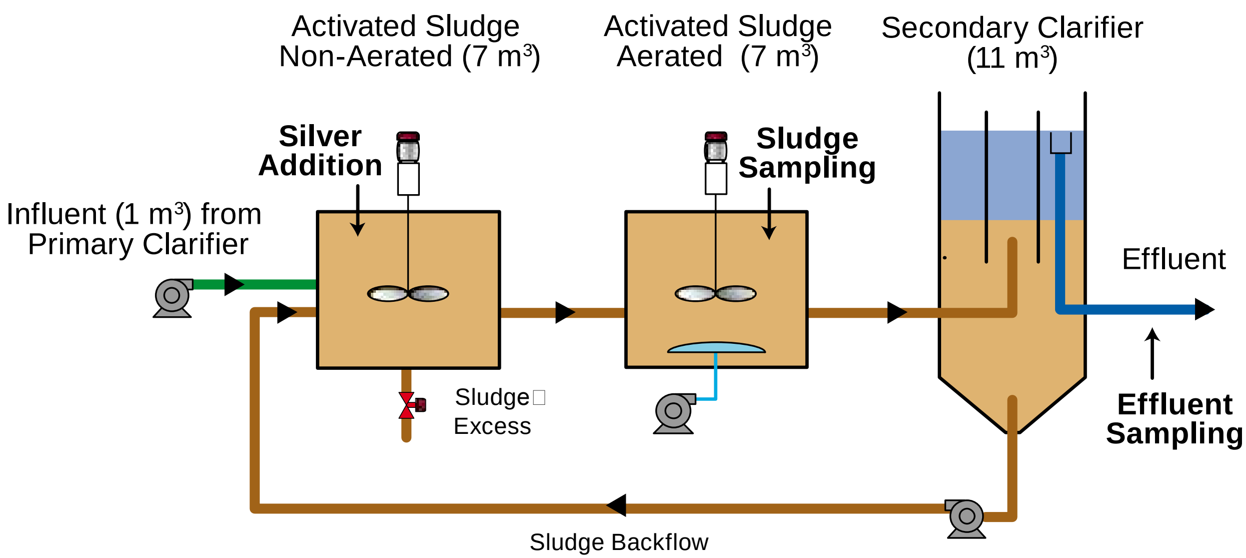
Conditions reflecting our scientific interest in processes (25 g Ag /kg TS overburdened the test system)

Outline of Presentation

1. Objectives
2. Nitrification Process
3. **Pilot Scale WWTP**
4. Full Scale WWTP
5. Conclusions

Mass Flow in Pilot Scale WWTP (70 Equivalent Inhabitants)

- Plant operated under conditions similar to full-scale WWTP
  - Inflow 1 m^3/h wastewater directly from combined sewer system
  - Activated sludge with 12 days age and 3 g/L dry matter (DM)
- Addition of “nanosilver A (nAg-A)” and “silver chloride (AgCl)” (25 days)
  - 2400 µg/L Ag for 1 day (pulse for rapid equilibrium)
  - 200 µg/L Ag for 24 days (continuous)
  - Sampling of effluent and sludge



Pilot WWTP

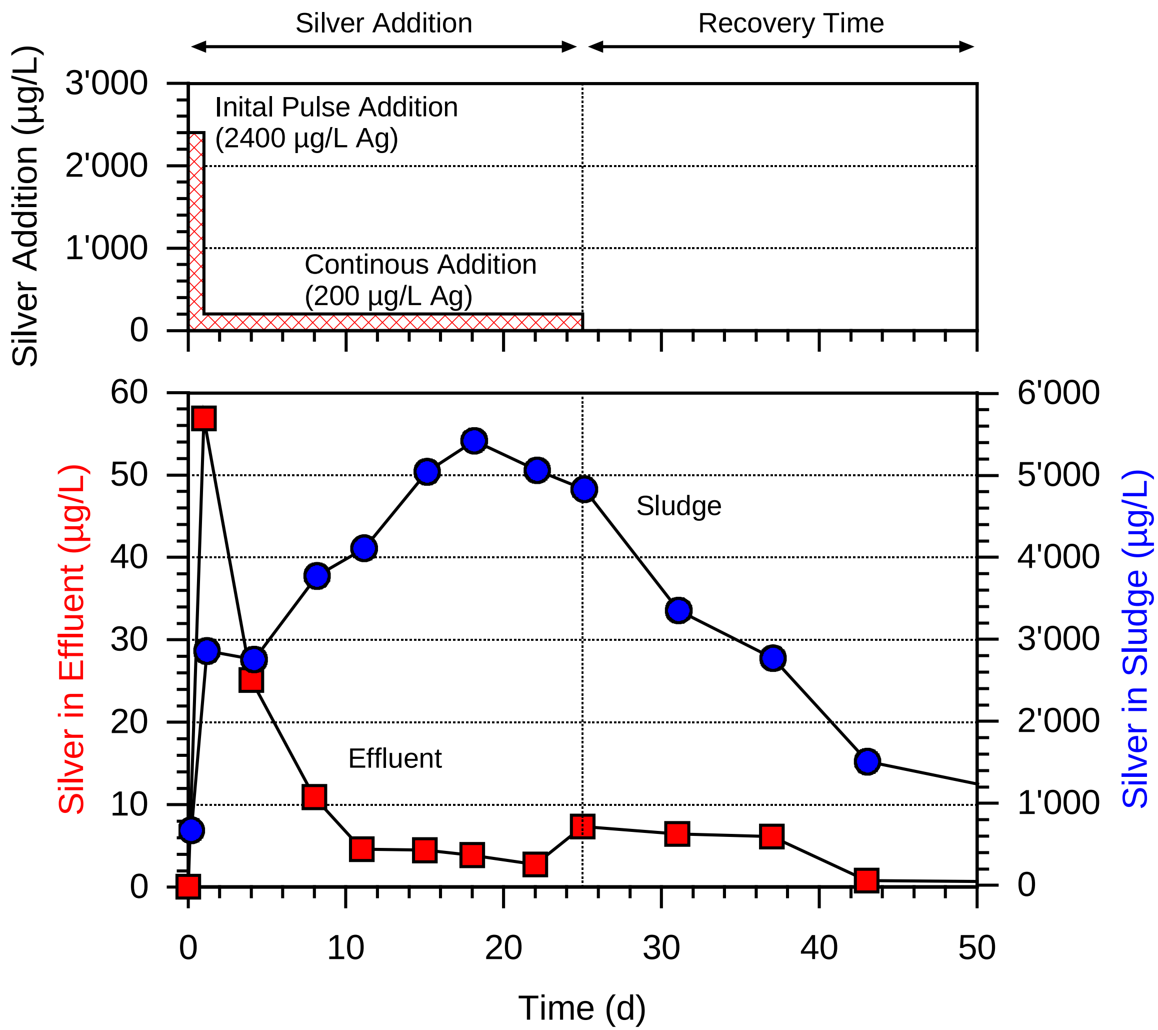
Addition of silver using pump

Effluent of secondary clarifier

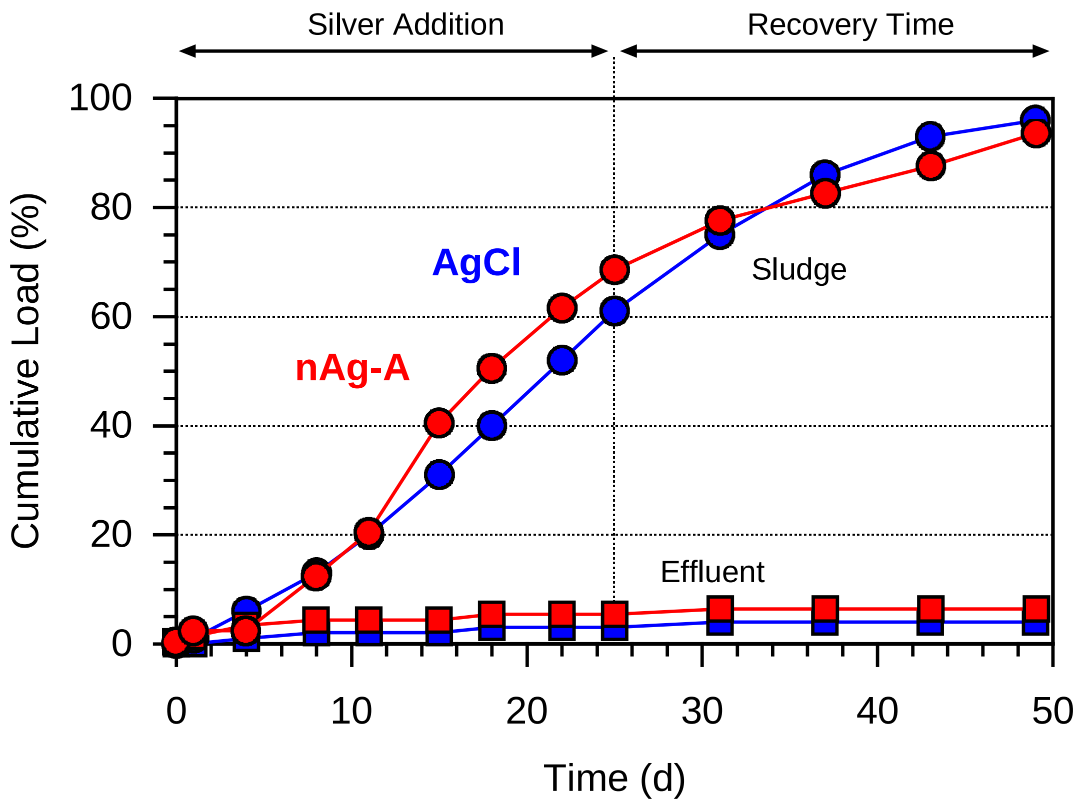
HSR
HOCHSCHULE FÜR TECHNIK
RAPPERSWIL

FHO Fachhochschule Ostschweiz

Silver Concentration in Effluent and Sludge



Cumulative Silver in Sludge and Effluent

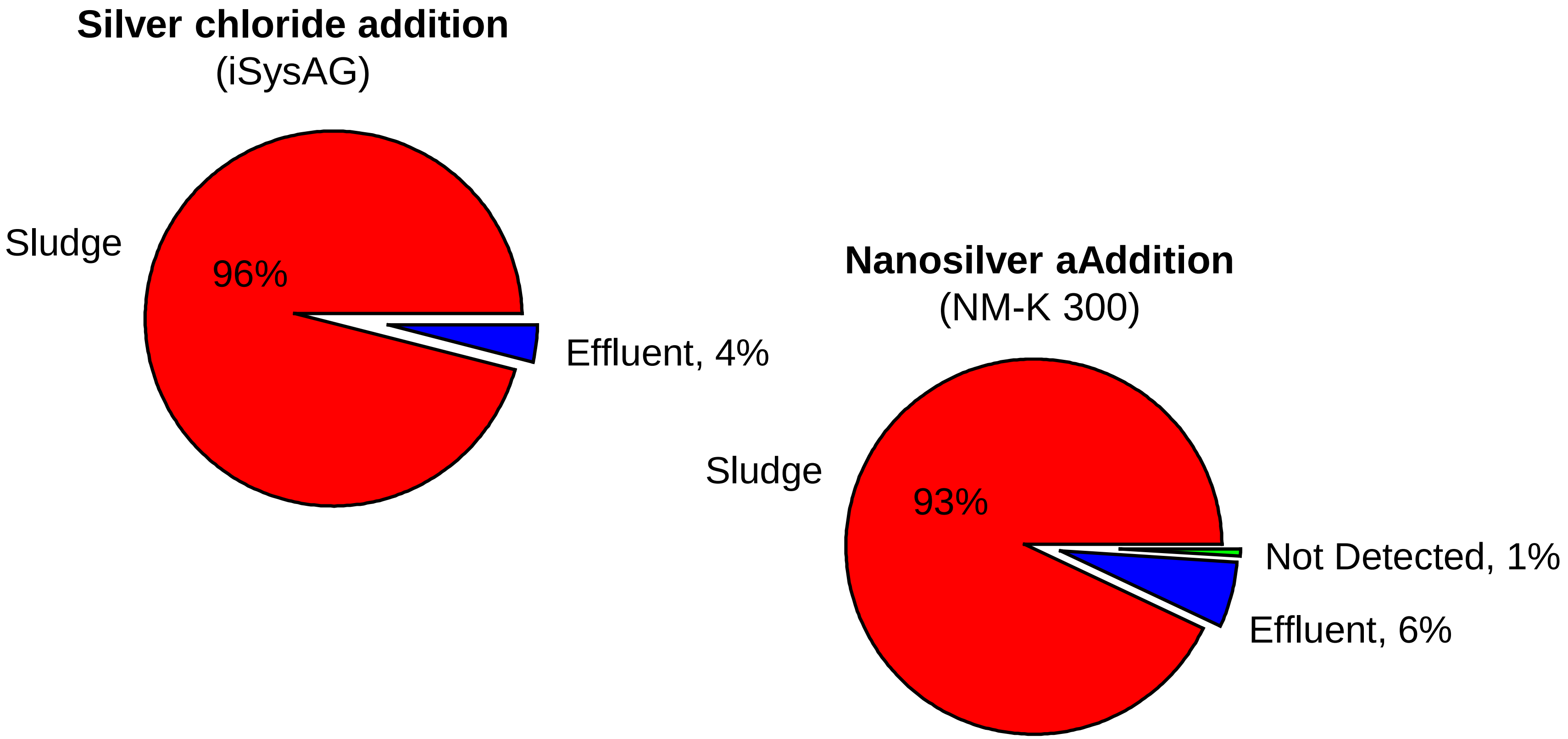


Excellent elimination of particulate silver in WWTP

HSR
HOCHSCHULE FÜR TECHNIK
RAPPERSWIL

FHO Fachhochschule Ostschweiz

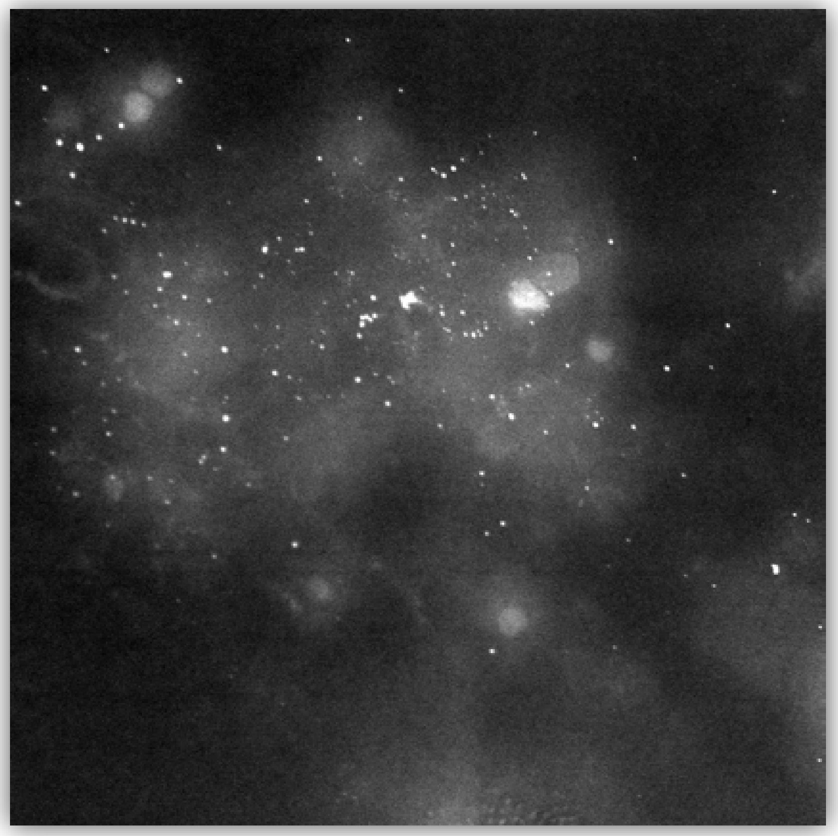
Mass Balance of Silver in Pilot WWTP

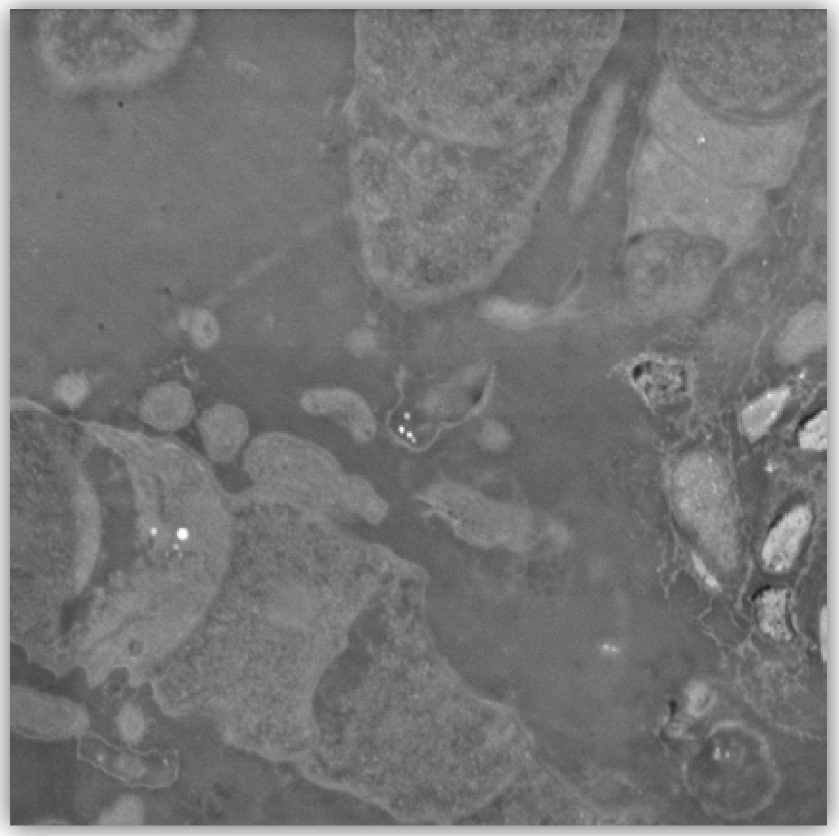


Strong correlation to suspended solids (dry matter)

Silver Particles attached to Activated Sludge Flocs

After Addition of Nanosilver A (NM-K 300)

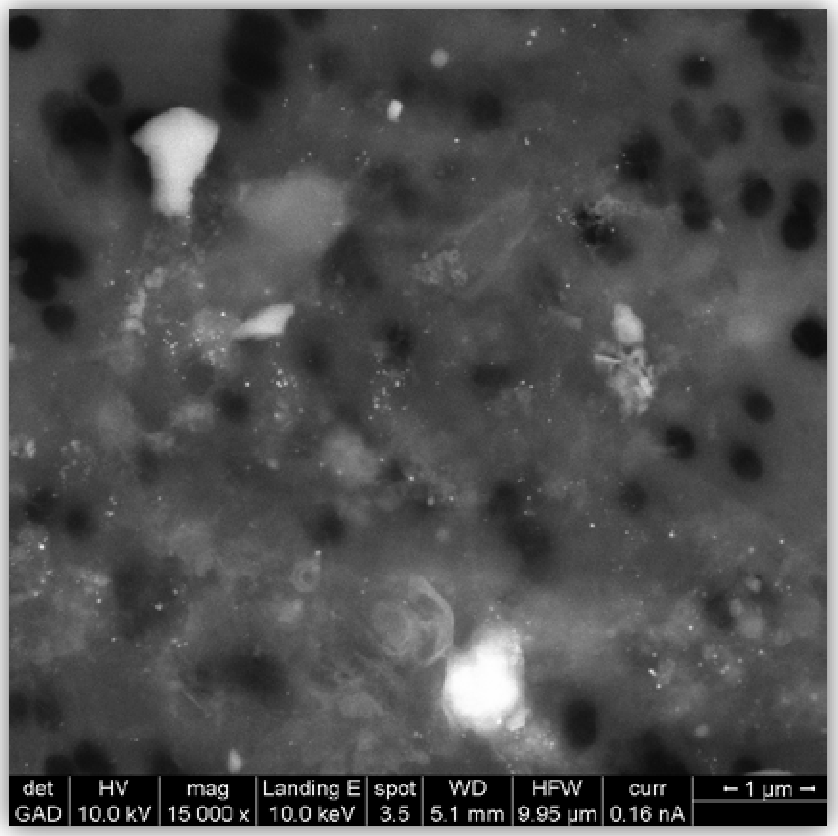


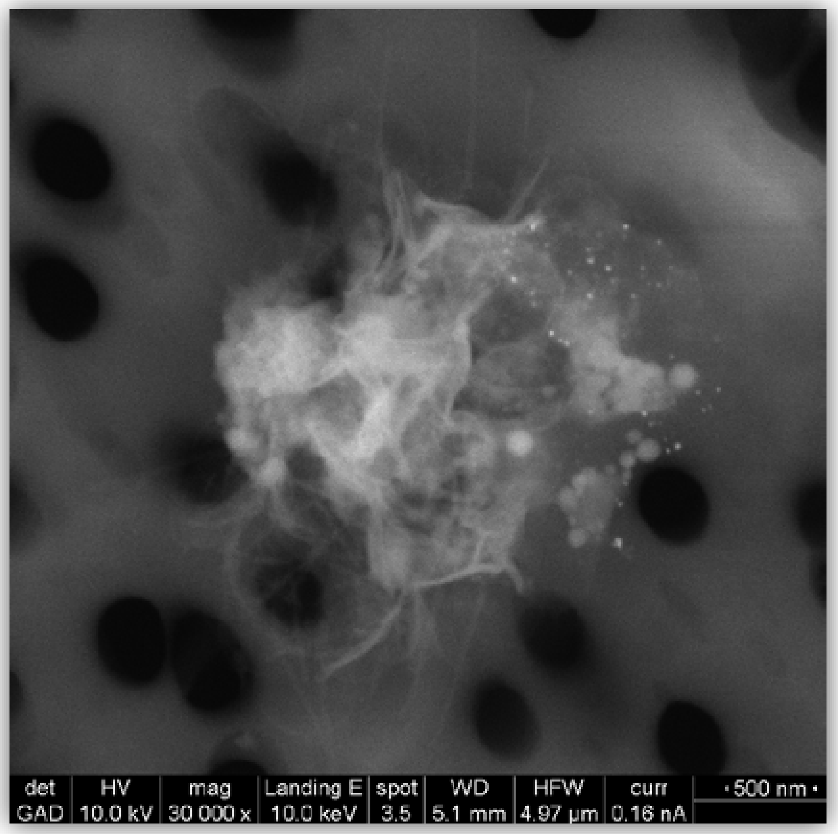


HSR
HOCHSCHULE FÜR TECHNIK
RAPPERSWIL
FHO Fachhochschule Ostschweiz

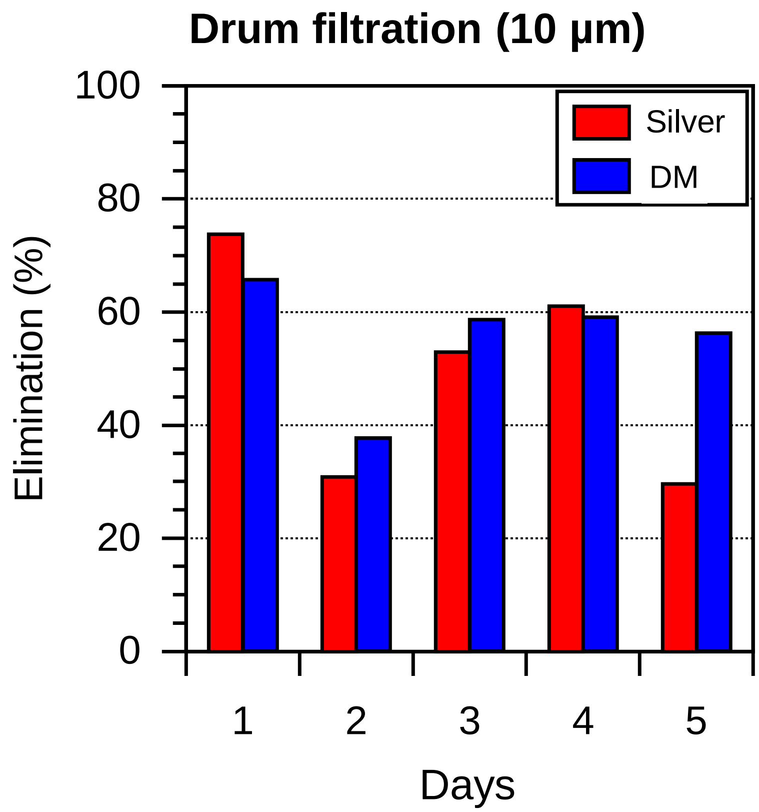
Silver Particles attached to Flocs in Effluent Water

After Addition of Nanosilver A (NM-K 300)





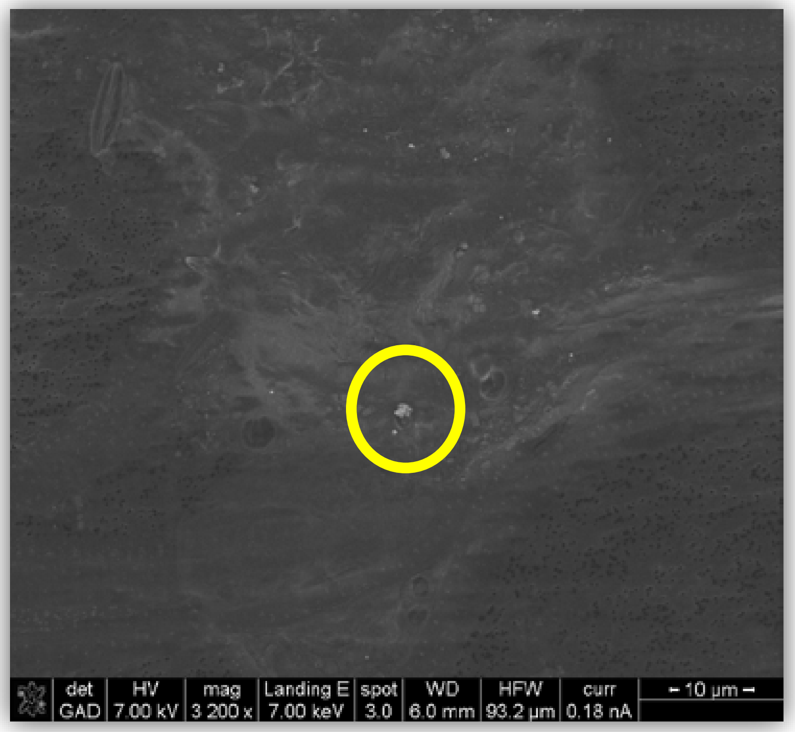
Technology for Tertiary Treatment

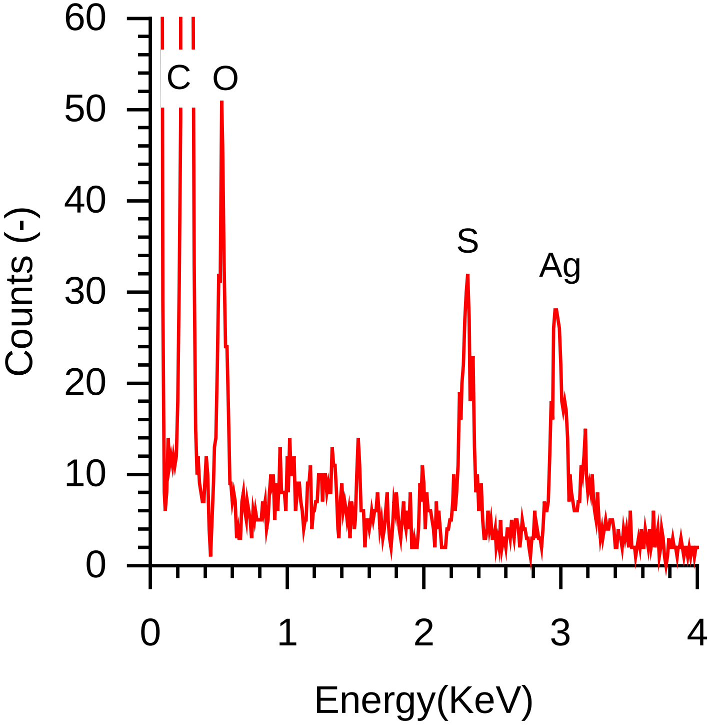


Similar barrier as sand filter

Silver Speciation using EDX

After addition of silver chloride





Rapid silver transformation to silver sulfide in real wastewater

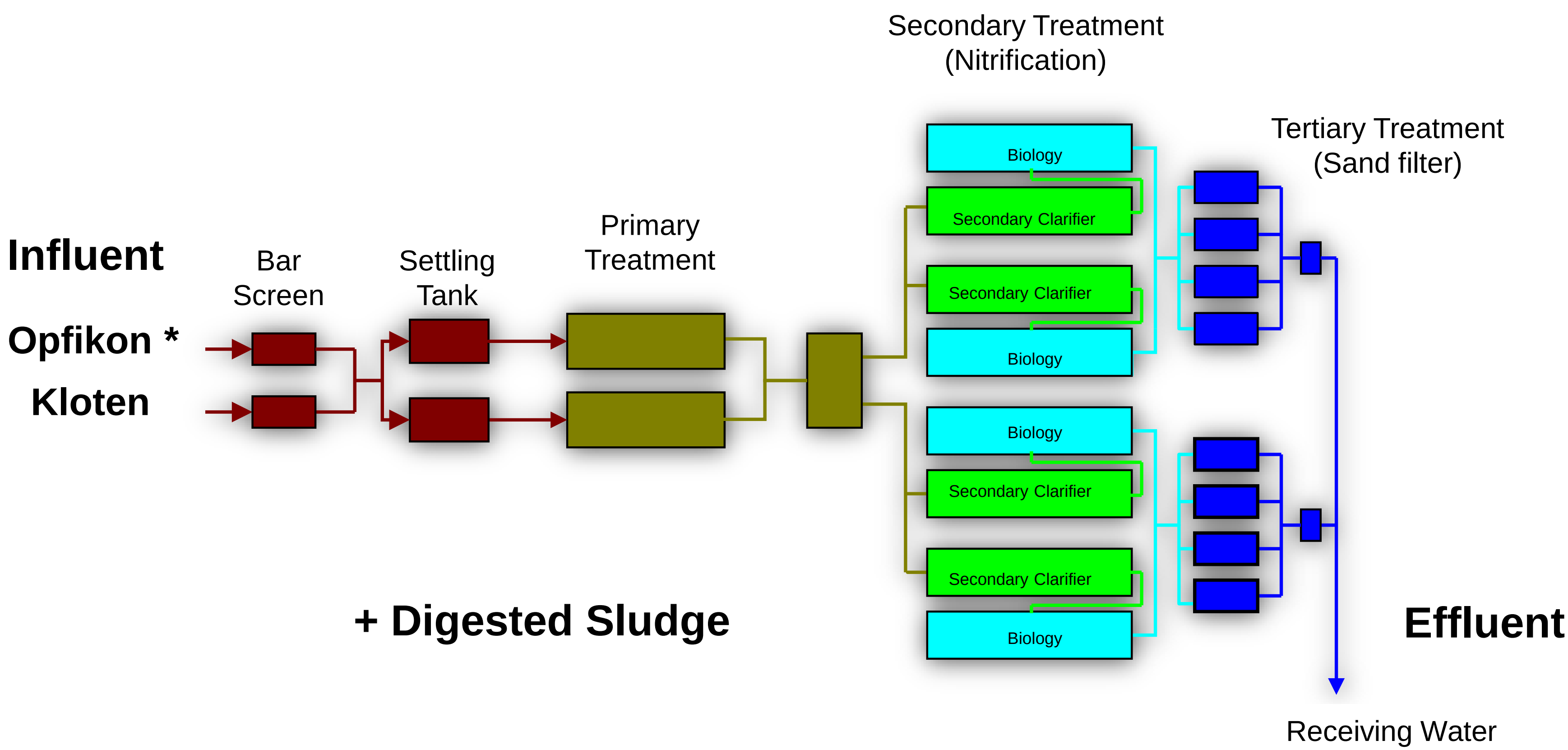
Outline of Presentation

1. Objectives
2. Nitrification Process
3. Pilot Scale WWTP
4. **Full Scale WWTP**
5. Conclusions

Silver Mass Flow in Full Scale WWTP

Kloten/Opfikon for 60'000 inhabitant equivalent

Sampling Scheme in WWTP



* Discharge of silver from an industrial laundry using AgCl. Application stopped completely 2010.

Mass Flow of Silver in WWTP

Daily composite samples of dry weather flow

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

* Worst-case related to industrial laundry (application stopped 2010)
** Corresponding with background concentration

→ **Silver present as silver sulfide**

Outline of Presentation

1. Objectives
2. Transfer Pathways
3. Sources
4. Fate
5. **Conclusions**

Conclusions to Nanosilver / Particulate Silver

Emission

- Small amounts release to wastewater (e.g. from coating, laundry)
- Low influent concentrations of WWTP (even under worst-case conditions)
- Occurrence mainly as AgS attached to larger particles

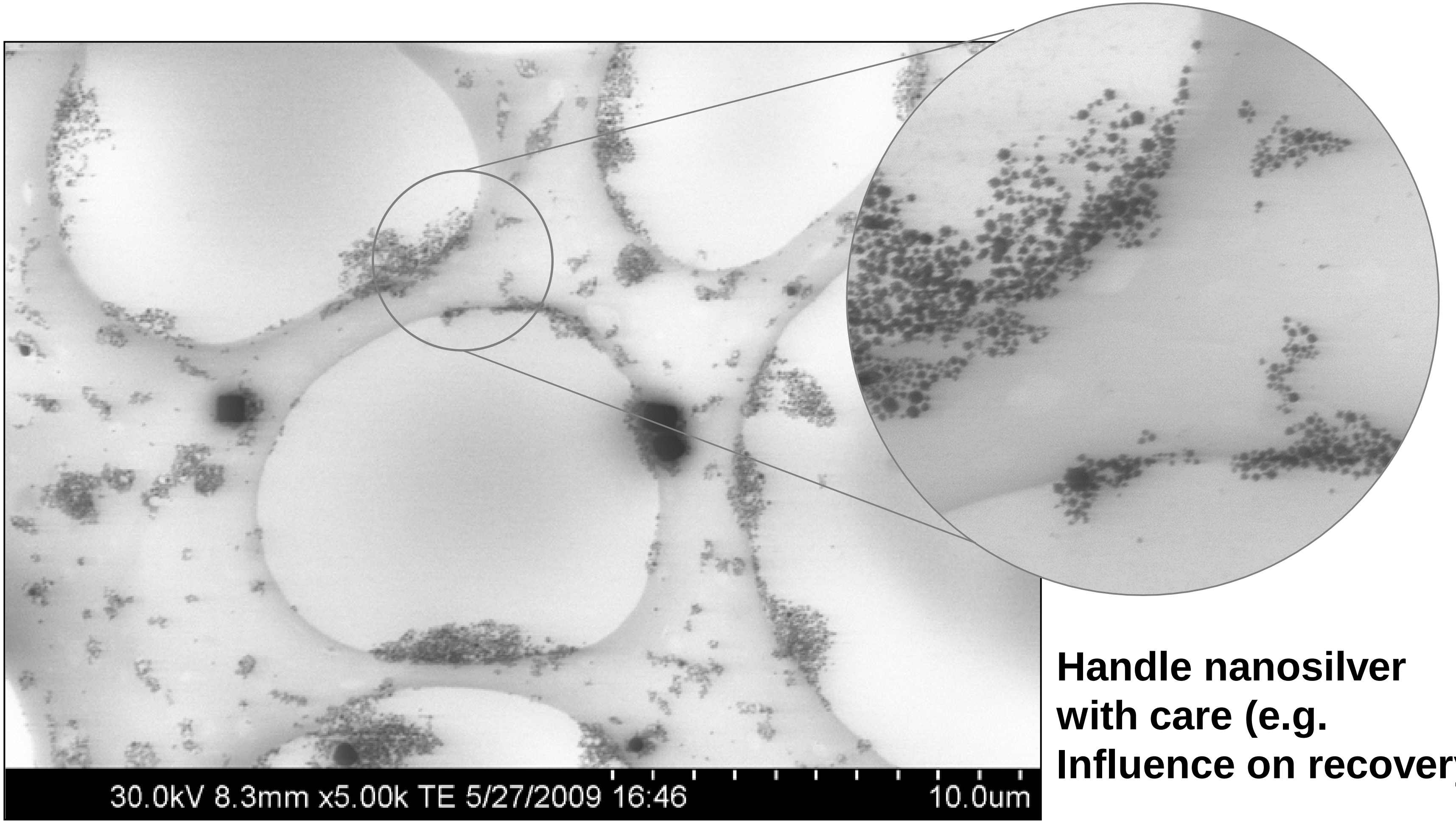
Fate in WWTP

- No effect on nitrification process (microbial activity not inhibited)
- Excellent elimination (95-99%) which is similar to CeO and TiO_2 (in Switzerland micropollutants elimination >80% in the future)
- Attached to sludge flocs (thus filtration possible)
- Rapid transformation to insoluble AgS

General remark

- Testing under artificial laboratory conditions (matrix, concentration, coating) gives limited insight to environmental behavior (but to processes)
- Up-to-date testing, sampling, analysis are required (chemical, physical, visual)

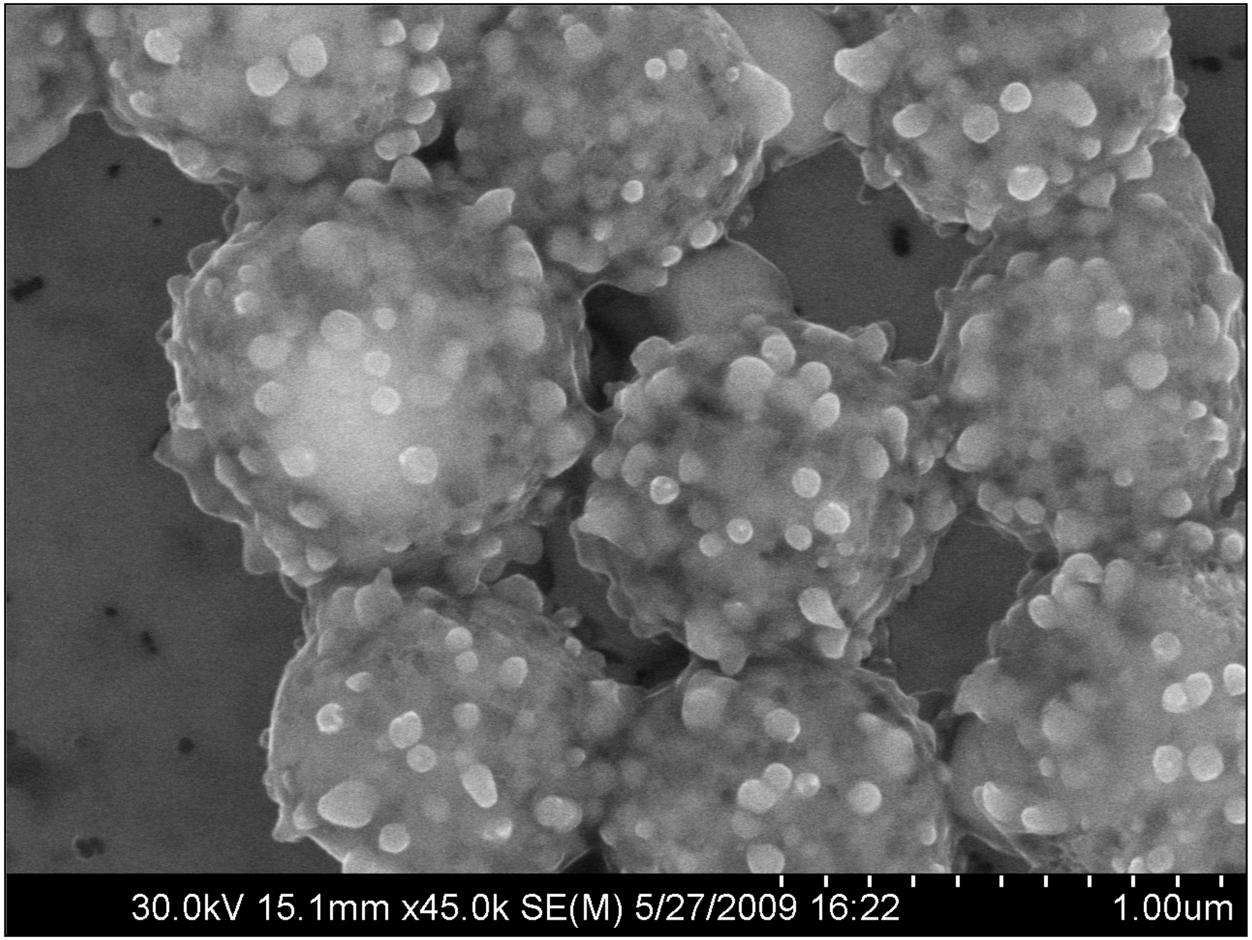
Adsorption at Air–Water Interfaces



Handle nanosilver with care (e.g. Influence on recovery)

HSR
HOCHSCHULE FÜR TECHNIK
RAPPERSWIL
FHO Fachhochschule Ostschweiz

Reduction of AgCl to Ag^0 by Electron Beam (SEM)



Handle AgCl with care in tests

Acknowledgements

Partner

- Eawag (Swiss Federal Institute of Aquatic Science and Technology)

Funding

- Swiss Federal Office for the Environment (FOEN), Berne
- Cantonal Office for Waste, Water, Energy and Air (AWEL), Zurich

Literature

- Burkhardt et al. (2009): Nanopartikel in Fassadenbeschichtungen - Charakterisierung, Auswaschung und Vergleich mit organischen Bioziden. BAFU-Bericht, 25 S.
- Zuleeg et al. (2009): Charakterisierung und Bilanzierung von Silberpartikeln in Abwasserreinigungsanlagen. BAFU-Bericht, 29 S.
- Kägi et al. (2010): Release of Silver Nanoparticles from Outdoor Facades. Environmental Pollution, 158:2900-2905.
- Burkhardt et al. (2010): Verhalten von Nanosilber in Kläranlagen und dessen Einfluss auf die Nitrifikationsleistung in Belebtschlamm. Umweltwissenschaften und Schadstoff-Forschung (UWSF), 22:529–540.
- Burkhardt (2010): Das Beispiel Nanosilber. Umwelt Perspektiven, 6:14-16.
- Kägi et al. (2011): Behavior of metallic silver nanoparticles in a pilot wastewater treatment plant. ES&T, 45:3902-3908.
- Burkhardt et al. (2011): Entsorgung nanosilberhaltiger Abfälle in der Textilindustrie - Massenflüsse und Behandlungsverfahren. Forschungsbericht, HSR Hochschule für Technik, Rapperswil, Schweiz.
- Kägi (2012): Fate and Behaviour of Silver Nanoparticles in Urban Wastewater Systems. Water Science & Technology (submitted)

Thank you for Attention !

Michael Burkhardt
HSR University of Applied Sciences Rapperswil
Institute of Environmental and Process Engineering (UMTEC)
Switzerland

Berlin, 8th/9th January 2012

HSR
HOCHSCHULE FÜR TECHNIK
RAPPERSWIL

FHO Fachhochschule Ostschweiz

UMTEC INSTITUT FÜR UMWELT- UND VERFAHRENSTECHNIK