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NANOWASTE AS A PART OF MUNICIPAL WASTE STREAMS: A REVIEW

NANOMATERIÁLY JAKO SOUČÁST TOKŮ KOMUNÁLNÍHO ODPADU

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Abstrakt

Nanomateriály představují jak technologickou, tak ekonomickou výzvu současnosti. Zatímco v nedávné minulosti nacházely tyto nové materiály využití především v elektrotechnickém průmyslu, v posledních letech se stávají běžnou součástí spotřebitelských výrobků, které získávají díky jejich přítomnosti mnoho specifických vlastností a vylepšení. Nanoprodukty, jak lze tyto výrobky zkráceně nazývat, si našly cestu do všech moderních domácností, a to zejména v podobě kosmetických výrobků a textilu. Nanomateriály však nejsou pouze přínosem, ale mohou představovat také rizika pro životní prostředí i pro lidské zdraví. Zejména nanočástice se mohou ze spotřebitelských výrobků nekontrolovaně uvolňovat, a to i prostým používáním, a vstupovat přímo do vodních ekosystémů, či nepřímo do životního prostředí přes procesy spojené s odpadovým hospodářstvím. Cílem tohoto příspěvku je shrnutí aktuálních poznatků týkajících se odpadu spojeného s nanoprodukty, který představuje zcela nový typ odpadu, o jehož produkci a chování v tocích komunálního odpadu existuje stále velmi málo informací.

Abstract

Engineered nanomaterials present a major contemporary technological challenge. Many specific functions, chemical or physical properties of frequently utilized products of daily use namely cosmetics and textile are nanotechnology-enhanced. The significant increase of consumer nanoproducts on the market will mirror the amount of future waste containing nanomaterials, for which the term nanowaste can be easy used. Nanomaterials and particularly nanoparticles from nano-based products in the end of their life cycle phase or during their use end up in municipal waste streams and due to ineffective waste handling or inappropriate waste management can enter the environment and cause many issues including the harmful effect for human health. This literature review summarizes actual knowledge about nanowaste and reports on currently proposed waste management systems how to deal with this new kind of waste.

Klíčová slova: *nanomateriál, nanoprodukt, nanoodpad, komunální odpad, odpadové hospodářství*

Key words: *nanowaste, nanoproducts, nanomaterials, municipal waste, waste management*

Introduction

Nanomaterials are defined as materials, "which should consist of 50 % or more of particles having a size between 1 nm to 100 nm" (European Commission 2011). These nanoscale materials could be also divided according to their dimensionality to one-dimensional nanomaterials such as layers, films, surface coatings, two-dimensional nanomaterials include for example nanofibres or nanotubes and three-dimensional nanomaterials are known as nanoparticles (Royal Commission on Environmental Pollution 2008), which seem to have highest potential health and environmental impacts (Filipová et al. 2012).

Nanomaterials are known as novel materials produced by industrial processes called nanotechnology during last decade, but they have been always present on Earth. Natural nanomaterials are produced by many processes in nature including photochemical reactions, eruptions of vulcanoes, forest fires and simple erosion (Buzea et al. 2007) and many others. Some nanoparticles are biosynthesized by algae (Rai and Posten 2013) or other organisms as specific bacteria and diatoms (Narayanan and Sakthivel 2011). Even several viruses can be classified as nanoparticles (Buzea et al. 2007).

Anthropogenic nanomaterials were created first time as by-products of combustion, metallurgy and other technological processes many thousands years ago, which is evident from many antiquities as Damascus swords (Daw 2012) or Roman dichroic glass cage cup called Lycurgus cup (Freestone et al. 2007). Anthropogenic nanomaterials, which are emerging recently by human activities, could be divided to two groups as by-products which are created during many physical and technical processes, and products of nanotechnology called "engineered nanomaterials" (Topinka 2011).

Products, whose functions, physical or chemical properties are enhanced by nanomaterials, are called nano-based products or simply nanoproducts. According to Bystrzejewska-Piotrowska et al. nano-based products can contain two main types of nanomaterials – surfaces coating or free nanoparticles (Bystrzejewska-Piotrowska et al. 2009). They find use in many areas such as electronic, biomedical, pharmaceutical, cosmetic, energy, environmental and material applications (Nowack and Bucheli 2007). The vast majority of nanomaterials consists of nanosilver, various forms of carbon, zinc oxide, titanium dioxide and iron oxide (Royal Commission on Environmental Pollution 2008; Musee 2011). Nanomaterials can be found currently in many consumer products. They are listed for example in nanotechnology Consumers Products Inventory Database that contains more than 1800 registered products (Consumer Products Inventory 2013). The most increasing amount of nano-based products are cosmetics and textiles as products of daily use, which represent more than 50 % of the market (Greßler et al. 2014).

Logical consequences of the widespread use of nanomaterials and nano-based products contribute to the appearance of new kinds of waste (Boldrin et al. 2014). The main aim of this literature review is to briefly summarize actual knowledge about nanowaste and report on currently proposed waste management systems for this new type of waste.

Discussion

Sources of nanomaterials released to the environment and nanowaste

Although nanomaterials can also offer the great tool for remediation of the environment through many applications called "environmental nanotechnology"(Biswas and Wu 2005), their uncontrolled release to the environment is highly undesirable. Both synthesized nanomaterials from commercial products and nanomaterials, which are released from industrial production and other processes, reach waste streams through many different ways (Biswas and Wu 2005). These novel materials can be released to the environment from point sources such as production facilities, waste handling and wastewater treatment plants or from non-point sources as simple using or wearing of nano-based products by consumers (Liu et al. 2008). According to Bismas and Wu one of the most critical operation, which can cause possible release of nanomaterials from industry to the environment, are cleaning operations of production chambers (Biswas and Wu 2005). Another possible way is an accidental release during production processes or transportation (Nowack and Bucheli 2007). All of these nanomaterials including nanomaterials from atmospheric deposition, can contaminate soils and both surface and underground water (Nowack and Bucheli 2007; Zweck et al. 2008; Bystrzejewska-Piotrowska et al. 2009).

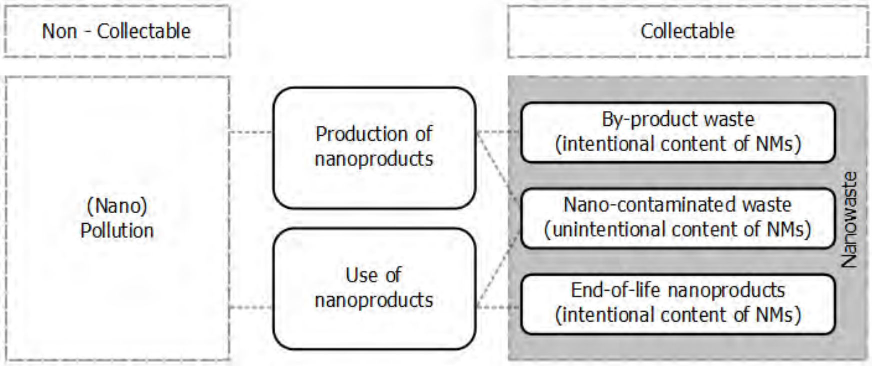

Fig. 1 Nanowaste versus nanopolution (Boldrin et al. 2014)

Legend*: The "NMs" is a commonly used abbreviation for "nanomaterials"*

The term "nanowaste" can be tracked back to 2008 (Liu et al. 2008). According Boldrin et al. "the term nanowaste could be first applicable when engineered nanomaterials come into contact with solid waste streams and can be separately collected or collectable" (Boldrin et al. 2014) (Figure 1). Single fraction of nanomaterials, by-products from industry contaminated by nanomaterials, waste materials containing engineered nanomaterials (*e.g.*, sludge from wastewater treatment plants) as well as nano-based products in the end of their life cycle could be called nanowaste (Boldrin et al. 2014). Boldrin et al. also point out other examples of engineered nanomaterials contamination, which should be rather called nanopollution. Keller et al. estimate that 63-91 % of global engineered nanomaterials production in 2010 ended up in landfills, 8-28 % were released into soils, 0,4 – 7 % entered water bodies and 0,1-1,5 % entered atmosphere (Keller et al. 2013). Boldrin et al. also define three critical factors by which the amount of nanowaste from commercial products is generated – the first is the amount of nano-based products produced and presented on the market, the second is the lifespan of these products, and the third is the exact progress of releasing nanomaterials from nanoproducts during the use phase (Boldrin et al. 2014).

The increasing number of publications focused on nanomaterials is stunning. Whereas in 1990's there was only few papers about this topic, currently Web of Science contains more than 68 thousands publications connected to the term "nanomaterials" (Figure 2). It is alarming, that only tens of publications connected with "nanowaste" is currently published according to Web of Science. On the other hand the number of citations of these papers is gradually growing, which reflects the emerging interest of this issue (Web of Science 2015). The lack of publications in this field seems to be alarming, considering particularly the fact that nanowaste is potentially the most important pathway of releasing nanomaterials into the environment (Zweck et al. 2008).

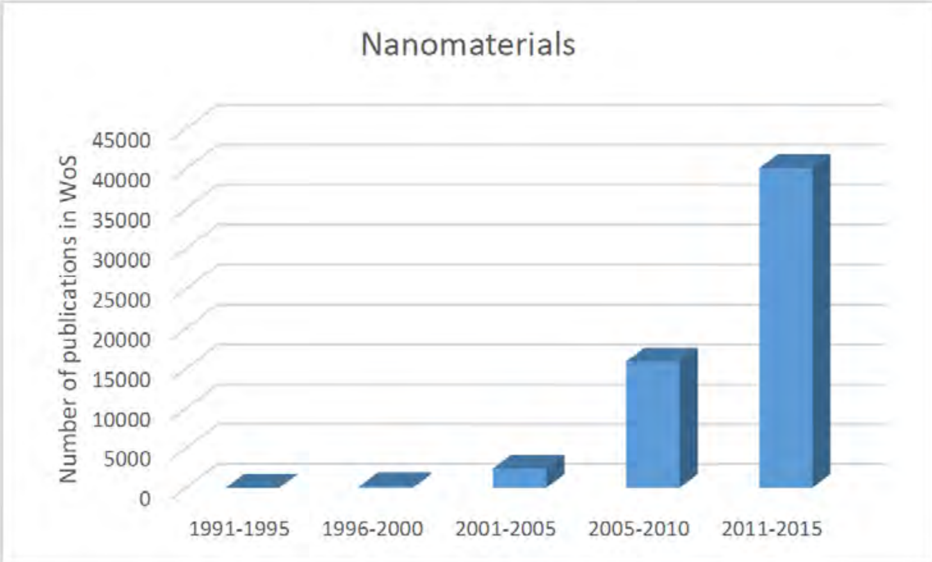

Fig. 2 Number of publications about nanomaterials (Web of Science 2015)

Examples of nanoproducts and their fate during disposal processes

As mentioned above, nano-based commercial products of daily use with their specific properties are widely spread in the market and their utilization is increasing continuously, namely nano-based cosmetics and personal care products (Zweck et al. 2008). According to Keller et al. almost 16 % of engineered nanomaterials are currently used in cosmetics worldwide (Keller et al. 2013). Sunscreens, which reflect UV light due to titanium oxide nanoparticles, products containing nanosilver, which has outstanding antibacterial properties, or anti-aging skin treatments containing nanoparticles of gold, are very popular (Zweck et al. 2008). In correlation with this consuming behaviour, nanoparticles from cosmetics can easily enter waste streams and contaminate directly aquatic ecosystems through processes as bathing or swimming in the nature, or indirectly through waste water treatment plants after showering (Zweck et al. 2008; Bystrzejewska-Piotrowska et al. 2009). Müller and Nowack estimate that 95 % of nanoparticles from cosmetics are released during use (Müller and Nowack 2008).

Different situation is in nano-based textiles, where there are more ways in which nanonaterials can be released to waste streams (Pourzahedi and Eckelman 2015). Many properties of textiles are nanotechnology-enhanced as UV protection, antibacterial activity, easy-care and self-cleaning or other specific functional finishes, such as medical textiles, flame-retardant and odour eliminating textiles (Wei 2009). Most frequently used nanomaterials for textile improvement are silver nanoparticles, which have a very large specific area leading to their contact with bacteria or fungi causing bactericidal and fungicidal effects (Samal et al. 2010). These nanoparticles can be released namely during wash cycles from both municipal and industrial sources, and as a part of sludge from wastewater treatment plants, which is incinerated or can be spread as a soil fertilizer on agriculture fields (Blaser et al. 2008), can reach the environment (Buzea et al. 2007; Benn and Westerhoff 2008). According to Lee et al. nano-based textile fabrics lost the antibacterial activity after 20 cycles of washing (Lee et al. 2003). Apart from nanosilver, titanium dioxide can be also released during washing from nano-based textiles (Keller et al. 2013). Processes of waste water treatment are ineffective for this kind of nanoparticles (Rejinders 2006). In addition, chemical dry cleaning of textiles can probably cause the release of nanoparticles (Greßler et al. 2014) as well as simple wearing or using of nano-based textiles (Rejinders 2006). Musee mentions results, which showed, that conventional water treatment processes in waste water treatment plants (*e.g.*, alum coagulation) are able to remove less than 80 % of nanoparticles presented in waste water, and around 90 % are removed by membrane filtration in addition as a final step of water treatment (Zweck et al. 2008). Other nanoparticles can escape to the environment.

Although nanoparticles from consumer products of daily use mentioned above probably will be emitted mostly into waste water (Keller et al. 2013), they can be also released during both municipal or industrial waste handling (*e.g.*, *via* abrasion during re-using and recycling processes (Greßler et al. 2014) and disposal processes as landfilling or waste incineration (Wei 2009; Pourzahedi and Eckelman 2015). However, Keller at al. estimate that the vast majority (30 - 95 %) of nanomaterials from textiles in their end of life phase will end up in landfills (Keller et al. 2013). Exact behaviour of nanowaste in landfills and incineration plants is still known very little (Greßler et al. 2014). According to current data, only nanomaterials in the 100 nm and bigger are effectively filtered and probably 20 % of nanomaterials smaller than 100 nm can be released through filtration system of incinerators (Musee 2011). Nanoparticles of silver, titanium dioxide and zinc oxide were also presented in the bottom ash after incineration, which is usually landfilled, whereas carbon nanotubes were almost completely combusted (Müller et al. 2012).

Although some research was done by using Life Cycle Assessment (LCA) method for estimation of nanomaterials fate, currently the market product analysis seems to be the most suitable for quantification (Boldrin et al. 2014). This analysis can mirror the situation in waste streams, since nanowaste data are not available.

Toxicity of nanomaterials and the risk assessment in the environment

While the antibacterial properties of nanosilver have been known for hundreds of years (Pourzahedi and Eckelman 2015), some exceptional properties of other nanomaterials are being observed and discovered for the very first time (Royal Commission on Environmental Pollution 2008). These new properties and functionalities of engineered nanomaterial as well as totally different nanomaterial behavior compared to those in bulk form, can lead to different mobility and toxicity in organisms and the environment (Royal Commission on Environmental Pollution 2008). The lack of information about both novel properties and health effect raises still some uncertainty, which parameters are the most important for nanomaterials risk assessment. According to Oberdörster there are three most significant parameters in determining the health effect of nanomaterials: the three D‘s - dose, dimension and durability (Oberdörster 2002).

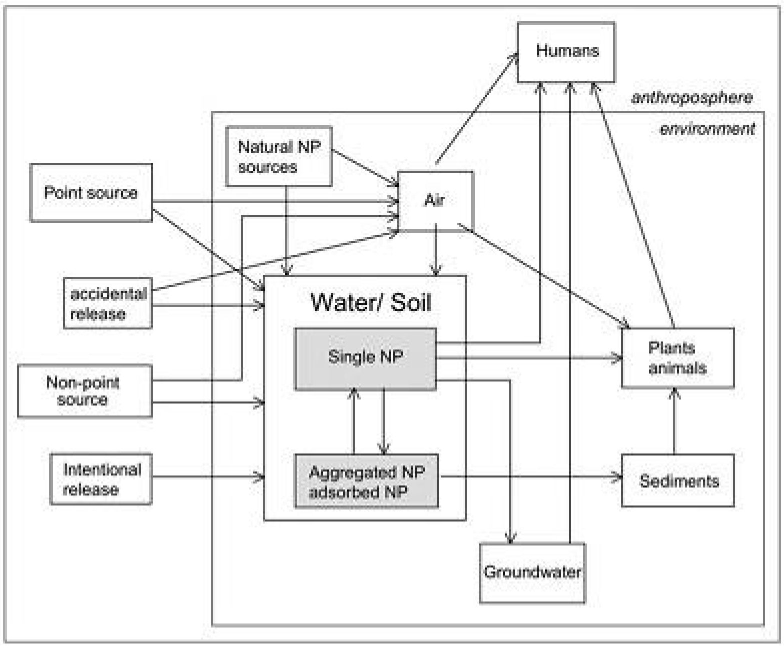

Fig. 3 The pathway of nanoparticles from the athrophosphere into the environment, reactions in the environment and exposure of humans. (Nowack and Bucheli 2007)

Legend: *The "NP" is a commonly used abbreviation for "nanoparticle"*

Biswas and Wu described three ways, how nanoparticles can enter the human body – through skin, lungs or the gastrointestinal tract (Biswas and Wu 2005), where nanoparticles are able to enter cells and interact with subcellular structures (Buzea et al. 2007). A lot of research is currently focused on bioaccumulation of nanomaterials in aquatic organisms. First results suggest that nanoparticles could be available for dietary uptake at lower trophic levels and transferred and appear within a food chain (Zhu et al. 2010; Judy et al. 2011) and seem to be a possible pathway for human exposure (Zhu et al. 2010). Although still more information about nanomaterials behaviour and toxicity is needed, many *in vitro* studies already proved the cytotoxic effect of some nanoparticles (Royal Commission on Environmental Pollution 2008). The pathway of engineered nanoparticles as well as nanoparticles from natural sources in the environment, interaction between the antroposphere and the environment and possible ways of human exposure to nanoparticles are described in figure 3.

One of the well-known examples of harmful effects of engineered nanomaterials in humans was presented in 1997 by Dunford et al. They showed that titanium dioxide or zinc dioxide engineered nanoparticles from sunscreens, which reflect UV light in sunlight, can cause DNA damage in human cells (Dunford et al. 1997). The crucial question remains: is the penetration of these nanoparticles possible through the skin, remains? Diseased, sunburned skin or skin affected by allergies is probably an insufficient barrier against entering of nanoparticles to the human body (Jacobs et al. 2010).

Well-known is also negative effect of silver nanoparticles on wastewater treatment systems and anaerobic digestion. Almost 30% of the worldwide production of silver nanoparticles are used into medical supplies and devices due to their antibacterial properties (Keller et al. 2013) and also in many other consumer products. As well as other microorganisms, also nitrifying bacteria are very susceptible to silver nanoparticles and higher concentration of this nanomaterial entering the wastewater treatment plant in biomass inhibits its microbial activities (Hu 2010). Blaser points out that silver nanoparticles released to the waste water accumulate to the sewage sludge and can be spread further on agriculture fields (Blaser et al. 2008).

Legal regulations of engineered nanomaterials and future nanowaste management

Legal regulations are one of the most crucial issues. Currently the waste containing nanomaterials are treated as any other waste without any specific requirements (European Commission 2012). There are no specific regulations for nanotechnologies or nanomaterials in Europe and all processes connected with manufacturing , use and disposal of nanomaterials are covered namely by REACH - Registration, Evaluation, Authorisation and Restriction of Chemicals and very little by some specific regulations for pharmaceuticals, veterinary medicines, pesticides and biocides, toys and cosmetics (Royal Commission on Environmental Pollution 2008). Also The Waste Electrical and Electronic Equipment Directive – WEEE and Regulation on classification, labelling and packaging of substances and mixtures - CLP are marginally linked to nanomaterials (European Commission 2012).

Although REACH seems to be the most important and very strong regulatory instrument for both bulk material and nanoforms of the same substance (Schwirn et al. 2014), it was not designed for engineered nanomaterials, nanomaterial-based products and their applications and it is necessary to undertake a review of this regulation and try to deal with these novel materials (Royal Commission on Environmental Pollution 2008; European Commission 2012). Besides REACH, the mostly overlooked EU Water Framework Directive WFD could potentially play a key role in the future (Hansen et al. 2011). Also the EU Waste Framework Directive should receive much more attention, because currently there are no legal regulations directly connected to nanowaste. Since engineered nanomaterials handling and nanowaste management have no specific legal regulations on their own, the use of the precautionary principle as a first step prevention of harmful effect on the environment and human health is highly recommended (Health Council of the Netherlands 2011) as well as minimising of nanowaste volumes production and other prevention from entering waste streams (Health Council of the Netherlands 2011; Greßler et al. 2014).

Together with the steep increase of nano-based products on the market, the question of nanowaste management is currently more and more emerging. One of the first studies connected with nanomaterials and nanowaste handling held in United Kingdom was published in 2008. This study "Novel Materials in the Environment: The case of nanotechnology" probably for the first time discusses product take-back requirements of nano-based products as an effective way how to prevent entering of nanomaterials to the environment. These products collected in that way would be returned to their original producers for recycling. However, this study shows that this take-back procedure probably cannot be implemented namely due to the large variability of nano-based consumer products (Royal Commission on Environmental Pollution 2008). Almost all recent studies point out that nanowaste must be treated differently in comparison with conventional methods of waste management, although basic principles of waste hierarchy according to EU Waste Framework Directive should be followed (Directive 2008/98/EC 2008). For instance the report of Health council of the Netherlands mentions as key factors waste prevention and safe handling of nanomaterial-containing waste (Health Council of the Netherlands 2011).

Tab. 1 Nanowaste classification (Musee 2011)

Nanowaste classes	Description	Comments/description	Examples of waste streams in terms of nanoproducts
Class I	*NM hazard:* non-toxic; *Exposure:* low to high	Concerns on waste management may only arise if the bulk parent materials (Trojan horse effects) can cause toxicity to humans and the environment through accumulation beyond a certain threshold concentration limit. Otherwise, nanowaste can be handled as benign/safe. No special disposal requirements. Risk profile: *none to very low*.	Display backplanes of television screens, solar panels, memory chips, polishing agents
Class II	*NM hazard:* harmful or toxic *Exposure*: low to medium.	Toxicity of NMs may warrant establishing potential acute or chronic effects to determine the most suitable and optimal management approach during handling, transportation or disposal processes. Risk profile: *low to medium*	Display backplane, memory chips, polishing agents, solar panels, paints and coatings
Class III	*NM hazard:* toxic to very toxic; *Exposure:* low to medium	Protocols appropriate for managing hazardous waste streams in the entire waste management chain are desirable/recommended. Need for research to determine if current waste management infrastructure is adequate to deal with hazardousness of waste streams due to nanoscale materials. Risk profile: *medium to high*	Food packaging, food additives, wastewater containing personal care products, polishing agents, pesticides
Class IV	*NM hazard:* toxic to very toxic; *Exposure:* medium to high	Waste streams should be disposed only in specialized hazardous wastes designated sites. Inadequate WM could lead to serious threats to humans and environmental systems. Risk profile: *high*	Paints and coatings, personal care products, pesticides, etc.
Class V	*NM hazard:* very toxic to extremely toxic; *Exposure:* medium to high	Dispose only in specialized hazardous waste streams designated sites. Poor waste management can cause extensive nanopollution to diverse ecological and water systems, which may prove to be costly, laborious, and time consuming to remediate. Immobilization and neutralization techniques among the most effective treatment techniques. Risk profile: *high to very high*	Pesticides, sunscreen lotions and food and beverages containing fullerenes in colloidal suspensions

Based on recent toxicology data, first concepts of nanowaste classification have emerged. Musee divides nanowaste into five classes according to toxicity and exposure potency of nanomaterials in nano-based products (Musee 2011) (Table 1). Unfortunately there are no nano-specific regulations in the European or Czech waste legislation as well as no presence of nanowastes in Waste catalogue as a single item.

Apart from relatively common methods of waste treatment and disposal, processes of remediation could be also used in case of nanowastes. According to Bystrzejewska-Piotrowska et al. the main contemporary challenge is to find specific microorganisms, fungi or plants, which can bioaccumulate, utilise, decompose or immobilise namely metal nanoparticles from this kind of waste, despite the fact that the process of bioaccumulation is still not well known (Bystrzejewska-Piotrowska et al. 2009).

Conclusion

The increase of nano-based products on the market together with lack of information about nanowaste as well as the absence of nano-specific legal regulations is alarming. The amount of future nanowaste is partly predictable since the production of engineered nanomaterials will mirror the development in near future. The global population has now a unique opportunity to find the solution of this issue by establishing the environmental policy concerning nanomaterials and nanowaste management as soon as possible, because conventional methods as waste handling seems to be not appropriate enough.

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