# Measurement of manufactured nanomaterials in environmental samples

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**on behalf of**

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Scientific Stakeholder Meeting on

Nanomaterials in the Environment

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# Nanomaterials in the aquatic environment

NP origin, challenges & solutions

**challenges for the determination of NPs in environmental samples:**

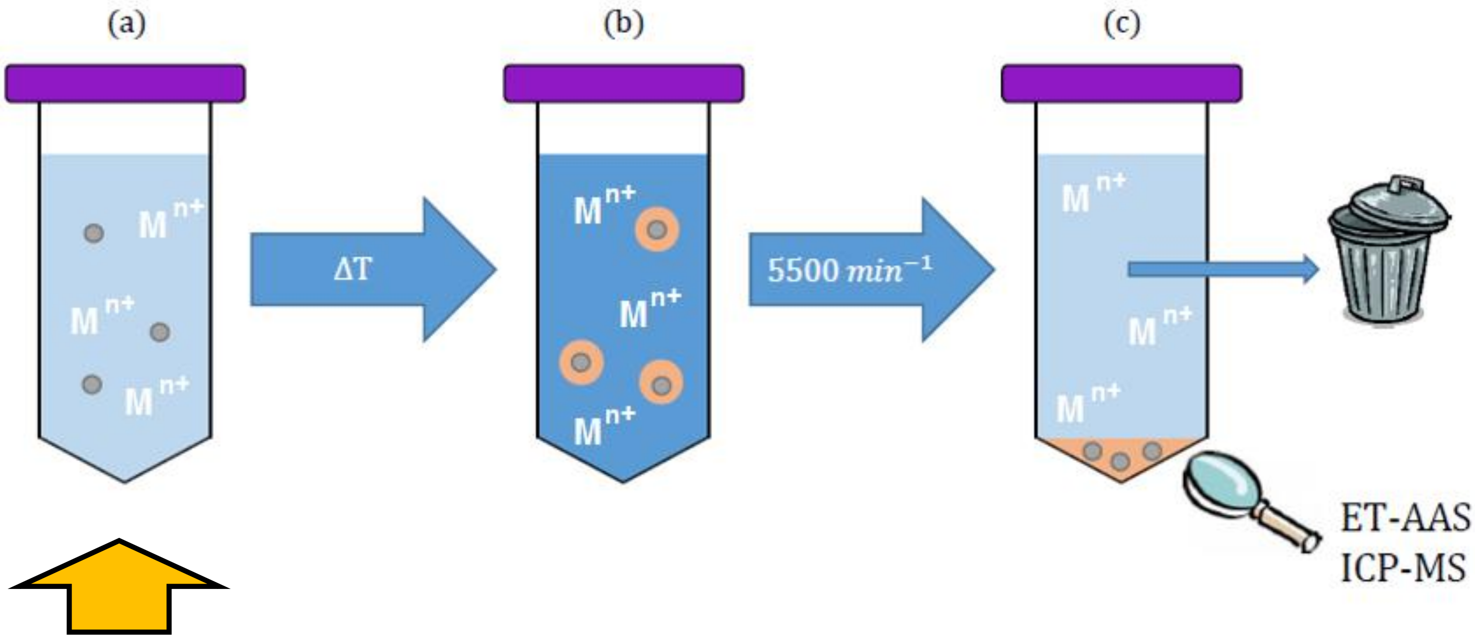
- low particle concentrations in the **ng/L**-range
- complicated **matrices** and interferences
- **separation** of soluble and particular species (i.e. Ag(I) / AgNP)

**solution approach:**

- separation (and enrichment) of particles from the matrix
- hyphenation to selective and sensitive determination techniques
- no particle mutation

# Cloud-Point-Extraction (CPE)

general procedure




+ Triton TX-114 (surfactant)
+ pH buffer
+ complexing agents

Hartmann, Hutterer & Schuster, J. Anal. At. Spec. **2013**
Hartmann & Schuster, Anal. Chim. Acta **2013**
Hartmann, Baumgartner, Schuster; Anal. Chem. **2014**
Duester, Fabricius, Jakobtorweihen, Philippe, Weigl, Wimmer, Schuster, Nazar, Anal. Bioanal. Chem. **2016**

# Cloud-Point-Extraction

a versatile toolbox for nanomaterial analysis in the environment

Ag-NP

Au-NP

Rh-NP


ET-AAS

fast & cheap quantification

sp-ICP-MS

quantification & particle size distribution

TEM (EDX)

particle sizes, morphology & composition

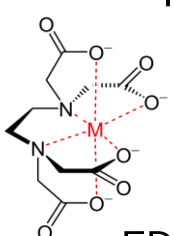
# CPE for AgNPs



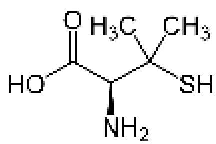
**Is there any co-extraction of ionic silver?**

→ ionic co-extraction reaches a **minimum** after ligand addition for Ag(I)

complexing agents for Ag(I)

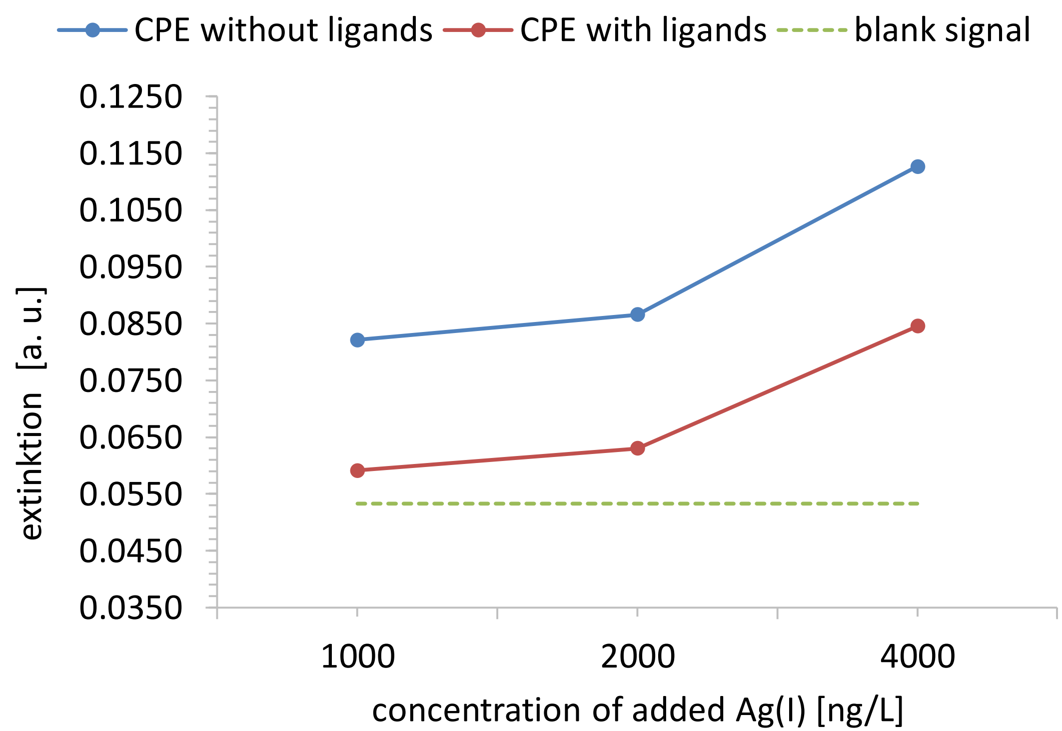


EDTA




D-Penicillamine

**down to** Ag(I) 100 ng/L
(environmental relevant!)
→ co-extraction < 15 %

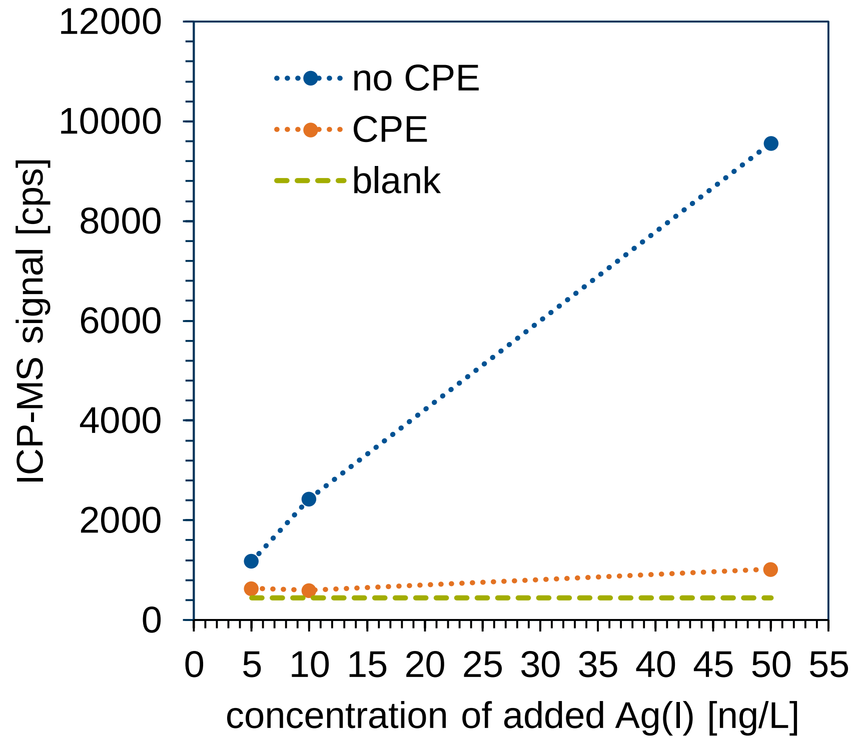


# CPE for AgNPs


## Does the natural matrix influence the co-extraction of Ag(I)?

**validation experiments**

determination of
**co-extraction rates** for Ag(I)
during CPE using
**real water matrix**
(stream, no silver background,
TOC ≈ 2.5 mg/L)




real water samples
spiked with Ag(I) (5, 10, 50 ng/L)

samples were prepared twice: **CPE** and **no CPE**
samples were of the same volume and same matrix

measured co-extraction of Ag(I) in real water matrix
ranges form 6.3 to 25.3 %

→ no significant influence of the natural matrix!

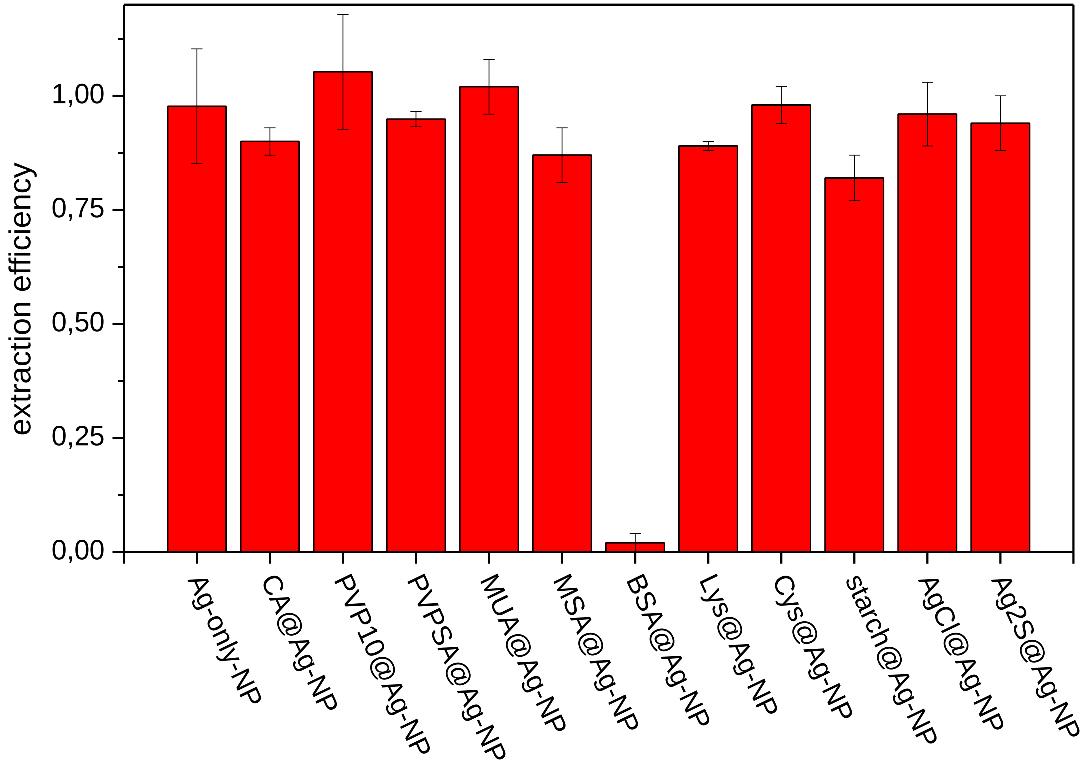
# CPE for AgNPs


## Is there any influence of particle coatings on the CPE efficiency?

**recovery rates with 13 different AgNPs:**

Ag-only-NP: Laserablation from Ag(0) in $H_2O$
CA@Ag-NP: Citrate
PVP10@Ag-NP: Polyvinylpyrolidone (PVP, 10 kDa)
PVPSA@Ag-NP: PVP Sigma Aldrich
MUA@Ag-NP: 12-Mercaptoundecanoic Acid
MSA@Ag-NP: Mercaptosuccinic Acid
BSA@Ag-NP: Boval Serum Albumine
Lys@Ag-NP: Lysine
Cys@Ag-NP: Cysteine
starch@Ag-NP: Starch
AgCl@Ag-NP: Chloride
Ag2S@Ag-NP: Sulfide
Ag3PO4-NP: Phosphate

Analytics: TEM-EDX and ATR-FT-IR




→ extracted AgNP = Σ ($Ag_2S$, AgCl, … NP)

G. Hartmann, T. Baumgartner, M. Schuster; Anal. Chem. **2014**, 86, 790−796

# CPE for AgNPs


## **additional validation**

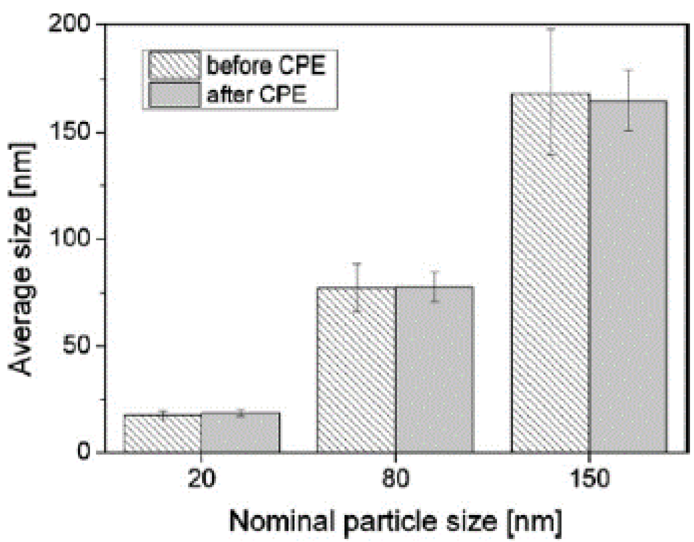
- **no influence** of natural occurring **matrix components** (ammonium, chloride, phosphate, nitrate, humic acid, $TiO_2$-µ-particles) on the **extraction efficiency of AgNPs** and **Ag(I) co-extraction**
- **no influence** on **particle size distribution** before and after CPE

# CPE for AuNPs

pH adjustment by adding HCl

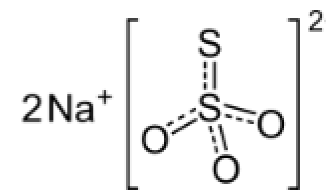
extraction efficiency for AuNPs 89 – 95 %

CPE does not affect AuNPs' size distribution




sepecies separation
dissolved Au vs. AuNP

addition of
Sodium thiolsulfate




Au(III) → Au(I)

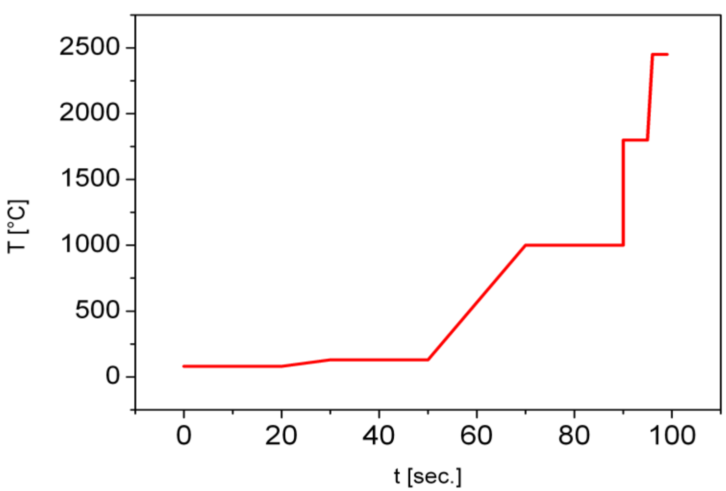
↓

$[Au(S_2O_3)_2]^{3-}$

→ only 2 % co-extraction
of dissolved Au (1 mg/L)

Hartmann & Schuster, Anal. Chim. Acta **2013**

# CPE hyphenated to ET-AAS

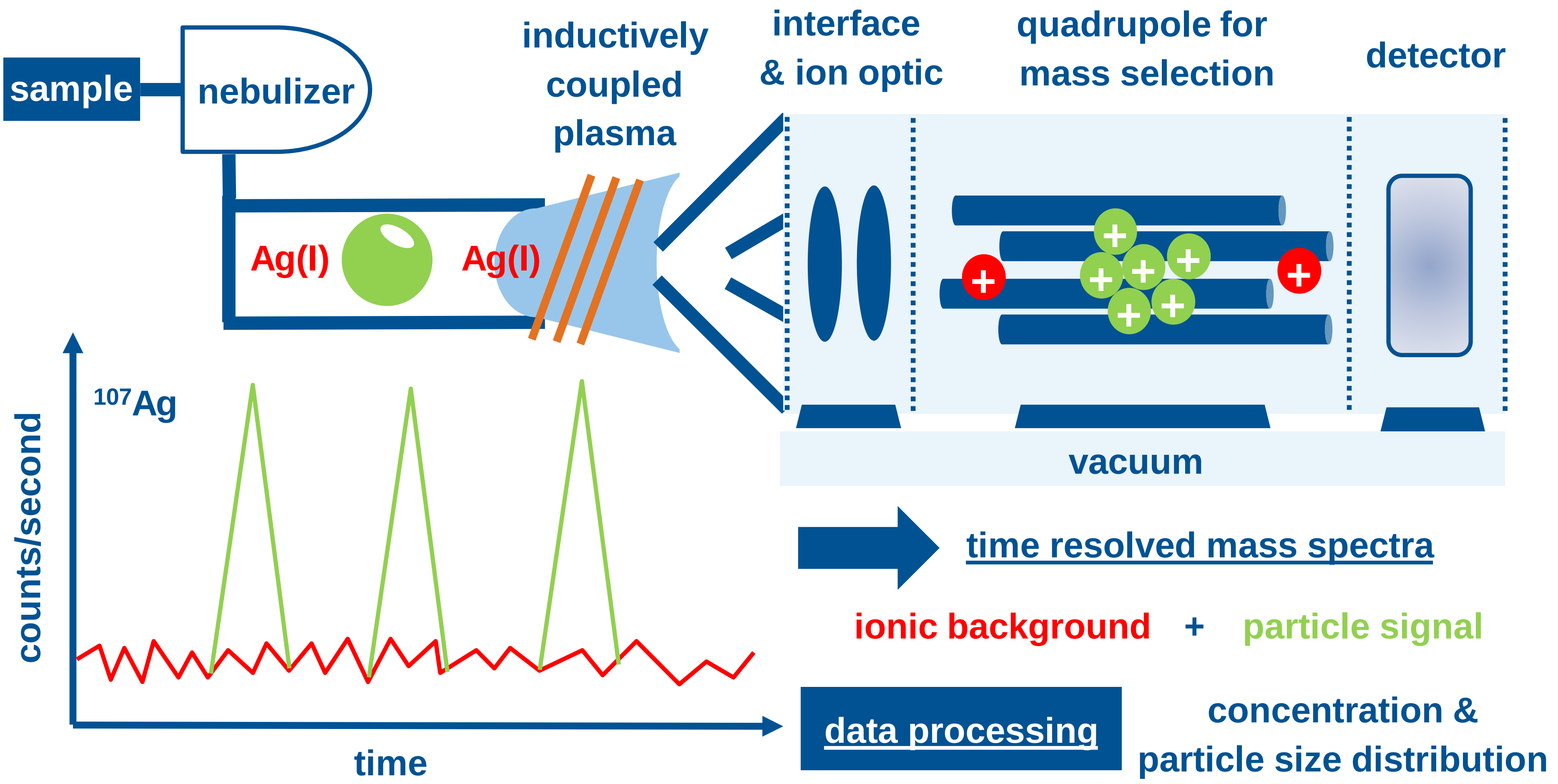

**advantages of CPE-ET-AAS:**

- ✓ very low detection limits < 1 ng/L
- ✓ high selectivity (Zeeman correction)
- ✓ high matrix tolerance
  (CPE + temperature program of ET-AAS)
- ✓ small sample volumes needed (20 µL)
- ✓ no nebulizer needed
- ✓ surfactant rich phase is measured after low dilution (100-400 µL) → Excellent enrichment factors

no size information


# CPE hyphenated to sp-ICP-Q-MS

single-particle Inductively Coupled Plasma Quadrupole Mass Spectrometry



# CPE hyphenated to sp-ICP-Q-MS

determination of particle size distributions down to 10 nm


**ETAAS**
concentration

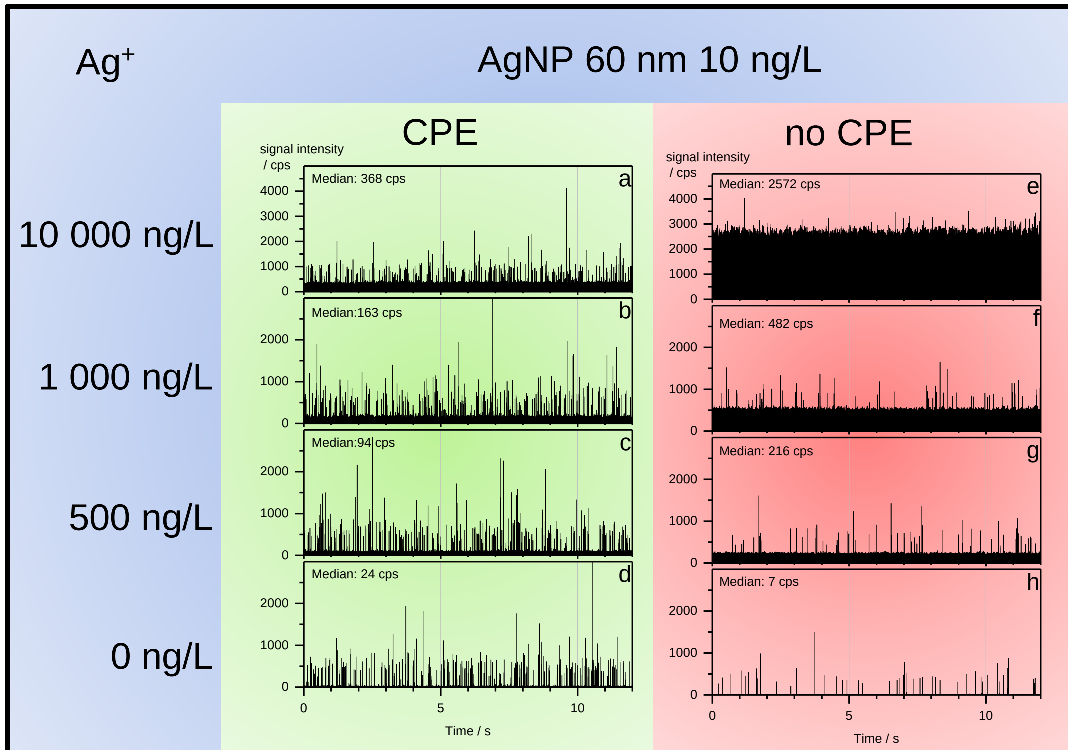
some challenges:
nebulizer-system, dilution, …

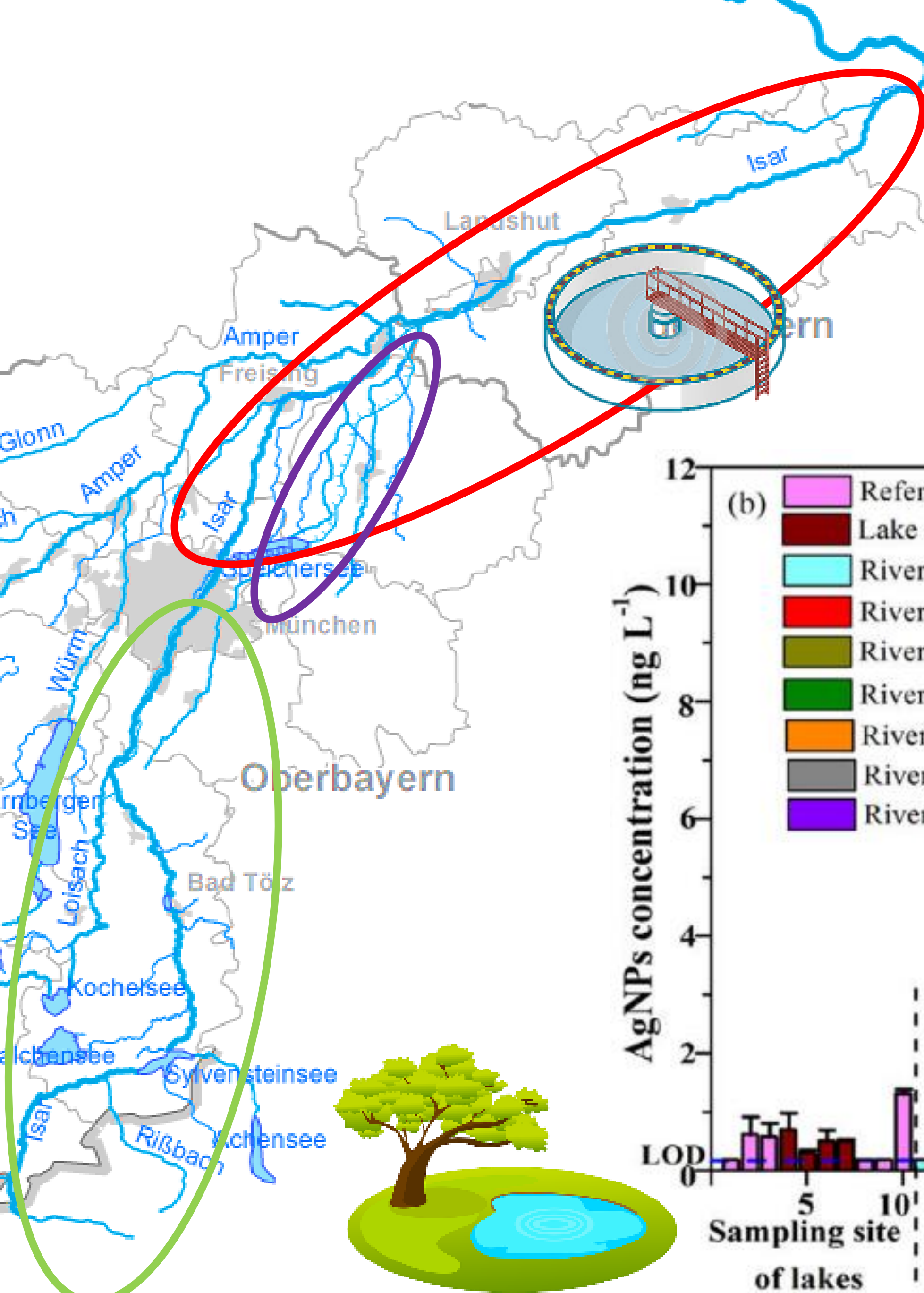
**sp-ICP-MS**
concentration + particle size

CPE reduces the ionic background caused by dissolved Ag(I) species

formally hidden particle signals become now visible

→ very small particles are detectable (depending on the element, Ag 10 nm, Rh 3 nm) – up to 2 ng/L

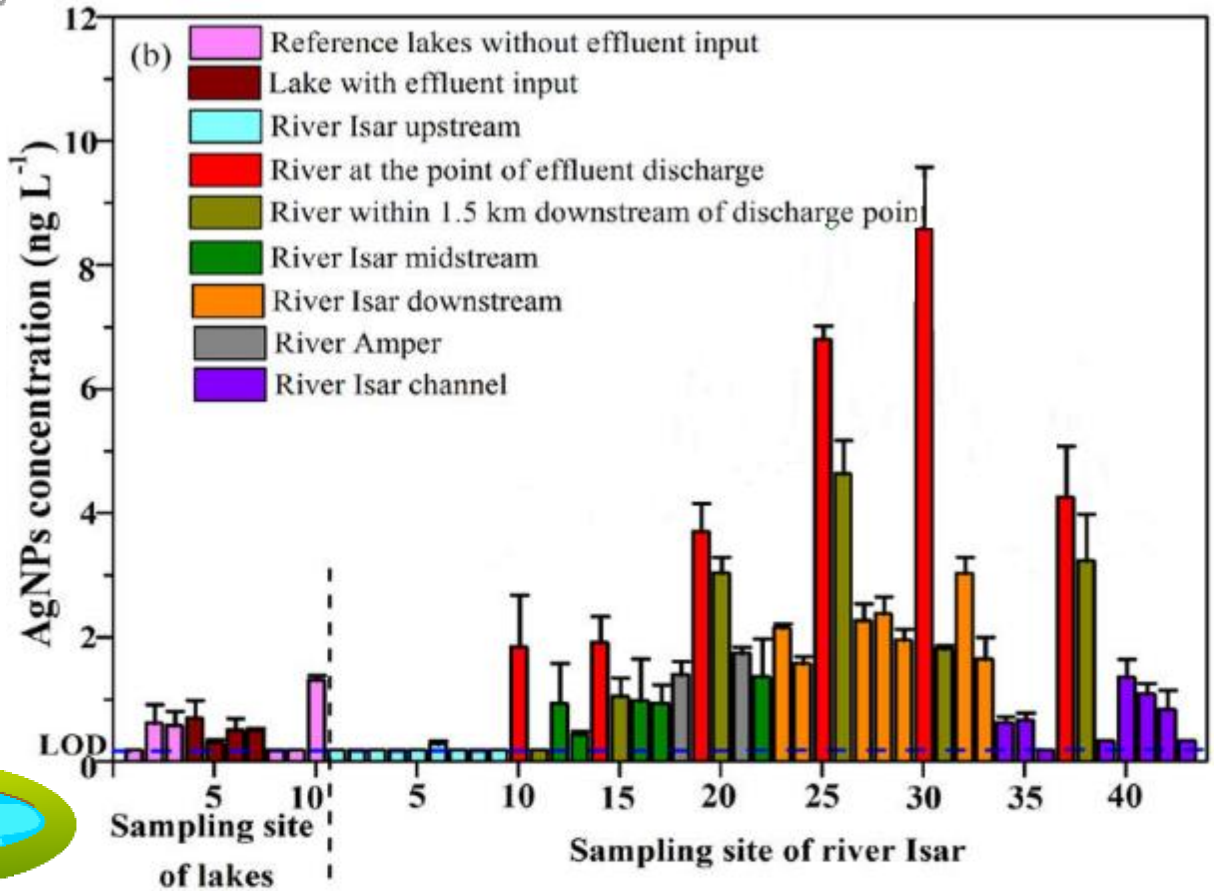





→ AgNPs are **anthropogenic** and can be **attributed to WWTP effluent** discharge

→ surprising: measurable **natural background** of AgNPs

Li, Stoiber, Wimmer, Xu, Lindenblatt, Helmreich & Schuster, Environmental Science and Technology, **2016**



# Thank you for your attention!

# Any questions?

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funded by
Bavarian State Ministry of the
Environment and Consumer Protection

# for more information…

**CPE method and validation**

Species selective preconcentration and quantification of gold nanoparticles using cloud point extraction and electrothermal atomic absorption spectrometry. Georg Hartmann, Michael Schuster. *Analytica Chimica Acta 761* (**2013**) 27-33.

Ultra-trace determination of silver nanoparticles in water samples using cloud point extraction and ETAAS. Georg Hartmann, Christine Hutterer, Michael Schuster. *Journal of Analytical Atomic Spectrometry 28* (**2013**) 567-572.

Influence of Particle Coating and Matrix Constituents on the Cloud Point Extraction Efficiency of Silver Nanoparticles (Ag-NPs) and Application for Monitoring the Formation of Ag-NPs from Ag+. Georg Hartmann, Tanja Baumgartner, Michael Schuster. *Analytical Chemistry 86* (**2014**) 790-796.

Can cloud point-based enrichment, preservation, and detection methods help to bridge gaps in aquatic nanometrology? Lars Duester, Anne-Lena Fabricius, Sven Jakobtorweihen, Allan Philippe, Florian Weigl, Andreas Wimmer, Michael Schuster, Muhammed Faizan Nazar. *Analytical and Bioanalytical Chemistry* (**2016**) (DOI 10.1007/s00216-016-9873-5, open access).

# for more information…

**Examples for application to determine AgNPs in environmental samples**

Quantification of Nanoscale Silver Particles Removal and Release from Municipal Wastewater Treatment Plants in Germany. Lingxiangyu Li; Georg Hartmann, Markus Doeblinger et al. *Environmental Science & Technology 47* (**2013**) 7317-7323.

To What Extent Can Full-Scale Wastewater Treatment Plant Effluent Influence the Occurrence of Silver-Based Nanoparticles in Surface Waters?. Lingxiangyu Li, Monika Stoiber, Andreas Wimmer, Zhenlan Xu, Claus Lindenblatt, Brigitte Helmreich, Michael Schuster. *Environmental Science and Technology* 50 (**2016**) 6327-6333 (DOI 10.1021/acs.est.6b00694).

# Appendix

# AgNPs in WWTPs

**Water sample collection**

→ 24 h composite samples
every 2 h sampling

→ 2 full-scale municipal plants with different biological treatment techniques and sewer systems

**Water sample pretreatment and AgNP concentration and size analysis**

→ CPE + ET-AAS / sp-ICP-MS

**Aims**

→ Removal efficiency in different treatment steps

→ Is there any season dependence?

→ AgNP sizes in influent and effluent

Environmental Science & Technology
Article
pubs.acs.org/est

**To What Extent Can Full-Scale Wastewater Treatment Plant Effluent Influence the Occurrence of Silver-Based Nanoparticles in Surface Waters?**

Lingxiangyu Li,[†] Monika Stoiber,[†] Andreas Wimmer,[†] Zhenlan Xu,[‡] Claus Lindenblatt,[§] Brigitte Helmreich,[*,§] and Michael Schuster[*,†]

DOI: 10.1021/acs.est.6b00694
*Environ. Sci. Technol.* 2016, 50, 6327−6333

# Waste Water Treatment Plant – Scheme

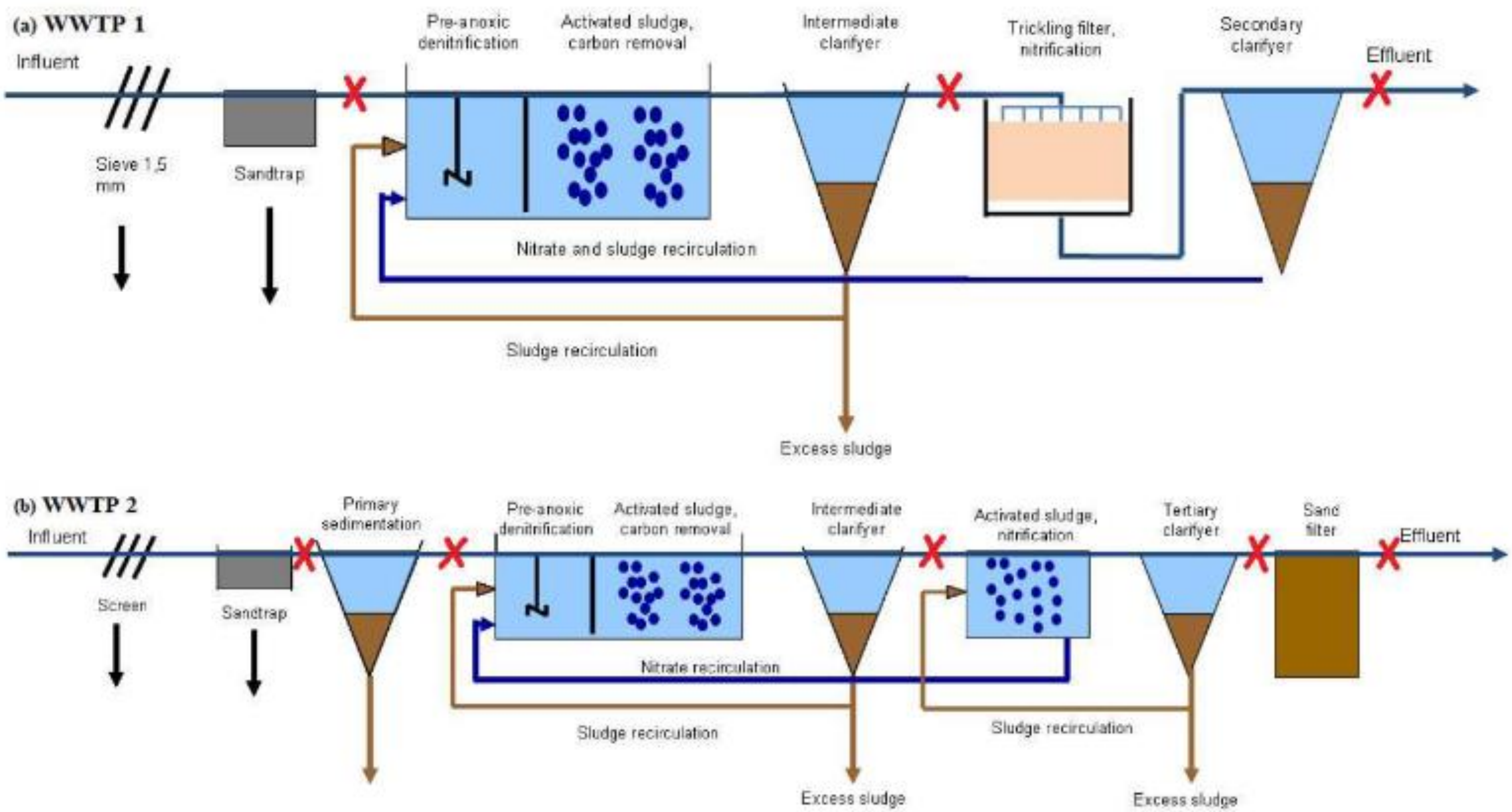
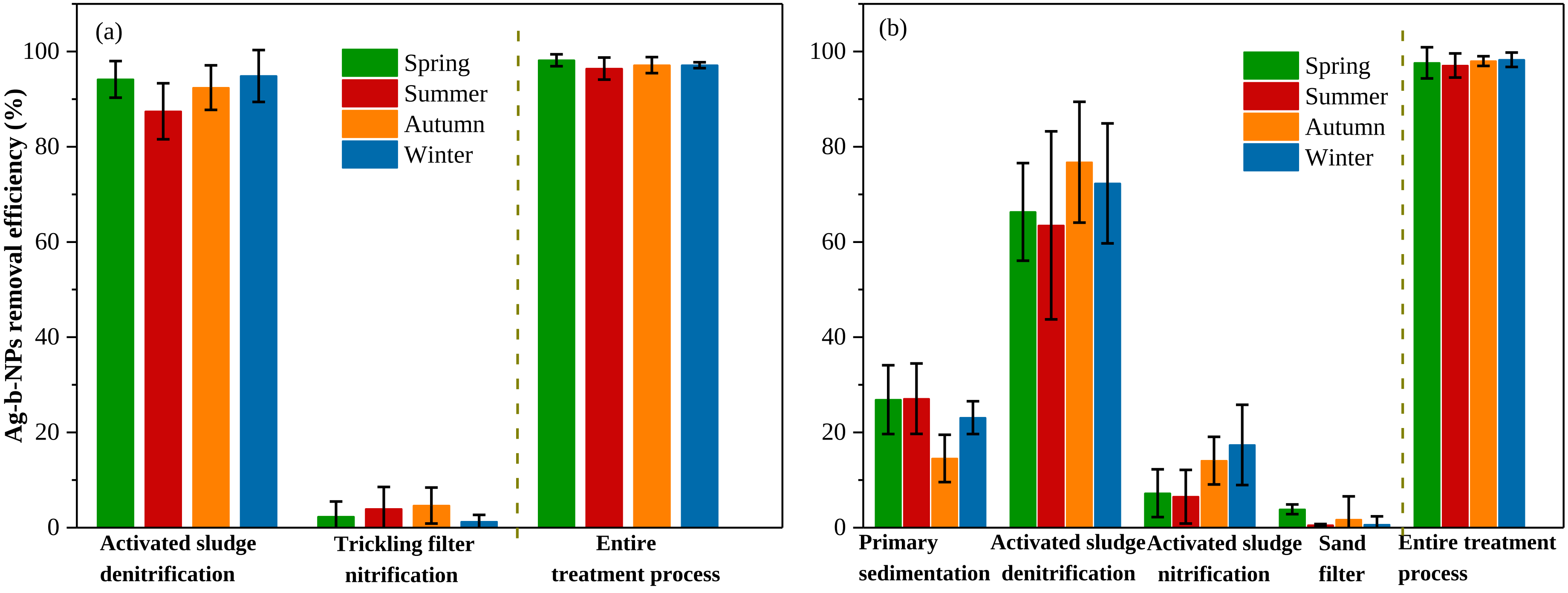



**Fig S1.** Schematic diagrams of the investigated full-scale WWTPs. The crossings in red present sampling sites along the wastewater treatment process. (a) WWTP 1 with average flow rate of 5,300 $m^3$/d (population served ~26,000). (b) WWTP 2 with an average flow rate of 160,000 $m^3$/d (population served ~850,000) .

# Characterization of AgNPs in WWTP Waters

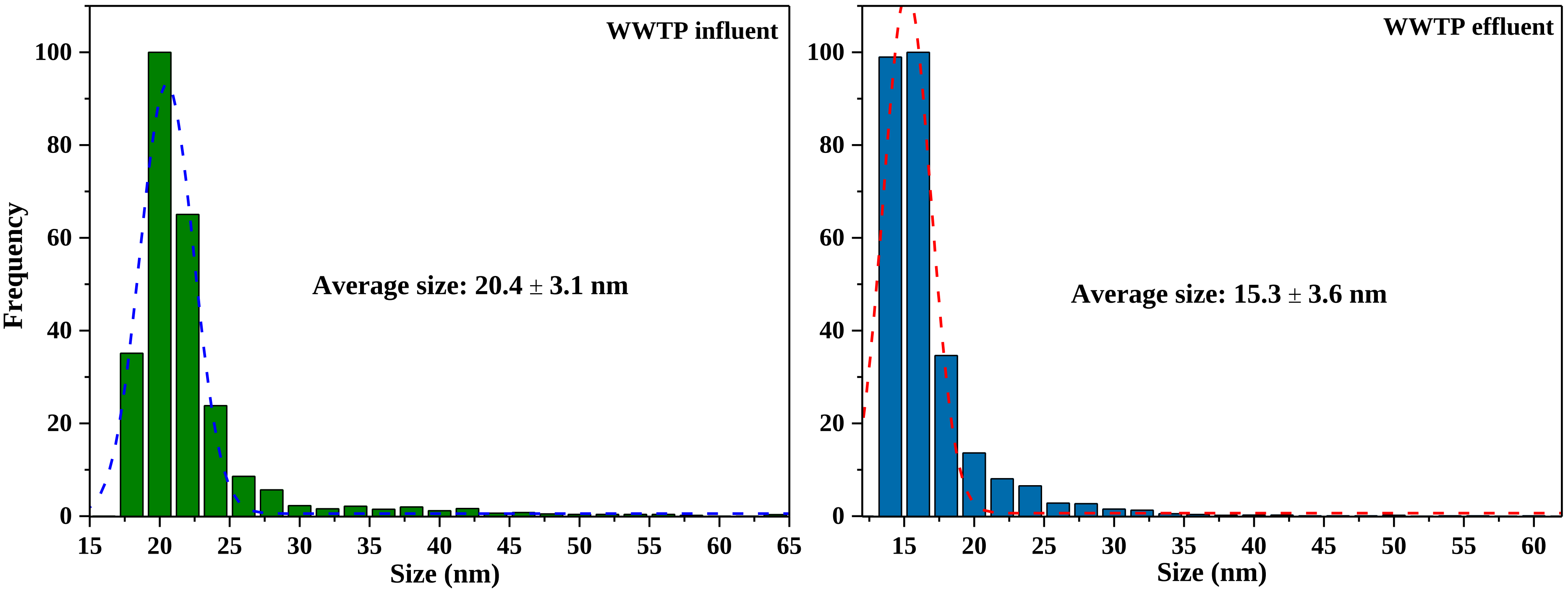
- → Significant decreases in AgNP concentrations along the treatment process
- → Main removal step: **activated sludge denitrification** (> 96.4 %)
- → **Season-independent** removal
- → Influent: 357 ng/L (winter) to 10.1 ng/L (summer) / Effluent: < 11 ng/L
- → Activated sludge (WWTP b) >> Trickling filter (biofilm,WWTP a)



# Characterization of AgNPs in WWTP Waters

→ sp-ICP-MS measurement of WWTP samples

→ Slight variation in size distributions of AgNPs through WWTP




Li, Stoiber, Wimmer, Xu, Lindenblatt, Helmreich & Schuster, ES&T **2016**