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Grouping concept for metal and metal oxide nanomaterials with regard to their ecotoxicological effects on algae, daphnids and fish embryos

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ABSTRACT

Manufactured nanomaterials (NMs) are being developed in many different variations such as size, shape, crystalline structure and surface modifications. To avoid the testing of each single nanomaterial variation, grouping and read-across strategies for nanomaterials similar to classical chemicals are discussed. Grouping and read-across aim to identify NM groups with analogous sets of properties or properties that enable reasonable predictions of a NM hazard without additional testing. This will contribute to save costs and time in the risk assessment. So far the knowledge is still limited how modifications of NMs and their properties affect ecotoxicity.

This study was initiated to support the discussions on grouping regarding aquatic ecotoxicological effects and for the identification of relevant properties as well as the development of a grouping concept addressing aquatic ecotoxicity. A comprehensive and homogenous data set based on fourteen nanomaterials was established. The selected NMs were modifications of five chemical species (Ag, ZnO, TiO_2, CeO_2, Cu). As the focus was on the applicability for regulatory purposes, for ecotoxicity the OECD test guidelines 201 (algae), 202 (daphnids) and 236 (fish embryo) were considered. The physico-chemical properties of the chosen NMs were determined in deionized water and the test media applied for the ecotoxicological tests. Reactivity, ion release, morphology and ecotoxicity of the chemical composition (information from the bulk material) were identified as the most relevant grouping properties regarding nanomaterial's ecotoxicity. A grouping scheme and procedure was proposed considering these properties. The scheme was validated with a set of additional nanomaterials (TiO_2, SiO_2, Fe_2O_3).

A rough, but reliable grouping of NMs with different chemical composition was possible. The separation of NMs with the same chemical composition, into different groups was only feasible, if the NMs show major differences in one of the relevant properties (e.g. different shape). Based on the available data set it is unknown whether either further physico-chemical properties have to be considered or whether the impact of the selected variations on ecotoxicity is too minor to result in significant ecotoxicological differences. In order to further advance the grouping concept for regulatory testing, future developments should include the specification of threshold values with regard to the properties solubility and reactivity as well as for the characterization of the morphology. Additionally, test methods addressing the sorption tendency of NMs to algae could contribute to an improvement of the ecotox-scheme with regard to the consideration of physical effects by shading resulting in limited growth.

1. Introduction

Manufactured nanomaterials (NMs) are already used in numerous manufacturing processes and products and a release into the environment during their life cycle can occur (Nowack et al., 2012). For the different applications NMs are developed in many different variations such as size, shape, crystalline structure and surface modifications. Dependent on the variation, a different behavior of a NM with similar chemical composition is expected and it has to be evaluated how the variations may affect ecotoxicity. To avoid the testing of each single nanomaterial variation, grouping and read-across strategies for NMs similar to classical chemicals are discussed. Grouping and read-across aim to identify groups of substances/forms of a substance with specific sets of properties or properties that enable reasonable predictions

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hazard without additional testing. For grouping and read-across of NMs the main discussion is whether and how it can be performed for NMs of one chemical composition to address the various variations. This approach is required when considering regulations such as REACh (European Union, 2006). There, grouping and read-across can be used as instruments to fill data gaps within the regulatory information requirements.

In 2016, a workshop was held in Brussels (OECD, 2016) on grouping and read-across for the hazard assessment of manufactured nanomaterials. The workshop dealt especially with the OECD Guidance on Grouping of Chemicals and it was concluded that the existing grouping and read-across strategy for traditional chemicals is also applicable to NMs if some NM specific needs are taken into account. Additional properties, standardized methods, guidance and case studies are required to develop knowledge on how to connect physico-chemical (PC) properties of NMs with behavior and effects intended to be predicted in the grouping and read-across exercise.

For the prediction of effects from NM-associated PC-properties various concepts were developed ranging from overarching strategies to approaches with comparable high levels of detail. Most of the approaches focus on human toxicity (Arts et al., 2015; Arts et al., 2016; Jagiello et al., 2016; Kuempel et al., 2012; Low-Kam et al., 2015; Oomen et al., 2015; Winkler, 2016; Wyrzykowska et al., 2016; Zhang et al., 2012). Lynch et al. (2014) postulated that the toxicity of a specific NM is caused by at least one of four mode-of actions namely, release of toxic chemical constituents from NMs; direct effects from physical contact with NMs; inherent properties of the material such as photochemical properties; capacity of NMs to act as vectors for the transport of other toxic chemicals. They assume that it should be possible to characterize the toxicity by three categories of properties i.e. intrinsic factors, extrinsic properties, composition, which include many individual properties.

For ecotoxicity only a limited number of studies are available dealing with this topic. In the approach of Tamm et al. (2016) numerous PC-properties are included, but the authors did not identify the properties which are the main drivers for ecotoxicity. In other approaches selected PC-properties are linked with ecotoxicological tests but the applied test procedures such as microbial tests are not relevant in the scope of regulation (Patel et al., 2014) and the transferability of the identified properties to regulatory relevant ecotoxicological tests is unknown.

Several studies demonstrate that for ion releasing NMs released ions are one driver of the ecotoxicity (Ivask et al., 2014a; Ivask et al., 2014b; Notter et al., 2014; Xiu et al., 2012). Therefore, solubility should be a suitable indicator. Nevertheless, particular effects and unknown mechanisms of toxicity are also discussed (Gagne et al., 2013; Ivask et al., 2014a). DNA or RNA-profiling showed different expression patterns in organisms upon exposure to NMs and dissolved metal salts, supporting the hypothesis of additional toxicity mechanisms for NMs apart from the sole toxicity of the ions alone (Garcia-Reyero et al., 2014). These differences between NMs and ions may be driven by different uptake mechanisms or toxicokinetics (Bohme et al., 2017; Novo et al., 2015). Properties such as reactivity (e.g. the formation of reactive oxygen species, ROS (Ma et al., 2013)) or the zeta potential are indicators for reactivity and dispersion stability/agglomeration behavior (Meißner et al., 2010; Nickel et al., 2015; von der Kammer et al., 2010) and can affect the availability of the NMs for the test organisms. For non-ion releasing NMs the formation of ROS in the test medium as a property for ecotoxicity was demonstrated for CeO_2 by Booth et al. (2015). However, other studies have reported that CeO_2 NMs exhibit a scavenging ability and can reduce oxidative stress (Amin et al., 2011). For photocatalytic active NMs such as TiO_2 the crystalline structure could be of relevance. The crystalline structure anatase shows a substantially higher photoreactivity than rutile (Xu et al., 2011), but mixed-phase titanium catalysts can show an even greater photoreactivity (Hurum et al., 2003).

Independent of the chemical structure, size and surface area of the NMs are recommended as indicators of the degree of ecotoxicity as they determine the degree of surface dependent effects (Kim et al., 2015; Sendra et al., 2017). Thereby, it has to be considered that for ion-releasing NMs size and solubility are related.

The development of concepts regarding grouping using literature data is difficult as there are multiple modifications of the applied test designs such as the preparation of the test dispersions, the applied test media, organisms and endpoints as well as incubation periods. All these modifications can affect the results and hence the conclusions regarding the influence of selected PC-properties on ecotoxicological effects. Further, inconsistent reporting hampers the use of data from literature, as many studies do not provide full details as needed for the purpose of grouping.

To support the discussions on grouping regarding aquatic ecotoxicological effects and for the identification of relevant properties as well as the development of a grouping concept addressing aquatic ecotoxicity, a comprehensive and homogenous data set was established. In total, fourteen NMs were selected for systematic testing. They related to five chemical compositions (Ag, ZnO, CeO_2, TiO_2, Cu) with three to four sub-types (except Cu with only one sub-type). The sub-types per NM differed in properties such as size, shape, crystalline structure, solubility, reactivity. NMs featuring specific surface coatings were not considered to get a basic grouping concept in a first step and avoid establishing groups predominated by coating effects. Intrinsic properties as well as PC-properties (e.g. agglomeration size, zeta potential, pH, isoelectric point, solubility, reactivity) of the NMs in deionized water and in the test media were determined. Numerous statistical approaches were applied to establish relationships between the test results and the respective properties. Based on the results a concept for the grouping of NMs with regard to their ecotoxicological effects on algae, daphnids and fish embryos was developed. In the following, the most relevant steps of the investigations and concept development are described. An extensive report on the study, entitled “Considerations about the relationship of nanomaterial's physical-chemical properties and aquatic toxicity for the purpose of grouping” is available at the homepage of the German Environment Agency (http://www.umweltbundesamt.de/en/publications).

2. Material & methods

2.1. Selected NMs

Ion-releasing as well as non-ion releasing metal and metal oxide NMs which differed in size and shape, crystalline structure, reactivity and zeta-potential were selected. The selection aimed at covering a range of different properties with regard to chemical composition, shape, size and solubility, among others. Intrinsic properties are listed in Table 2 and medium dependent properties in supplementary material SM 1.

2.2. Suspension preparation

For the determination of the PC-properties and for the ecotoxicological tests NM suspensions were prepared. The suspension preparation procedure followed a protocol established in the EU SIINN project nanOxiMet (www.nanOxiMet.eu).

In the first step a stock suspension of the NMs was prepared water by mixing 40 mg ± 4 mg of the powder of the NMs or 40 µL of the NM-300 K suspension with 40 mL deionized (DI) water to reach a concentration of 1 g/L or 10 g/L for the silver NM, respectively. The suspension was sonicated for 10 min using a cup horn (Bandelin, Germany), and a pulse of 2 (0.2 s/0.8 s). The final energy input of 0.6 W/mL was calorimetrically measured (Taurozzi et al., 2011). The other two silver NMs (Ag 110,525 and 1340) were available as suspensions (10 g/L) and were not sonicated to avoid any structural