Nano matters: building blocks for a precautionary approach

van Broekhuizen, J.C.

Citation for published version (APA):
Chapter 8

Conclusions
Chapter 8 Conclusions

This thesis deals with two issues regarding the responsible development of nanotechnologies. The first issue concerns the precautionary principle: how should this principle be applied to the manufacture, processing and use of nanomaterials. The focus is on the positioning of stakeholders involved in this deliberative process about application of the precautionary principle, especially on the demands of environmental NGOs and trade unions (Civil Society Organizations – CSOs). These demands regard the way that industry and government should deal with nanomaterials given the lack of sufficient hazard and risk data. This thesis also deals with the attitude of the industries, which use nanomaterials, especially of small and medium sized enterprises (SME), regarding their understanding of the precautionary principle and their willingness to make the principle operational for a safe workplace.

The second issue regards the operationalization of the precautionary principle and how to embed this in a risk management strategy for the workplace. The focus is on nano reference values (NRVs), which were proposed to be used as a provisional alternative for the so far lacking health-based occupational exposure limits (HB-OEL). So far HB-OELs are not available for nanomaterials. The concept of NRVs was further developed to a level that might make them acceptable as a tool for risk management when uncertainty regarding hazard and risk data prevails. NRVs were applied at workplaces where manufactured nanomaterials (MNMs) and nano-enabled products were used. The NRV-concept was also compared with other concepts to support occupational risk management such as the control-bandung approach.

Chapter 2 of this thesis deals with the role of the CSOs in the debate on the responsible development of nanotechnologies and what they propose to make the precautionary principle operational. The positions developed by trade unions and environmental NGOs show large similarities. The trade unions positioned themselves collectively under the umbrella of the European Trade Union Confederation (ETUC) with a resolution on nanotechnologies and nanomaterials in 2008 and 2010 (ETUC 2008, ETUC 2010). The Environmental NGOs formulated their position in the EEB position paper (EEB 2009).

A key point in the position statements of CSOs is the demand for openness and transparency by industry about manufactured nanomaterials (MNMs) applied in products. The CSOs ask for a full life cycle analysis regarding release of MNMs in all stages of the nano-enabled products’ life cycle and an assessment of the associated environmental and occupational health risks. The CSOs emphasize that the precautionary principle should be applied when using MNMs and nano-enabled products for which knowledge on the health hazards is insufficient or ambiguous and risks cannot be properly assessed. As viewed by the CSOs, the application of the precautionary principle does not only relate to industry and its environmental and health & safety policy but regards also the task of governmental authorities to provide a (legal) frame that guarantees the safe use of MNMs.

The CSOs’ demands are summarized in “building blocks for a precautionary approach” (see table 1).
Table 1  Building blocks for a precautionary approach

| No data → no exposure and no data → no emission. |
| Reporting of the content and type of nanomaterials in products (traceability) |
| Registration of workers possibly exposed to nanomaterials |
| Transparent communication about known and unknown risks |
| Derivation of workplace exposure limits |
| Development of an early warning system |
| Pre-marketing approval for all applications and nanotechnologies and nanomaterials as a central element of the policy and regulatory framework |

The building blocks mentioned in Table 1 play a role in (ongoing) European initiatives to create openness and transparency and to assure the safe use of nano-enabled products. Among these are the publications of Codes of Conduct (CoC) by the European Commission and some large companies manufacturing nanomaterials, adaptations in the REACH regulation to fit nanomaterials in the regulatory system, the recommendation of a definition of nanomaterials by the European Commission, the French initiative to make reporting of the use nanomaterials in products mandatory, initiatives in Member States to set up a database of nano-enabled products at the market and many others. The first six building blocks also are the basis for the advice of the Dutch Social and Economic Council (SER 2009) on the safe use of nanomaterials and provide a frame for the Dutch governmental environmental and occupational health and safety (OHS) policy.

Industrial openness and transparency about MNMs used in marketed products appears to be problematic. The studies presented in this thesis about the construction industry, the furniture industry and paint value chain (chapter 3) show that market penetration of MNMs in products was limited and that awareness of the majority of the end-users, employers and employees of the building and furniture industry participating in the studies about the availability of nano-enabled products and about their actual use appears to be very low. For most of the participants it appeared to be very difficult to find out whether manufactured nanomaterials are applied in the products they use, there is much ignorance on the availability of nano-enabled products at the market and about the identity of the nanomaterials used in these products. This appears to be even worse for sectors that are active in cleaning and maintenance. An example is the sector of car repair. Car repair shops are generally not informed about nanomaterials used in car components as coatings, bumpers, rubber particles etc. The transparency of the nanomaterials use is further obscured by the tendency of downstream product manufacturers to keep R&D activities confidential that they carry out with nanomaterials to improve the performance of their products. And when downstream product manufacturers are using nano-enabled products in their processes and products many of them are reluctant to make this public as to avoid a critical reaction from the public due to the worldwide social debate on health and safety issues and related uncertainties.

Also information about hazards and risks of MNMs is poorly developed. A collective industrial effort to generate as yet lacking toxicity data for nanomaterials and the exchange of data bears similarities to those for chemical substances under REACH, for
which a mandatory participation was foreseen in substance information exchange fora (SIEF) to assure and stimulate the exchange of industrially “owned” toxicity data (REACH 2006). For nanomaterials such initiatives were not identified. Only for a few nanoparticulate substances, such as CNTs, TiO₂ and Ag more detailed information, including proposals for health-based limit values have been provided. With the exception of CNTs (where some industrial companies provided proposals for an OEL) this information was largely provided by research institutes. The limited information supply about hazard and risks is not only a problem for CSOs and consumers, but also for downstream professional users of nano-enabled products. They are held ignorant to a large extent about hazards and risks of MNMs used in the products supplied, neither are they informed by their supplier about gaps in knowledge about hazards and risks or what they should do to avoid risks or how to apply a precautionary approach.

The no data, no exposure principle (building block 1 in table 1) calls upon the industry to apply effective control measures. It allows the use of MNMs in products, but demands for a precautionary approach in occupational settings to fully control all exposures to MNMs with insufficient hazard data, including control during accidental release and maintenance and cleaning operations. The need to apply effective control measures also applies to environmental emissions of MNMs, along the full life cycle. The safe option to achieve this would be a moratorium, i.e. to avoid the use of MNMs (and nano-enabled products). This option is not advocated by the CSOs that participated in the study. Nevertheless, it is generally acknowledged that when a choice is made to apply MNMs, releases cannot be prevented (at all foreseeable and unforeseeable moments) and consequently a zero-exposure or a zero-emission is an illusion. Considering the derivation of acceptable exposure levels for airborne MNMs generates the dilemma that the existing gaps in toxicological knowledge make a derivation of health-based exposure levels impossible. Regulators and industrial stakeholders in the Netherlands have agreed that postponing the derivation of limit values for occupational exposure until more hazard data come available is not an acceptable option, as that would imply acceptance of the situation as it is, allowing exposure to emerging concentrations at the workplace.

In view thereof, the concept of nano reference values (NRVs) (building block nr 5 in table 1) has been developed (IFA 2009, Dekkers et al 2010, this thesis) and framed for provisional use at the workplace. The starting point was to derive particle number–based NRVs for four groups of nanomaterials. This was preferred over a mass-based approach. Size, form, biopersistence, and density were used as parameters to distinguish the groups. For granular nanomaterials, assuming a sphere-like shape and standardized at a diameter of 100nm, number-based benchmarks were derived equivalent to a mass concentration of 0.1mg/m³. (This implies that the equivalent mass-concentration for smaller nanoparticles is lower, e.g. for particles with a diameter of 50nm this is 12.5μg/m³). For nanofibers (including carbon nanotubes) the asbestos OEL was used as reference. For soluble and non-biopersistent nanoparticles a NRV was assigned according to the applicable OEL for the coarse (or molecular) form because regarding hazard, these particles are supposed to behave like ‘conventional’ substances.

The NRVs are defined as 8-hour time-weighted averaged (8hr-TWA) concentrations, intended to be a warning level: when they are exceeded exposure control measures should
be taken to assure an exposure below this level (see table 2). For short-term peak exposures of maximum 15 minutes it was proposed to use a maximum level of twice the value of the NRV: \( \text{NRV}_{15\text{min-TWA}} = 2 \times \text{NRV}_{8\text{hr-TWA}} \). This is in line with the discussions of an international workshop presented in chapter 7.

**Table 2** Nano Reference Values (NRVs) for 4 classes of manufactured nanomaterials

<table>
<thead>
<tr>
<th>Class</th>
<th>Description</th>
<th>Density</th>
<th>NRV (8-hr TWA)</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rigid, biopersistent nanofibers for which-effects similar to those of asbestos are not excluded</td>
<td>0.01 fibers/cm³</td>
<td>SWCNT or MWCNT or metal oxide fibers for which asbestos-like effects are not excluded</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Biopersistent granular nanomaterial in the range of 1 and 100 nm</td>
<td>&gt;6,000 kg/m³</td>
<td>20,000 particles/cm³</td>
<td>Ag, Au, CeO₂, CoO, Fe, Fe₂O₃, La, Pb, Sb₂O₃, SnO₂</td>
</tr>
<tr>
<td>3</td>
<td>Biopersistent granular and fiber form nanomaterials in the range of 1 and 100+6,000 kg/m³</td>
<td>40,000 particles/cm³</td>
<td>Al₂O₃, SiO₂, TiN, TiO₂, ZnO, nanoclay Carbon Black, C₆₀, dendrimers, polystyrene Nanofibers with excluded asbestos-like effects</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Non-biopersistent granular nanomaterial, in the range of 1 and 100 nm</td>
<td>Applicable OEL</td>
<td>e.g., fats, NaCl</td>
<td></td>
</tr>
</tbody>
</table>

The study presented in chapter 5 of this thesis indicates that most companies working with nanomaterials accept NRVs as a tool to prevent hazard and risk. Companies tend to be proactive toward using the NRVs for risk assessment and management. An important driver to use NRVs seems to be a temporary certainty employers experience regarding their legal obligation to take preventive action. A contribution to the positive attitude of companies towards the NRV may also be the reassuring finding that conventional exposure control measures are generally adequate as well to control airborne MNMs. Many of the companies and regulators welcome the voluntary character of NRVs, but trade unions and a few companies advocate giving the NRVs a more binding status. Important preconditions for compliance to use NRVs relate to appropriate and easy available measurement strategies at low cost and an appropriate information supply about nanomaterials used in products and their possible release during intended use. Regulators can benefit from the positive motivation posture of companies. To enhance the use of NRVs regulators are recommended to emphasize the trust building function of NRVs. The Dutch Government accepted the approach and regards the provisional NRVs as reflecting the best available science and as state of the art approach for risk assessment of nanomaterials (Atsma 2009; Donner 2010).

As shown in chapters 3 and 4 of this thesis, the exposure to manufactured nanomaterials was measured at a variety of workplaces: in the construction industry (mixing and drilling nano-enabled concrete), the furniture industry (applying nanopaint and abrasion of (nano)-painted surfaces), electroplating, nanopaint manufacturing, manufacturing of pigment concentrates, production of non-reflective glass, manufacturing of fluorescent tubes, car repair and refinishing and as a control the manufacturing of conventional non-nano wall paint and the long-term testing of wear lubrication. An exposure assessment strategy was developed to distinguish exposure to manufactured nanomaterials from the ambient background concentration and from the concentration of nanoparticles generated at the workplace by processes and equipment used. This assessment strategy allows for applying nano reference values without necessarily examining the chemical composition of
workplace samples. It was found that the use of solid, dispersable manufactured nanomaterials gives sometimes rise to high airborne NP concentrations near the source with a rapid dilution further away from the source. Use of manufactured nanomaterials contained in a fluid, or machining (e.g. abrasion) of surface coated articles with nanomaterials-containing paint or coating shows only a very limited or no emission of airborne NPs. For most operations the exposure can be characterized by short-term high peak emissions, but the 8hr-TWA exposure to manufactured nanomaterials remained in most cases below the NRV_{8hr-TWA}. The NRV_{15min-TWA} is incidently exceeded at some workplaces.

The measurements presented in chapters 3 and 4 of this thesis show that manufactured nanoparticles are not the only source of workplace exposure to nanoparticles. Also important can be process-generated nanoparticles (PGNPs). The handling of some conventional paint components may generate airborne NPs, due to a nanoparticulate fraction in these compounds, and may give rise to a larger NP-emission than the emission generated by the manufactured nanomaterials used. Combustion processes (e.g. the use of diesel engines), the use of electro motors and continuously running machines may also generate PGNPs. That the contributions of process-generated nanoparticles to the total nanoparticles’ exposure cannot be ignored in risk assessment, was acknowledged by the Dutch Social and Economic Council (SER) that made this finding part of their advice on the use of nano reference values (SER 2012). It was also taken up by the 7th Joint EU/US conference on occupational safety and health (EU/US 2012) of trade unions, employers’ organizations and governmental authorities. This conference adopted this issue in their overarching principles as follows: *Develop harmonized exposure assessment measurements and control strategies for nanomaterials and processes - Process generated nanomaterials cannot be ignored when assessing nanomaterials at the workplace.*

The finding that it is relevant to take process-generated nanoparticles into account may reach far beyond the risk assessment of workplaces with manufactured nanomaterials or nano-enabled products. For activities with emissions for which a HB-OEL has been established, like for example welding operations, it is advisable to reconsider the health basis of this OEL and to apply the knowledge that is available nowadays on the risks of exposure to nanoparticles. This thesis advises to apply the NRVs also to the process-generated nanoparticles because the toxicity is not necessarily different from the assumed toxicity of manufactured nanomaterials. The Dutch Social Economic Council decided differently, and decided to distinguish between manufactured nanoparticles and process-generated nanoparticles, and to advise the Minister of Social Affairs to develop a generic health-based OEL for process-generated nanoparticles (SER 2012).

The NRV approach was integrated in a laymen-oriented guidance for working safely with nanomaterials and nanoproducts (the Guidance). In chapter 6 this approach was compared with two qualitative tools that support safe working with manufactured nanomaterials: the Control Banding Nanotoo (CBN) and the Stoffenmanager Nano (SMN). The Guidance and CBN estimate the emission potential, the SMN estimates the immission potential. The tools provide a model to estimate the risk when working with nanomaterials, may provide defaults for lacking hazard data and recommend a level for engineering control. It was
found that the three tools, when applied at the same workplaces, estimate differences in risk levels, but they do not necessarily lead to differences in recommended engineering control. The CBN and the SMN estimate a high risk especially when hazard data are lacking. The Guidance estimates a high risk level when dispersive MNMs are used. It was observed that the sensitivity for hazard data is high in the SMN, and low in the CBN and the Guidance, while the sensitivity for exposure data is high for the CBN and low for the SMN and the Guidance. The neglect of process-generated nanoparticles in the three tools may lead to an underestimation of the exposure to workplace-related nanoparticle emissions, and as a consequence to an underestimation of the potential risks. It was concluded that the tools studied may have a function in increasing the awareness of workers and SMEs about the possible risks of nanomaterials. The tools make explicit what hazard and exposure data are urgently needed to fill the gaps to make a reliable risk assessment.

The NRV-concept was also compared with the approach of the British Standards Institute (BSI), which is a scaling-down methodology that derives benchmark levels for nanomaterials based on the OEL as established for the coarse particles. The NRV-approach was furthermore compared with the generic approach proposed by Pauluhn, who assumes lung-overload to be the critical effect for most nanoparticles, derives an algorithm with the particles’ density as key element to calculate a derived no-effect level for the specific nanoparticle. It was shown that the NRV approach as proposed here gives rise to stricter exposure limits than the mass-based proposals of Pauluhn and often to stricter exposure limits than the mass-based BSI proposal.

References


ETUC (2008) Resolution on nanotechnologies and nanomaterials Resolution adopted by the ETUC Executive Committee in their meeting held in Brussels on 24-25 June 2008


IFA (2009): Technical Information → nanoparticles at the workplace:


Available at http://www.ser.nl/medie/Files/Internet/Talen/Engels/2009/200901/200901.ashx