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Uptake and accumulation of wastewater-borne nanomaterials and released metals by the benthic amphipod *Hyalella azteca* under environmentally relevant conditions

Background

The increasing production and use of engineered nanomaterials (ENMs) inevitably leads to increasing inputs of these materials into wastewater streams. Physicochemical transformation of ENMs in wastewater systems may alter the behavior and fate of ENMs. In the wastewater treatment plant (WWTP), ENMs primarily hetero-aggregate with sludge flocs and are thus removed efficiently from the wastewater stream and accumulated in the sludge phase. Thus, ENMs are released to the environment, either in small amounts via the effluent of WWTPs (bound to sludge flocs) or by using the sewage sludge as fertilizer on agricultural land. Most studies on the fate and transformation of ENMs released by WWTP and their potential bioavailability to organisms in various aquatic systems have been conducted with pristine ENMs. A few cases were conducted with synthetic wastewater to mimick the transformation processes in WWTPs, but these studies were using ENM concentrations far exceeding model predictions.

The aim of this study was, therefore, to elucidate the impact of the physicochemical transformation of ENMs in WWTPs on their uptake and accumulation potential in aquatic invertebrates.

Hypotheses

- Even low ENM concentrations in wastewater and sludge matrices can lead to measurable body burdens in aquatic species after short-term exposure
- The wastewater treatment process alters the bioavailability and accumulation potential of ENMs for aquatic invertebrates

Approach

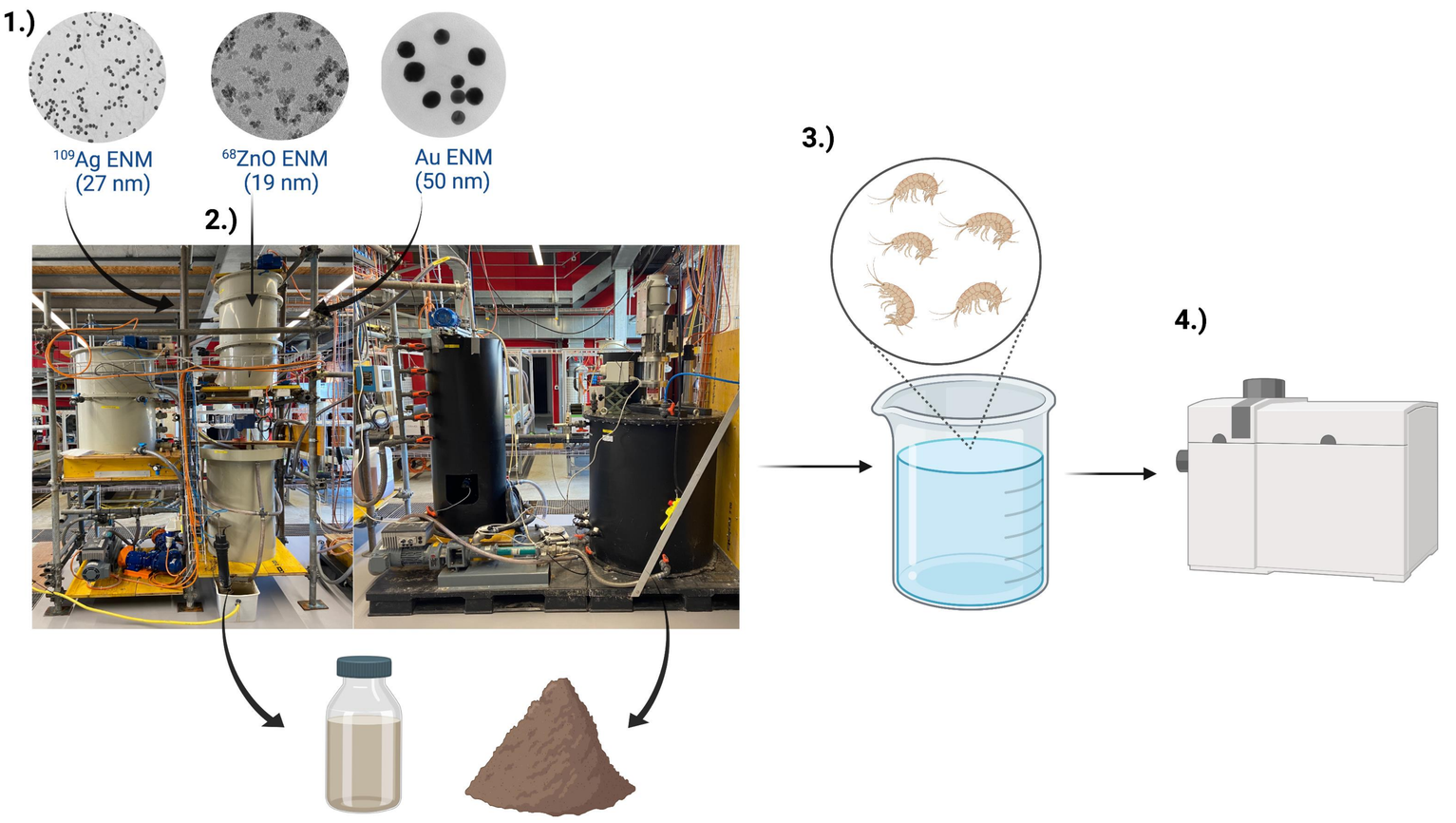

Fig 1. Schematic overview of the experiment. For each ENM type a separate WWTP experiment was conducted (duration up to 3 weeks). Concentrations in the different WWTP matrices were monitored using samples taken every 2 hours and measured by ICP-MS. For each ENM type a separate exposure study with *H. azteca* was condutced.

1) Isotopically enriched ENMs (^{109}Ag & ^{68}Zn) were synthesized to allow ENM tracing at low concentrations in complex matrices with high natural background of the respective metals.

2) The synthesized ENMs and Au ENMs were spiked into a pilot WWTP (operating with municipal wastewater, inflow of 17 L/h) and the effluent & digested sludge were collected.

3) 7-day aqueous exposure studies with *H. azteca* and ENM - containing WWTP effluents, biosolids or pristine ENMs spiked to control WWTP effluent or culture media were conducted.

4) The animal body burden was measured by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) and single particle ICP-MS (sp-ICP-MS) to estimate the impact of the wastewater treatment on the uptake and accumulation of the metals, but also to assess the presence of individual ENMs in the samples after optimized sample processing/ digestion.

Results and Conclusion

- Environmentally relevant concentrations of approximately 3 (Au), 20 (Ag) and 90 (Zn) mg/kg (dw of digested sludge) were reached by the ENM spiking in the pilot WWTP.
- Preliminary data obtained using isotopically enriched ENMs revealed that detection and differentiation of low ENM concentrations in WWTP matrices and *H. azteca* against natural background is possible.
- Exposure to Au ENMs- containing effluent (54 and 114 ng/L) led to measurable body burdens and revealed a reduced uptake and/or accumulation by *H. azteca*, compared to pristine Au ENMs.
- Analysis for experiments with exposures of *H. azteca* to ^{109}Ag and ^{68}Zn ENMs are ongoing.

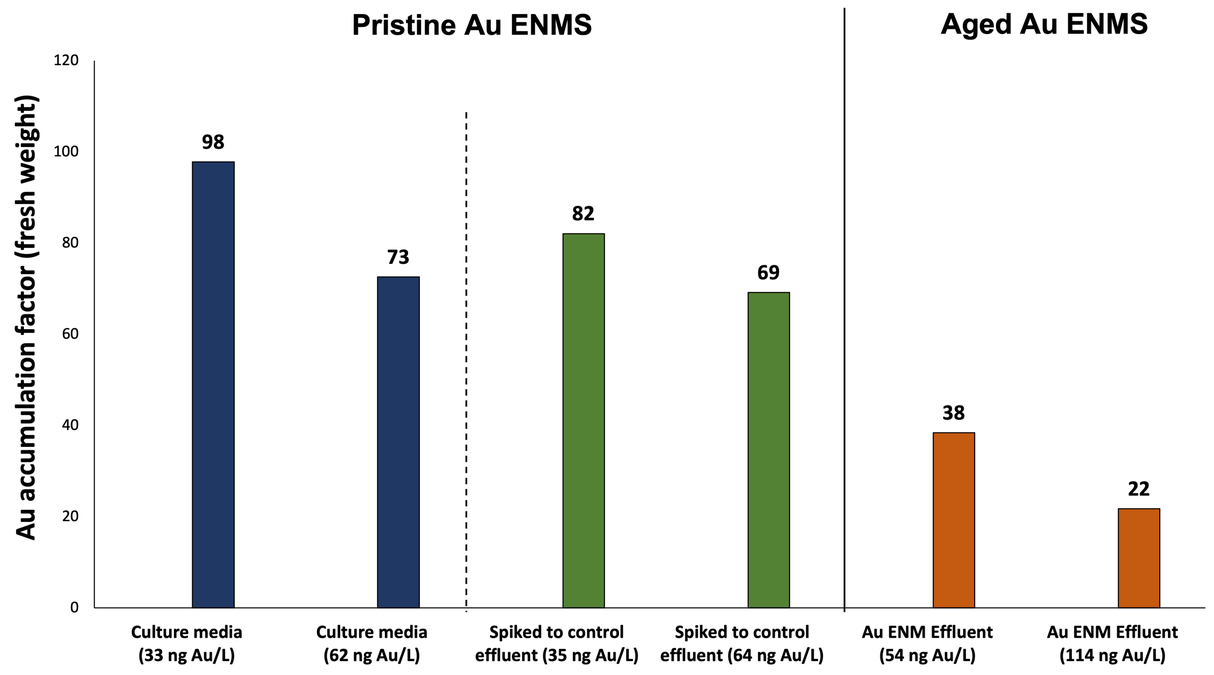

Fig 2. Accumulation factors of Au in *H. azteca* (body burden divided by the exposure conc., in mg/L). Au concentrations of the treatments are total metal concentrations in culture media and control WWTP effluent spiked with Au ENMs or effluent from ENM spiked WWTP.

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NIVA at SETAC 2022

The project has received funding from the Norwegian Research Council (Nano2021 Call, Agreement number 302378/F20)
https://www.niva.no/en/projectweb/entrans