Appendix 20

Literature review of the impact of nanoparticles

Dixon.Brosnan

environmental consultants

Project		**Supplemental report to the NIS for a proposed Resource Recovery Centre and associated works at Ringaskiddy, Co. Cork**		
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DixonBrosnan The Cedars, Bridewood, Ovens, Co Cork
Tel 086 851 1437| carl@dixonbrosnan.com | www.dixonbrosnan.com

Date	Rev	Status	Prepared by	
05/05/16	0	Issue to client	Carl Dixon MSc.	
			Dr. Ed Porter (AWN Consulting)	
			Dr. Fergal Callaghan (AWN Consulting)	
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			Dr. Fergal Callaghan (AWN Consulting)	

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1. Introduction

During the oral hearing for the Strategic Infrastructure Development application for a Resource Recovery Centre at Ringaskiddy, Co. Cork, supplemental information was requested by Dr. Jervis Good of the National Parks and Wildlife Service (NPWS, Department of the Arts, Heritage and the Gaeltacht) in relation to possible impacts from engineered nanoparticles. The NPWS submission, (which is attached as **Appendix 1** of this report) recommended that a review of the scientific literature on effects of engineered nanoparticles likely to originate from the proposed waste to energy facility (incinerator) is undertaken, and an assessment of their potential effects on Cork Harbour SPA be included as a supplement to the Natura Impact Statement (NIS).

There are two possible pathways by which engineered nanoparticles, from the waste to energy facility (incinerator), could enter the environment and have a potential impact on a Natura 2000 site. One possible pathway is via emissions to air from the stack. The other possible pathway is via the flue gas cleaning residues if there was a spillage during transport or disposal.

This supplemental report to the NIS is structured as follows;

Section 1 Introduction

Section 2 Literature review of the potential biological/ecological impacts from engineered nanoparticles

Section 3 reviews the potential for such particles to be generated by waste-to-energy facilities

Section 4 looks at the potential risk related to transport of residues

Section 5 provides a conclusion on the potential impact on Natura 2000 sites.

Section 6 Reference list

This report was reviewed in 2018 and updated where required.

2. Literature review - Potential biological and ecological impacts from engineered nanoparticles.

Nanoparticles (NPs) are in the 1-nano-metre (nm) to 100-nm size range. Nanoparticles can be composed of many different base materials (carbon, silicon and metals, such as gold, cadmium and selenium) and they have different shapes. Nanoparticles in the environment may be either engineered nanoparticles or nanoparticles from a range of natural or combustion sources. New engineered nanoparticles are different to naturally occurring nanoparticles because they are being fabricated from the "bottom up". Nanoparticle properties differ compared with those of the parent compounds because about 40–50% of the atoms in nanoparticles (NPs) are on the surface, resulting in greater reactivity and potentially will have different biological effects to naturally occurring nanoparticles. The surface properties and the very small size of NPs provide surfaces that may bind and transport toxic chemical pollutants, as well as possibly being toxic in their own right by generating reactive radicals (Farré et al, 2009).

While nanoparticles occur naturally in the environment, the use of engineered nanoparticles has seen a recent spike and use is likely to increase significantly in the future. Metal-based nanoparticles such as silver (Ag) and titanium dioxide (TiO_2) are widely used in industrial and household applications. Because of the increasing use of such engineered nanoparticles and their release into the natural environment, NPs are likely to have a widespread geographic distribution (Dong-Ha Nam, 2014).

2.1 Possible ecosystem impacts

Recent efforts to characterize the toxicity of engineered nanoparticles have focused on the environmental implications, including exploration of toxicity to organisms (Walser et al, 2012). Concern has been expressed about the possible ecological impacts from the accumulation and aggregation of NPs in the aquatic environment, mainly in bottom sediments (Farré et al. 2009). Concern has been also expressed about the impact of such nanoparticles on the functioning of ecosystems. For example Andreia et al, (2016) found that release of nanosilver (nAg) in aquatic ecosystems may modify their functioning via impacts on the functional role of a freshwater shrimp (*Gammarus roeseli*).

Ekvall et al (2017) looked at the long-term effects of tungsten carbide (WC) nanoparticles in pelagic and benthic aquatic ecosystems. They evaluated the potential long-term exposure effects of WC nanoparticles on a pelagic (*Daphnia magna*) and a benthic (*Asellus aquaticus)* organism. No long-term effects were observed in the benthic system with respect to population dynamics or ecosystem services. However, long-term exposure of *D. magna* resulted in increased time to first reproduction and, if the particles were resuspended, strong effects on survival and reproductive output. Hence, the considerable differences in acute vs. long-term exposure studies revealed here emphasize the need for more long-term studies.

Nuzzo et al (2016) assessed the impact of bio-palladium nanoparticles (bio-Pd NPs) on the activity and structure of a marine microbial community. They concluded that considering all the factors evaluated, bio-Pd NPs could be deemed as non-toxic to the marine microbiota in the conditions tested.

The study reported a statistically significant reduction in cell viability, algal biomass and the photosynthetic pigments at 10, 50, 100, 150 and 200 mg/L of ZnO NPs from 24 h onwards. The reduction in photosynthetic pigments and cell growth might be due to oxidative stress induced by the interaction of ZnO NPs on algal cells, which led to cell death

Djearamane et al, (2018) looked at cytotoxic effects of zinc oxide nanoparticles on cyanobacterium *Spirulina (Arthrospira) platensis.* The study reported a statistically significant reduction in cell viability, algal biomass and the photosynthetic pigments at 10, 50, 100, 150 and 200 mg/L of ZnO NPs from 24 h onwards. The reduction in photosynthetic pigments and cell growth might be due to oxidative stress induced by the interaction of ZnO NPs on algal cells, which led to cell death.

2.2 Possible impacts on invertebrates including estuarine/marine invertebrates

Shannon K. (2013) noted that estuarine and marine sediments are a probable end point for many engineered nanoparticles due to enhanced aggregation and sedimentation in marine waters, as well as uptake and deposition by suspension-feeding organisms on the seafloor. They tested whether three heavily used metal oxide engineered nanoparticles, zinc oxide (ZnO), copper oxide (CuO), and nickel oxide (NiO) were toxic to an estuarine amphipod, *Leptocheirus plumulosus* and found that the accumulation of metals in amphipod tissues increased with exposure concentrations for all three NPS, suggesting possible exposure pathways to higher taxa.

Baun et al (2008) noted a lack of data in the field and noted that the limited number of studies has indicated acute toxicity in the low mgl^{-1} range and higher of engineered nanoparticles to aquatic invertebrates, although some indications of chronic toxicity and behavioural changes have also been described at concentrations in the high μgl^{-1} range.

Gagne et al (2008) looked at toxic effects of cadnium-telleuride (CdTe) quantum dots on freshwater mussels at various concentrations greater than 1mg/l. Some physiological impacts were recorded at these high concentration levels. Peyrot et al. (2009) reported similar effects. Conway et al. (2014) looked at the implications of trophic transfer and accumulation of cerium oxide CeO_2 nanoparticles in a marine mussel (*Mytilus galloprovincialis*) through two exposure methods namely direct and through sorbtion to phytoplankton. Approximately 99% of CeO_2 was captured and excreted in pseudofeces and average pseudofeces mass doubled in response to CeO_2 exposure. Clearance rates increased with CeO_2 concentration but decreased over time in groups exposed to CeO_2 directly, indicating stress.

Mouneyrac et al (2014) found that metal-based NPs in general were highly agglomerated/aggregated in seawater. Both metal forms (nanoparticulate, soluble) were generally bioaccumulated in two marine invertebrates, the bivalve mollusc *Scrobicularia plana* and the annelid polychaete *Hediste diversicolor.* Cozzaria et al, (2015) found that when the marine annelid polychate *N. diversicolor* is exposed to dissolved, nano and bulk silver (Ag) via spiked sediments, it showed an oxidative stress response.

Canesi et al, (2012) concluded that bivalves represent a particularly suitable model for investigating the effects and mechanisms of action underlying the potential toxicity of NPs in marine invertebrates. As suspension-feeders, they have highly developed processes for cellular internalization of nanoparticles integral to key physiological functions such as intra-cellular digestion and cellular immunity.

Baker et al, (2013) notes that benthic, sediment-dwelling and filter feeding organisms are most at risk. In marine systems, metal oxide (MeO) NPs can absorb to micro-organisms with potential for trophic transfer following consumption. The author also notes that environmentally-realistic metal oxide NPs concentrations are unlikely to cause significant adverse acute health problems, however sub-lethal effects e.g. oxidative stresses have been noted in many organisms, often deriving from dissolution of Ag, Cu or Zn ions, and this could result in chronic health impacts on such organisms.

2.3 Potential impacts on fish

Ostaszewska et al, (2016) looked at effects of silver (AgNPs) and copper (CuNPs) nanoparticles on larval Siberian sturgeon (*Acipenser baerii*) after 21 days of exposure. Toxicity tests were done in triplicates for each concentration of AgNPs 0.1, 0.5, 1.5 mg L^{-1} and CuNPs 0.01, 0.05, 0.15 mg L^{-1}. The results indicate that AgNPs and CuNPs exposure at these high levels negatively influenced survival; body length and mass; and morphology and physiology of the epidermis, gills, and liver of Siberian sturgeon larvae.

Handy et al (2011) notes that exposure to nanoparticles in the water column can cause respiratory toxicity involving altered ventilation, mucus secretion and gill pathology. Sub lethal concentration of various nanoparticles for fish ranged from 100 μg L^{-1} to 1 mg L^{-1}, while the lethal concentration of nanoparticles reach the milligrams per liter range.

Mehmet (2013) looked at sub-lethal effects of exposure of low and high concentrations of titanium dioxide nanoparticles (TiO2 NPs) on goldfish (*Carassius auratus*) and no significant accumulation in the muscle and brain of the fish was detected. However, titanium oxide (TiO2) NPs exposure inhibited growth of the goldfish. Scwon et al, (2010) showed that exposure of silver NPs to rainbow trout, at concentrations close to current estimations of environmental levels, can result in accumulation of silver in the gills and liver of fish and can affect likely oxidative metabolism in the gills.

Remya et al (2015) examined the impact of iron oxide nanoparticles hematology, iono regulation and gill Na^{+}/K^{+} ATPase activity in Indian major carp, *Labeo rohita.* The results indicated that high Fe_2O_3 NP concentrations in the aquatic environment may have adverse physiological effects on fish and the authors note that the results of the present study highlight the need for safe disposal and protocols for these metal oxides.

Ale et al (2018) looked at nanosilver toxicity in gills of tropical fish in relation to accumulation, oxidative stress, histopathology and other physiological effects. The results confirmed that the presence of low AgNP concentrations, in short and subchronic exposures, generates alterations in stress biomarkers and in the structure of this vital organ that are the gills.

2.4 Potential impacts on birds and mammals

Information looking at the potential impacts of nano-particles on wild mammal and bird populations, either through direct toxicity or bioaccumulation, is very limited. A review of published studies by Shah (2010) found that no studies were published on the toxicity of nanoparticles to birds. Some information on domestic birds is available. Sawosz et al. (2009) found that nanoparticles of silver do not affect growth, development and DNA oxidative damage in chicken embryos when hydrocolloids (0.3 ml), containing 50 ppm of nanoparticles, were injected in ovo prior to incubation of eggs. However, most such studies focus on the potential beneficial use of nanoparticles as food supplements for commercial poultry.

2.5 Limitations of available data

As an emerging field, a number of researchers have pointed out that data is lacking. A review of published studies by Shah (2010) found that that 42% of the studies involved measuring the toxicity of nanoparticles against pure microbial cultures, 18% of the ecotoxicity studies used fish or fish cells, 20% used daphnids and shrimp, 8% used plants, and fewer than 5% used worms. Although the pool of literature may seem quite large, glaring absences are apparent including birds and honey bees.

Matrangaa (2012) points out that whilst there is not much data available for gauging the effects of engineered nanoparticles on marine wildlife, the ultimate ecotoxicological impacts of chronic exposure to ENPs should be investigated further using laboratory tests and field studies. Mehmet (2013) notes that although aquatic species are at risk of exposure to the NPs, there is currently little known about their uptake, potential toxic effects, and behaviour in aquatic systems.

Handy et al, (2012) notes that rapid and reliable measurement methods for engineered nanoparticles in the tissues of organisms are needed to understand uptake and bioavailability, but also to ensure correct interpretation of ecotoxicity test results for risk assessments. Research with ecologically relevant test species and in real environmental scenarios is needed.

Lead et al (2018) reviewed developments in studies of nanomaterials (NMs) in the environment. They noted that although Ag, zinc oxide (ZnO), copper oxide (CuO), cerium dioxide (CeO_2), titanium dioxide (TiO_2), iron oxide (FeO), fullerenes, carbon nanotubes (CNTs), and a small number of others remain the most widely used and researched NMs, some newer NMs have been produced in recent years. The greatest interest and development has been in broad classes of materials including nanocomposites and nanohybrids, sometimes referred to as either multiple-component core-shell nanocrystals or oligomer NMs. The authors concluded that there is a developing consensus that NMs may pose a relatively low environmental risk, but because of uncertainty and lack of data in many areas, definitive conclusions cannot be drawn. In addition, this emerging consensus will likely change rapidly with qualitative changes in the technology and increased future discharges.

2.6 Conclusions

In general the literature review on the potential for biological and ecological impacts from engineered nanoparticles indicates that NPs in general can be aggregated in seawater and marine/estuarine bottom sediments. Lethal effects have been reported at high concentrations (generally in the mg/l range) in laboratory studies. Sub-lethal impacts such as oxidative stress have been reported and could potentially occur at environmentally realistic levels with respect to fish and invertebrates. Macro-invertebrate suspension feeders such as mussels may be at greater risk although work to quantify such effects via field studies is generally lacking. Some workers have reported impacts on fish but there is a paucity of information in relation to birds and mammals such as otter.

Although there are theoretical pathways by which impacts could occur at higher trophic levels, researchers have noted the paucity of information relating to ecosystem impacts or impacts on vertebrates such as birds. At the present time there is no clear scientific evidence which indicates that the levels of nanoparticles likely to realistically occur in the environment represent a significant risk to birds feeding on macro-invertebrates in estuarine sediments or to piscivorous birds listed as features of interest for the Cork Harbour SPA.

3. Conclusions on Nanoparticle air Emissions From Waste-To-Energy Facilities

Research has been conducted over the last fifteen years on emissions from incinerators in terms of nanoparticle size and numbers[1]. Nanoparticles (also referred to as ultra-fine particles (UFPs)) range in size from 1 - 100 nm. Nanoparticles in the environment may be either engineered nanoparticles or nanoparticles from a range of natural or combustion sources. As a worst-case, it has been assumed that the levels of nanoparticles reported in the literature studies below are 100% engineered nanoparticles.

A paper undertaken in 2001 (Zurcher et al, 2001) studied the emission of nanoparticles from modern municipal waste incinerators including a detailed investigation of particle numbers and particle size distribution. The study concluded that:

"The removal efficiency for PM_{10} of the flue gas treatment systems in all plants is very good. The number concentration of most plants is in the same order of magnitude as ambient air. According to our measurements we can state that waste incineration plants with up-to-date flue gas cleaning systems are not a relevant source for the emission of ultrafine particles into the environment. Particles above 1 micron are almost completely eliminated".

More recent research has been undertaken by an Italian research team (Buonanno et al, 2011a, Buonanno et al, 2011b, Buonanno et al, 2010) which focussed on a series of modern waste-to-energy facilities in Italy.

One of these papers (Buonanno et al, 2011b) reviewed emissions from five facilities in Italy with a range of furnaces and flue-gas cleaning technology. The facilities included moving grate, roller-type grate and fluidized bed reactors. In terms of abatement, the technology included wet, semi-dry and dry processes, spray absorber systems and fabric filters. Four of the five incinerators installed fabric filters, the exception being a facility which processed biomass which had a wet scrubber as the preferred abatement technology.

At two of the incinerators, measurements of nanoparticles were taken both prior to and after the fabric filter in order to determine the abatement efficiency of the fabric filter in the nanoparticle range. The results from the efficiency test were that fabric filters could achieve an efficiency of 99.99% over the entire measurement range (from 6 nm – 1000 nm) in terms of particle numbers.

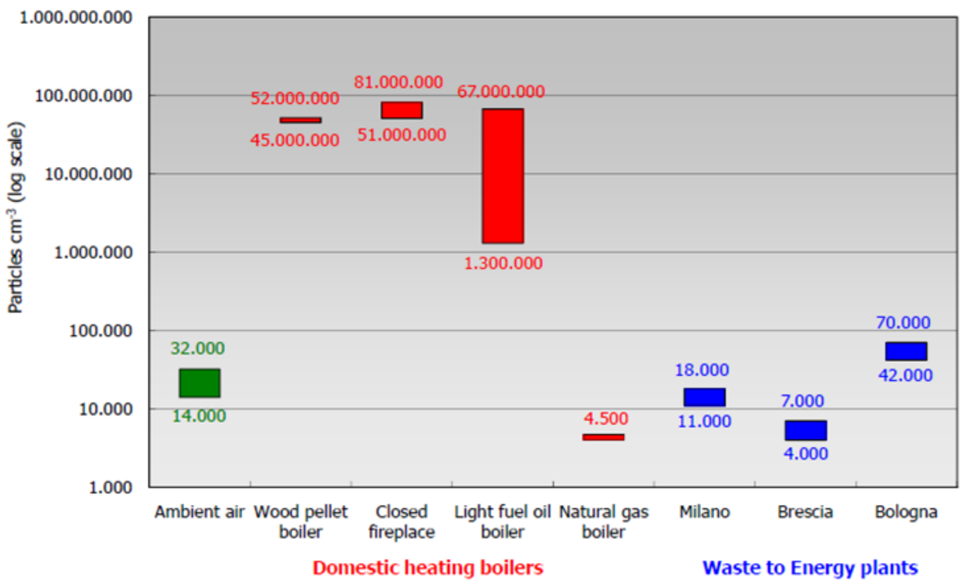
[1] Refer also to the evidence provided by Dr Edward Porter in which this research is considered

In terms of the overall results from the four MSW incinerators, the average concentration ranged from 0.4 – 6.0 x 10^3 particles cm^{-3}. The study concludes by stating:

*"**Implications**: The main implication of the study is that the use of a fabric filter in the flue gas treatment section of incinerators is able to guarantee very low concentrations in the stack in terms of UFPs. As regards the incineration plants, a further implication of the proposed study is that an a priori negative social response seems to be unjustified when referred to the ultrafine particle emissions."*

Buonanno et al, (2010) undertook a review of nanoparticles in ambient air downwind of a waste-to-energy facility in 2010. The facility was a modern moving grate facility with a semi-dry abatement system (SNCR, spray absorber system and a fabric filter). The average total number concentration was lower than 1.0 x 10^4 particles cm^{-3}. The study concluded that the results were typical of a rural site and that most of the elements could be attributed to long-range transport from other natural and/or anthropogenic sources.

Another study, by Cernuschi et al (2010), found that emissions of nanoparticles (in terms of particle numbers) from WTE facilities with fabric filters were typically similar to or lower than ambient air as shown in Figure 1. The results were compared to other combustions sources, such as wood pellet boilers, closed fireplaces and light fuel oil boilers, which were typically orders of magnitude higher.



Taken from "Cernuschi et al (2010) Emissions of Fine and Ultrafine Particles from Stationary Combustion Plants – Final Summary (LEAP, 2010)."

awnconsulting

The Tecpro Building, Clonshaugh Business and Technology Park, Dublin 17
T: +353 1 847 4220 F: +353 1 847 4257

Project
Indaver Ringskiddy Resource Recovery Centre

Reference
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Figure 1
UFP Particle Number (particles cm^{-3}) – Three Modern Incinerators In Italy Compared To Ambient Air & Other Combustion Sources

Buonanno et al (2009) also assessed the emissions of nanoparticles from incinerators and compared them to emissions from other sources:

> *"In terms of total particles emitted, 20 vehicles (with a percentage of HGVs between 6% and 8%) moving along a 3 km highway length in typical traffic conditions, are equivalent to one hour emission of the waste-to-energy plant."*

A recent review undertaken by a team lead by Roy Harrison in the UK (Kumar et al, 2013) stated the following in terms of nanoparticles from incinerators:

> *"However, the work of Buonanno et al. (2008, 2009a, 2011) and Angelucci et al. (2010) indicates that the flue gas treatment used on current technology incinerators is highly efficient, reducing nanoparticle concentrations in stack gases to levels comparable with ambient air. Consequently, the UFPs associated with MSW incineration are likely to be considerably smaller in quantity compared with a major source such as road traffic emissions."*

4. Potential impacts from engineered particles in Boiler Ash and Flue Gas Cleaning Residues - NIS conclusions

Circa 2,000 tonnes per annum of boiler ash and circa 9,104 tonnes per annum of flue gas cleaning residues will be produced in the waste-to-energy facility at Ringaskiddy. The flue gas cleaning residues will be in the form of fine particles which will include engineered nanoparticles. As noted in sections 4.5.8 and 4.5.9 of the NIS, these residues will be disposed of to a landfill for hazardous waste after treatment if necessary or recovered to a salt mine, either in Ireland, if one is available, or abroad. Potential impacts on Natura 2000 sites were screened out due to the following:

- The shipping containers used for transport are designed and operated in line with international standards. The regulation of the transport of the boiler ash and flue gas residues would be subject to Trans Frontier Shipment (TFS) licence which is a licence which must be approved by the origin/destination/transit authorities consenting to the movement/transit and acceptance of wastes between EU member states.
- The residues will be collected on the site in sealed silos. The silos are emptied into a tanker via a sealed connection. This will ensure that there are no fugitive releases on the site.
- It is noted that the accident risk during shipping of the boiler ash and flue gas residues is low. Van Den Bosch are the preferred international logistic services provider which transports such residues for Indaver. They note that in the 51 years of their history no container has ever fallen overboard and no ship has sunk with their containers on board.
- The addition of water leads to the residues solidifying. Thus in event of a shipping accident and if the transport container were to lose integrity, the residues would solidify on contact with water and solidified residues will be salvaged from the sea bed.

Section 4.5.8 of the NIS (DixonBrosnan, 2015) concluded that *"Given the extremely low risk of an accident, the low risk of leakage from the transport containers, the fact that the residues will solidify on contact with water, no appreciable impacts on Natura 2000 sites along the shipping route from the disposal of this material will occur."*

5. Conclusions

The Natura Impact Statement appraised the potential for significant impacts arising from the proposed development on Natura 2000 sites within a 20km radius. Following screening the only Natura 2000 site for which potential impacts had been identified was the Cork Harbour

SPA which is located approximately 0.5km from the proposed development site at its closest point.

Theoretically impacts on the SPA could arise if high levels of NPs were to reach the aquatic environment, via emissions or accidental spillage of flue gas residues.

A literature review (Section 2) indicates that engineered nanoparticles could theoretically impact on marine macro-invertebrates and fish, including species which may form part of the diet of birds listed as features of interest for the Cork Harbour SPA. At the present time however, there is no clear scientific evidence which indicates that the levels of nanoparticles likely to realistically occur in the existing environment represent a significant risk to birds feeding on macro-invertebrates in estuarine sediments or to piscivorous birds listed as features of interest for the Cork Harbour SPA.

A literature review (Section 3) on nanoparticle emissions from Waste-To-Energy facilities concluded that the use of a fabric filter in the flue gas treatment systems leads to very low levels of engineered nanoparticles in air emissions. The air emissions from the facility are not predicted to be a significant source of engineered nanoparticles and it is further noted that the Cork Harbour SPA is located 0.5km from the proposed facility at its closest point.

Nanoparticles will be present in flue gas residues. It was concluded by the NIS (Section 5 above) that the risk of accidental release of flue gas residues during transport is not considered significant and this potential impact was screened out in the NIS.

There will be no process aqueous discharges from the facility. The only aqueous discharges to the marine environment during construction or operation will be surface water and there will be no pathway for engineered nanoparticles to enter the surface water. There is no direct pathway to water, it is indirect and the particle concentrations in air associated with the waste to energy plant are effectively insignificant when compared with background. Particles in air may over time deposit on water but in this case the water body is Cork Harbour with a daily tidal flux of some 57 million m3/day, providing many orders of magnitude dilution of any particles depositing on water.

For the receptor to be impacted there needs to be a significant concentration of particles in the water. From literature it is indicated that significant effects are most likely to occur at the mg/l level, whereas with the available dilution and the insignificantly small emission, it is not possible that the mg/l levels could ever be reached. Therefore, the potential for significant impacts on prey items for birds within the Cork Harbour SPA from engineered nanoparticles is considered extremely remote for the foreseeable future.

Following on from this comprehensive assessment of the potential impacts on the qualifying interests and conservation objectives for Natura 2000 sites, it has been concluded that the proposed development will not have an adverse effect on the integrity of any Natura 2000 sites including the Cork Harbour SPA.

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