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Nanomaterials and the European Water Framework Directive

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Abstract

Besides the European Union (EU) Regulation on Registration, Evaluation, Authorization and Restriction of CHemicals (REACH), the EU Water Framework Directive (WFD) is probably the single most important piece of environmental legislation in Europe when it comes to dealing with nanomaterials in the future given their widespread and dispersive use. Despite of the importance of the WFD, the WFD has come under little academic scrutiny in this regard. While REACH deals with the manufacturing and import of chemicals, the Water Framework Directive is directed towards reducing the presence of dangerous chemicals (i.e. 'priority substances') in European waters. In this article, we first introduce to the key elements of the WFD and we analyze and discuss the challenges that hamper the implementation of the WFD, if nanomaterials were to be covered by the WFD as effectively as e.g. xenobiotic organic chemicals and heavy metals.

These challenges include whether nanomaterials could be considered as possible candidates to be selected as priority substances, how European Member States are to establish Environmental Quality Standards (EQSs) for nanomaterials, how European Member States are to undertake environmental monitoring of nanomaterials and finally, the applicability of Best Available Techniques and associated emission limit values when it comes to reducing point and diffuse sources of nanomaterials. We recommend that emerging (eco)toxicological evidence as well as the possibility of widespread environmental contamination of certain nanomaterials is used to select priority substances and that resources are allocated toward obtaining a deeper scientific understanding of the environmental processes that form the basis for deriving EQSs today. Instead of focusing on environmental monitoring downstream, 'upstream monitoring' should be implemented by systematically mapping nanomaterial production volumes, product concentrations, market penetration, dispersive vs. non-dispersive uses, etc. to map out the trends of environmental exposure in a given river basin district and finally, that focus is increased on engineering environmentally benign nanomaterials in order to prevent future point and diffuse sources of pollution.

1. Introduction

In regard to regulation of nanomaterials in Europe, the EU Regulations on Authorization and Restriction of CHemicals (REACH) is probably is single most important piece of legislation. Whereas REACH deals with the manufacturing and import of chemicals, the Water Framework Directive (WFD), which was adopted in October 2000, deals with cleaning up and reducing dangerous chemicals (i.e. 'priority substances') in European surface waters and groundwaters. Given the increasing use of nanomaterials, environmental exposure seems inevitable and hence there is an urgent need to analyze and discuss how and under what conditions nanomaterials fall under the scope of the WFD.

In this article, we first the discuss the scope and key elements of the WFD and go on to review the status of implementation. This includes an introduction to key deadlines and terms such a 'river basin management plans', 'good ecological potential' and 'good surface water chemical status' and 'priority substances' and 'Environmental Quality Standards' (EQS). The WFD establishes a river basin approach to water management, whereby Member States have to develop river basin management plans that specify the measures to be taken to meet the environmental objectives. This requires the establishment of a monitoring programme to determine the river basin's 'ecological potential' and 'chemical status', as well as the development of a plan of measures designed to achieve good ecological potential and good chemical status by 2015 (EP & CEU 2000). These requirements represent a number of challenges when it comes to nanomaterials, which we introduce and discuss in the second part of the article. These include whether nanomaterials are possible candidates as priority substances, how European Member States are to undertake environmental monitoring of nanomaterials and the feasibility of European Member States establishing EQS for nanomaterials. Finally, we provide a set of recommendations.

2. The EU Water Framework Directive

2.1 Aim and scope of the WFD

The key aims of the WFD are to protect surface waters, transitional waters, coastal waters and groundwater, to promote long-term sustainable water use and to prevent the further deterioration and to protect and enhance the status of aquatic ecosystems. In addition, the WFD aims to protect and improve the aquatic environment through specific measures for the progressive reduction of discharges, emissions and losses of priority substances and the cessation or phasing-out of discharges emissions and losses of priority hazardous substances (EP & CEU 2000, Art. 1). Thereby the WFD expands the scope of water protection to all waters, surface waters and groundwater and sets a goal of 2015 for achieving 'good status' for all waters in the EU, with a final deadline of 2027.

2.2. River basin management plans

The WFD establishes water management by a river basin approach with cooperation and joint objective-setting across Member State borders even in some cases beyond the EU territory. The geographical and hydrological formation of each river basin determines which Member States need to establish a so-called 'river basin management plan'. The river basin management plan, which needs to be updated every six years by the Member States, specifies the measures to be taken to meet the environmental objectives for surface waters, for groundwater and for protected areas. Furthermore, it specifically requires a summary of the measures taken to address pollution from priority substances. For instance, for surface waters, Member State shall implement necessary measures to prevent deterioration, restoration of artificial and heavily modified water bodies with the aim of achieving 'good ecological potential' and 'good surface water chemical status' ideally by 2015, and by the latest by 2027. This has to be done along with a progressively reduction of pollution from a set of 'priority substances' and 'ceasing or phasing out emissions, discharges and losses of priority hazardous substances' (EP & CEU 2000, Art. 4).

In addition, the river basin management plan is to include an analysis of the characteristics of the river basin (region, salinity, depth, etc.), as well as a review of the impact of human activity on the status of surface waters and on groundwater (e.g. water abstraction for urban, industrial, agricultural and other uses and impact of significant water flow regulation, including water transfer and diversion) (EP & CEU 2000, Art. 5, Annex II). This includes an economic analysis completed by the Member States of water use, involving relevant calculations of the recovery costs of the services that water brings as well as the volume, prices and costs associated with these water services, taking account of long term forecasts of supply and demand for water into account. Finally, the analysis should make judgments about the most cost-effective combination of measures with respect to water uses to be included in the programme of measures (EP & CEU 2000, Art. 5, Annex III).

2.3. Good ecological status and good chemical status

In order to ensure ecological protection for all surface waters the WFD sets a number of 'general requirement for ecological protection' as well as a 'general minimum chemical standard'. 'Good ecological status' is defined in terms of the quality of the biological community, the hydrological characteristics and the chemical characteristics, while 'good chemical status' is defined in terms of compliance with all the quality standards established for chemical substances at EU level (EP & CEU 2000, Art. 4, Annex V). Because of ecological variability, no absolute standards for biological quality can be set which would apply across the European Community. Controls are specified so that they allow for some limited deviation from the biological community to be expected had there only been minimal anthropogenic impact on this biological community. The definition of 'Good chemical status' is especially relevant to nanomaterials as it is defined in terms of compliance with all the quality standards established for chemical substances at European level. Presently, the WFD focuses on a relatively limited number of priority substances for which environmental quality standards have been set and though more substances will be added, nanomaterials have to the best of our knowledge not been considered (EP & CEU 2000, Art. 16).

2.4 Groundwater

One of the important innovations of the implementation of the WFD is that it integrates groundwater and surface water management for the first time at the European level. The requirements for groundwater in the WFD are complemented and extended by Directive 2006/118/EC on the protection of groundwater against pollution and deterioration. Compared to the requirements for 'good ecological status' and 'good chemical status' on surface waters, the situation is somewhat different for groundwater as management is based on the overall presumption that groundwater should not be polluted at all and hence all direct discharges to groundwater are prohibited. The Groundwater Directive sets chemical quality standards for nitrates, pesticides and biocides which must always be adhered to and are not intended to serve as an acceptable level of pollution (EP & CEU 2006, Annex I). In order to detect indirect discharges to groundwater the WFD further entails a requirement to monitor groundwater bodies to detect changes in chemical composition, while the Groundwater Directive sets requirements for the identification and reversal of any significant and sustained upward trends in concentrations of pollutants (EP & CEU 2000, Art. 17).

3. Implementation of WFD

The timeline of the implementation of the WFD into national legislation consists of a number of stages. By 2004, the Member States should have identified River Basin Districts and Authorities, as well as having completed a characterization of each river basin in terms of pressures and impacts, including the economic analysis. Monitoring networks and river basin management plans should be established and finalized by 2006 and 2009 respectively. In 2012 operational measurement programmes are to be established, in 2015 the second river basin management plans have to be initiated and by 2027 at the latest the objectives of the river basin management plans should be met.

Reporting from the Member States to the European Commission show that around 57,000 monitoring stations have been set up on surface waters and 51,000 for groundwater. Of these, more than 41,000 are for operational monitoring of ecological and/or chemical status. Most stations have been set up in the UK, Italy, Germany and Denmark, with the majority of stations located on rivers (75%), lakes (13%) and coastal waters (10%) (CEC 2009). The European Commission has identified a number of gaps and deficiencies in the design of the monitoring programmes set up by the Member States, including: 1) no clear incorporation of specific monitoring of protected areas e.g. in water dependent habitat and species protection areas; 2) a lack of reporting on international coordination mechanisms being in place in many international river basins; 3) assessment methods for biological quality element are not in place and 4) little information on the levels of confidence and precision of the overall monitoring programs - in particular the assessment methods for ecological status (CEC 2009).

4. Exposure pathways and estimations of concentrations for nanomaterials entering European waters

Given the widespread production and use of nanomaterials, it is inevitable that nanomaterials will be released into EU waters either directly or via soils (Boxall et al. 2007). Environmental routes of exposure are multiple and can stem from:

- nanomaterials employed in environmental remediation of soils and groundwater;
- operations related to the production of nanomaterials such as cleaning of production chambers;
- spills from production, transport, and disposal of nanomaterials or products;
- the use and disposal of products containing nanoparticles including incomplete waste incineration and disposal in landfills;
- wastewater overflow and ineffective sewage treatment plants (STP) unable to hold nanoparticles back or degrade them;
- degradation of products containing nanomaterials (Biswas and Wu 2005, RS & RAE 2004, Boxall et al. 2007, Grieger et al. 2010).

In addressing water pollution, the WFD distinguishes between point and diffuse sources of pollution. Point sources could be emissions of wastewater from industrial manufacturing facilities that either produces nanomaterials or nanoproducts. Point sources could further include effluent from urban wastewater treatment facilities stemming from e.g. cosmetics and sunscreens washed off the users' body or face (Mueller and Nowack 2008), detergents, nanotextiles (Benn and Westerhoff 2008) and from in- and outdoor paints (Kaegi et al. 2008). Nanomaterials can also be used to disinfect water (Li et al. 2008) and in wastewater treatment (NanoIron 2009) and hence these types of direct use might constitute a point source as well. Diffuse sources of nanomaterials could include: 1) nanomaterials leaching from landfills into groundwater and then into surface waters, 2) nanomaterial containing pesticide run-off from cultivate areas and sewage sludge, and 3) spilled fuels and lubricants washed off roads into storm water discharges as well as 4) atmospheric deposition of nanomaterials from, for instance, automobile engines and incinerators.

The total environmental load from current uses of nanomaterials is unclear (Muller and Nowack 2008, Luoma 2008). So far only Kaegi et al. (2008) have reported quantitative measurements of transport of nanomaterials in the environment. Kaegi et al. (2008) compared the leaching of $TiO2$ nanoparticles from a newly painted model facade and a real façade and traced leached nanoparticles from paint on house façades into receiving water bodies. It was found that the leaching from a newly painted model façade resulted in a titanium concentration of 600 µg l-1 of which 90% of the leached nanoparticles had a size range between 20 and 300 nm. Even after two years of exposure to weathering, the painted real façade resulted in a leaching of only 10 µg l-1 for titanium, while the urban run-off contained 8 µg l-1. For the real façade, the size of particles was similar to the newly painted façade and hence around 20-300 nm for 90% of the particles, but for the urban run-off 50% of particles were < 300 nm. Besides Kaegi et al. (2008), various estimates have been made both for individual products, nanomaterials and applications as well as product types and these are reviewed below as they help provide a feel for the current and future emissions of nanomaterials into the environment and especially European waters.

4.1 Nanosilver

Luoma (2008) estimated mass release of nano-silver from nano-silver socks, nano-silver wash machines and swimming pools in which nano-silver is used as a biocide. Silver discharges from nano-silver socks were estimated to be in the range of 6-930 kg per year in a scenario where 10% of the US population wore nano-silver sock and 180-2790 kg per year in a scenario where 30% wore nano-silver socks, with the range depending on the nano-silver content in the socks. Assuming that households that are wealthy enough will buy nano-silver washing machines, the contribution from nano-silver wash machines was found to be 2850 kg per year. In a context where 1 million pools use nano-silver as a biocide, the contribution from swimming pools was by far the largest found, estimated to be at 30 tons. In another scenario, Luoma estimated the total future discharges to be 457 tons assuming that there will 100, 10, and 5 products in the future with a comparable nano-silver discharge rate to socks, wash machines and the swimming pools, respectively. After waste treatment this could be reduced to 128 tons provided that 80% of the discharges are treated sufficiently to remove 90% of the silver.

Blaser et al. (2008) estimated the silver emission into wastewater by multiplying the amount of silver in biocidal plastics and textiles with the release rate of silver ions from these products and the period the products are in contact with water. Assuming that the wastewater removal in the sewage treatment plant ranges between 99-85%, Blaser et al. (2008) found that the predicted environmental concentration (PEC) for nano-silver from sewage treatment plants would be 18 µg/L whereas PECwater and PECsediment would be 320 ng/L and 14 mg/kg, respectively.

4.2 Cosmetics and personal care products

Based on available information on applied concentration of nanoparticles in cosmetics, personal care products and paints, Boxall et al. (2007) used a series of algorithms (for, among others, pesticides, medicinal products, and ultrafine particles) to estimate the predicted environmental concentrations of nanoparticles in soil and water. Although anticipating that 10% market penetration probably provides a conservative estimate (with the exception of sunscreens), Boxall et al. calculated the PEC for three scenarios assuming that 10%, 50% and 100% of the products on the market contained nanoparticles. The highest total predicted concentrations in water was found to be for latex nanoparticles (103-1025 µg/L) stemming from laundry detergents followed by zinc oxide (76.0-760 µg/L) and titanium oxide (24.5-245 µg/L) used in, among others, paints and sunscreens. The use of hydroxyapatite in toothpaste and fullerene in cosmetics is estimated to lead to an environmental concentration of between 10.1-101 and 0.31-3.13 µg/L, respectively. Predicted concentrations in soil range from 4.3-43 mg/kg for nanolatex to <0.01 for cerium oxide.

Mueller and Nowack (2008) modeled the predicted environmental concentration for nano-Ag, nano-TiO_2 and carbon nanotubes (CNTs) for air, water and soil in Switzerland. The calculations by Mueller and Nowack (2008) were based on a quantitative substance flow analysis of how nanoparticles from various product categories such as textiles, cosmetics, coatings, plastics, sports gear, electronics, etc. enter the environment through abrasion, outlet from the sewage treatment plants and/or waste incineration plants and landfills. Given the lack of information, numerous assumptions and estimates had to be made about worldwide production volumes, concentrations of nanomaterials in the products, levels of incombustible nanoparticles and behaviour during wastewater treatment. For CNT, for example, it is estimated to be realistic that the worldwide production in 2007/2008 is 350 tons and that these are evenly incorporated into plastics and electronics. For the CNT that end up in the waste incinerator, it is furthermore assumed that 50% will be burned, of which 25% will end in the slag and 25% will become airborne. Of the 25% that become airborne, 99.9% will be caught in the filters of the waste incineration plant leaving 0.1% to enter the atmosphere. In a high exposure scenario, Mueller and Nowack (2008) assumed a worldwide production of 500 tons annually and that only 25% are burned, with 99% of the airborne CNT caught by the filters of the incineration plant.

In comparing these results, Boxall et al. (2008) estimated PECs for nanoparticles in cosmetics and personal care products whereas the scope of the analysis of Muller and Nowack included among others textiles, metal products and cosmetics. Still Muller and Nowack found PECs that were lower - although in the same order of magnitude - as Boxall et al. (2008) for Ag in water and soil, and for TiO_2 in air. This was the case even for the high exposure scenario, whereas estimates differ substantially for TiO_2 in soil with several orders of magnitude. Boxall et al. (2008) assumed that no nanoparticles would be retained in the sewage treatment plants whereas Mueller and Nowack (2008) assumed that 97% and 90% of the nanoparticles would be cleared in the realistic and the high exposure scenario, respectively. This could help explain some of the difference between the PECs observed by Boxall et al. (2008) and Mueller and Nowack (2008).

Building on the work of Mueller and Nowack (2008), Gottschalk et al. (2010) included estimates of sediment and groundwater concentration as well as production, manufacturing and recycling processes. Using Monte Carlo and Markov Chain Monte Carlo computer simulations, Gottschalk et al. (2010) found that surface water concentrations (TiO_2

0.02 mg/L; CNT 0.003 ng/L; Ag 0.72 ng/L) differed substantially from concentrations in the sewage treatment plant effluent (TiO2 4.3 mg/L; CNT 11.8 ng/L; Ag 38.7 ng/L) and sewage treatment plant sludge (TiO2 211 mg/kg, CNT 0.069 mg/kg; Ag1.88 mg/kg). High rates of sedimentation led to remarkable annual deposition in sediment (TiO2 499 mg/kg; CNT 0.229 mg/kg; Ag 1.2 mg/kg).

5. Engineered nanoparticles as priority substances

Although environmental exposure estimates differ, environmental exposure of nanomaterials is inevitable. Hence a key question in regard to the Water Framework Directive is whether nanomaterials are possible candidates as priority substances.

Currently, the list of priority substances has to be reviewed and adapted by the European Commission at least every four years. As an overarching principle, the list of priority hazardous substances should include

1. hazardous substances agreed for phase-out or for cessation of discharges, emissions and losses in international agreements as well as
2. 'hazardous substances which give rise to 'an equivalent level of concern' as substances that are persistent, toxic and liable to bioaccumulate (PTBs)' (EP & CEU 2001).

Directive 2000/60/EC introduces in Article 16(2) a scientifically based methodology for selecting Priority substances on the basis of their significant risk to or via the aquatic environment. This methodology is based on scientific principles, taking particular account of:

1. evidence regarding the intrinsic hazard of the substance concerned, and, in particular, its aquatic ecotoxicity and human toxicity via aquatic exposure routes,
2. evidence from monitoring of widespread environmental contamination, and
3. other proven factors which may indicate the possibility of widespread environmental contamination, such as production, use volume and use pattern of the substance concerned.

On this basis, the European Commission has developed a Combined Monitoring-based and Modelling-based Priority Setting (COMMPS) scheme, in collaboration with experts from interested parties (Klein et al. 1999). The COMMPS scheme is a so-called scoring method in which functional relationship and weight factor are combined into one or more ranking lists of substances (Lerche et al. 2002). The COMMPS scheme follows a number of sequential steps:

- Step A: Selection of candidate substances for the ranking procedure from various official substance lists and monitoring programmes such as List I and II of Council Directive 76/464/EEC, OSPAR list of individual candidate substances and HELCOM lists of priority substances.
- Step B: Calculation of exposure indices based on surface water monitoring data and modeling data (using the Mackay I distribution model) for organic substances in the aquatic compartment. Exposure lists are also established for pollutants adsorbed by sediments and for metals (several scenarios) based only on monitoring data.
- Step C: Calculation of effect indices based on test data on direct and indirect effects on aquatic organisms as well as selected effects on humans (carcinogenicity, mutagenicity, reproductive and chronic effects from oral uptake) for organic pollutants and metals in the aquatic compartment and sediments.
- Step D: Computation of the risk-based priority index leading to ranked lists of substances derived by multiplying the exposure and the corresponding effects index for each substance. A number of lists are generated i.e. for organic substances based on aquatic monitoring data and on modelling data, respectively, one list is obtained based on sediment monitoring data and several lists are obtained for metals.
- Step E: Expert screening of the generated risk-based ranking lists in order to identify and select a subset of candidate priority substances from each of the lists leading to a recommendation for the inclusion/exclusion of these candidate substances into the priority list (Klein et al. 1999).

Each of the various steps in the COMMPS scheme hold obstacles when it comes to nanomaterials and some elements of the COMMPS work directly against the possibility of any nanomaterials being included as a candidate substances in the priority list.

First of all, no nanomaterial is currently listed on any of the official substance lists and monitoring programmes from which candidate substances are selected (Step A of the COMMPS scheme).

Second, surface water monitoring data is currently not available for any nanomaterial and the detection and monitoring of even widespread environmental presence of nanomaterials in natural waters presents some profound challenges. Environmentally relevant concentrations of nanomaterials are currently projected to be low as highlighted above in regard to nanosilver and nanoparticles used in cosmetics and personal care products. As detection limits for most monitoring methods are not sufficiently low (probably in the range of ng L-1-pg L-1 (Hasselöv et al. 2008), detection of nanomaterials in the environment by existing methods seems highly unlikely. Furthermore, there is no information about initial background levels of nanomaterials in the environment and there is currently no manner in which one can tell the difference between an engineered nanoparticle and a natural nanoparticle (Tiede 2008, Hassellöv et al. 2008). The use of modeling data based on production volumes, use pattern, environmental distribution and biodegradation as input parameters is an alternative option in the COMMPS scheme when there is a lack of monitoring data. However, the Mackay models currently suggested in the COMMPS scheme (Step B) are not applicable to nanomaterials since they are based on equilibrium assumptions and distribution coefficients that are not applicable to neither organic nor inorganic nanomaterials (Quick et al., 2011).

Third, the effect scores in the COMMPS Step C are based on scoring of the direct and indirect aquatic effects, e.g. using available Predicted No Effect Concentrations (PNECs) which, if existing for nanomaterials, are extrapolated from chronic or acute data according to the methods laid down in the Technical Guidance Documents on chemicals (ECB 2003). Such chronic and acute data is rarely available even for the most tested nanomaterials such as C60, carbon nanotubes, etc. (Baun et al. 2009, Stone et al. 2009). Furthermore, the reliability and interpretation of the available ecotoxicity data is impeded as a result of factors such as: particle impurities, suspension preparation methods, release of free metal ions, and particle aggregation (Baun et al. 2009, Stone et al. 2009, Hartmann et al. 2010).

The indirect aquatic effect scores are calculated from the measured bioconcentration factors (BCF) or the octanol-water partitioning coefficient (Kow) as a measure for the bioaccumulation potential. For nanomaterials, reliable measured BCFs are at present not available for the most commonly tested nanomaterials (Stone et al., 2009) and the traditionally used extrapolations based on Kow-values are not meaningful for nanomaterials. Finally, effects on humans such carcinogenicity, mutagenicity, reproductive and chronic effect from oral uptake of nanomaterials remain largely unexplored (Stone et al. 2009).

Based on the COMMPS scheme, Decision 2455/2001/EC of The European Parliament and of the Council of 20 November 2001 establishes a list of priority substances, whereas Directive 2008/105/EC lays down the environmental quality standards (EQS) for these priority substances and certain other pollutants as required under Article 16 of the Water Framework Directive. Annex I of Directive 2008/105/EC currently lists 33 substances, including Cadmium (Cd) and Nickel (Ni). Some nanomaterials are currently based on Cd and Ni and may therefore be stated to be included as priority substances in the annex I of this Directive. However, no consideration of potential nano-specific issues has been included in the setting of the EQS set for Cd and Ni.

6. Establishing EQS for nanomaterials

If a nanomaterial were to be included in the list of priority substances, an EQS would have to be defined (EP & CEU 2000). However, at present this presents big, and unresolved, scientific challenges due to limited reliability of the traditionally used test systems and methods for valid prediction of the ecotoxicity, persistency and bioaccumulation behaviour of nanomaterials (Baun et al., 2009).

As noted in relation to the COMMPS scheme, estimating EQS for nanoparticles is currently hampered by lack of ecotoxicological data, questionable reliability of available ecotoxicity data due particle impurities, suspension preparation methods, etc. In addition, the reliability of current test guidelines is uncertain, given that were originally developed for soluble chemicals and not dispersed nanomaterials (Baun et al. 2009, Hartmann et al. 2010). Besides these issues, mainly related to the lack of relevant data, it is also questionable whether the principles for deriving EQSs for chemicals can be directly transferred to nanomaterials. The physico-chemical properties of nanoparticles means that the potential adverse effects is not solely linked to the mass concentration of the nanoparticles in the biological sample, which is the fundamental premise of existing principles for deriving EQSs (Baun et al., 2009).

7. Environmental monitoring of nanomaterials

Besides laying down the EQS that Member States have to apply to water bodies, Directive 2008/105/EC also requires Member States to arrange for the long-term trend analysis of concentrations of those priority substances that tend to accumulate in sediment and/or biota. Monitoring programmes have to be established as well within six years after the date of entry of the WFD. For instance in regard to surface waters '...such programmes shall cover among other things 'the ecological and chemical status and ecological potential' (EP & CEU 2000, Art. 8). The frequency of monitoring should provide sufficient data for a reliable long-term trend analysis and should, as a guideline, take place every three years. Arrangement of long-term monitoring furthermore entails a responsibility on Member States to take measures to ensure that such concentrations do not significantly increase in sediment and/or relevant biota.

As mentioned above, monitoring in natural waters represents some profound challenges when it comes to nanomaterials. Besides issues related to developing methods with sufficiently low detection limits and being able to distinguish between natural and unintentionally produced nanoparticles, there is furthermore a lack of suitable methods to complete *in situ* analyses of samples in natural media and to complete nanoparticle characterization. Finally, it is important to recognize that even the slightest change in physico-chemical properties can make two nanomaterials of the same molecular form very different from each other in terms of characterization and environmental fate and behaviour.

Hence any environmental monitoring programs must be targeted towards specific nanomaterials, which will be extremely challenging and not something that is expected to be easily overcome (Tiede 2008, Hasselöv et al. 2008).

8. Triggers for action to reduce pollution

In the case that a nanomaterial should be included on the list of priority substance and assuming that the material could furthermore be detected and monitored for in EU waters, Art. 10, 11 and 16 of the WFD outline the specific measures that should be implemented to reduce environmental outlets. In order to reduce point source and diffuse discharges into surface waters, Art. 10 prescribes a so-called combined approach which entails the application of Best Available Technique (BAT) or relevant emission limit values to point sources, along with the application of Best Environmental Practice to diffuse sources.

BAT Reference Documents (BREF) is published to inform the operators of industrial installations of BAT for the reduction of point source emissions. Currently the BREF do not specifically address nanomaterial emissions and the emission limit values associated with the BAT in the BREF were not established with consideration of the nanoform. The current level of coverage of nanomaterials and ultra-fine particles within the BREFs is limited, although there is some mention of the effectiveness of techniques in reducing sub-micron size particles in relation to emissions to air. In order to achieve the objectives under Article 4, including good water status Member States must establish a programme of measures for each river basin district. This includes the requirement for point sources to have a specific authorization or a registration based on general binding rules laying down emission controls for pollutants. Diffuse sources must also be regulated by authorization or registration, with controls periodically reviewed and updated (EP & CEU 2000, Art. 11).

Article 16 of the WFD requires the European Parliament and the Council to adopt strategies aimed at the progressive reduction of water pollution by individual pollutants, as well as groups of pollutants. For priority hazardous substances these strategies should be aimed at the cessation or phasing out of discharges, emissions and losses (Article 16(1)). According to Article 16, the Commission is required to identify the appropriate cost-effective - and proportionate - combination of product and process controls for point and diffuse sources (Article 16(6)). The Commission is furthermore called on to submit proposals for emission controls for point sources for priority substances two years following their categorization as priority substances (Article 16(8)). In the absence of agreement on a community level, the Member States shall establish controls after six years (2014). This means that if one or more nanomaterials should be added to the list of priority substances, key point sources could be targeted for point source emission reductions. Proposals for point source controls should be based on a consideration of all technical reduction options, which in the case of nanomaterials may be limited and costly. Fabric filters, electrostatic precipitators and wet scrubbing are some of the techniques typically employed to capture releases of particulates to air from industrial installations and although these might also be effective in abating the nano-scale fraction, it is to be expected that efficiency will typically be less than for coarser particles. With regards to releases to surface waters, options available for controlling releases include both end-of-pipe techniques (for example for sedimentation and filtration of industrial effluents, and reduction of wastewater emissions from municipal waste water treatment plants) and up-stream legislation to eliminate the sources.

9. Discussion

The aim and scope of the WFD is focused on the overall protection of EU waters from further deterioration as a result of human activities and the production and use of nanomaterials are, in theory, no exception to this broad overall aim. Despite this, a number of limitations of the WFD have been identified, especially with regards to: 1) the COMMPS scheme which is currently used to selected substances as candidates for the list of priority substances; 2) the data requirements and procedures used to derive EQSs; 3) the requirements of evidence from monitoring of widespread contamination and finally, 4) the applicability of Best Available Techniques and associated emission limit values when it comes to reducing point and diffuse sources of nanomaterials. In the following, these limitations will be discussed and recommendations will be provided on how to address them.

9.1 Nanomaterials, COMMPS and list of Priority Substances

Some nanomaterials can at best be classified as emerging pollutants e.g. nanosilver and zinc oxide as quite low concentrations of nanosilver and zinc oxide have been observed to cause adverse impacts on various environmental species (fish, daphnia, algae) in the laboratory (Stone et al. 2009). Hence most nanomaterials would never even be considered under the COMMPS scheme, as only candidate substances from official lists of well-known and established pollutants are selected. These established pollutants either fulfil the PBT-criteria or are known to have a deleterious effect on the aquatic environment. In that manner the COMMPS scheme is inherently reactive and fundamentally directed towards prioritizing among known pollutants and not directed towards dealing with emerging pollutants. Even if one or more nanomaterials were to be considered under the COMMPS scheme, the heavy reliance on monitoring and modeling data as well as the lack of ecotoxicological data will hamper the usability of COMMPS scheme for most nanomaterials for some time to come. Deriving the exposure and effect scores required in the COMMPS scheme is simply not possible for the time being.

The overall goal of the WFD is to prevent deterioration of all bodies of surface water and groundwater and promote long-term sustainable water use and to enhance the status of aquatic ecosystems. It therefore seems to work against this overall aim that one would always have to wait for evidence of environmental harm to emerge before prioritizing a substance, while knowing that environmental exposure of the substance is increasing exponentially, although we cannot detect and monitor it for the time being. Thereby any opportunity to prevent harm is missed. When it comes to nanomaterials, we recommend that the COMMPS scheme is not used and that the more loose 'scientific principles' cited in the article 16 of the WFD, are considered such as 'evidence regarding the intrinsic hazard of the substance concerned' (including aquatic ecotoxicity and human toxicity via aquatic exposure routes) and 'other proven factors which may indicate the possibility of widespread environmental contamination such as production or use volume of the substance concerned, and use patterns' (EP and CEU 2000, art. 16).

Some applications of nanomaterials involve direct contact with the water cycle and do therefore call for attention as potential priority substance, e.g. due to their use for water disinfection (Li et al. 2008) and wastewater treatment (Nano Iron 2009), as well as the direct use of specific nanomaterials to treat soil and groundwater contamination (Li et al. 2006). Given the widespread and diffuse use of nanomaterials in a range of consumer products along with the hazard characteristics (ecotoxicity, persistency, etc.) of some nanomaterials, we would argue that for instance carbon nanotubes, nano-scale silver and zinc oxide should and could be considered as candidates to be added to the list of priority substances. In the case of silver, the nano-scale of the particles has enabled a range of uses that not hitherto was possible. Since silver in its 'non-nano' forms is a well-know environmentally hazardous metal and there is substantial evidence that nano-silver is at least as toxic (Stone et al. 2009), it seems appropriate to re-evaluate the inclusion of silver - and its nano-forms - as a priority hazardous substance under the WFD.

9.2 Data requirements and procedures used to derive EQSs

Should a nanomaterial be including on the list of priority substances, the establishment of an EQS is required. However, the establishment of the EQS for any given nanomaterial is hampered by the lack of ecotoxicological data on toxicity, persistency and bioaccumulation even for the most tested nanomaterials such as fullerenes, carbon nanotubes, titanium dioxide, zinc oxide, and silver. This makes it virtually impossible to set an EQS for nanoparticles. The reliability and interpretation of the available ecotoxicity data is furthermore impeded as a result of factors such as: particle impurities, suspension preparation methods, release of free metal ions, and particle aggregation (Baun et al. 2009). Besides these issues, mainly related to the lack of relevant data, it is also questionable whether the principles for deriving EQSs for chemicals can be directly transferred to nanomaterials. Thus, there is an urgent need for a deeper scientific understanding of the processes influencing the exposure concentrations used in the standardized test systems that form the basis for deriving EQSs today. Without such knowledge, any extrapolation will at best be very uncertain, and at worst invalid, in order to obtain the WFD goals of protecting and enhancing status of aquatic ecosystems in Europe.

9.3 Environmental monitoring of nanomaterials

Should EQSs be established for one or more nanomaterials in the future, monitoring would then be required as for other priority substances under WFD. However, monitoring of nanomaterials holds a number of technical challenges such as insufficiently low detection limits for most methods, high background of natural and unintentionally produced nanoparticles in environmental samples. Setting up monitoring programmes for nanomaterials does not make much sense at the moment due to these technical limitations and although substantial progress has been made recently, it will still be some time before we can consistently monitoring environmental concentrations of nanomaterials in situ.

It is a fact that nanomaterials are increasingly being produced and used and that the diffuse applications make environmental exposure inevitable. Despite numerous limitations in our knowledge about production and environmental releases of nanomaterials (Luoma 2008, Boxall et al. 2007, Mueller and Nowack 2008, Gottschack et al. 2010, Kaegi et al. 2010), production and uses of nanomaterials is much more easily determined, accessible and obtainable compared to quantitative environmental monitoring data and hence this information should be used proactively to implement 'upstream monitoring' of nanomaterials rather than 'downstream monitoring'. By systematically mapping production volumes, product categories (food, cosmetics, etc.), product concentrations, market penetration, end-of-life projection, etc. as well as the nature of use (dispersive vs. non-dispersive) one could begin to map out the trends that environmental exposure would follow in a given river basin district.

9.4 Reduce point and diffuse sources of pollution

Although BAT might not be available specifically for nanomaterials, there are plenty of ways in which one could reduce the environmental outlet of nanomaterials.

First, the use of nanomaterials in products and applications could be made a lot smarter by exploring the possibility of changing the location of the nanomaterial in a given product, so that it serves the same function, but exposure is minimized or completely eliminated. For instance, environmental exposure of dispersive nanoproducts that are sold in liquid form to coat various surfaces such as bathroom tiles, kitchen hardware, etc. could be reduced if manufacturers produced these products with the nanoparticles bound to the surface. Another option is to completely eliminate emissions of nanoparticles in use phase by developing dirt-repelling nanostructured surfaces that do not involve the use of nanoparticles at all (see figure 1).

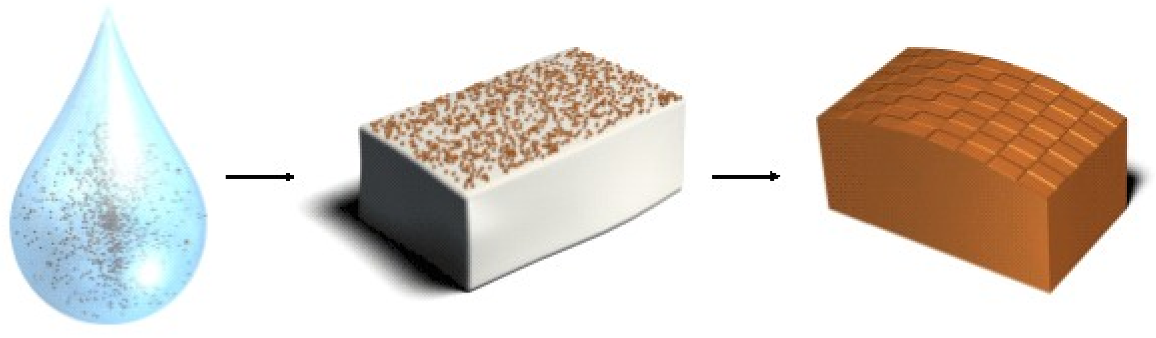

Figure 1: Illustration of how changing the location of the nanoelement in a given application changes the environmental exposure potential of the nanomaterial. In the liquid form the likelihood of emissions to the aquatic environment is higher than if the particles are bound to a surface. Finally, if the materials are nano-structured, no emissions of nanoparticles can occur.

Second, nanomaterials may be engineered so that they become less of a concern by engineering them to be more biodegradable, less persistent, and less toxic i.e a safety bu design approach.

Finally, the use of certain nanomaterials may be limited to cases in which their inclusion is truly 'necessary,' whereby the potential benefits of using nanos clearly outweigh the risks (Baun et al. 2009)

10. Conclusion

Given the widespread and dispersive use of nanomaterials, the EU Water Framework Directive (WFD) could potential play a key role when it comes to dealing with nanomaterials in the future. Despite this, the WFD has come under little academic scrutiny in this regard. In this article, we have analyzed the WFD and identified a number of limitations when in comes to dealing effectively with nanomaterials. These limitations are related to: 1) the COMMPS scheme which is currently used to selected substances as candidates for the list of priority substances; 2) the data requirements and procedures used to derive EQSs; 3) the requirements of evidence from monitoring of widespread contamination and finally, 4) the applicability of Best Available Techniques and associated emission limit values when it comes to reducing point and diffuse sources of nanomaterials. In order to overcome these limitations when it comes to nanomaterials, we recommend that:

1. emerging (eco)toxicological evidence as well as the possibility of widespread environmental contamination of certain nanomaterials is used to select priority substances;
2. that resources are allocated toward obtaining a deeper scientific understanding of the environmental processes that form the basis for deriving EQSs today;
3. 'upstream monitoring' is implemented by systematically mapping nanomaterial production volumes, product concentrations, market penetration, dispersive vs. non-dispersive uses, etc. to map out the trends of environmental exposure in a given river basin district and;
4. focus is increased on engineering environmentally benign nanomaterials in order to prevent future point and diffuse sources of pollution

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