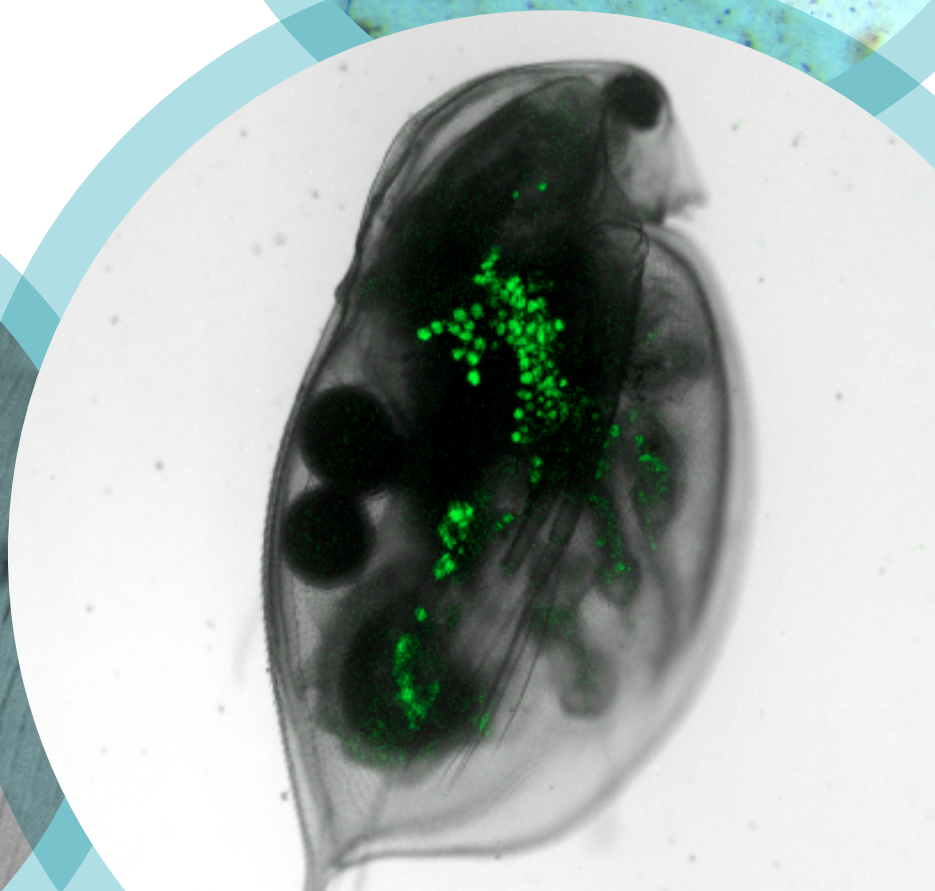
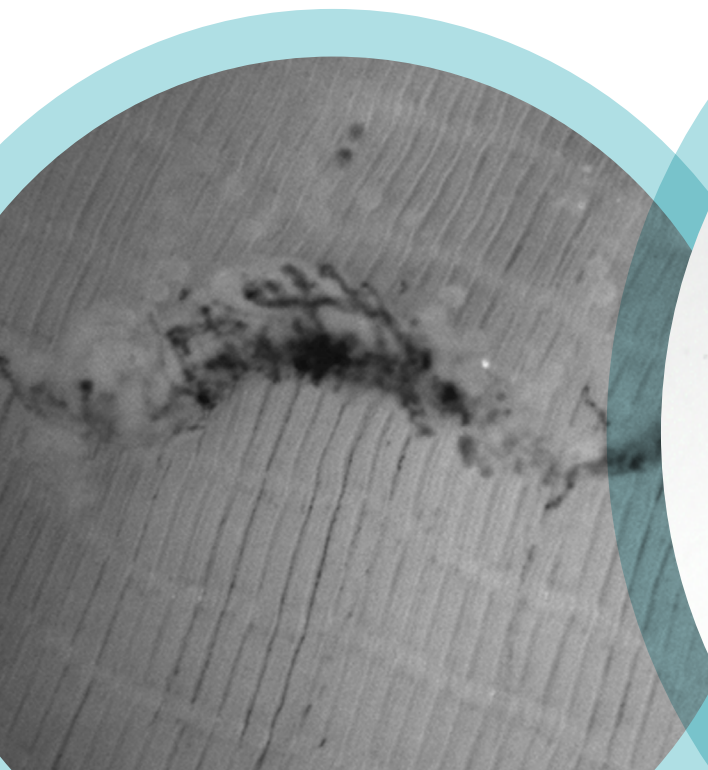
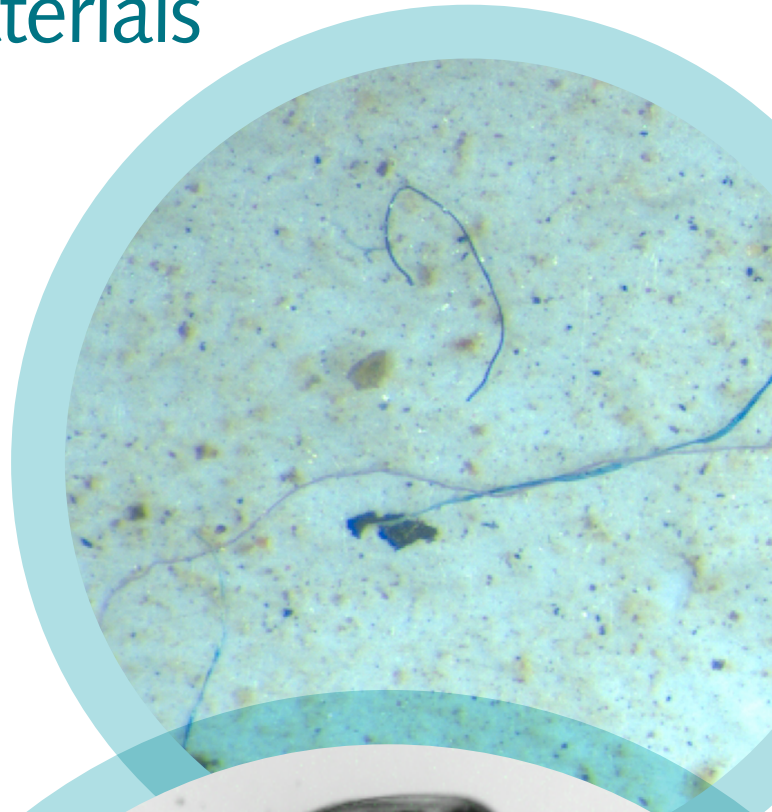




Scotland's centre of expertise for waters

# Review of existing knowledge – emerging contaminants

Focus on nanomaterials  
and microplastics  
in the aquatic  
environment





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# Executive Summary

## Key Points

### Nanomaterials

The nanotechnology industry is expanding fast with an ever increasing number of products containing nanomaterials (nanoscale <100nm on at least one dimension). In many cases the lifecycle analysis of these materials (production, use, disposal) is incomplete or lacking, especially for nano-composite materials, where the entry route to the environment is not immediately apparent. It is also becoming clear that there is a lack of understanding concerning how nanomaterials interact with other contaminants. The knowledge gaps we highlight in this report currently make reliable risk assessment difficult or even impossible.

### Microplastics

Litter in the environment is not a new phenomenon. However, the realization that microscopic plastic particles (microplastics) <5mm and synthetic microfibrils occur in the aquatic environment has recently drawn a lot of public attention. One particular concern is growing evidence for the ability for microplastics to move up the food chain and therefore potentially affect human health. We highlight a number of gaps in our understanding of microplastic behaviour in the environment, particularly their interaction with microorganisms and the ability to sequester and therefore concentrate other non-polar contaminants, thus potentially exposing organisms that have come into contact with microplastics to higher contaminant concentrations. We review a number of NGO supported and Scottish Government initiatives that have led to changes in consumer behaviour and draw attention to the inability to measure the impact of these measures owing to the lack of appropriate microplastic baseline concentrations.

## Introduction

Emerging technologies can deliver great benefits, but may also carry risks to the environment and/or human health. Furthermore, existing contaminants in the environment may increase in importance with our improved understanding of their behaviour and interaction with relevant organisms in a changing environment. Whilst nanomaterials are an example of the former, microplastic particles represent the latter. The present report is the result of a review of the existing knowledge of emerging contaminants relevant to Scotland, with a focus on nanomaterials and microplastics. The aim was to identify gaps in the current knowledge and provide recommendations on research needs to support relevant Scottish Government policies.

## Policy Implications

### Nanomaterials

- The lack of detection methods for monitoring the presence of NMs in the environment and in environmental media

means that few reliable data<sup>1</sup> currently exist on the quantities released into the environment (it is not actively monitored in Scotland).

- Encourage research to develop environmentally relevant testing strategies to produce the data required to validate risk assessment models for NMs.
- Given the published information available on establishments in Scotland producing or working with NMs it is unlikely that the situation is more acute to what is taking place in other European countries. Although records are not fully available it is expected that the number of establishments which fit into those categories is not very large. Therefore, it is proposed that the situation continues to be monitored and that regulatory developments will follow the lead from the work currently taking place at European level.
- Specific regulations on the production use and disposal of NMs may be required.

### Microplastics

- A fully-funded large-scale baseline study for the Scottish marine environment is required in order to separate fresh input from historic material and understand temporal trends.
- Develop standardized methods for sampling, sorting and identification of environmental microplastic polymers. This includes developing categories for reporting that would allow data from different survey types to be compared, similar to the OSPAR beach litter survey. This is currently being discussed at European level with the Austrian EPA as lead, but the timeframe is as yet unclear (SEPA, personal communication). Scotland needs a strong representation in relevant international bodies (OSPAR, GESAMP, JCR, EU-EPA) to help devise these standardized methods suitable for the Scottish situation, which may be very different from other countries in terms of climate, plastic usage and end of life treatment etc.
- More research is required to understand the potential harm of microplastics, including source and fate in the marine environment (trophic mobility), as well as the development of appropriate biomarkers of exposure in marine organisms and implications for human health.
- Instigate studies to better understand how microplastics interact with contaminants in the environment and how they may act as vectors for the potential facilitated entry of chemical pollutants into the food chain.
- Instigate studies to help understand biofilm formation on microplastics and its role in microplastic dynamics.
- Following recent realization that sewage can account for a large amount of particularly fibrous microplastic material, the development of fabrics that release fewer fibres during washing as well as appropriate filters that can remove these microplastic fibres from the sewage stream needs to be encouraged.
- Recent public engagement through investigative media pieces needs to be built on and the reduction of waste encouraged. If alternative materials are not available further incentives for increasing recovery and recycling rates need to be created, such as the one recently piloted by the Scottish Government's Zero Waste initiative.
- Industry and retail need to be further incentivized to use less packaging material.

# 1 Introduction

## 1.1 Background to Emerging Contaminants - Nanomaterials and Microplastics

As defined by CREW, "A comprehensive review is required of the sources, impacts, risks and monitoring of water related 'known-unknowns', including potential emerging contaminants of concern within Scottish watercourses; data availability; impact assessment on ground and surface water including WFD compliance (and coastal environments-Bathing Water Directive); and current and future risks, monitoring and assessment methodologies for emerging contaminants of concern within Scottish watercourses."

## 1.2 Definitions of Emerging Contaminants

Emerging contaminants can be defined as previously undetected foreign chemical species or substances that have only recently been shown to occur in the environment, and identified as being of potential concern to the environmental and/or public health, and for which adequate data do not exist to evaluate their potential risk<sup>2</sup>. It has been noted that the term "contaminants of emerging concern" (CEC) is more appropriate than emerging contaminants given that many chemical species have been noted for their inherent toxicological potential for some time<sup>3</sup>.

# 2 Nanomaterials as Contaminants of Emerging Concern

According to the latest European Commission (EC) definition (European Parliament's Resolution on Regulatory Aspects of Nanomaterials (2008/2208(INI) 24.4.2009.), a "nanomaterial" refers to any "natural, incidental or manufactured material containing particles, in an unbound state, aggregate or as an agglomerate, and where, for 50% or more of the particles in the number size distribution, one or more external dimensions are in the size range 1nm to 100nm"<sup>4</sup>. Conventionally it has been accepted that nanomaterials (NM) have one or more dimensions within the nanoscale (1-100 nm) whereas nanoparticles (NPs) have three dimensions in the nanoscale<sup>5</sup>. When particles are synthesized at the nanoscale their properties often change in comparison to larger particles of the same material: for example the magnetism of iron NMs can be greatly enhanced at the nano-scale compared to the bulk form, as is the reactivity of gold NPs. These unique properties make NMs useful in developing new materials with applications in almost every sector of the world's economy, such as in healthcare (magnetic resonance imaging (MRI), anticancer treatments<sup>6</sup>, and in a host of consumer products), in electronics and construction industries (sensors and creation of durable light weight resistance materials<sup>7</sup>), the food industry<sup>8</sup>, environmental remediation<sup>9</sup>, and the energy sector (efficient energy storage)<sup>10</sup>.

NMs can be classified as CECs because there is limited published information and understanding of their source, occurrence and distribution in the environment. Biogenic and anthropogenic NPs have occurred in the environment for millennia, and engineered NMs have been in commerce for decades. Thus, while we have been exposed to NPs for a long time the increasing production and use of a wide variety of NMs, that vary in composition and physicochemical characteristics, are raising concerns about their potential impact on human health and the environment<sup>11, 12</sup>.

## 2.1 Classification of Nanomaterials

The defining property of an NM is its size. However, NMs have specific physical chemical properties making them useful in all areas of commerce. It is important therefore to try to organise this diverse range of materials into some classification system. It is not yet possible to classify NMs according to their environmental behaviour, bioavailability, and mechanism of toxicity; however, with regards to NMs that are relevant in the aquatic environment the best way to begin classifying them is according to their chemical makeup<sup>12-14</sup>. This can be complicated because NMs can contain more than one material, and their interaction with complex biological matrices can affect their characteristic properties such as size, shape, surface area and charge, that can be influenced by external abiotic environmental factors such as salinity, pH, water hardness, and presence of organic matter. Therefore, consideration needs to be paid to the material structure, the shape, and the physical behaviour of NMs in the environment<sup>14</sup>, including the impact of any coatings or dispersants. In 2010 the International Standards Organisation (ISO) published "Nanotechnologies Methodology for the classification and categorization of nanomaterials" (ISO/TR 11360:2010), in which they propose an approach for the definition of NMs in relation to their environmental effects,

fate, and behaviour, eventually expediting priority ecotoxicity testing/monitoring of NMs of the most concern.<sup>12, 13, 15.</sup>

## 2.2 Nanotechnology in Scotland

In 2002, two government funded reports<sup>16</sup> highlighted the low contribution of UK companies to the nanotechnology sector, and as a result pledged £90m of funding, of which £50m was allocated to an "applied research programme", and £40m was allocated to a UK Micro and Nano Technology (MNT) Network, with the aim of promoting nanotechnology centres to make the most of nano-related commercial opportunities and gain a position in the global nanotechnology market. This funding can be seen as the beginning of the nano age in Scotland that resulted in the establishment of 24 MNT facilities between 2003-2007, which has come to form an integral part of the UK's nanotechnology infrastructure<sup>17</sup>. Despite Scotland's recognized electronics and semiconductor sector, and the well-developed research base and commercialisation opportunities for nanotechnology<sup>18</sup>, the initial governmental funding has yet to translate to a major nano-related industry; this puts Scotland behind on a global scale with regards to nanotechnological research and development.

## 2.3 Sources of Exposure from Current and Predicted Applications of NMs in Scotland

It is expected that the widespread and expanding use of NMs will result in increased release to the environment throughout the product lifecycle, resulting also in potential increasing organism exposure through multiple pathways<sup>19</sup>. The number and extent of companies involved in the manufacture of nanomaterials is not extensive in Scotland, nevertheless, there are many small and medium sized Scottish industries and small research centres producing nanomaterials.

Environmental exposure through surface run off or release from fabrication/manufacture is possible but these would be considered potential incidental point source exposures. Other types of potential point sources include:

Release from consumer products healthcare, textile, semiconductor and electronics industry ([http://www.nanotechproject.org/inventories/consumer/analysis\\_draft/](http://www.nanotechproject.org/inventories/consumer/analysis_draft/)).

Leaching from paint/facades/textiles/building materials treated with so-called functionalised smart coatings. For example self-cleaning, or stain and scratch resistant, or antimicrobial surfaces<sup>7, 20, 21</sup>.

Environmental remediation (land remediation, treatment of drinking water, air quality, and also monitoring biosensors)<sup>9</sup>. However in Scotland this is currently not a likely source of NMs, because a 2004 British Royal Society and Royal Academy of Engineering report<sup>22</sup> recommended that a moratorium on the use of NMs in the UK be applied, which remains in place, although experimental trials are known to have taken place in the UK. However, NMs are used elsewhere in pioneering remediation technologies<sup>9</sup>. Consequently, the European Commission's Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) has consistently called for further risk research, while acknowledging environmental remediation technology as one of nanotechnology's potential benefits<sup>5</sup>

Agricultural. A potential source of NMs to the environment in the future may arise from the application of NMs in agriculture and in the food industry. NMs have potential applications in crop cultivation, pesticides and fertilizers, and in animal feeds. However, in Scotland and Europe this is not yet an issue as the technology is not yet cost effective<sup>23</sup> and no wide scale use of NMs in agriculture has been reported.

Food industry<sup>8, 24, 25</sup>. The applications of NMs in the food sector, although currently a new development, are predicted to grow rapidly, especially in packaging technology. Many of the major food companies are investing/applying nanotechnology to food<sup>8</sup>. There is no complete list or inventory of NMs used in the food industry, in particular in food packaging, on the UK or EU market, although they are known to be available on the global market. The Food Standards Agency (FSA) has expressed interest in developing a register, and the EC produced an inventory in 2010<sup>26</sup>, but no subsequent updates were available at the time of compiling this report.

## 2.4 Other/Global Sources of NMs

Although it is difficult to accurately estimate global annual quantities of NM produced, the main NMs on the market include carbon based NMs, metallic<sup>27-31</sup> and non-metallic NMs, organic NMs, and composites<sup>32</sup> (see table 2 in the Appendix). In the wider scope of global events it is tempting to only consider localised sources of NM environmental exposure as relevant in Scotland. However research on contaminants of emerging concern show that they are present in the environment on a global scale, and can occur even in relatively undeveloped areas<sup>33, 34</sup>. As there is a lack of suitable detection devices, models developed to achieve a comprehensive understanding of Scotland's nanotechnologies' supply chain, manufacturers, importers, service providers, end users, and disposal cannot be adequately validated, and the results may therefore not reflect the current situation of NMs in Scotland's aquatic environment.

## 2.5 Transport and Fate of NMs

The life cycle of NMs, from manufacture, production and synthesis, to their use, transport and disposal, provides multiple possible entry points into the aquatic environment. The major exposure pathways therefore will include release from sewage treatment plants (in water and through landfill application), agricultural runoff, release from solid waste disposal depots, and atmospheric precipitation. To gain an understanding of the transport and ultimate fate of NMs in the aquatic environment it is important to consider how NMs behave in different environmental compartments, and how physicochemical conditions might affect their stability/reactivity, bioavailability and persistence<sup>35</sup>. For example, NMs may exist in either a free form or bound in a matrix which could affect their mobility; additionally, the presence of organic matter has a capacity to absorb, bind, and aggregate NMs in ways which may affect their transport, bioavailability, and toxicity in some compartments, or conversely may enhance their stability, thus leading to increased exposure times and in turn increased toxicological potential<sup>36</sup>. Finally, interaction with NMs with other chemical substances may also promote the toxicity of other substances, such as metals, that would otherwise be present in the environment at benign concentrations<sup>37</sup>.

There are many tools available for modelling the fate of chemical compounds in different environmental compartments. Although the body of work on modeling the environmental fate of NMs is growing, particularly in freshwater<sup>38, 39</sup>, it still lags behind that of conventional chemical models, making it difficult to apply these confidently to environmental NM behaviour, and thus limiting the ability to adequately assess the risk of NMs<sup>13, 38</sup>.

## 2.6 Climate Change and Potential Implications on NM Behaviour

The Climate Change (Scotland) Act 2009 aims to reduce emissions of greenhouse gases (as carbon dioxide equivalents) by at least 80% by 2050. Nevertheless, it is a reality that climate change is already affecting the Scottish environment. According to SEPA's Strategic Environmental Assessment Report of December 2007, the average temperature in Scotland has risen by over 1°C since 1961, and Scotland is on average 20% wetter<sup>40</sup>. The 2011 SEPA report on the soil quality in Scotland has described how predicted changes in temperature and rainfall patterns in Scotland are likely to have significant effects on Scottish soils<sup>41</sup>. Based on climate change models, the predicted effects of climate change for Scotland include continued warmer seas, increases in average temperatures, milder temperatures and wetter conditions, particularly during the winter, and a higher intensity of rainfall and longer periods without rain, particularly during summer. Increased rainfall, higher temperature, and soil quality have a knock on effect on water quality as these are interconnected. These changes will affect how NMs (and other CECs) are transported, and the fate of NMs in the aquatic environment.

## 2.7 Legislation

Based on available predictive and limited quantitative data it can be argued that, given the wide range of NM-applications, it is a certainty that NMs are entering the environment, although it is unclear in which form. Given the new potential risks<sup>22</sup> these materials hold over their bulk counterparts, the key question arises whether existing legislation is sufficient to safeguard the environment. At present there are no international regulations regarding NM exposure and no internationally agreed or standardized protocols for toxicity testing and environmental monitoring<sup>13</sup>. Although the European Commission has published a definition for NM and engineered nanomaterials (EMNs)<sup>4</sup>, there is no internationally agreed definition. In the UK the precautionary principle is currently advocated owing to the knowledge gaps regarding the potential hazards of NMs. Reports from the UK Department of Trade and Industry (DTI)<sup>42</sup> and UK Council for Science and Technology<sup>43</sup> provide a good overview of the existing regulatory framework, and highlight gaps for occupational health and safety, consumer and environmental protection, and waste regulation in regards to NMs. In particular, setting threshold levels and classifying NMs in products as well as the difficulties associated with their implementation, owing to the lack of availability of monitoring technologies<sup>13</sup>, are identified as major gaps in the current legislation.

The Ministerial Group on Nanotechnologies published their UK Nano Strategy in 2010. This governmental report outlines clear environmental health and safety (EHS) aims, and highlights how the UK government will explore the approaches to EHS research – to work within the European framework with regards to NMs. This strategy outlines how the government will develop further

the current voluntary reporting scheme to include products as well as materials containing substances at the nanoscale – an expansion on the voluntary reporting scheme set up by the Department of Environment, Food and Rural Affairs (DEFRA). It reports how it aims to monitor the implementation of the upcoming amendments to the novel foods and cosmetics directive in REACH (Registration, Evaluation, Authorisation and Restriction of Chemical) to ensure NMs are covered.

European legislation (Regulations, Decisions, and Directives) will impact Scotland's approach to management and monitoring of NM entry to the environment. The European Commission notes that NMs fall under the scope of existing health, safety, and environmental regulation: namely, the Water Framework Directive (2000/60/EC), the Protection of Groundwater against Pollution Directive (2006/118/EC), the Drinking Water Directive (98/83/EC), the Environmental Quality Standards Directive (2008/105/EC), the Urban Waste Water Directive (91/271/EC) and the directive concerning the release of Dangerous Substances into the aquatic environment (Directive 2006/11/EC)<sup>44</sup>. Furthermore, as most nanomaterials are considered chemical substances, REACH<sup>32</sup>,<sup>45</sup> has become the cornerstone of nanotechnology oversight in Europe, even if NMs are not explicitly mentioned. Thus, the current position of the Health and Safety Executive (HSE) in the UK is that the existing EU regulations provide adequate regulatory coverage for NM-related risks, and no new specific regulations are required at this point, although the situation may change in the future as work in this area continues to progress<sup>47, 48</sup>. However, "Where nanomaterials have an uncertain or not clearly defined toxicology and unless, or until, sound evidence is available on the hazards [...] a precautionary approach should be taken to the risk management"<sup>46</sup>. Therefore, currently legislation for the regulation of NMs in the environment lies within the current regulations for environmental protection. However, when considering the multiple pathways by which NMs can enter the environment, a broader outlook should be applied in order to consider potential needs for future amendments of legislation covering the entire NM life cycle, especially with regard to the important issue of tonnage thresholds.

### Gaps in REACH legislation with regards to NMs

- No specific guidelines for NMs
- Threshold Tonnage restrictions hamper registration of NMs

### Gaps in WFD with regards to NMs

- Mass based threshold limits do not apply to NMs
- Limitations in the availability of monitoring techniques for detection of NMs causing inability for NMs to become priority hazardous substances
- Setting to EQS; currently not specifically applicable to NMs, because of the uncertainties attached to environmental behaviour and fate of NMs.

## 2.8 Monitoring Methodologies

The current lack of data on NM concentrations in the environment is one major obstacle that hinders the adoption of the existing environmental regulatory frameworks for NMs. This lack of data stems from the fact that currently there is no quantitative knowledge on the rates of release of NMs to the environment, and although many predictions of NM concentrations have been made<sup>32</sup> to date, water monitoring

data are not available for any NMs. This is due to the fact that monitoring of NMs in natural waters presents some major challenges. For example, the ability to measure metal NMs in natural waters is impeded by the presence of background levels of trace metals, and although methods are under development, NMs represent a large diversity of materials that challenge the technical capabilities of standard methods<sup>49</sup>. Current methods cannot distinguish between an artificial NM and a naturally occurring NM, and detection limits for most monitoring methods are in the range  $\text{ng L}^{-1}$  to  $\text{pg L}^{-1}$ ; this may not be sufficiently low to detect NMs<sup>50</sup>.

One area of NM monitoring that is rapidly developing is the use of product databases. Whilst there is no national database for Scotland on sources or predicted quantities of NMs in the environment, data are emerging at a global scale<sup>32</sup>.

### 3 Microplastics as Contaminants of Emerging Concern

Marine litter has been defined by the United Nations Environment Programme (UNEP) as “any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment. Marine litter consists of items that have been made or used by people and deliberately discarded into the sea or rivers or on beaches; brought indirectly to the sea with rivers, sewage, storm water or winds; accidentally lost, including material lost at sea in bad weather (fishing gear, cargo); or deliberately left by people on beaches and shores”<sup>51</sup>. The development of several regional programmes to address the issue (WIOMSA – West Indian Ocean Region; COBSEA – East Asian Seas; CPPS – Southeast Pacific; OSPAR – OSPAR region (North Atlantic))<sup>52</sup>, is indicative of the international dimension of the problem from which Scotland is not immune. According to the UK’s Marine Conservation Society, Scotland had the second highest litter levels on UK beaches surveyed in 2009, down 26% from 2008, 2,581 items/km to 1,907 items  $\text{km}^{-1}$ , respectively<sup>54</sup>, and more recent surveys in 2013 show a further slight drop (MCS press release 19<sup>th</sup> March 2015: <https://www.mcsuk.org/press/view/617>) The cost of marine litter to the Scottish economy, from cleaning beaches, loss of tourism revenue to damaged fishing gear and lost commercial catches in fisheries, is approximately £16.8m per annum, although without reliable data this is likely to be an underestimate of the true cost<sup>55</sup>.

Plastics are a major constituent of marine litter. The generic term “plastics”, which are anthropogenic, non-metallic high molecular weight polymers, includes a wide range of materials, such as rubbers, technical elastomers, textiles, technical fibers, thermosets, and thermoplastics. The plastics family is very diverse and includes Styrene Acrylonitrile Copolymer (SAN), polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), polyethylene terephthalate (PET), nylon, polyvinyl alcohol (PVA), acrylonitrile butadiene styrene (ABS), expandable Polyester Resins (EPS), and synthetic rubbers. According to data provided by the Association of Plastics Manufacturers ([www.plasticseurope.org/](http://www.plasticseurope.org/)), production of primary plastics and plastic products in the EU is a multi-billion Euro industry, showing strong growth during the 1990’s. The current economic crisis has strongly affected the industry, and, following a brief recovery in 2010/11, production is now displaying a downward trend. The management of plastic waste material remains a major world-wide problem. According to the USEPA only 7% of US plastic waste was recovered in 2008<sup>56</sup>. In the EU an estimated 45 million metric tonnes of plastics were consumed in 2009 of which approximately 29% was recovered and of which 42% were recycled. Germany, the highest plastic waste producer in the EU, recovers 80% and recycles about 35% of it, whereas the UK with the second highest plastic waste production recovers only 26%<sup>53</sup>. Whilst in many other countries around the world, including Mauritania and several European countries, the use of plastic bags has either been banned or a levy introduced, significantly reducing the use and occurrence of bags as litter in the environment, NI, Wales, and England have yet to implement a pledge to charge for plastic bags. In October 2014, following a lengthy consultation process, Scotland started levying a charge on single-use plastic shopping bags.



Plastic debris in the marine and freshwater environment has been recognized as a problem for decades, mainly because of its visibility as flotsam, accumulation of “litter” on beaches and the seafloor<sup>57, 58</sup>, and detrimental interaction with high-profile aquatic organisms<sup>59</sup>. Most plastics, because of their polymeric nature are not easily biodegradable, although they generally start to become brittle after prolonged exposure to UV light and degradation through other weathering processes (e.g. loss of volatile organic plasticizers). The resulting persistence of plastics in the environment, which is part of their appeal as a material of choice for manufacturers, means that their main route of degradation is through mechanical abrasion leading to ever smaller plastic particles, so-called microplastics. Although plastic litter and pellets are not a new problem<sup>57, 60, 61</sup>, the awareness of microplastics in the environment and their propensity to cause environmental damage is a relatively recent development<sup>62</sup>, which is now attracting an increasing amount of attention<sup>53, 58, 63</sup>.

### 3.1 Classification of Microplastics

Microplastics can be defined as plastic particles and fibres smaller than 5mm and/or that are retained in a neuston net (~333µm mesh size)<sup>63</sup>, to date the only standardized sampling technique for microplastics in the water column, making recovery data of smaller microplastics difficult to compare. Generally microplastics are grouped by usage and origin as either (1) primary microplastics, which are used as a raw material in the plastics industry, and in consumer products such as abrasives and personal care products, and (2) secondary microplastics, which are fragments resulting from degradation of larger plastic items<sup>63</sup>. Brightly coloured microplastic fibres are easily distinguished from natural particulates, but non-fibrous microplastic particles from cleaning and personal care products (PCP) and fragmentation of macroplastic litter will be discoloured by biofilms and exposure to light. Better methods are therefore required to easily distinguish microplastics from naturally occurring particulates.

### 3.2 Transport, Fate and Effects of Microplastics in Aquatic Environments

A significant gap in current knowledge is the uncertainty of the importance of primary and secondary sources of microplastics<sup>63</sup>, as well as the identification of sinks and hot-spots for plastics and microplastics. In this context, as in any environmental biomarker study, good local and/or regional Scottish reference sites need to be identified. The origin of plastic debris entering the marine environment lies in wind-blown material from terrestrial sources (mainly packaging), sewage outfall (including plastic particle additives to personal care products, such as scrubs), as well as from shipping<sup>64</sup>, including discarded fishing gear, lost cargo (including plastic pellets for industrial plastic production: [www.pelletwatch.org](http://www.pelletwatch.org)) and debris from aquaculture developments and offshore installations<sup>65</sup>. Whereas the disposal of litter at sea is strictly regulated by the IMO (MARPOL 73/78), and enforced in territorial coastal waters by its member states, dumping at high sea is more difficult to detect. However, the discovery of large accumulations of floating debris in the North Pacific gyres suggests this cannot be ruled out as a source of entry of microplastics into the sea. As indicated above, degradation of plastic debris has until recently been cited as the main source of microplastics in the marine environment.

However, a large proportion of microplastic polymers identified in UK sediments include Polyester and acrylic, often found in fibrous form. Wastewater treatment plant effluent has been shown to contain similar fibres, suggesting that in addition to microplastic particles from degradation of larger debris, a hitherto overlooked major source of microplastics to the marine environment is through washing of clothes rather than from degradation of macroplastic litter alone<sup>66</sup>.

Whether density plays a part in their respective distributions is still being debated, but appears to be size dependent<sup>62, 67</sup>. In one study macroplastic debris exhibited patterns of distribution for less dense items (mainly wind-driven floating litter), while for microplastic particles the patterns were more distinct for denser material, that tended to sink<sup>67</sup>.

#### 3.2.1 Interaction of Microplastics with Aquatic Organisms

The high profile cases of ensnared marine mammals, sharks, and turtles<sup>59</sup> in discarded fishing gear, as well as colonial seabirds using plastic as nesting material<sup>68</sup>, are well-known examples of animals interacting with plastic debris. However, floating plastic debris, such as microplastics, can also act as a substrate and vector for exotic and invasive species<sup>69</sup>, including microbes, as well as persistent organic pollutants, contaminating otherwise pristine ecosystems<sup>70</sup>. Many of these chemical pollutants enter the aquatic environment from various sources and the upper surface layers are prone to quite high inputs of these chemicals. Upon their entry into surface waters, chemical pollutants may become subjected to abiotic (e.g. photolysis; chemical oxidation; adsorption to inert surfaces) and biotic (e.g. adsorption to bio-surfaces; microbial degradation) influences that will ultimately dictate their fate. Published reports have shown the presence of priority toxic substances, such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethan (DDT) and polycyclic aromatic hydrocarbons (PAHs), to be associated with plastic pellets collected from marine waters<sup>71, 72</sup>. The adsorption and accumulation of these chemicals from seawater onto the surface of plastic pellets can be explained by the low polarity attraction between them.

##### 3.2.1.1 Ingestion

Plastics are ingested by aquatic organisms that mistake them for food. The best known example is the case of turtles ingesting floating plastic bags, mistaking them for medusae, in many cases their main source of food. A variety of organisms have also been shown to ingest microplastics, such as plankton<sup>73, 74</sup>, the mussel *Mytilus edulis*<sup>75</sup>, sea cucumbers<sup>76</sup>, turtles<sup>59, 77</sup>, Norway lobsters (*Nephrops norvegicus*)<sup>78</sup>, both pelagic<sup>79, 80</sup> and demersal<sup>80-82</sup> fish species, and sea birds<sup>83-88</sup>. The concern is that if microplastics are ingested, they could obstruct feeding appendages or accumulate in the digestive tracts of exposed organisms<sup>75</sup> leading to nutritional impairment and general decline in condition<sup>88</sup>. There is also evidence of an inflammatory response in the blood compartment plus pathologies in other tissues following such accumulation of particulate materials in filter-feeding mussels<sup>89</sup>.

##### 3.2.1.2 Exposure to Chemicals Associated with Microplastics

Furthermore, ingested microplastics may also facilitate exposure to metals<sup>70, 71, 90-95</sup> and persistent organic pollutants<sup>71, 92-95</sup> adsorbed to the plastic or plasticizers leaching from the

plastic particles and residues of metal catalysts<sup>96</sup>. As some of the chemicals are carcinogenic and associated with increasing the susceptibility of animals that ingest the contaminated particles to disease, this is a significant concern. For example, the mass of plastic found in the Great Shearwater *Puffinus gravis* has been correlated to concentrations of PCBs in its tissues<sup>88</sup>. Some plasticizers, such as bisphenol-A are known endocrine disruptors potentially interfering with the reproduction of affected organisms<sup>94, 95, 97</sup>. However, the mechanisms by which xenobiotics desorb from plastic particles under varying conditions are still poorly understood. Tests need to be carried out under relevant environmental conditions in order to develop appropriate models to assess the risk to potentially vulnerable organisms and habitats. These substances may be accumulated and magnified up the food chain to become highly concentrated in higher trophic levels, particularly top predators, that are often a source of food for humans, posing a potential socio-economic risk<sup>96</sup>. Plastic particles may hence be considered as important vehicles for transporting toxic chemicals in the marine environment and into marine and terrestrial food webs. The adsorption and accumulation of low polarity (i.e. hydrophobic) chemicals onto the surfaces of micro-plastics would be expected to attract microorganisms that are capable of utilizing these chemicals, because the latter would act as an available source of carbon and energy. Since almost any environment contains some source of energy, microbes will adapt or evolve to exploit it. Therefore, in the marine environment, the adsorption of these chemicals to micro-plastics is likely to result in some bacteria migrating. There is potentially a spatial and temporal association between micro-plastics and certain types of bacteria that are capable of metabolizing the adsorbed chemicals. Very little is understood about the role of biological processes involved in the degradation of micro-plastics. Microorganisms, in particular bacteria, are likely to contribute importantly here. Bacteria harbour an immense genetic diversity and, over relatively short timescales, evolve novel degradation pathways, such as for the biodegradation of industrially-synthesized xenobiotic compounds that have eventually found their way into the environment using monooxygenase enzymes, such as Cytochrome P450<sup>98</sup>.

Analogous to the physical interaction of chemical pollutants with micro-plastics, dissolved organic matter (DOM) in the marine water column could also be prone to adsorbing onto the surface of micro-plastics. In the oceans, DOM is the largest and possibly least understood pool of carbon, comparable in mass to the carbon in atmospheric CO<sub>2</sub><sup>99</sup>. Much of this DOM exists as biopolymers that undergo reversible transition between colloidal and dissolved phases<sup>100, 101</sup>. A major fraction of marine DOM derives from the synthesis and release of exopolysaccharides (EPS) by bacteria and eukaryotic phytoplankton<sup>102, 103</sup>, that can have high levels of uronic acid<sup>104</sup>, which confer EPS macromolecules with an ability to interface with low polarity substances, such as hydrocarbons<sup>105-107</sup>. Amino acids and proteins are also often found to be associated with marine bacterial EPS, which can confer hydrophobic characteristics to these polymers<sup>103, 107, 108</sup>. It would therefore seem reasonable to include EPS into the list of substances that could adsorb and accumulate on the surfaces of micro-plastics.

### 3.2.1.3 Biofouling

Bacteria are protagonists in the initial colonisation and development of biofilms on most submerged surfaces. Upon

entry of microplastic particles into the marine environment, their surface would commence to adsorb any hydrophobic chemicals within the immediate vicinity of the surrounding seawater. At the same time, or soon afterward, the surface of the particles would become subjected to a sequence of stages leading to a biofilm formation. The adsorption and accumulation of certain chemicals to the particle surface will dictate the first bacterial colonizers, which are likely to be species with an 'appetite' for any of the chemicals adsorbed (e.g. PCBs, DDT, PAHs or other). These chemicals could act as a selective trigger for the first microbial community to colonise the plastic particles and, hence, influence the next types of colonisers in the sequence of biofilm development. The subsequent colonisation of eukaryotic phytoplankton (e.g. diatoms, dinoflagellates) and protozoa would also involve the production and release of large quantities of EPS, that will encase and protect the microbial community from external assaults. A microplastic particle with a fully-formed biofilm could act as a "hot spot" of microbial activity. This description of biofilm formation on microplastic particles is hypothetical and largely based on preliminary data and on biofilm formation on other submerged surfaces in the marine environment.

## 3.3 Climate Change – Microplastics

Evidence exists to suspect that climate change and associated shifts in large scale oceanographic processes could affect the distribution of debris in the marine environment<sup>109</sup>. However, there is no information available regarding the effects of climate change on the degradation of plastic debris or the behaviour of microplastics in relevant environmental conditions. For instance, would higher water temperatures lead to accelerated degradation, either through increased microbial activity, likely increase in solar irradiation or a potential drop in pH from ocean acidification?

## 3.4 Microplastic Monitoring Methodologies

As with any form of environmental contamination, it is important to develop a set of internationally recognized standardized sampling techniques that enable comprehensive monitoring programmes. Whilst there are well-established protocols for sampling of plastic litter at the macro scale (OSPAR, HELCOM 29/2, UNEP/ICO, EPA, NOAA)<sup>52</sup>, characterized as material >2.5cm, there are no corresponding sets of guidelines available for meso scale debris (<2.5cm >5mm) and microplastics (<5mm). There have been a number of international initiatives and workshops towards establishing this aim for microplastics<sup>52</sup>. Much of this work appears to be focusing on the water column as this is seen as the most likely place to find and monitor input of fresh plastic material. There are currently three steps needed in this monitoring process i) sampling, ii) detection, and iii) identification and sorting.

- i) Devices for sampling suspended particulate matter in the aquatic environment have been in use for several decades, notably for the sampling of plankton. These devices usually consist of conically shaped nets, with a mesh size of around 300µm and a mouth of known circumference, and a detachable collecting container at the tail end of the net. The net is usually towed behind a vessel, whereby the water is forced through the net and the residue driven towards a collecting container. Knowledge of the area enclosed by the

mouth of the net together with the flow through the net indicates the volume of water filtered per time and allows the estimation of particulate concentration. Other devices, such as the continuous plankton recorder (CPR), operate by trapping plankton between two slowly moving bands of silk that are rolled up into a storage vessel containing formalin for preserving the plankton. Preserved CPR samples have been used to obtain historical microplastic particle concentrations in the marine environment from the 1960s to compare them with present day levels, showing a significant increase<sup>62, 110</sup>. Other techniques that have been discussed are the use of pump-fed filters in order to standardize flow, avoid atmospheric contamination, and allow sampling from stationary platforms with potential for automation<sup>111</sup>. Sampling of intertidal sediments typically occurs at the strand line, the location where buoyant macro litter tends to accumulate in the intertidal. Sampling from the intertidal zone is achieved by hand collecting replicated samples of sediment typically with a small metal scoop or trowel. Sampling is normally from the top layer of sediment (top few centimetres), whereas subtidal sediments are often sampled using traditional means, such as grabs, box cores, or multicorers. The latter are used where information about the sediment stratification, including surface layer integrity, is required<sup>112</sup>.

- ii) The most commonly reported separation and sorting approach is to extract plastic particles from the non-plastic plankton net residue or sediments using a high density flotation technique, typically by agitating the filtrate or sediment in a saturated sodium chloride solution. The supernatant, containing any positively buoyant plastic, is separated onto filter paper, which is then examined under a dissecting microscope. Small fragments are either identified by visual examination or preferably are removed for further analyses. The density of a saturated NaCl solution is around 1.2. For most polymer types this is sufficient using the flotation technique. However some polymers, such as PVC and Polyester have higher densities, 1.4 and 1.39, respectively, and are likely to be under-reported using this technique. An alternative approach has been reported using Ludox-TM 40 with eight centrifuge cycles and a 32 µm filtration step<sup>113</sup>.
- iii) Identification and sorting. Early approaches to identifying and classifying microplastics by polymer type have applied Fourier Transform infrared (FT-IR) spectroscopy<sup>62</sup>. Polymers conclusively identified by this method in UK waters were acrylic, poly (ethylene:propylene), polyamide (nylon), polyester, polyethylene, polymethylacrylate, polypropylene, and polyvinyl-alcohol. However, FT-IR requires time-consuming sample preparation, as high background is generated by moist or biofilm coated samples, and the spectral patterns are not very distinct for aged or nontransparent particles. Raman spectroscopy, although traditionally more expensive, requires no sample preparation, samples do not need to be transparent and it has greater size resolution. Advances in Raman development are making this system more affordable and therefore a more attractive option for the future<sup>114</sup>. Nevertheless, these are rather laborious processes and consequently there is a drive towards automating the process. Although to our knowledge no such system exists at present, automation will most likely be achieved for water samples

first. A pump-based filtration system could conceivably be fitted with in-line analytical systems, such as Ferrybox Systems, an onboard pumping and analysis system for monitoring general background aquatic parameters, such as temperature, salinity, oxygen, and turbidity that are used to assess the health of a given body of water. These systems are currently being developed to expand their capability towards other important parameters, such as Chlorophyll *a*, nutrients, pH, pCO<sub>2</sub>, plankton organisms, and in the future specific contaminants and possibly even specific particulates such as microplastics. In the meantime identification could be made easier, quicker, and cheaper by developing a putative microplastics identification key, much like the procedures used in the forensic examination of synthetic polymers using polarized light microscopy<sup>115, 116</sup>.

### 3.5 Legislation Governing Microplastics

The EU Marine Strategy Framework Directive (MSFD), which applies to coastal water bodies, outlines 11 descriptors to define the environmental status of marine water. One of them, descriptor 10 ([http://ec.europa.eu/environment/marine/good-environmental-status/descriptor-10/index\\_en.htm](http://ec.europa.eu/environment/marine/good-environmental-status/descriptor-10/index_en.htm)), concerns marine litter. The main goal of the directive is to foster legislation that will help to achieve “Good Environmental Status” (GES) in its member states. GES in the context of litter is defined as “properties and quantities of marine litter that do not cause harm to the coastal and marine environment”. The focus is on plastic litter, and has recently acknowledged the increasing perception of the problem of microplastics driven by the growing body of evidence in the scientific literature. Consequently, as a follow up to the Commission’s Decision on criteria and methodological standards on GES of marine waters (2010/477/EU), the Marine Directors requested the Directorate-General for the Environment (DG ENV) in 2010 to establish a technical subgroup under the Working Group on GES in relation to the Marine Strategy Framework Directive 2008/56/EC (MSFD) for further development of Descriptor 10, Marine Litter. In 2011 the technical subgroup on Marine Litter produced a report published by the European Commission’s Joint Research Centre and Institute for Environment and Sustainability<sup>52</sup>. A road map for 2012 was established, proposing that a monitoring strategy needs to be developed and harmonized across the regions and the EU, including further development of monitoring tools to include microplastics. Amongst the requirements are harmonized tools for assessing harm of plastic debris and microplastics, litter categories, sources and source weighting. Although the potential impact of microplastics is becoming an increasing concern, the European Commission’s Registration, Evaluation, Authorisation & Restriction of Chemicals (REACH) does not apply to microplastics.

The European Union has recently funded a number of relevant consortia with the aim of understanding the problems associated with plastics in the marine environment, including MARLISCO, a project promoting the Social Awareness and CO-Responsibility, FP7 BIOCLEAN, an international consortium dedicated to the biodegradation of plastics, and FP7 CLEANSEA, addressing the specific problem of marine litter. In Scotland, Marine Scotland Science, a branch of the Scottish Government, is responsible for implementing GES under the MSFD. In order to address the marine litter problem outlined

in Descriptor 10 of the MSFD, litter monitoring was included in the Clean Seas Environment Monitoring Programme (CSEMP) in 2009, and data submitted to the Marine Environmental and Assessment National database (MERMAN) held at the British Oceanographic Data Centre (BODC) which includes litter data from the Marine Conservation Society (MCS). The Scottish Government also supports a range of initiatives and, advised by the Scottish Marine Litter Strategy Steering group, is taking action to help prevent and also deal with the consequences of litter. This includes “Fishing for Litter” that encourages fishermen to remove marine litter from the sea with the aim of correct disposal in port in accordance with the EU Port Waste Reception Directive (Directive 2000/59/EC), and a number of relevant charities through the Zero Waste Scotland programme. The Zero Waste Scotland programme contains a number of regulations aimed mainly at industry and municipal authorities, preventing plastics from going to incineration or landfill, and improving the recovery and recycling rates of waste plastics. Curiously, there is no mention of plastic or litter in the Marine (Scotland) Act 2010. Although litter is mentioned in UK Marine Policy Statement 2011, there is no specific reference to plastic. DEFRA includes plastics in its Marine Programme Evidence Plan 2011/12 and reports that “litter, particularly plastics, is being found on all surveyed beaches”, but that there is “little evidence available to assess levels and impacts of [...] litter and microplastics”. In 2011, Marine Scotland organized a Marine Litter workshop in light of the Marine (Scotland) Act 2010 and the implementation of the MSFD. Although microplastics are mentioned briefly, the main focus of the report is on macroplastic debris<sup>55</sup>. Similarly, as of May 2013, there were

1,497 hits on the SEPA website containing the term “plastic”. However, only three hits were returned on searches containing the terms “microplastic” or “micro-plastic” or “micro plastic”. These include draft minutes of a meeting of the Clyde Area Advisory Group from 25<sup>th</sup> March 2011<sup>17</sup>, and draft and final minutes of the Argyll Area Advisory Group from the 6<sup>th</sup> March 2008<sup>18</sup>.

Public awareness of microplastics and the potential problems have been greatly increased by recent media events, both broadcast and in print. The most notable examples, especially as they are still available on the internet, are a BBC Newsnight ([www.bbc.co.uk/news/science-environment-21259593](http://www.bbc.co.uk/news/science-environment-21259593)) piece that was broadcast 30<sup>th</sup> Jan, 2013, and a piece in the Scotsman on the 20<sup>th</sup> February, 2013. A host of social networking platforms are also raising and improving awareness, most notably Twitter (@mscuk – scrub it out, @PlasticPollutes, @ProjectGreenBag, @RiseAbovePlstcs, @LifeWoutPlastic @plasticsoupfoun) and Facebook (Plastic Pollution Coalition, My Plastic Free Life, Plastic Oceans), as well as associated blogs, driving internet traffic towards the primary literature, much of which is slowly becoming Open Access. The resulting public pressure from campaigns such as the Beat The Bead has led to several high-profile industry initiatives to directly reduce microplastic pollution. For example, Unilever have announced on their website that they will phase out the use of plastic micro beads as a scrub material in all of their personal care products globally by 2015, and this has since been widely reported. In addition, Lush have announced an end to using plastic glitter in products.

## 4 Recommendations

### 4.1 Nanomaterials

- Specific regulations on the production, use, or disposal of NMs may be required, as there is still limited understanding of their impact on the ecosystem and human health.
- The lack of detection methods for monitoring the presence of NMs in the environment and in environmental media means that few reliable data<sup>1</sup> currently exist on the quantities released into the environment (it is not actively monitored in Scotland).
- Research from the past decade has seen more papers published on developing models predicting NM concentrations in the environment. There are limited data available to validate these models.
- Develop environmentally relevant testing strategies for assessing risks.
- Need to better understand the behaviour of NMs in complex environmental media, such as fresh- and seawater, sediments and sediment-pore water systems.
- Given the published information available on establishments in Scotland producing or working with NMs, it is unlikely that the situation is more acute than what is taking place in other European countries. Although records are not fully available, it is expected that the number of establishments which fit into those categories is not very large. Therefore, it is proposed that the situation continues to be monitored and that regulatory developments follow the lead from the work currently taking place at European level.
- Instigate studies to help understand biofilm formation on microplastics, and its role in microplastic dynamics.
- Scotland needs strong representation in relevant international bodies (OSPAR, GESAMP, JCR) to help devise standardized methods suitable for the Scottish situation, which may be very different from other countries in terms of climate, plastic usage, and end of life treatment, etc.
- Following recent realization that sewage can account for a large amount of particularly fibrous microplastic material, the development of fabrics that release fewer fibres during washing as well as appropriate filters that can remove these microplastic fibres from the sewage stream needs to be encouraged.
- Recent public engagement through investigative media pieces needs to be built on and the reduction of waste encouraged. If alternative materials are not available, further incentives for increasing recovery and recycling rates need to be created, such as the one recently piloted by the Scottish Government's Zero Waste initiative.
- Industry and retail need to be further incentivized to use less packaging material.

### 4.2 Microplastics

- A fully-funded large-scale baseline study for the Scottish marine environment is required. This will help to better identify sources of microplastics and hotspots, as well as establish relevant local reference sites. This is particularly important for separating fresh input from historic material, and understanding temporal trends.
- Develop standardized methods for sampling, sorting and identification of environmental microplastic polymers. This includes developing categories for reporting that would allow data from different survey types to be compared, similar to the OSPAR beach litter survey.
- More research is required to understand the potential harm of microplastics, including source and fate in the marine environment (trophic mobility), as well as the development of appropriate biomarkers of exposure in marine organisms, and implications for human health.
- Instigate studies to better understand how microplastics interact with contaminants in the environment, and how they may act as vectors for the potential facilitated entry of chemical pollutants into the food chain.

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## 6 Web Resources

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FP7 Intelligent testing strategy for nanomaterials  
<http://www.its-nano.eu/> Last accessed 20.10.13

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EU Marine Strategy Framework Directive (MSFD), descriptor 10: [http://ec.europa.eu/environment/marine/good-environmental-status/descriptor-10/index\\_en.htm](http://ec.europa.eu/environment/marine/good-environmental-status/descriptor-10/index_en.htm)  
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