Aquatic toxicity of palladium: A grouping and read-across approach for some palladium substances and why others need separate assessments

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INTRODUCTION

- **Palladium (Pd)** is used in catalysis and found in air, soil, and water
- **Ecotoxicity Data:** Limited data on algae, invertebrates, fish
- **Alternative Assessment Approaches** to facilitate ecotoxicological assessment

Table 1: Overview of key differences properties between read-across palladium substances and Palladium dinitrate, Palladium (II) di(4-oxopent-2-en-2-oate), and Palladium(II) Acetate. These distinctions explain the exclusion of the latter three Pd- compounds from the proposed grouping and read-across approach.

	Read-across Compounds*	Palladium dinitrate	Palladium (II) di(4-oxopent-2-en-2-oate)	Palladium (II) acetate
Type	Inorganic	Inorganic	Organometallic (lipophile)	Organic metal salt
Ligand	e.g. Chloride; Ammonia	Nitrate	Acetylacetonate	Acetate
Expected aquatic respeciation	Respeciation to $Pd(OH)_2$	Hydrolysis to mixed aquato-nitrato species, ultimately forming $Pd(OH)_2$	Slow and limited respeciation; retains molecular structure	Hydrolysis to mixed aquato-acetato species ultimately forming $Pd(OH)_2$
Acute Toxicity (µg Pd/L (± sd)	Algae at 5.56 ± 2.6 µg/L Invertebrates at 50.6 ± 3.6 µg/L Fish at 267.8 ± 25.8 µg/L	Algae: 25.3 µg/L Invertebrate: 681.7 µg/L Fish: 46 516 µg/L	Algae: 28.3 µg/L Invertebrate: 75.9 µg/L Fish: 5.48 µg/L	Algae: 1.27 µg/L Invertebrate: 36 µg/L Fish: n.a.

STUDY OBJECTIVES

- **Read-across:** Grouping Pd compounds by similar speciation
- **Quantitative Ion Character-Activity Relationships (QICAR) modelling** (Le Faucheur *et al.*, 2021)

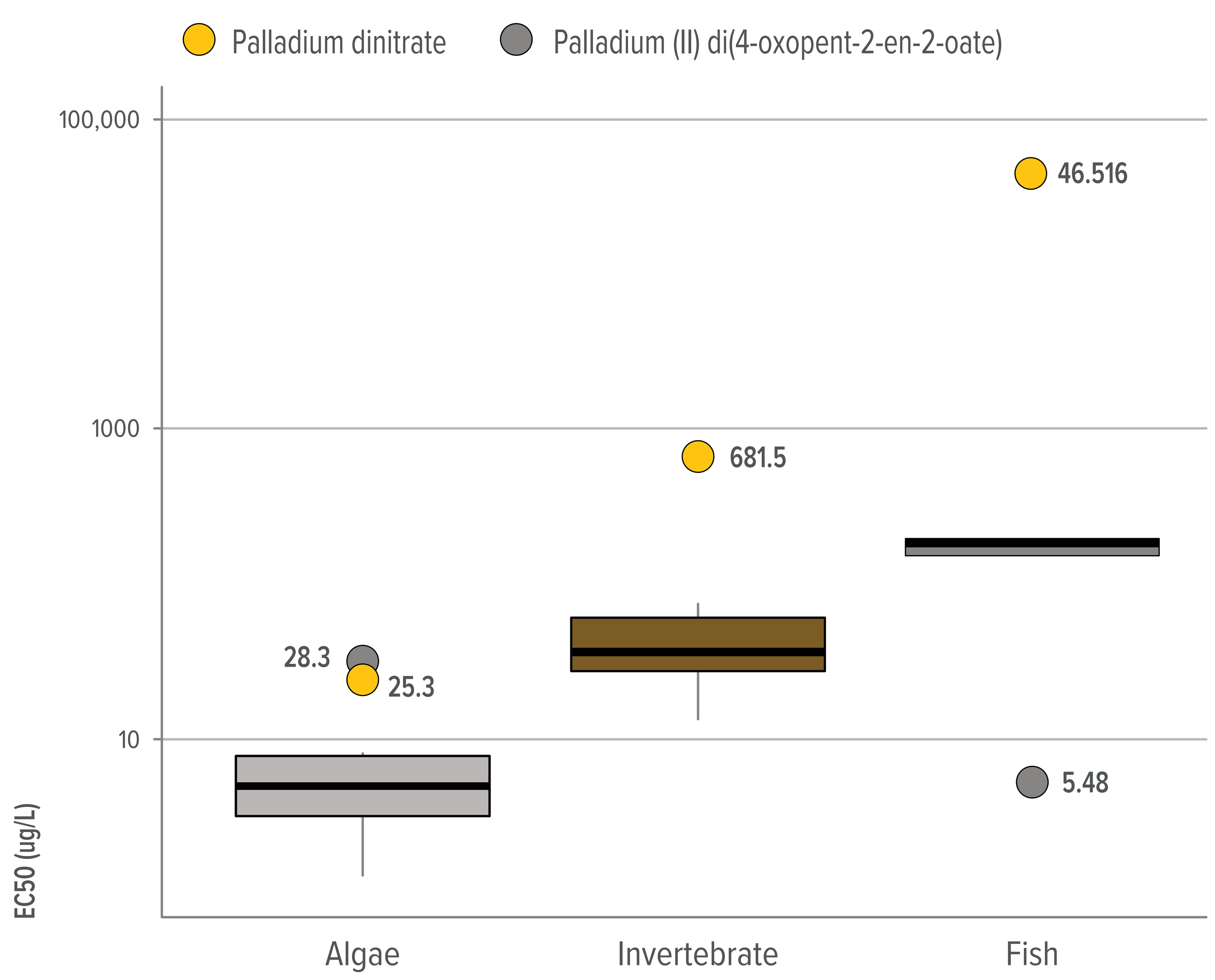

Fig. 1: Boxplot of EC50 values grouped by algae (n =10), invertebrates (n=7), and fish (n=5). Outlier substances by IQR method depicted.

METHODS

- **Literature Review** (Klimisch score 1-2) and OECD/GLP compliant study reports from industry
- Collection of **acute & chronic effective concentrations (EC50, EC10) of alga, invertebrates, and fish**
- Identify outliers unsuitable for read-across
- **Analyze Pd respeciation** (freshwater) & establish grouping

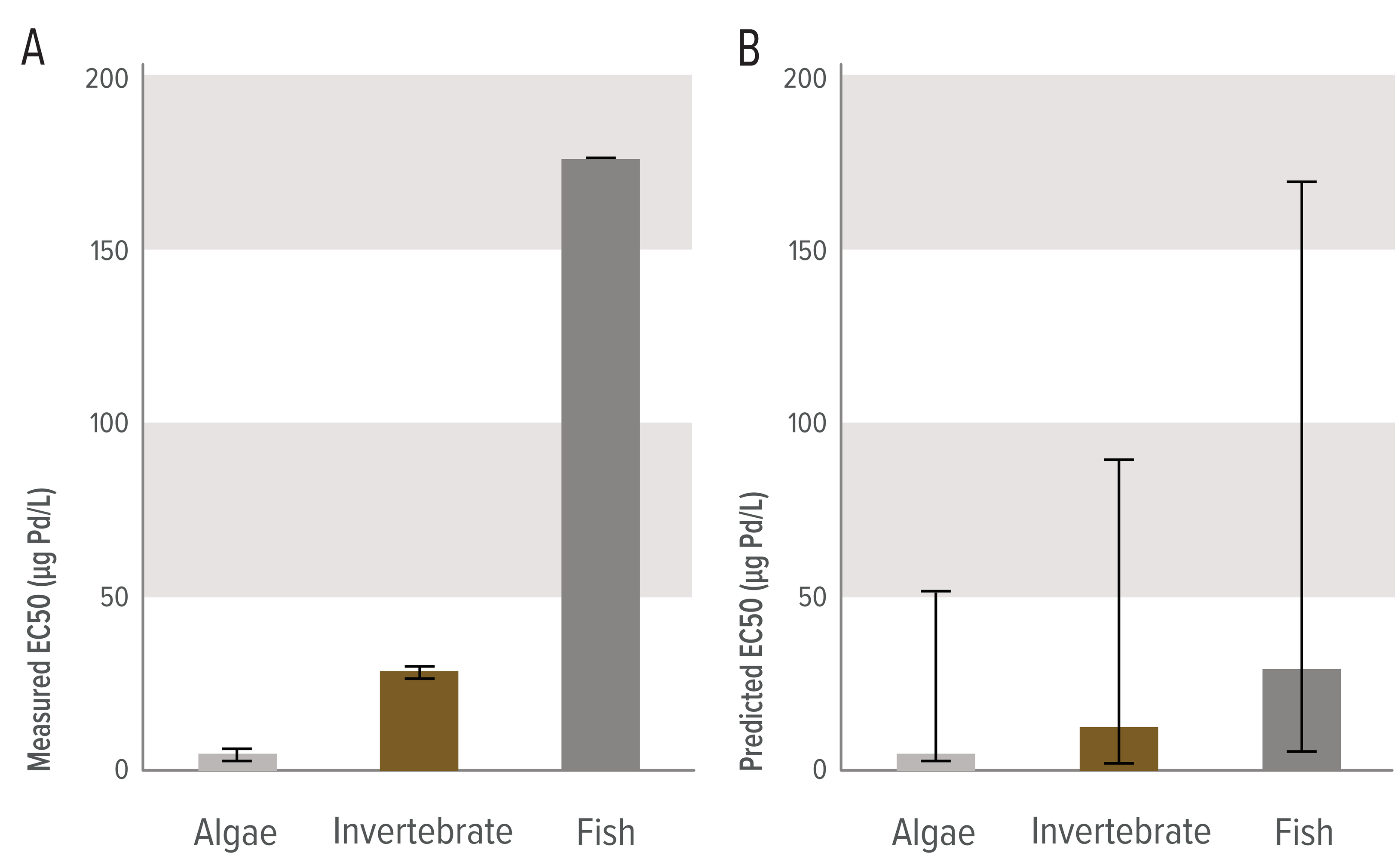

Fig. 2: Comparison of experimentally measured EC50 values (A) and QICAR modelled values (B) across three trophic levels for the grouped Pd compounds.

** Read-across Compounds:*

- simple inorganic Pd salts (e.g. Pd dichloride, Pd dihydroxide or Pd sulphate)
- tetraamminepalladium compounds
- tetra-and hexachloropalladium compounds
- mixed ammine/chloride salts (diamminedichloropalladium)

RESULTS & CONCLUSION

1. **Toxicity Variations:**
   - Algae most sensitive species
   - Outlier:
     - Palladium (II) di(4-oxopent-2-en-2-oate) & Palladium dinitrate (Fig. 1)
     - Palladium dinitrate (chronic; not shown)
2. **Toxicity Variations:**
   - Prediction matches with measured values for algae and invertebrate, but conservative for fish (Fig. 2)
3. **Speciation Effects** (Table 1):
   - **Grouped substances** (inorganic Pd-salts): Respeciation in water to common $Pd(OH)_2$ species
   - **Palladium dinitrate:** hydrolyzes to complexes with lower bioavailability & toxicity than grouped substances
   - **Palladium (II) di(4-oxopent-2-en-2-oate):** limited respeciation; unique toxicity profile due to lipophilic mechanism
   - **Palladium (II) Acetate:** speciation unclear, but comparable toxicity than grouped substances

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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.**

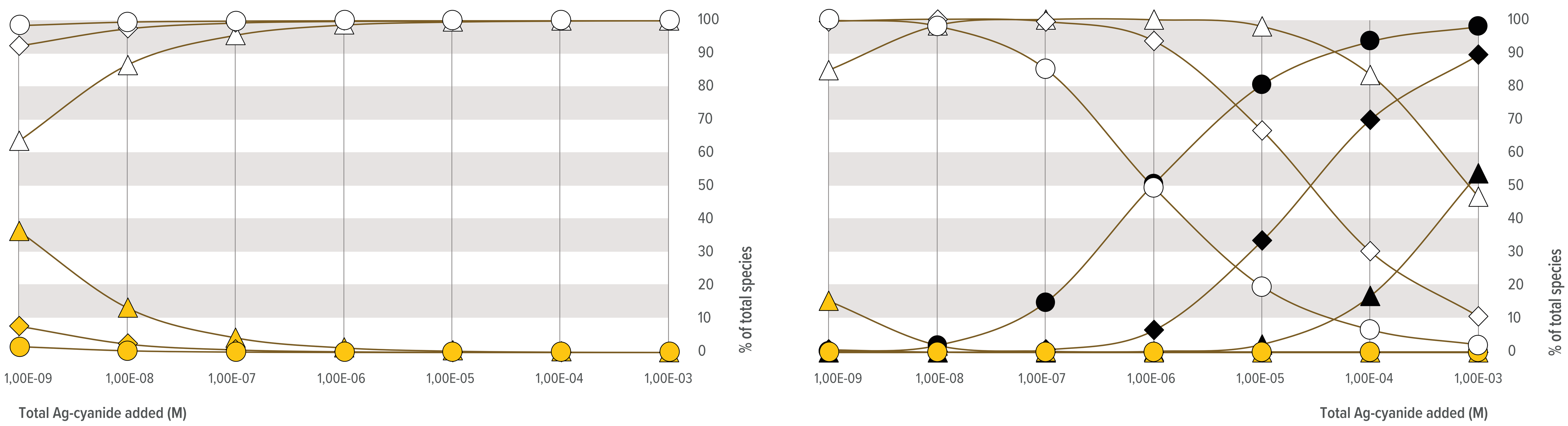

Figure 1: Modeled distribution (using MINEQL) of Ag^+ (yellow), AgCN (white) and $Ag(CN)_2$ (black) at pH 5.5 (triangles), 7 (diamonds) and 8.5 (circles) in water after addition of AgCN (left figure) or $KAg(CN)_2$ (right figure) at concentrations of $1x10^{-9}$ to $1x10^{-3}$ M

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)

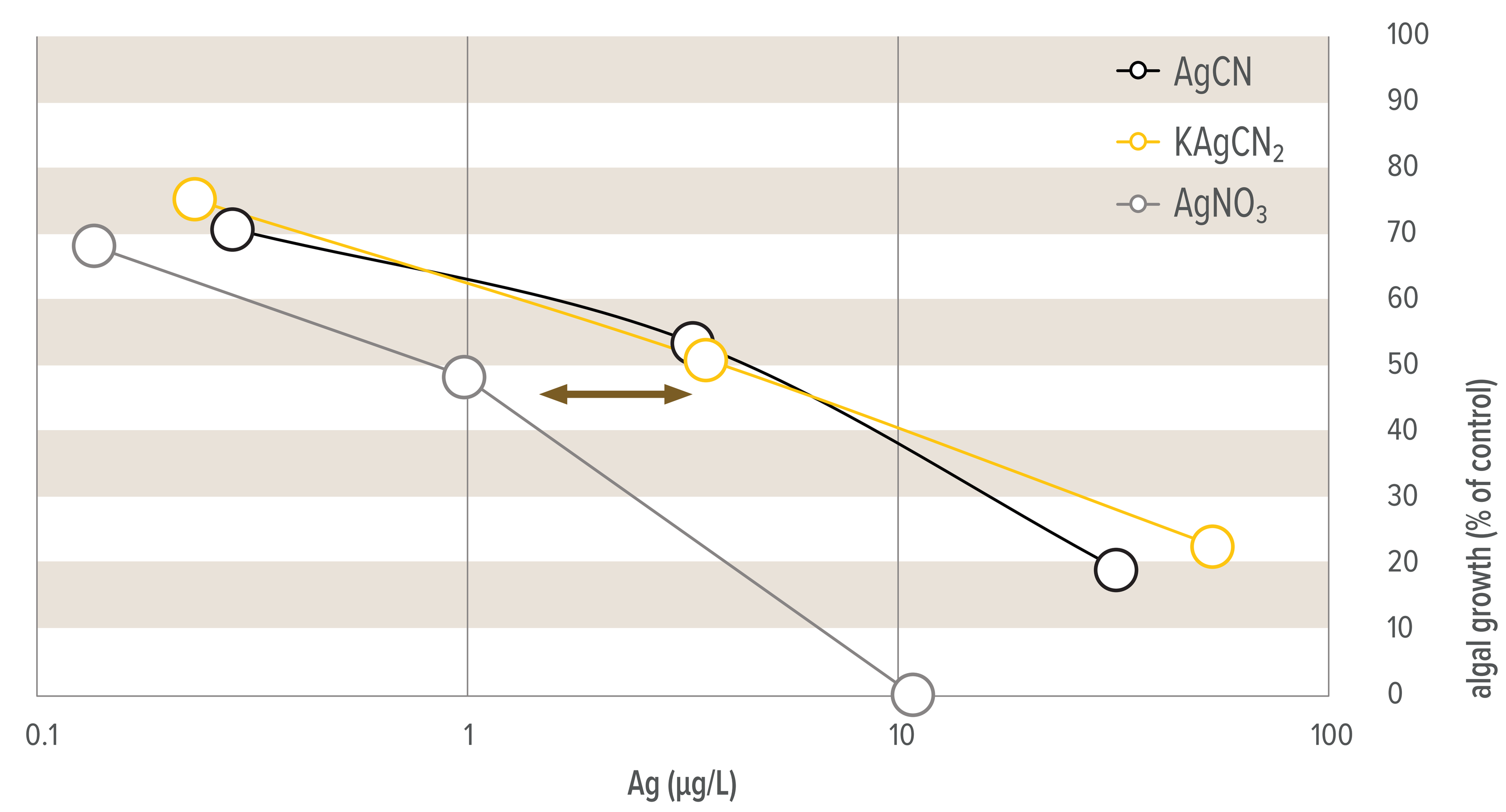

***Figure 2:** Results of the dose-range finding study with $AgNO_3$ (grey), $KAg(CN)_2$ (yellow) and AgCN (black). Algal growth (% of control) as a function of measured dissolved Ag concentrations.*

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]

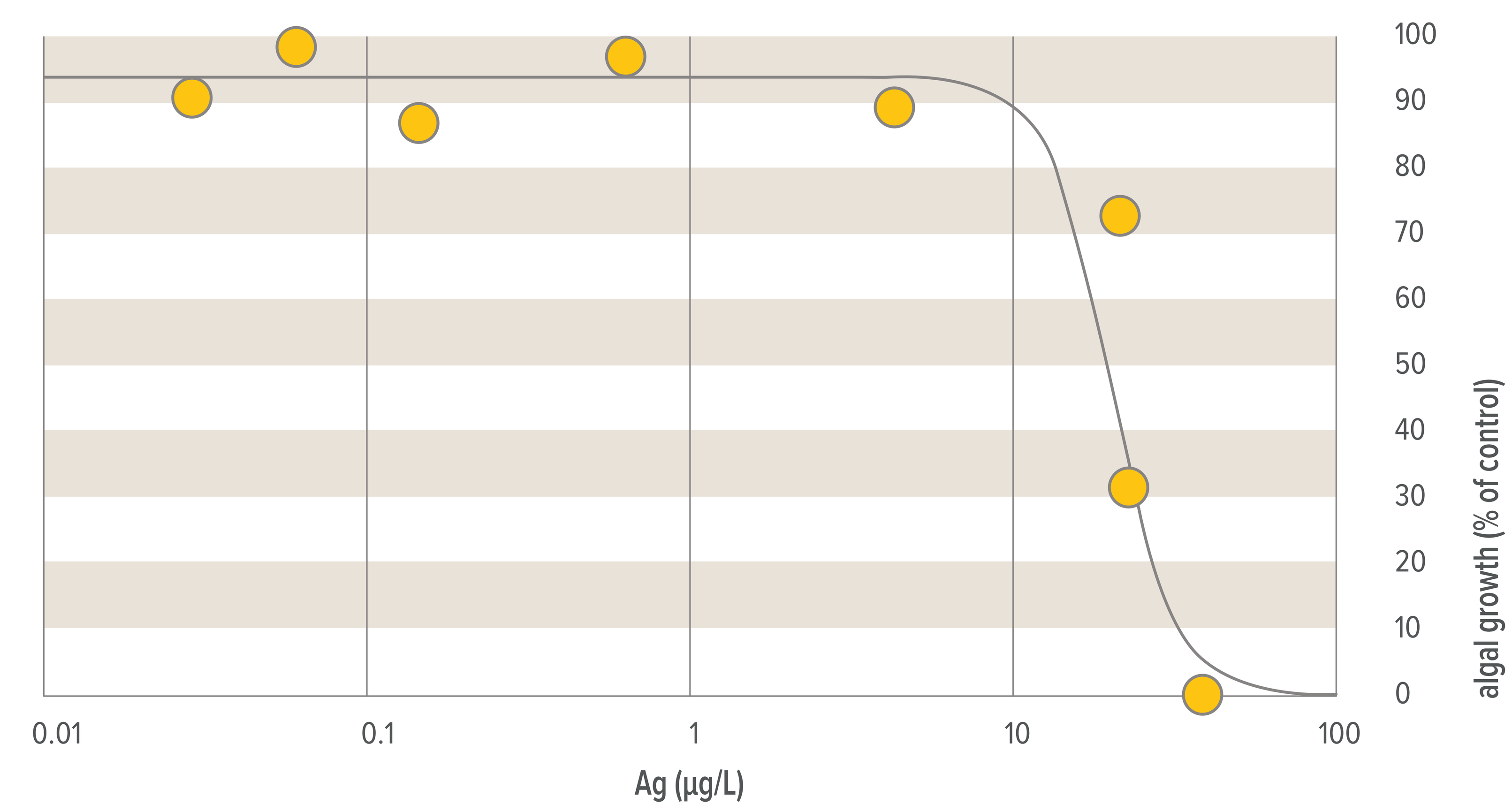

***Figure 3:** Results of the main study with AgCN. Algal growth (% of control) as a function of measured dissolved Ag concentrations.*

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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