Algal acute toxicity of Silver Cyanide in freshwater environment

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INTRODUCTION

- Silver ions (**Ag^+**) are known for their natural antimicrobial properties and have a recognised high ecotoxic potential.
- **Silver nitrate** is commonly used as test item for Ag^+ in ecotoxicity tests.
- **Algae** are identified as most sensitive aquatic species towards Ag^+ toxicity (Arijs *et al.* 2021).
- **Silver-cyanide complexes** are assumed to be stable at ecologically relevant conditions (Xue *et al.* 1985), but are currently void of reliable ecotoxicity test data.
- **Aim of this work: investigate the comparative toxicity of silver nitrate vs. silver-cyanide complexes towards algae.**

INITIAL CONSIDERATIONS

- Two industrially relevant silver-cyanide complexes registered under EU-REACH: **silver cyanide [AgCN] and potassium dicyanoargentate [$KAg(CN)_2$].**
- Water solubility: AgCN 1.1 µg/L vs. $KAg(CN)_2$ 200 g/L.
- Speciation calculations (MINEQL) in simple aquatic systems (fixed pH of 5.5, 7 or 8.5; total added Ag concentration 10^{-3} – 10^{-9} M) suggest **dominance of Ag-cyanide complexes over Ag^+ at ecotoxicologically relevant Ag-cyanide concentrations.**

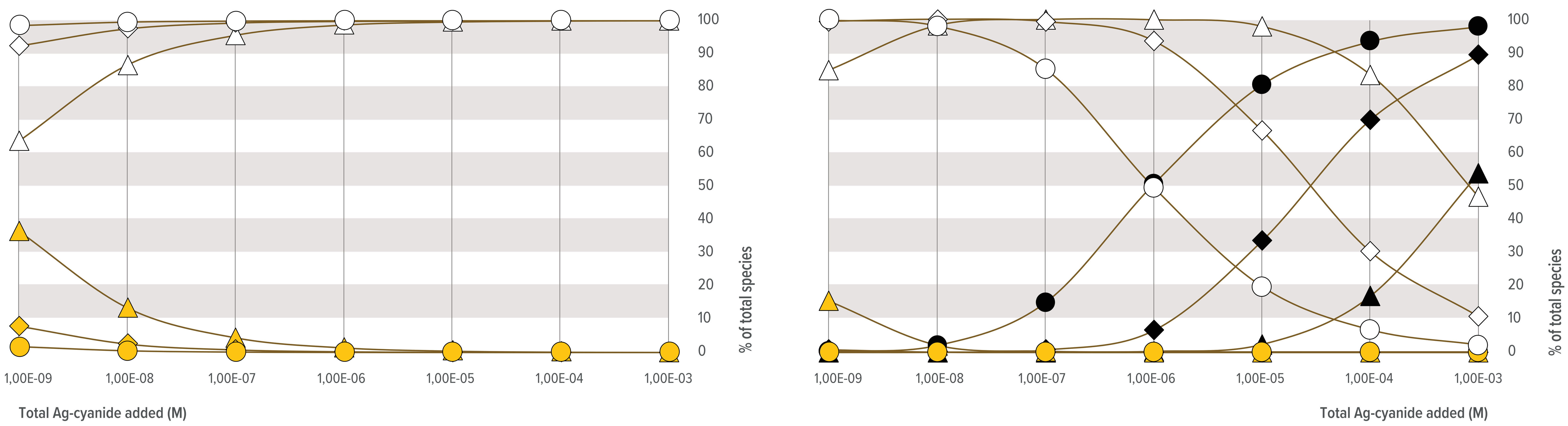

Figure 1: Modeled distribution (using MINEQL) of Ag^+ (yellow), AgCN (white) and $Ag(CN)_2$ (black) at pH 5.5 (triangles), 7 (diamonds) and 8.5 (circles) in water after addition of AgCN (left figure) or $KAg(CN)_2$ (right figure) at concentrations of $1x10^{-9}$ to $1x10^{-3}$ M

DOSE-RANGE FINDING STUDY

- **$AgNO_3$** and **$KAg(CN)_2$** tested at 0,5 – 50 µg Ag_{total}/L, **AgCN** tested at 25 – 2500 Ag_{total}/L
- Measured dissolved Ag (% of total added Ag): 1.1-1.3% for AgCN, 47-100% for $KAg(CN)_2$ and 20-27% for $AgNO_3$
- Experimental data covering ±25-75% reduction in algal growth (*Raphidocelis subcapitata*)
- **Indicative Ag concentrations at 50% growth inhibition [EC50 value]:**
  $AgNO_3$ (0.55 µg Ag/L) < AgCN = $KAg(CN)_2$ (2.6 - 3.4 µg Ag/L)

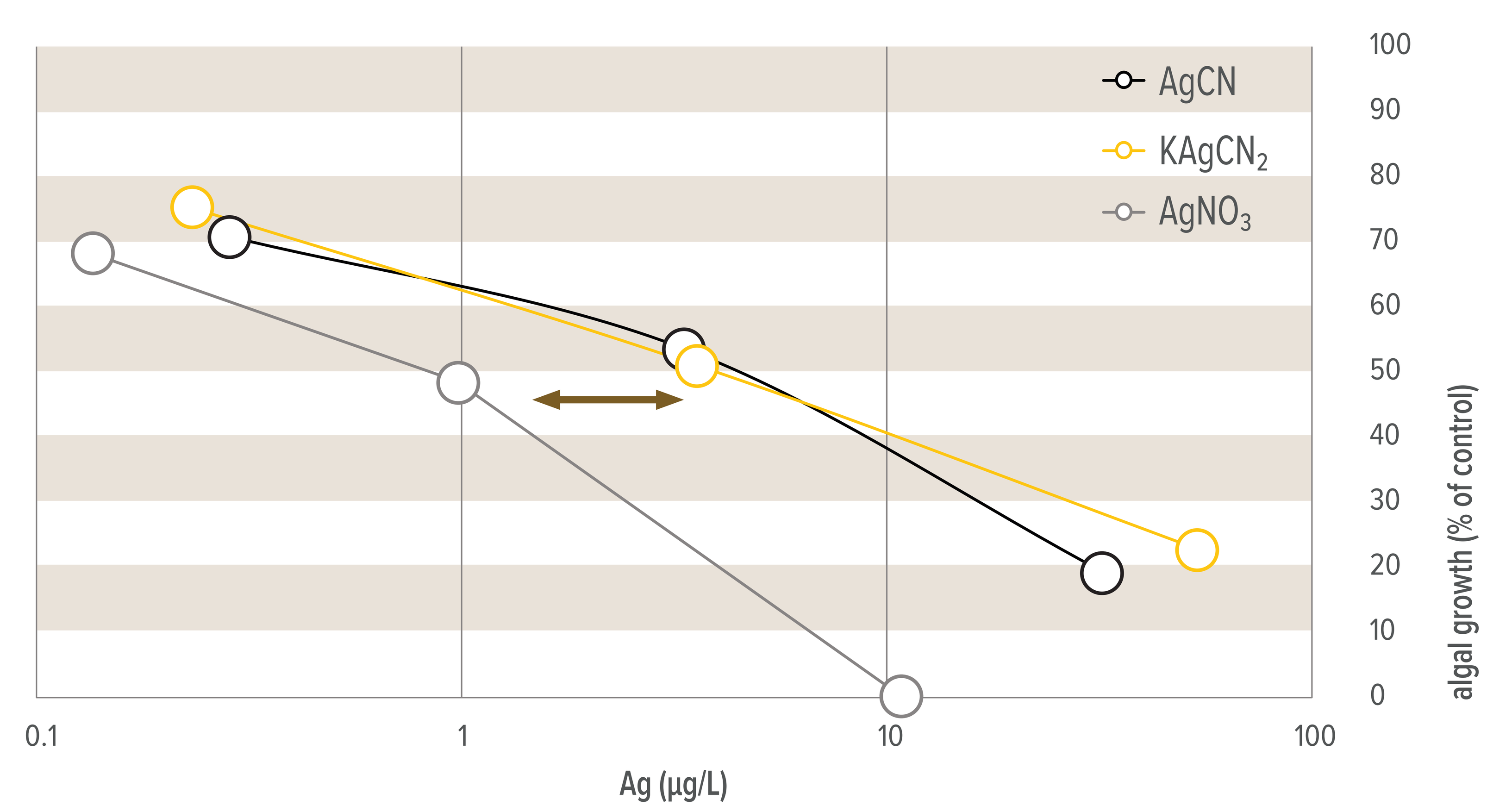

Figure 2: *Results of the dose-range finding study with $AgNO_3$ (grey), $KAg(CN)_2$ (yellow) and AgCN (black). Algal growth (% of control) as a function of measured dissolved Ag concentrations.*

MAIN ALGAL TOXICITY STUDY

- **AgCN** as test item; added at 6 test concentrations (0.005 - 15 mg Ag_{total} /L)
- Algal toxicity test (*R. subcapitata*) according to OECD guideline 201; GLP compliant
- 72 hour-growth inhibition as endpoint, dissolved Ag measured via ICP-MS
- **EC50 value: 16.2 µg Ag/L** [95% confidence interval: 11.3 – 23.1]

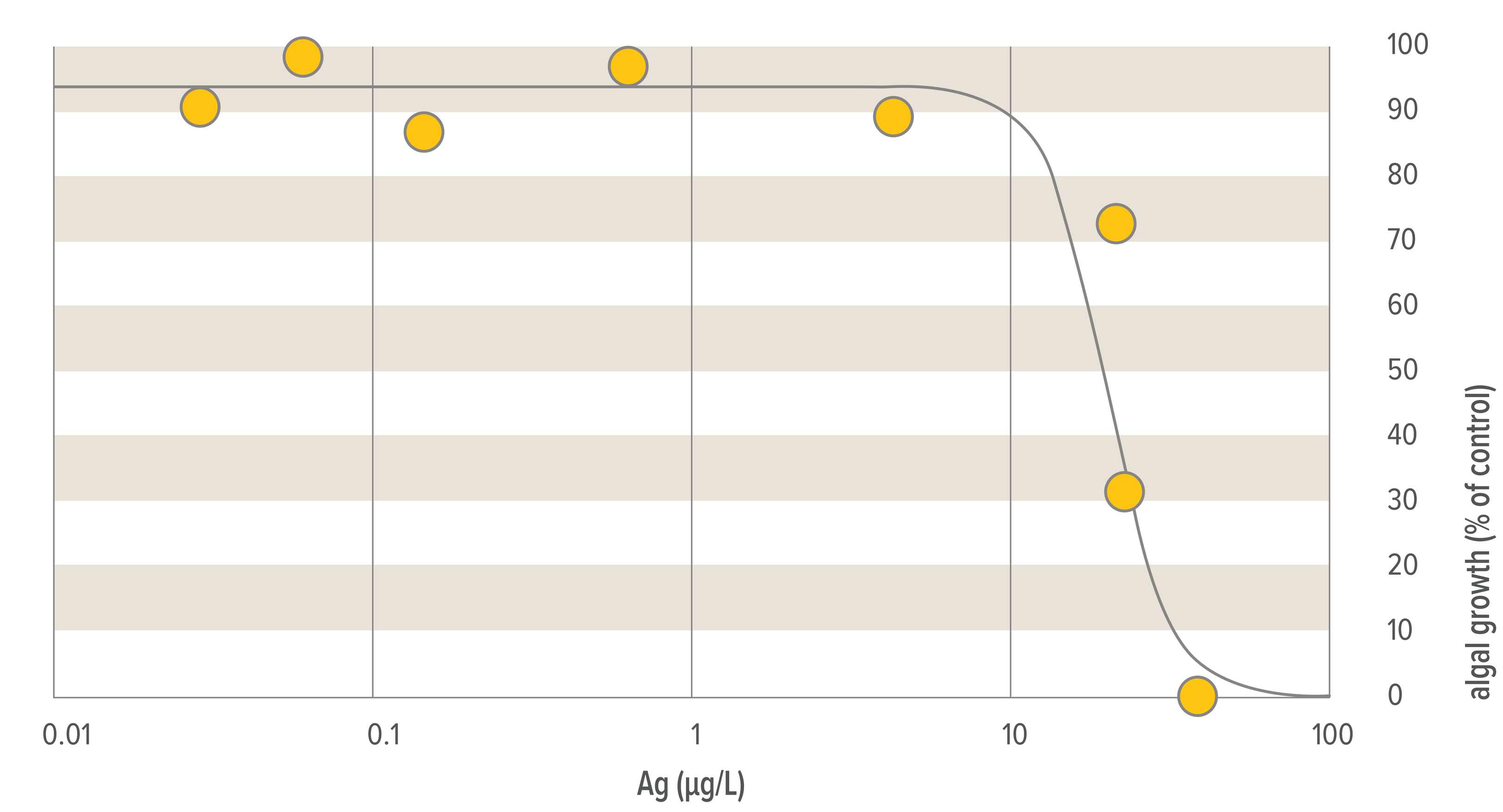

Figure 3: *Results of the main study with AgCN. Algal growth (% of control) as a function of measured dissolved Ag concentrations.*

CONCLUSION

- **Speciation modelling suggests stability of silver-cyanide complexes at ecotoxicologically relevant concentrations.**
- **Results from a dose-range finding study with *Raphidocelis subcapitata* confirm**
  - **a comparable toxicity of AgCN and $KAg(CN)_2$**
  - **a lower toxicity of AgCN and $KAg(CN)_2$ compared to silver nitrate.**
- **The toxicity of AgCN in a guideline conform test with *R. subcapitata* results in an EC50 value of 16.2 µg Ag/L.**
- **The toxicity of silver-cyanide complexes is more than 15-fold lower than of silver nitrate, based on EC50 values (EC50 silver nitrate 0.96 µg Ag/L; Schlich 2016).**
- **Next step, in this research program, is the determination of the ecotoxicity of silver-cyanide complexes towards invertebrates and fish.**

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