

Silver Particles in Wastewater Treatment Plants

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Outline of Presentation

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



Antibacterial Effect of Silver Nanoparticles Produced by Fungal Process on Textile Fabrics and Their Effluent Treatment

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Microorganisms play an important role in textile effluent remediation through reduction of silver ions. Studies demonstrated that silver ions may be reduced extracellularly using *Fusarium* to generate stable gold or silver nanoparticles in water. These particles can be incorporated into textile fabrics to provide antibacterial activity.

Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics

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Manufacturers of clothing articles employ nanosilver (n-Ag) as an antimicrobial agent, but the environmental impacts of n-Ag released from commercial products are unknown. The quantity and form of the nanomaterials released from consumer products should be determined to assess the environmental risks of nanotechnology. This paper investigates silver released from commercial clothing (socks) into water, and its fate in wastewater treatment plants (WWTPs). Six types of socks contained up to a maximum of 1300 µg Ag/g-sock and leached as much as 100 µg of silver in 500 mL of distilled water. Microscopy conducted on sock material and wash water revealed the presence of silver particles from 10 to 500 nm in diameter. Physical sequestration and ion selective electrode

toxicity of nanoparticle silver to bacteria suggesting that the antimicrobial effects of silver are detrimental to aquatic ecosystems. Therefore, to characterize (as colloidal or ionic) and quantify n-Ag released from commercial products, n-Ag could potentially compromise the health of ecosystems. For example, household washing or n-Ag could potentially compromise the health of ecosystems. For example, household washing or n-Ag could potentially compromise the health of ecosystems. For example, household washing or n-Ag could potentially compromise the health of ecosystems.

Ecosystem protection by effluent bioremediation: silver nanoparticles impregnation in a textile fabrics process

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Abstract Nanosilver particles (n-Ag) impregnated in textile fabrics can be used for antimicrobial protection. However, the release of n-Ag into the environment via agricultural land application of wastewater biosolids. If n-Ag proves to be difficult to remove in a wastewater treatment system, n-Ag remaining in a treated effluent stream may enter surface water environments, potentially disrupting numerous biological ecosystems. This paper investigates n-Ag release from commercial clothing (specifically, socks) into water, as well as the form of this silver and the adsorption characteristics that determine its fate in WWTPs. The amount of n-Ag in the sock fabric was quantified before determining the concentration and form (nanoparticle or ionic) of the silver released during repeated washings of the socks with distilled water. Batch adsorption isotherm studies were conducted with wastewater biomass and two sources of silver: (1) silver released from the socks into the wash water (nanoparticle or ionic), and (2) inorganic ionic silver. These isotherms were then used with a nitrification

the elimination of silver nanoparticles remaining in the wash water. The bacteria after biosorption were morphologically transformed, but the normal morphology after stress culture was completely recovered. The process also allowed the recovery of silver material that was leached into the effluent. In situ nitrification avoiding any effect in the eco-environment.

Keywords Silver nanoparticles • *Fusarium* • *Chromobacterium* • Bioremediation • Eco-environment • Health effects • EHS

Who cares on Silver Release and Pathways to Water?

Release
(Emission)

Façade



Laundry

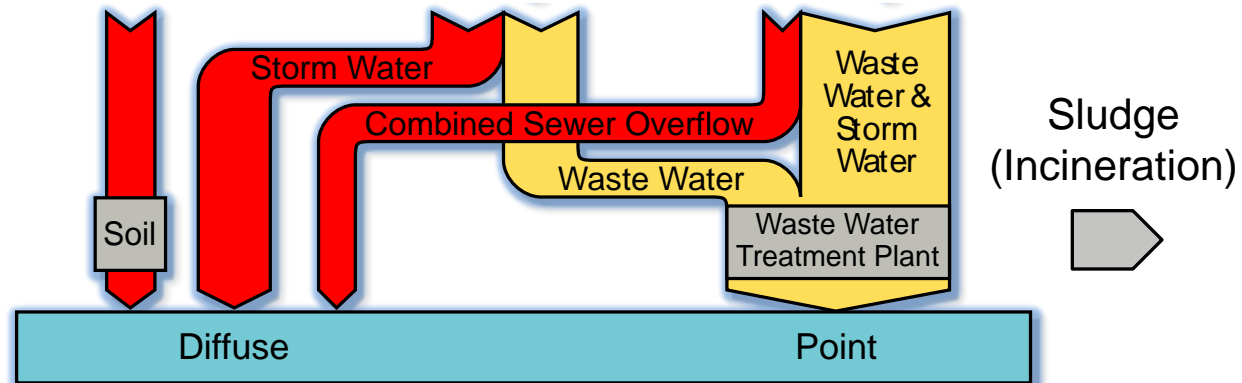


Pathways

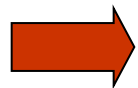
Stormwater
Infiltration

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”?*

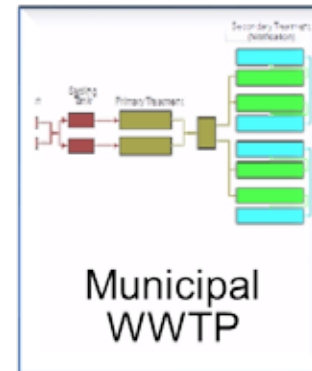
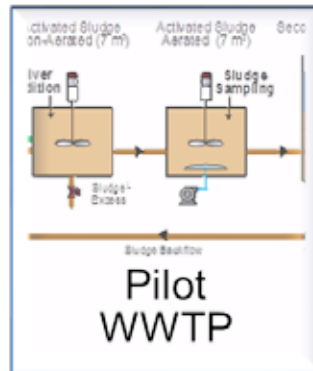
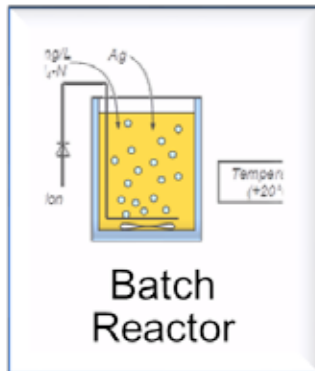
- n In Europe <50 t/a particulate silver in use, <4 t/a Ag for textiles (90% AgCl)
- n 30% of all nano-projects dealing with “nanosilver” (Maynard 2006)

	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

- n Influence on nitrification in activated sludge
(silver chloride, metallic nanosilver, metallic microcomposite silver)
- n Mass balance in a pilot WWTP with 70 equivalent inhabitants
(silver chloride, metallic nanosilver)
- n 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**

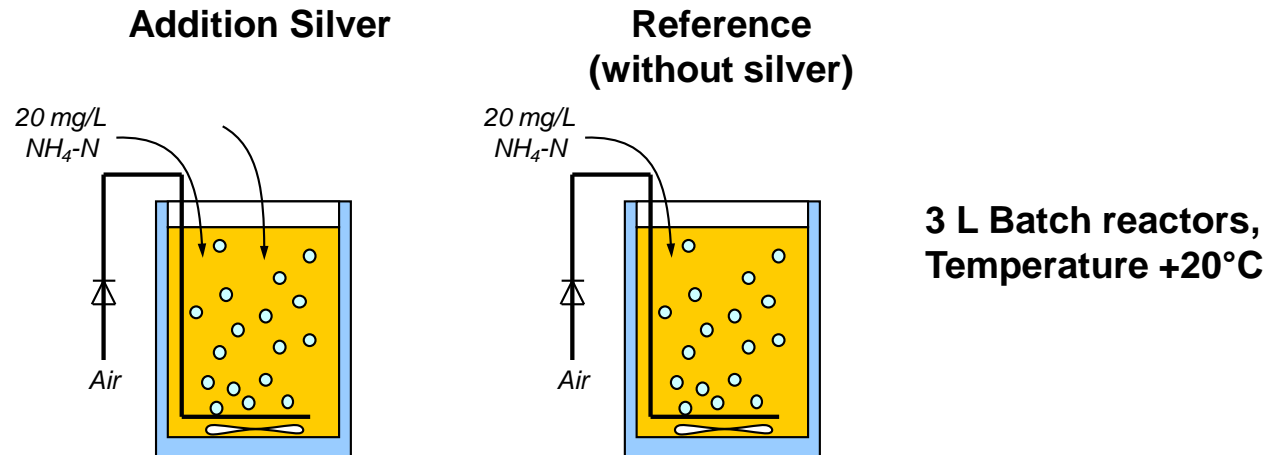
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- 2. Nitrification Process**
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Nitrification Inhibition Test with Real Activated Sludge

Aerated batch reactors operated with 3 L activated sludge

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

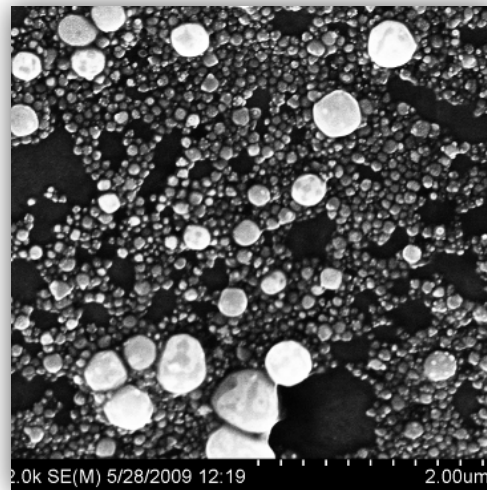


Tested Silver Forms (Market Products)

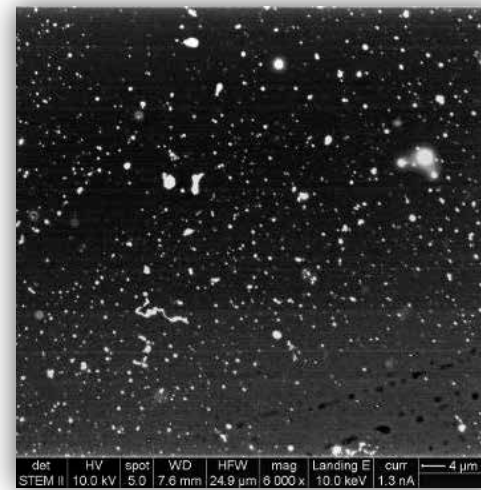
Silver Forms		Product
Silver nitrate (Reference)	AgNO_3	-
Silver Chloride	AgCl	iSys AG
Metallic Nanosilver A	nAg-A	AgPure WS10 *
Metallic Nanosilver B	nAg-B	SmartSilver Pro
Metallic Microcomposite Silver	Micro	HeiQ AGS-20

* Similar to JRC
NM-300 K

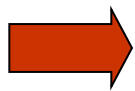
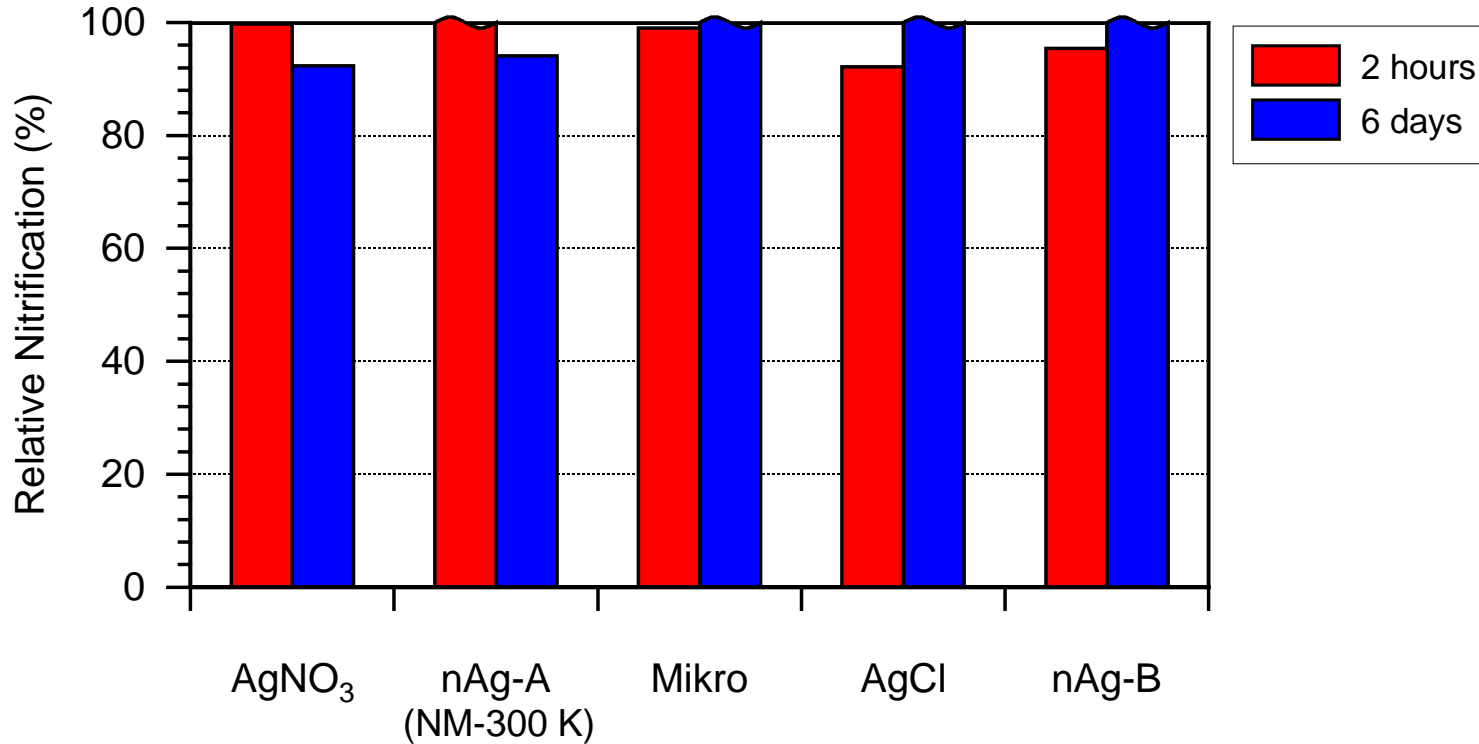
**Silver Chloride
(iSysAG)**



**Metallic
Nanosilver A
(NM-300 K)**

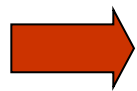
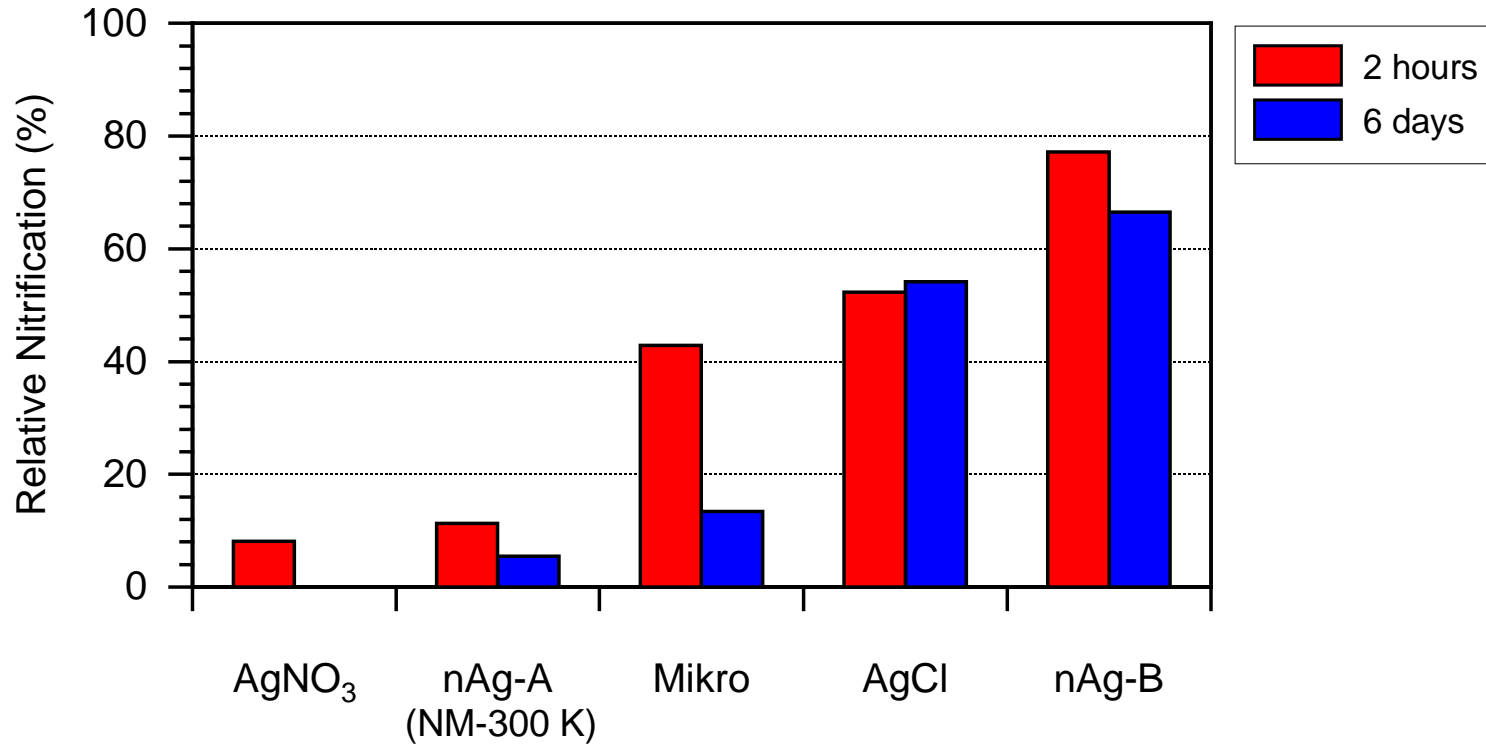


Nitrification Results of 1 mg/L Silver Addition



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



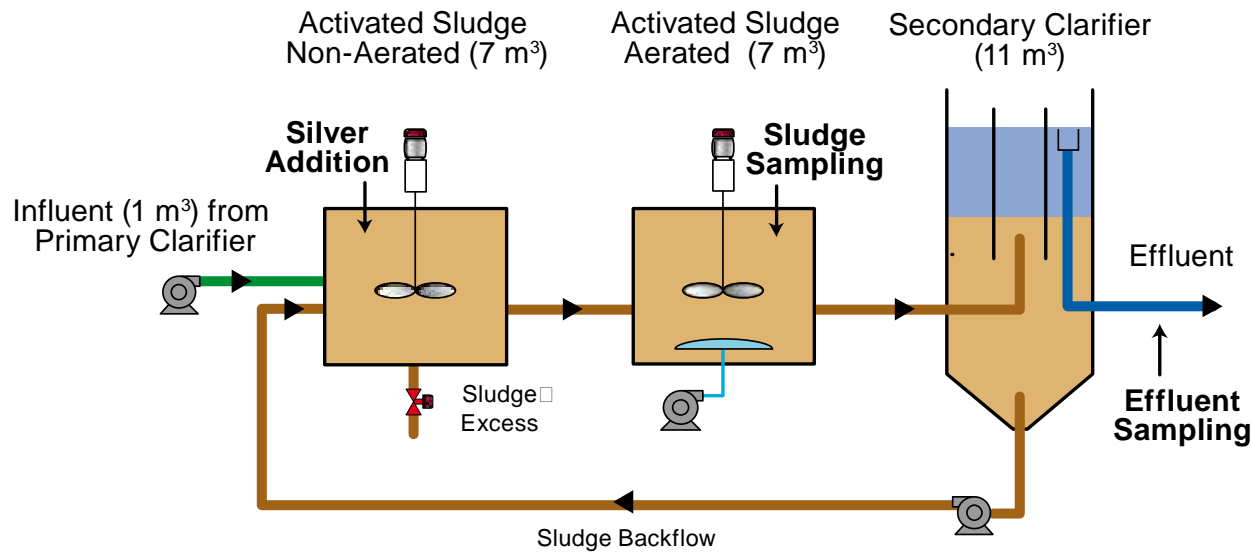
Conditions reflecting our scientific interest in processes (25 g Ag /kg TS overburdened the test system)

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Mass Flow in Pilot Scale WWTP (70 Equivalent Inhabitants)

- n Plant operated under conditions similar to full-scale WWTP
 - n Inflow 1 m³/h wastewater directly from combined sewer system
 - n Activated sludge with 12 days age and 3 g/L dry matter (DM)
- n Addition of “nanosilver A (nAg-A)” and “silver chloride (AgCl)” (25 days)
 - n 2400 µg/L Ag for 1 day (pulse for rapid equilibrium)
 - n 200 µg/L Ag for 24 days (continuous)
 - n Sampling of effluent and sludge



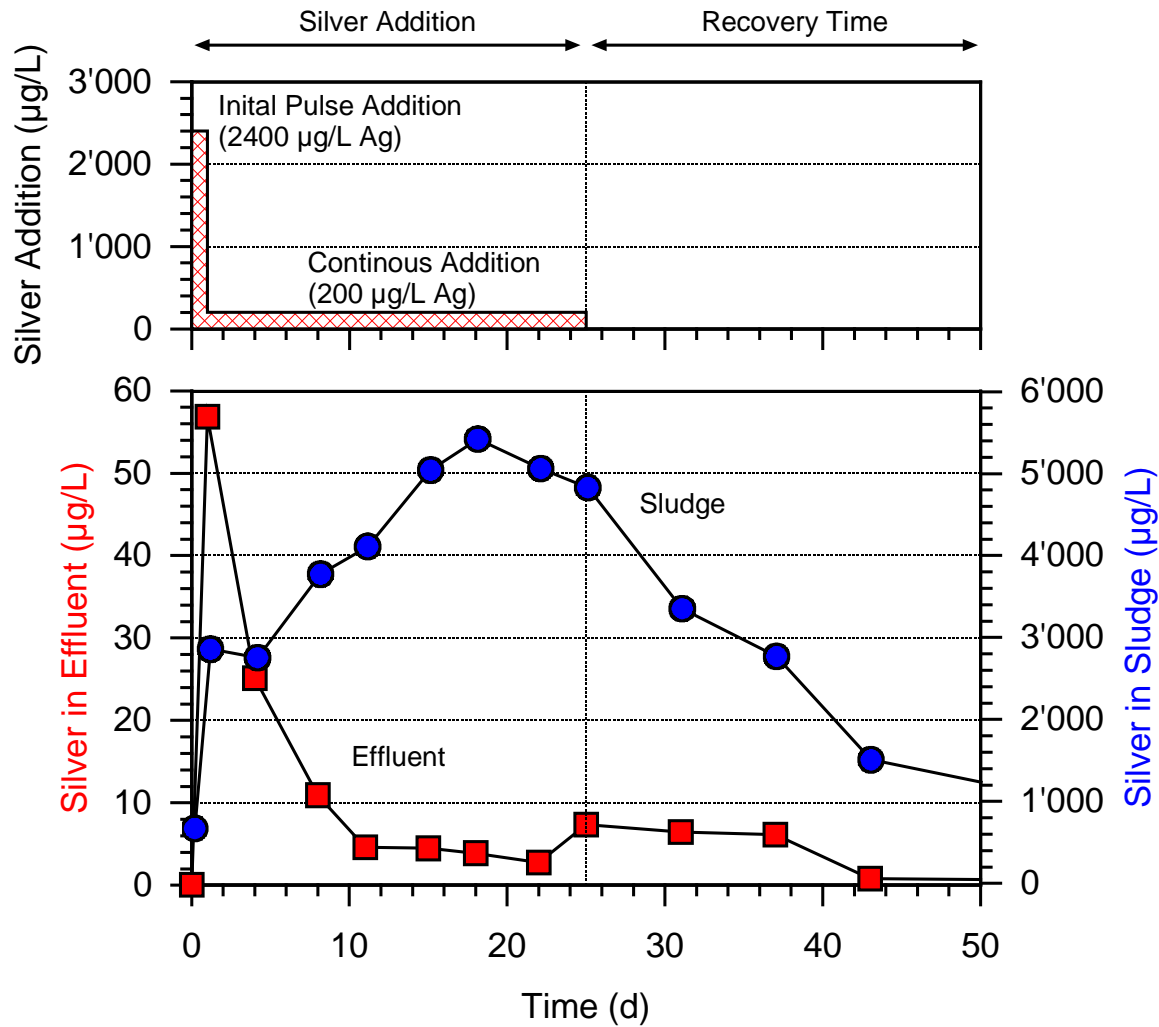
Addition of silver using pump



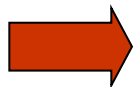
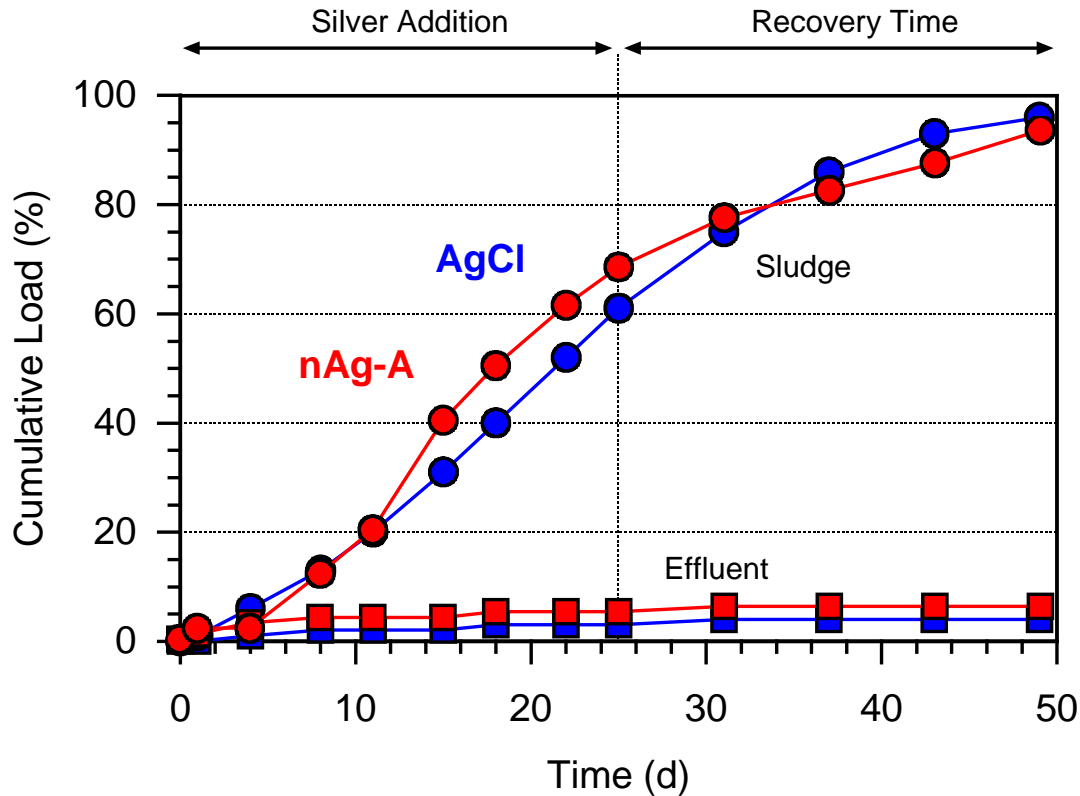
Effluent of secondary clarifier



Silver Concentration in Effluent and Sludge



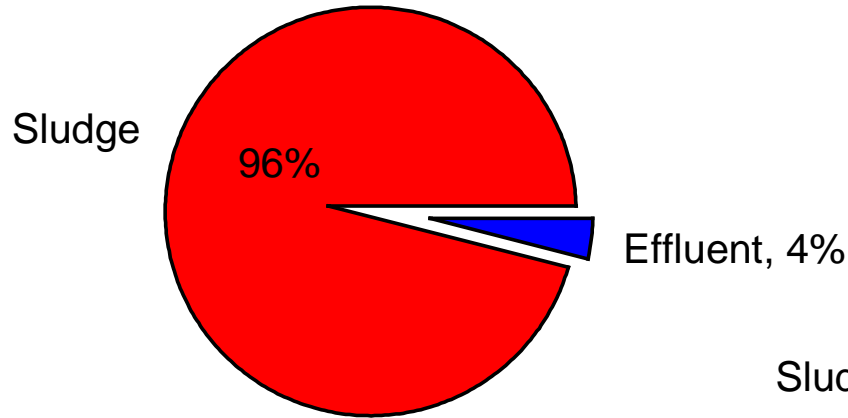
Cumulative Silver in Sludge and Effluent



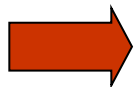
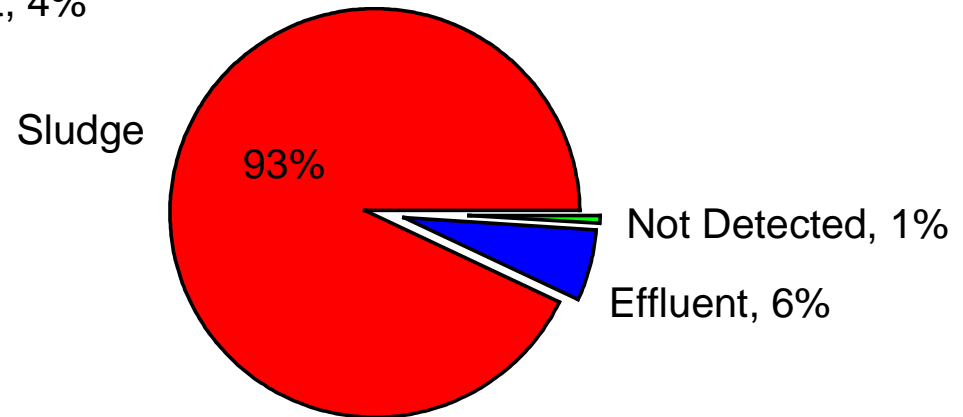
Excellent elimination of particulate silver in WWTP

Mass Balance of Silver in Pilot WWTP

**Silver chloride addition
(iSysAG)**



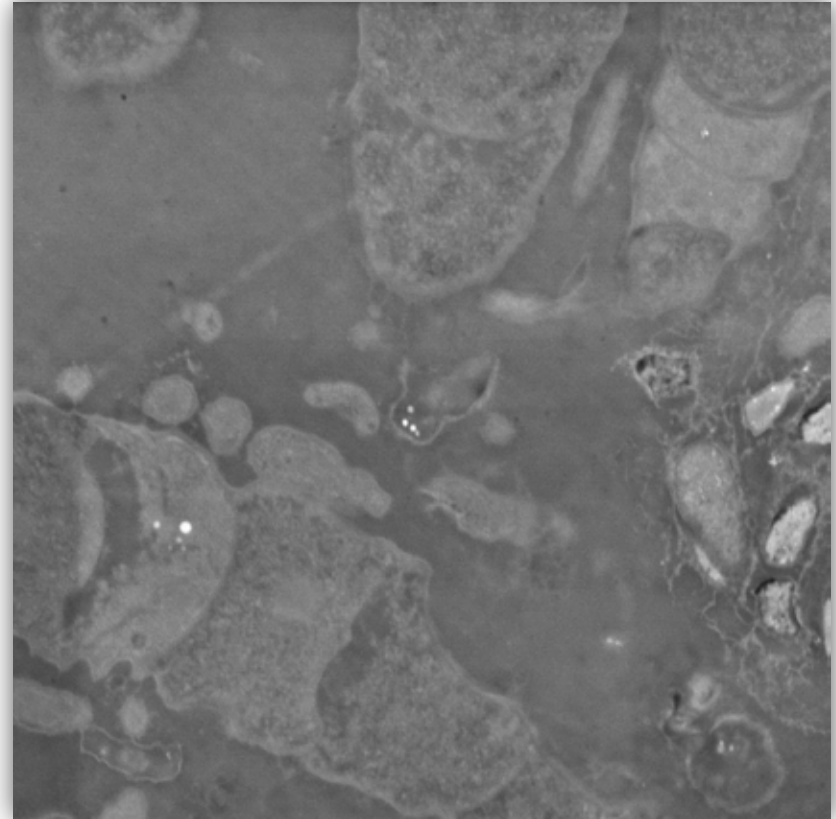
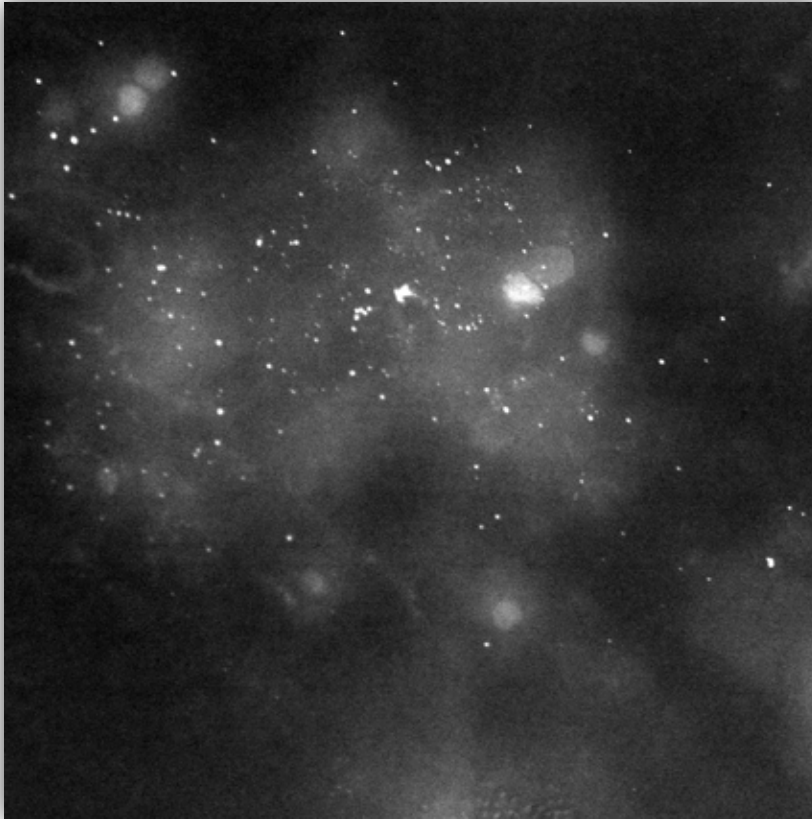
**Nanosilver addition
(NM-K 300)**



Strong correlation to suspended solids (dry matter)

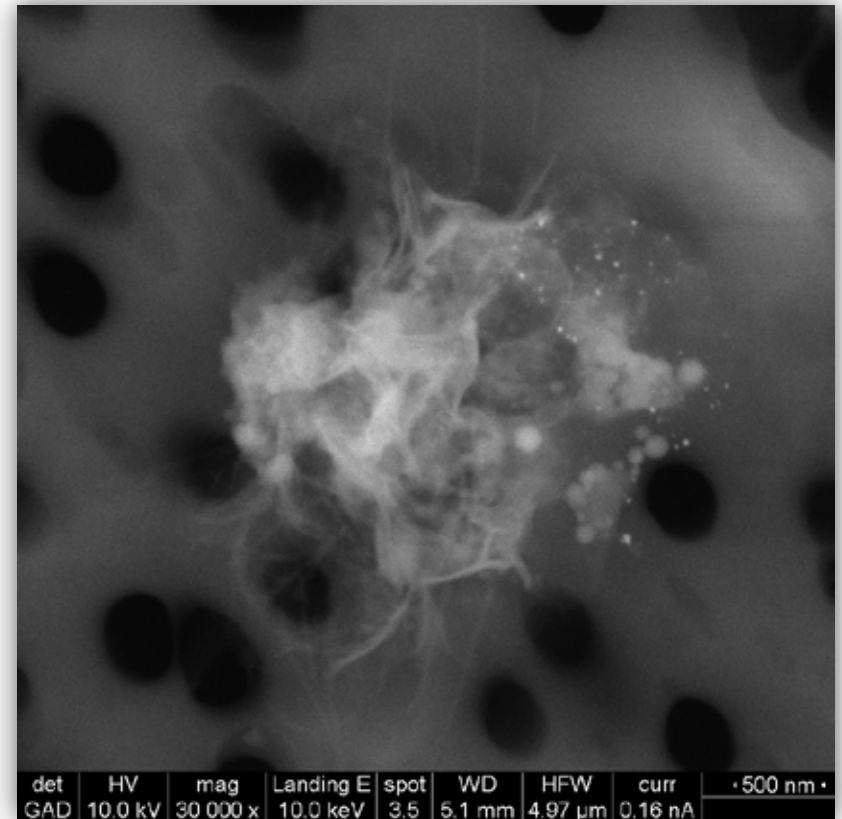
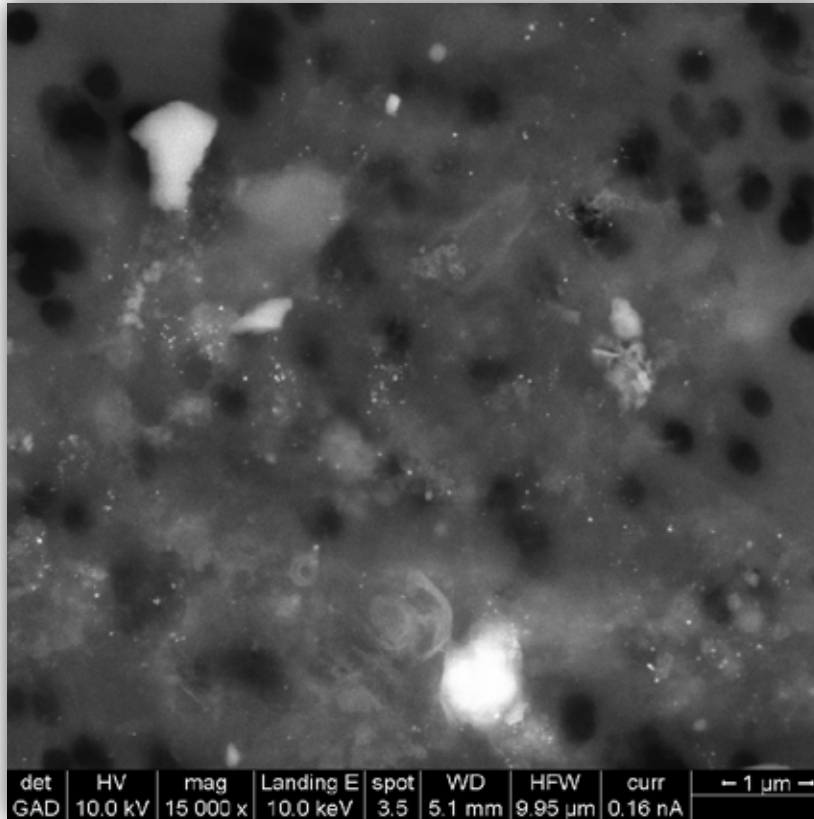
Silver Particles attached to Activated Sludge Flocs

After Addition of Nanosilver A (NM-K 300)

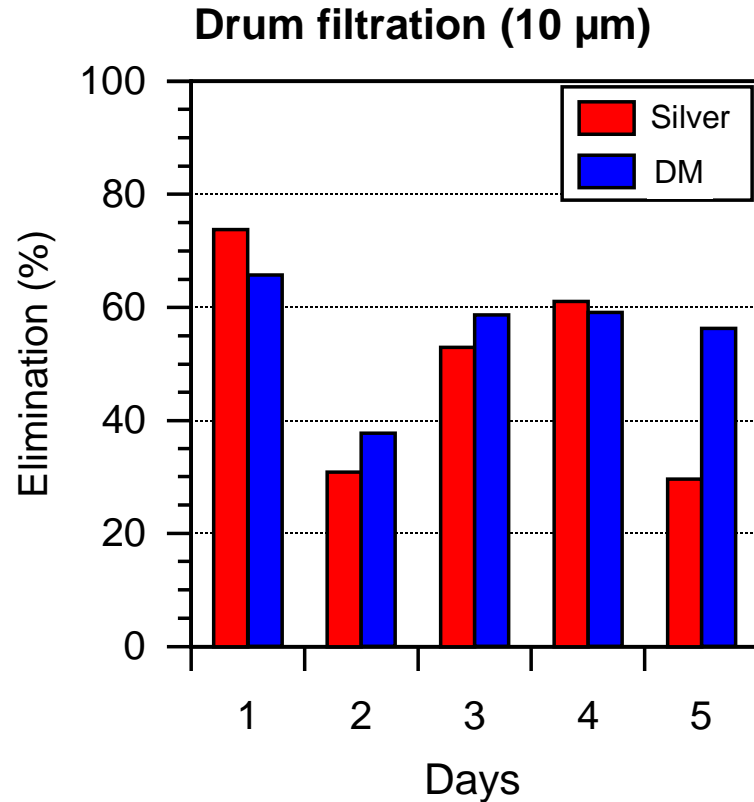


Silver Particles attached to Floccs in Effluent Water

After Addition of Nanosilver A (NM-K 300)



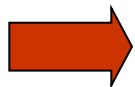
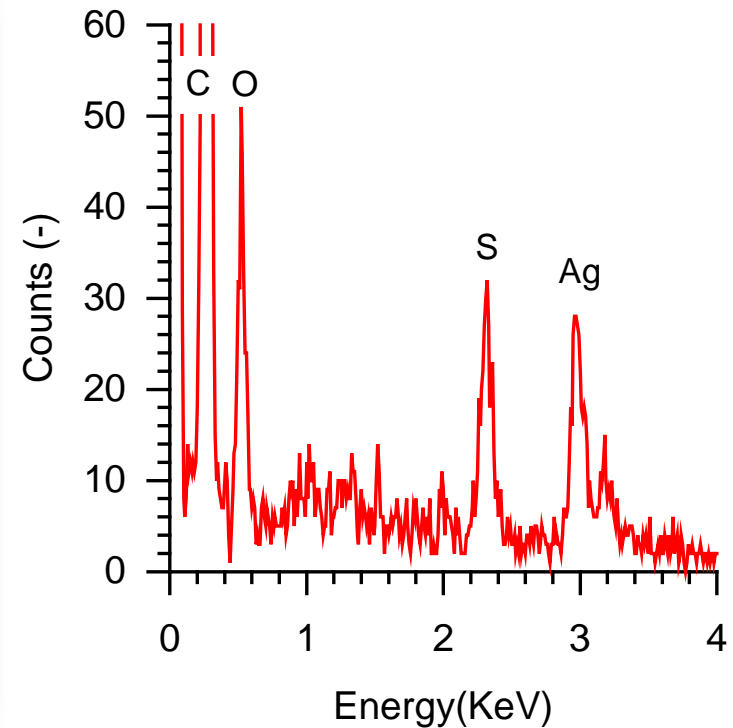
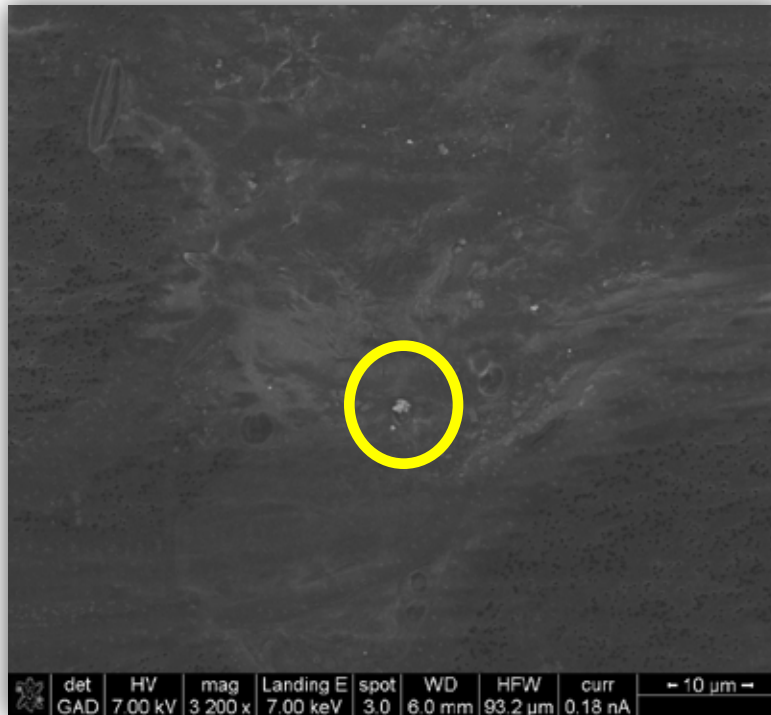
Technology for Tertiary Treatment



 **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

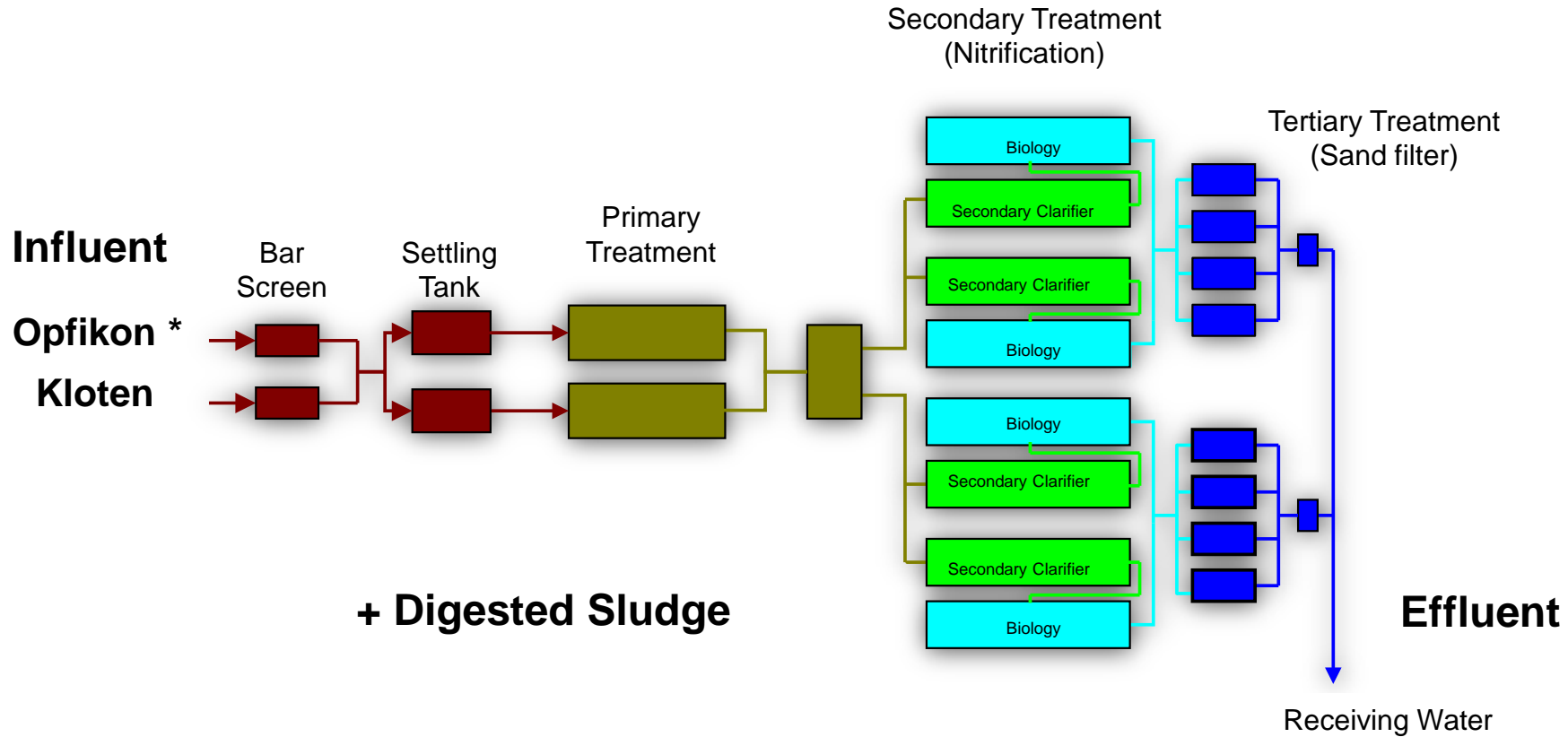
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Silver Mass Flow in Full Scale WWTP

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 ($\mu\text{g Ag /L}$)		Outflow ($\mu\text{g Ag /L}$)		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

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

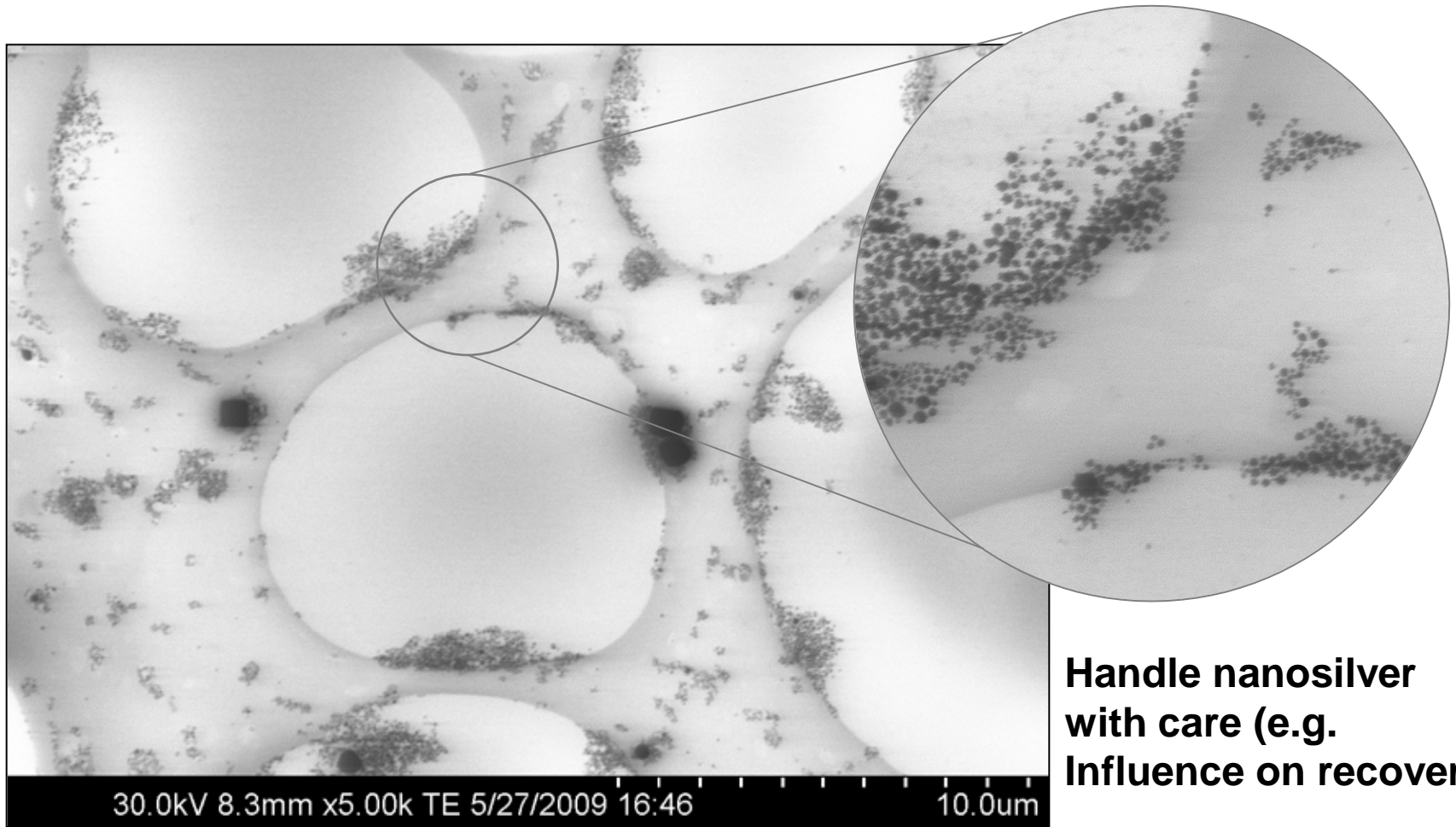
Fate in WWTP

- n No effect on nitrification process (microbial activity not inhibited)
- n Excellent elimination (95-99%) which is similar to CeO and TiO₂
(in Switzerland micropollutants elimination >80% in the future)
- n Attached to sludge flocs (thus filtration possible)
- n Rapid transformation to insoluble AgS

General remark

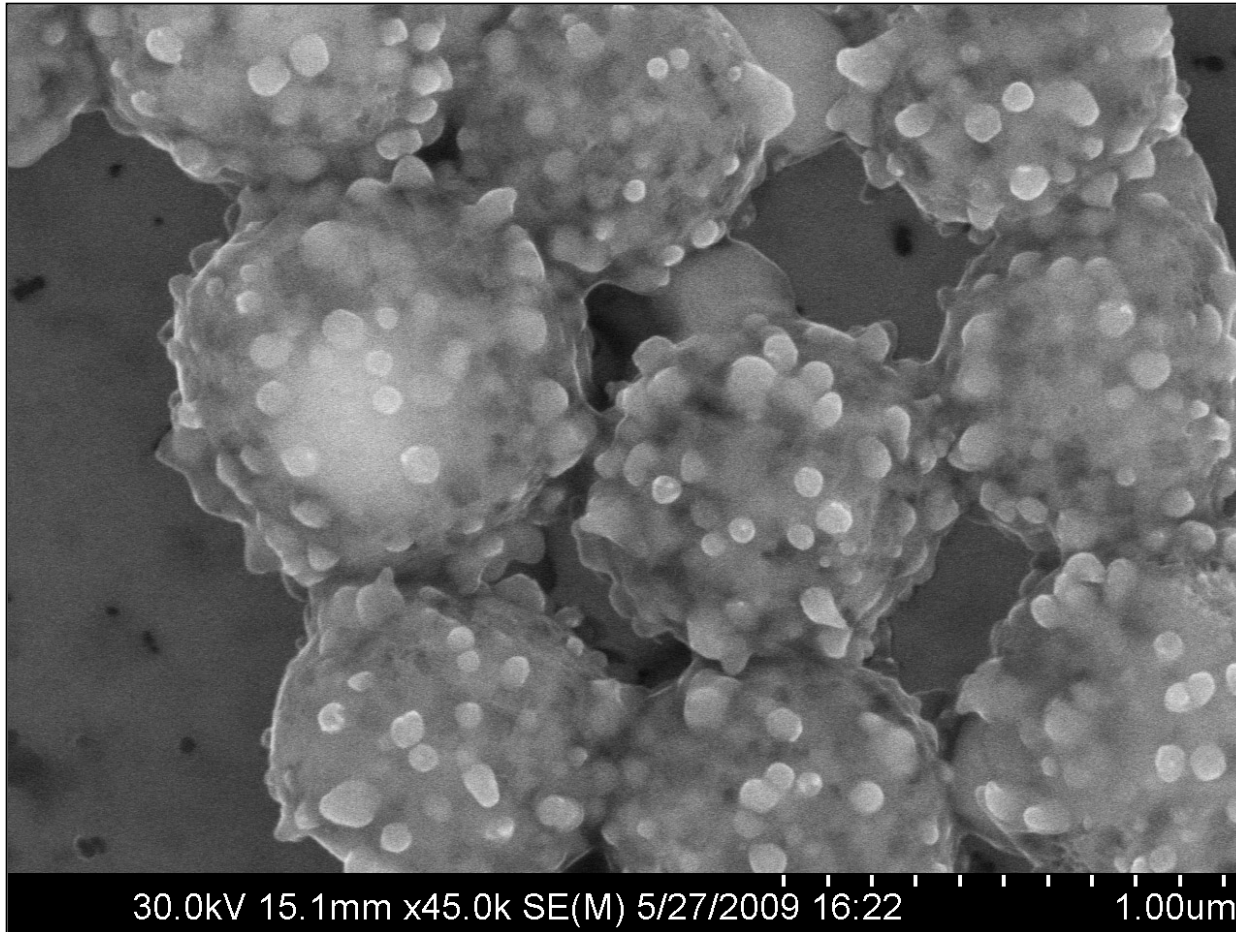
- n Testing under artificial laboratory conditions (matrix, concentration, coating)
gives limited insight to environmental behavior (but to processes)
- n Up-to-date testing, sampling, analysis are required (chemical, physical, visual)

Adsorption at Air–Water Interfaces



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

Reduction of AgCl to Ag⁰ by Electron Beam (SEM)



**Handle AgCl
with care in tests**

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- n Cantonal Office for Waste, Water, Energy and Air (AWEL), Zurich

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Thank you for Attention !

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