ObservatoryNANO

WP5: Environmental, Health and Safety (EHS) Impacts

Technology Sector Evaluation: Agrifood V 1.0 July 2010

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1. Introduction

The agrifood industry is the largest manufacturing sector in Europe. According to the European Technology Platform Food for Life (ETP, 2008) 'the agricultural sector employs over 11 million people (2.3% of the population of the enlarged EU)' and 'the food and drink industry had a turnover of 810 billion euro in 2004, transforming over 70% of the EU's agricultural raw materials and employing over 4 million people, the majority within the SMEs sector.'

There are a number of issues facing the industry:

- Shifting demands (and their articulation) from fork to farm: In the past the agrifood industry was driven by improvements to mass production and supply. However, increasing consumer interest and concerns over how and where food is produced and processed, means that this situation is becoming reversed as consumer requirements play a larger role (at least in the developed world). An increase in consumer choice through production of a variety of options, as well as catering for (an ever increasing number of) niche markets, means a more diverse and complex agrifood industry,
- Adaptive supply chains from farm to fork: There is a shift from stable supply chain[1] relations to more flexible and agile relationships with shifts and reorientations based on the needs of the value chain. This means suppliers need to remain aware of the dynamics of the value chain and adapt meaning a constantly co-evolving situation between supply and value chains,
- Environmental sustainability and agricultural management: As with all industries, agrifood needs to be environmentally sustainable. This encompasses new legislation affecting the number of pesticides which can be used; decreasing agricultural waste (or finding novel uses for it), for example Europe's fruit and vegetable industries generate about 30 million tonnes of waste a year (GRUB S UP, 2009); and reducing the amount of waste at the end point (*e.g.* packaging),
- Decline in food scientists: With fewer students enrolling in food science programmes in universities, there could be a real shortage of trained personnel within the next decade. This would hamper development of new technologies and process innovations, at a time when there will be a greater pressure to deliver on the issues mentioned above namely environmental sustainability, more adaptive supply chains and shifting consumer demands.

Regarding nanotechnology, many different national and regional programmes dedicated to agrifood are already underway or under development. For example the EU finances a number of industrial collaborative projects through the Framework Programmes, and national programmes include Japan (CSTP Strategic S&T Priorities in Nanotech. & Materials)[2], US ("Nanoscale Science and Engineering for Agriculture and Food Systems", a part of the National Research Initiative (NRI)), Nano4Vitality in the Netherlands (€12M over 4 years).

1 Supply chain is taken as the provision of an element to a food product (such as wheat, barley, bioplastics for packaging etc.) and value chain is the chain of developments from raw materials to end product in the grocers, on the shelves of supermarkets or for sale directly from source. Thus the value chain is a complex interlinking of many supply chains, requiring a great deal of management and coordination. ICT is playing a large role in this adaptive supply chain management but is beyond the scope of this report (for more information on advanced supply chain management see Ivanov *et al* (2010)).

2 In particular, the strategic priority "Developing nano-particle processing technologies and nano-scale evaluation technologies for domestic farm products in order to develop safer and higher quality food".

Estimates vary for the number of companies involved in nanotechnology and agrifood global markets. For example, Cientifica estimates that 400 companies are applying nanotechnology to food at present, but points to difficulties in measuring the full scale of development because many companies regard their nanotech R&D products as sensitive, and the Helmut Kaiser Consultancy estimates that the global nanofood market will be worth 20.4 billion USD in 2010.

This report divides nanotechnology in agrifood into three subsectors: agricultural production; food processing and functional food; and food packaging and distribution.

Agricultural production: this section describes the processes to produce materials from plant cultivation and raising domesticated animals, including foodstuffs, fuel, and raw materials for other industries such as the pharmaceutical, textile, and construction industries. It covers novel sensors and diagnostic devices, delivery systems for pesticides and nutrients, and describes how nanomaterials are now being manufactured from agricultural waste and through biological processes.

Food processing and functional food: this section describes the processes and equipment involved in turning agricultural produce into consumer products. It also includes the mechanisms in place to ensure quality control, one of the key areas in industrialised food production. It covers mechanisms for quality control including sensors such as electronic tongue and noses; equipment coatings and filtration systems based on nanotechnology that could bring efficiency gains for food processing; and the manipulation of the nanostructure of foodstuffs to engineer novel sensations and to improve the nutritional quality of processed food. It also describes functional foods, and the growing field of nutraceuticals.

Food packaging and distribution: this section describes materials used to preserve and protect fresh and processed foods, and the procedures and systems in place to monitor supply chains and authenticate items. It covers nanocomposite materials used to improve the barrier and mechanical properties of plastics; new bionanocomposites that can be compostable and promise solutions to waste management issues and sustainability; active and smart packaging that currently provides visual indicators to a foods' freshness, and promises advanced innovations through active interaction of packaging with the internal environment and the food itself, through encapsulation technologies.

2. General Considerations for the Environment, Health & Safety Impact of nanomaterials

The key benefit from nanotechnologies is the ability to exploit the specific, novel and sometimes unpredictable properties that arise from structuring matter at this scale. Over the last 10 years, nanotechnologies have received extensive investment, and have emerged as major drivers of science based innovation and industry. This has led to the development of new processes, products and materials for a wide range of applications.

In 2004 the UK's Royal Society and the Royal Academy of Engineering (RS/RAEng) published a seminal review of the "opportunities and uncertainties" presented by nanotechnologies (Royal Society & Royal Academy of Engineering, 2004). Whilst indicating that for many nanotechnologies, there were no foreseeable risks to health or to the environment, the report concluded that for "nanoparticles and nanotubes" there were potential risks, and that not enough was known about them. This conclusion was based on evidence gained from many years of research that exposure to particles can cause ill health within individuals or exposed populations. For example, within the occupational setting, exposure to coal dust is evidentially linked to the onset of lung diseases including pneumoconiosis and chronic obstructive pulmonary disease (COPD), and exposure to asbestos is causative of asbestosis, mesothelioma and lung cancer. In an environmental context, evidence suggests that exposure to the particulate component of atmospheric pollution may be associated with increased hospitalisation rates and cardio-vascular disease (Seaton *et al.*, 2009).

Publication of the RS/RAEng report led to a huge increase in research activity concerning both human health and environmental consequences (Aitken *et al.*, 2009a). For example, in Europe the Framework 7 NMP programme has funded more than 20 major projects, with a total budget of more that €50million. This research activity has addressed *inter alia* the toxicity and ecotoxicity of many types of nanoparticles, the kinetics of nanoparticles within biological and environmental systems, the extent to which individuals or the environment can become exposed and the level of risk which would result. These investigations have examined numerous mechanisms, end points and processes and materials, and have generated an extensive body of literature, particularly in relation to toxicology and ecotoxicology.

2.1. Establishing a knowledge on the potential hazard and exposure to nanomaterials

Scientific data compiled to date demonstrates that adverse health effects due to exposure to nanoparticles cannot be ruled out (Aitken *et al.*, 2009a, Aitken *et al.*, 2009b, Van Zijverden & Sips, 2009). However, although awareness for the importance of risk research has increased, critical information still is lacking to enable estimation of the risks posed by nanoparticles with equal certainty to those of other non-nano substances. Nevertheless, hundreds of products containing nanomaterials are currently available commercially, a situation which clearly necessitates investigation of the exposure and toxicity of these materials in the near future. Unfortunately, the research questions to be answered are so numerous that it will take years to compile the relevant data.

The potential for nanoparticles to cause damage has also been implicated within the environment, both directly via uptake into plants or organisms (including soil bacteria, eukaryotes, invertebrates and vertebrate species), and indirectly via changes in environmental variables such as pH of aquatic systems, ionic strength or dissolved organic carbon content (Aitken *et al.*, 2009a). Carbon nanotubes (CNT) and silver nanoparticles have been shown to cause detrimental effects in zebrafish development (Cheng *et al.*, 2007), and copper nanoparticles have been shown to be highly toxic to fish, daphids and algae (Griffitt *et al.*, 2008), and to induce stunting of exposed plant seedlings (Lee *et al.*, 2008).

Man and the environment can come into contact with the use of nanotechnology through a wide range of application areas. Some of these applications are produced only with the aid of nanotechnology, others contain nanomaterials. For the risk assessor, this second category is important, particularly when the applications contain non-degradable, insoluble, and freely available nanoparticles. For this category of products there are already a great many different areas of potential use, including medical applications, food, and consumer products as well as environmental and energy technology. These applications can improve the quality of life and the environment and can also lead to significantly more sustainable products, but for which it is of particular importance to understand and control potential risk.

There are already hundreds of nanotechnology applications on the market. For example, nanoparticles of titanium oxide and zinc oxide are regularly used as UV reflectors in sunscreen creams. Nanotechnology is also used to make clothing crease- and dirt-resistant, and to make electronics ever smaller, faster and more multifunctional. However, the majority of potential applications for nanotechnologies are currently still in the research and development phase and are expected to appear on the market over the coming years.

Understanding and effective management of potential risks posed by manufactured nanoparticles and nanomaterials is pivotal for responsible and sustainable development of nanotechnology. This in turn is mandatory for societal acceptance and exploiting the significant economic potential of this technology to the full.

2.2. Risk Assessment considerations for nanomaterials

In assessing the risks of non-nano chemical substances and nanomaterials alike, the following general approach is applied:

RISK = HAZARD (TOXICITY) x EXPOSURE

The intrinsic hazard (toxicity) of a nanomaterial is determined by a number of factors, such as the ability of a nanoparticle to pass through certain barriers in humans, plants or animals and cause damaging effects. The actual exposure is also determined by various factors such as the form in which the nanomaterial occurs (*e.g.*, either bonded or as ‘free’ particles) he specific setting in which the nanoparticle is being manufactured applied or used (and thus likelihood of contact). Thus, a specific nanomaterial may be hazardous, but if the level of exposure is very small, the ultimate risk will always be limited. For example, a specific nanoparticle bound within ultra-high performance concrete used to construct a bridge will pose less of a potential risk to consumers (*i.e.* those using the bridge), than the same NP used within antimicrobial food packaging, where the potential for consumer exposure may be increased due to their close contact with the product in which the NPs are bound.

Two areas can be distinguished within risk research for nanotechnology. One area aims at risks related to exposure to nanomaterials and the second area aims at risks related to the rest of nanotechnology and its products. There is consensus that the uncertainties about these risks need to be addressed most urgently.

In 2009, the Dutch Knowledge and Information Point “Risks of Nanotechnology” (RIVM/KIR nano) recommended to focus research primarily on those questions that provide information critical to the assessment of risks to man and the environment

(Van Zijverden & Sips, 2009). Depending on the perspective – worker, consumer, patient, or the environment – the starting points can then be defined for controlling or limiting the risks.

From this and other literature on the topic, there may be identified several key challenges for the EHS appraisal and risk management of nanomaterials:

1. *There is a high urgency for relevant risk information:* One of the pitfalls of emerging technologies is the imbalance between technological development and attention for human health and environmental safety issues as is the case for nanotechnology. Risk information needs to be generated and shared as quickly as possible for products on the market, underpinning the societal acceptance of further applications of this technology.
2. *Validity of known test systems is questionable, and detection of nanomaterials still problematic.* Nanomaterials create a challenge for risk research as they (might) behave differently in regular assessment and testing systems. Equipment and methods to detect nanomaterials allowing large-scale application are lacking.
3. *National, international and interdisciplinary integration is a prerequisite.* A large variety of research questions need to be addressed before uncertainties about risks for man and the environment are at the same level as for other chemical substances.

Whilst this brief introduction provides an outline of the key issues, it is impossible to outline the current knowledge on the hazard, exposure and risk assessment for nanoparticles in full. Instead the reader is directed towards the ObservatoryNANO Baseline Studies (Ross *et al.*, 2009) where many of the seminal studies from the last few years are identified and described.

2.3. The ObservatoryNANO Approach: Integrating EHS considerations with development of novel applications for nanotechnologies

ObservatoryNANO is concerned with mapping scientific and technological development across 10 core technology sectors, and a key task of WP5 is to undertake an appraisal of these reports and to identify potential emerging environment, health and safety issues therein, thus integrating the development of novel applications with risk research, an approach which is urgently required.

There is considerable overlap between those nanoparticles used across these 10 sectors – what differs is their use, which varies according to the application. Therefore the aspect which is specific to the technical sector in considering those novel risks which may arise from development of novel applications, is the potential for exposure. For this reason, the approach which we have adopted is to consider the potential exposure which may arise from the new applications identified.

As far as possible, we have considered the life cycle of the applications identified, whether there were possible exposures within the occupational setting, or to consumers or release to the environment. We also considered whether there was the potential for release from disposal.

Our review process involved extraction of information from each technology sector report & gathering of additional information from their lead authors. This data was then analysed, and our findings outlined within the subsequent sections of this report. In addition to a short summary of the key exposure issues identified from our analysis, our report includes three key tables as follows:

1. A table summarising all information gathered together with consideration of the potential for exposure arising throughout the lifecycle of each application
2. A table outlining those nanoparticles/nanomaterials in use within each technology sector, according to application
3. A table highlighting those applications where we consider there to be a high potential for release.

Detailed information of the type required to make strong evidence judgments about possible exposures was only very rarely available, and this is indicated in table. In none of the scenarios was actual exposure data available. However, for some applications additional information was available from the peer reviewed literature, and where this has been used this is again indicated within the table. In the majority on settings identified, due to the paucity of data assessment of whether or not exposure is plausible is based on expert judgement and information available from other similar scenarios. In this respect, these judgements should be considered provisional and where possible, effort should be placed on collecting relevant specific primary exposure data. As the ObservatoryNANO Project progresses, it is expected that these knowledge gaps will be addressed (at least in part) and thus that later EHS reports will be able to reach more resolute conclusions on the risks posed by those nanomaterials in consideration.

3. Summary of materials which have potential EHS impact

Table 1 below outlines the exposure potential for nanomaterials in the different subsectors of the Agrifood sector. The exposure potential is subdivided for the different users (manufacturer, professional user, consumer and environment) and the disposal phase. It is assumed that when nanomaterials enter the environment there is human exposure via the environment as well, including exposure via fish and drinking water. In the table only those environmental compartments are mentioned that are initially exposed to the nanomaterials (*i.e.* possible distribution of nanomaterials from one environmental compartment to another is not included).

In Table the nanoparticles carrying potential EHS impact are summarized according to application.

Table 1: Overview of the exposure potential for nanomaterials in the different subsectors of the Agrifood sector.

SECTOR Agrifood [1)]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2)])	
	Application	Types of NP [3)]	Incorporation in products [4)]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
Agricultural production									
Sensors and diagnostic devices (*future applications not mentioned*)	1. Uni-molecular sensors (biosensors) in pesticides	Liposomes, CNT, Ag nanoparticles, and mono-saccharide self-assembled monolayers	Bound	High	Dermal, inhalatory uptake during spreading in field[5)]	Oral via consuming crops, meat and milk	Soil, surface water, non-target biota (via direct unintentional application)	Low	Air (incineration), surface water (STP), soil (landfilling)
	2. Bioarrays in different stages of food chain	Silicon nanoscale cantilevers, and nanowires	Bound	High	Low	Oral via consuming crops, meat and milk	Soil, surface water, non-target biota (via direct unintentional application)	Low	Air (incineration), surface water (STP), soil (landfilling)

SECTOR Agrifood [1)]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2)])	
	Application	Types of NP [3)]	Incorporation in products [4)]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
	3. Solid-state sensors for detection of gases above crops	Oxides of tin, Indium, aluminium, zinc or composites of these	Bound in core of sensor	High	Low	Low	Soil, surface water (after wear and tear)	Low	Air (incineration), surface water (STP), soil (landfilling)
Disease and pest control in crop plants	1. Nano-emulsions in pesticides	Nanoemulsions of λ-cyhalo-thrin*, nano-emulsions of CNTs	Bound	High	Dermal, inhalatory uptake during spreading in field[5)]	Oral via consuming crops, meat and milk	Soil, surface water, non-target biota (via direct unintentional application)	Low	Air (incineration)
	2. Other formulations as vehicle in pesticides, fertilizers, plant growth promoters	Silica, nanoclays, layered double hydroxides	Unbound, thin film	High	Dermal, inhalatory uptake during spreading in field[5)]	Oral via consuming crops, meat and milk	Soil, surface water, non-target biota (via direct unintentional application)	Low	Air (incineration), surface water (STP), soil (landfilling)
Disease and pest control in domesticated animals		Liposomes, polymeric nanoparticles, nanoshells, conjugated nanoparticles, nanoclays	Unbound	High	Dermal during application of medicines via injections or water; inhalatory uptake during application via feed and aerosols	Oral via consuming meat and milk	Air, surface water (STP), soil (manure)	Low	Air (incineration)

SECTOR Agrifood [1]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2])	
	Application	Types of NP [3]	Incorporation in products [4]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
Water and nutrient control	1. Water use in agriculture, water purification filters	Nanoclays, immobilised TiO_2 films (used as photo-catalysts in tank type reactors to degrade unwanted elements such as atrazine)	Unbound, thin film	High	Low	Oral via con-sumption of drinking water (due to wear and tear of filters). Chemicals adsorbed to nanoclay par-ticles may pose a risk as well.	Surface water (due to wear and tear of filters). Chemicals adsorbed to nanoclay par-ticles may pose a risk as well.	Low	Soil (landfilling), air (incineration). Chemicals adsorbed to nanoclay particles may pose a risk as well.
	2. Enhanced nutrient uptake, fertilizers in soil and water	Nanoclays	Unbound	High	Dermal and inhalatory uptake during application	Oral via consuming crops	Soil, surface water	Low	Soil (landfilling), air (incineration)
Genetic engineering of plants and livestock to improve productivity		Mesoporous silica nanoparticles for genetic engineering of crop species	Unbound	High	Dermal during working with the particles	Low (Plants treated with the nano-particles as DNA-carrier are not considered to be used for consumption)	Surface water (STP), soil	Low	Air (incineration)

SECTOR Agrifood [1]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2])	
	Application	Types of NP [3]	Incorporation in products [4]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
Agriculture as a means to produce nanomaterials	1. Synthesis of nanomaterials from plant materials to improve packaging	Nanoclays, bionano-composites using natural biopolymers such as cellu-lose, zein, collagen, egg white, whey proteins	Bound	High	Low	Dermal during use of pack-aging and, if migration from packing into food occurs, oral via con-suming con-taminated food Consumer will be exposed as some of these bionano-composites are designed to be eaten	Surface water (STP)	Edible, composting, recycling	Air (incineration), soil (landfilling and via street litter), surface water (street litter)
	2. Biogenesis of nanomaterials	Metal nano-particles such as gold, silver, nickel, cobalt, nickel-cobalt alloy	Unbound	High	Dermal during working with nanoparticle suspensions	Low (Consumers may become exposed when the manu-factured nano-materials are used for spe-cific applica-tions)	Soil, surface water(STP), depending on growth medium	Low (unless the manu-factured nanoma-terials are used for specific appli-cations)	Air (incineration), soil (landfilling and via street litter), surface water (street litter)

SECTOR Agrifood [1)]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2)])	
	Application	Types of NP [3)]	Incorporation in products [4)]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
Food processing and functional food									
Quality control	1. Sensors for detection of chemical contaminants								
	1.a Uni-molecular sensors	Biomolecules conjugated to an electrode or encapsulated in a matrix or cap-sule, the nano-structured materials include lipo-somes, self-assembled monolayers, carbon nano-tubes, nano-particles	Bound	High	Dermal and inhalatory uptake of free particles which could be released due to wear and tear	Dermal and inhalatory uptake of free particles which could be released due to wear and tear	Possible abrasion by liquid analyte	Low	Air (incineration), surface water (STP), soil (landfilling)
	1.b Sensor arrays	Composite electrodes containing gold nanoparticles and the can-tilever arrays conjugated to antibodies	Bound	High	Dermal and inhalatory uptake of free particles which could be released due to wear and tear	Dermal and inhalatory uptake of free particles which could be released due to wear and tear	Possible abrasion by liquid analyte	Low	Air (incineration), surface water (STP), soil (landfilling)

SECTOR Agrifood [1)]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2)])	
	Application	Types of NP [3)]	Incorporation in products [4)]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
	1.c Solid-state sensors	Tin, indium, aluminium, zinc oxides	Bound	High	Inhalatory uptake (unlikely)	Inhalatory uptake (unlikely)	Mostly applied to gas so less likely to have abrasion	Low	Air (incineration), surface water (STP), soil (landfilling)
	2. Sensors for detection of biological contaminants								
	2.a Electronic biosensors	Conjugated nanowires, carbon nano-tubes, CNT in combination with gold or platinum nano-particles or quantum dots	Bound	High	Low	Low	Surface water (STP) (after wear and tear)	Low	Air (incineration), surface water (STP), soil (landfilling)
	2.b Optical biosensors	Conjugated CNT's, silica, gold and latex nanoparticles	Bound	High	Low	Low	Surface water (STP) (after wear and tear)	Low	Air (incineration), surface water (STP), soil (landfilling)
	2.c Mass-change biosensors	Au nanoparticles	Bound	High	Low	Low	Soil, surface water (STP) (after wear and tear)	Low	Air (incineration), surface water (STP), soil (landfilling)
	3. Electronic noses and tongues	Tin oxide, zinc oxide	Bound, thin film	High	Low	Low	Soil, surface water (STP) (after wear and tear)	Low	Air (incineration), surface water (STP), soil (landfilling)

SECTOR Agrifood [1]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2])	
	Application	Types of NP [3]	Incorporation in products [4]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
Processing technology	1. Equipment coatings for disinfection	Nickel, PFTE*, Ag DLC (diamond like carbon)*	Bound in surface coating of equipment	High	Inhalation and dermal during coating of the equipment	Oral via contaminated food after migration of coating particles	Soil, surface water (also after wear and tear of coating), Also diamond like carbon has been demonstrated to be removed over time through cleaning cycles	Low	Air (incineration)
	2. Filtration	Nanoclays, TiO2	Bound	High	Low	Oral via consumption of drinking water	Surface water (after wear and tear of filters, possibly via bio-fouling?)	Low	Surface water (STP)
Functional foods	1. Delivery systems for nutrients	Natural food ingredients in nanoform: lipids*, lyco-pene*, whey proteins*	Unbound	High	Low	Oral exposure (longer than normal) to nutrient and carrier, higher bioavailability (overdosing)	Surface water, soil after excretion out of the human body	Low	Surface water (STP), soil (landfilling)
	2. Food structure - 'mouth feel'	Natural food ingredients in nanoform: Whey proteins	Unbound	High	Dermal during addition of nanocompo-nents in food	Oral exposure to nanostructured components in food	Surface water, soil after excretion out of the human body	Low	Surface water (STP), soil (landfilling)

SECTOR Agrifood [1)]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2)])	
	Application	Types of NP [3)]	Incorporation in products [4)]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
	3. Edible coatings	Natural food ingredients in the form of nanowhiskers, nanofibres or nanofilms: chi-tosan, starch, cellulose, casein, whey, collagen, egg white, tri-glycerides and fatty acids	Unbound	High	Dermal/inhalation during formulation of the coating, dermal during dipping application, inhalation during spray application	Oral exposure to nano-structured components in food migrated from coating	Surface water, soil after excretion out of the human body	Low	Surface water (STP), soil (landfilling)
Food packaging and distribution									
Barrier packaging		Nanoclays, TiO2, acrylic nanoparticles in packaging	Bound	High	Dermal during packaging of food	Dermal during handling of packaging, oral exposure to migrated nano-particles in food	Surface water, soil	Recycling	Air (incineration), surface water (street litter), soil (landfilling and street litter)
Antimicrobial packaging		Ag, Zn incorporated in polymers (polypropylene)	Bound	High	Dermal during packaging of food	Dermal during handling of packaging, oral exposure to migrated nanoparticles in food	Surface water, soil	Recycling	Air (incineration), surface water (street litter), soil (landfilling and street litter)

SECTOR Agrifood [1]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2])	
	Application	Types of NP [3]	Incorporation in products [4]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
Biodegradable packaging		Nanoclays, metal oxides in natural polymers, CNT	Bound	High	Dermal during packaging of food	Dermal during handling of packaging, oral exposure to migrated nanoparticles in food	Surface water, soil	Low	Air (incineration), surface water (street litter), soil (landfilling and street litter)
Active and smart packaging	1. Regulating the internal packaging environment	Nanoporous calcium silicate, nanocrystalline titania particles in an ethyl cellulose polymer film	Bound	High	Dermal during packaging of food	Dermal during handling of packaging, oral exposure to migrated nanoparticles in food	Surface water, soil	Low	Air (incineration), surface water (street litter), soil (landfilling and street litter)
	2. Self-healing composites	50-nm-thick silicon oxide (SiO_2) layer deposited on top of a 300-nm-thick PMMA film embedded with 3.8nm CdSe/ZnS nanoparticles	Bound	High	Dermal during packaging of food	Dermal during handling of packaging, oral exposure to migrated nanoparticles in food	Surface water, soil	Low	Air (incineration), surface water (street litter), soil (landfilling and street litter)

SECTOR Agrifood [1]									
				Exposure potential Use (*e.g.* activity, exposure route, what)				Exposure potential Disposal (*e.g.* incinerated, landfilling, recycled, STP [2])	
	Application	Types of NP [3]	Incorporation in products [4]	Manu-facturer	Professional user	Consumer	Environment	Human	Environment
	3. Sensor technologies in packaging	Fullerenes, TiO_2, nano-porous silica, nanocrystals of urethane-substituted polydi-acetylenes	Bound	High	Dermal during packaging of food	Dermal during handling of packaging, oral exposure to migrated nano-particles in food	Surface water, soil	Low	Air (incineration), surface water (street litter), soil (landfilling and street litter)
	4. RFID tags and tracking	Ag, Au, Cu	Bound	High	Dermal during packaging of food	Dermal during handling of packaging, oral exposure to migrated nano-particles in food	Surface water, soil	Low	Air (incineration), surface water (street litter), soil (landfilling and street litter)

[1] References: (Basavaraja *et al.*, 2008, Bouwmeester *et al.*, 2009, Chen *et al.*, 2008a, Chen *et al.*, 2008b, Eranna *et al.*, 2004, Geertsma, 2007, Johnston *et al.*, 2008, Joshi *et al.*, 2005, Lee *et al.*, 2005, McMurray *et al.*, 2006, Mills *et al.*, 2006, Mukherjee *et al.*, 2008, Poland *et al.*, 2008, Saikhwan *et al.*, 2006, Subramanian *et al.*, 2005, Sygenta, 2010, Van Zijverden & Sips, 2009, Viswanathan *et al.*, 2006, VWA, 2010, Yonzon *et al.*, 2004)
[2] STP: sewage treatment plant
[3] * application already on the market
[4] *e.g.* bound, unbound, enclosed
[5] apart from the professional user, also bystanders are at risk for this type of exposure

Table 2 **Nanoparticles carrying potential EHS impact, according to application.**

Agricultural production						
	Carbon Nano-tubes	**Lipo-somes**	**Nano-clays**	**Metal oxides**	**Metals**	**Various**
Uni-molecular sensors (biosensors) in pesticides	•	•			Ag	monosaccharide self-assembled monolayers
Bioarrays in different stages of food chain						Silicon nanoscale cantilevers, and nanowires
Solid-state sensors for detection of gases above crops				Oxides of Sn, In, Al, Zn or composites of these		
Nano-emulsions in disease and pest control in crop plants	•					λ-cyhalothrin
Other formulations as vehicle in disease and pest control in crop plants, fertilizers, plant growth promoters			•	SiO_2		layered double hydroxides
Disease and pest control in domesticated animals		•	•			polymeric nanoparticles, nanoshells, conjugated nanoparticles
Water use in agriculture, water purification filters			•	Immobilized TiO_2 films		
Enhanced nutrient uptake, fertilizers in soil and water			•			
Genetic engineering of plants and livestock to improve productivity				SiO_2		
Synthesis of nanomaterials from plant materials to improve packaging			•			bionano-composites using natural biopolymers such as cellulose, zein, collagen, egg white, whey proteins
Biogenesis of nanomaterials					Ag,Au, Ni, Co, Ni-Co alloys	
Food processing and functional food						
	Carbon Nano-tubes	**Lipo-somes**	**Nano-clays**	**Metal oxides**	**Metals**	**Various**
Uni-molecular sensors for detection of chemical contaminants	•	•			Ag	Biomolecules conjugated to an electrode or encapsulated in a matrix or capsule, the nano-structured materials include liposomes, self-assembled monolayers, carbon nanotubes, nanoparticles
Sensor arrays for detection of chemical contaminants						Composite electrodes containing gold nanoparticles and the cantilever arrays conjugated to antibodies

Food processing and functional food *(continued)*						
	Carbon Nano-tubes	**Lipo-somes**	**Nano-clays**	**Metal oxides**	**Metals**	**Various**
Solid-state sensors for detection of chemical contaminants				Oxides of Sn, In, Al, Zn		
Electronic biosensors for detection of biological contaminants	•				Au, Pt	Conjugated nanowires, carbon nanotubes, CNT in combination with gold or platinum nanoparticles or quantum dots
Optical biosensors for detection of biological contaminants	•			SiO_2	Au	Conjugated CNT's, silica, gold and latex nanoparticles
Mass-change biosensors for detection of biological contaminants					Au	
Electronic noses and tongues for quality control				SnO_2, ZnO		
Equipment coatings for disinfection					Ni, Ag	PFTE, DLC (diamond like carbon)
Filtration			•	TiO_2		
Delivery systems for nutrients						Natural food ingredients in nanoform: lipids, lycopene, whey proteins
Food structure – 'mouth feel'						Natural food ingredients in nanoform: Whey proteins
Edible coatings						Natural food ingredients in the form of nanowhiskers, nanofibres or nanofilms: chitosan, starch, cellulose, casein, whey, collagen, egg white, triglycerides and fatty acids
Food packaging and distribution						
	Carbon Nano-tubes	**Lipo-somes**	**Nano-clays**	**Metal oxides**	**Metals**	**Various**
Barrier packaging			•	TiO_2		acrylic nanoparticles
Antimicrobial packaging					Ag, Zn	Ag, Zn incorporated in polymers (polypropylene)
Biodegradable packaging	•		•	•		metal oxides in natural polymers
Regulating the internal packaging environment	•			Ca_2SiO_4	Ti	Nanoporous calcium silicate, nanocrystalline titania particles in an ethyl cellulose polymer film
Self-healing composites	•			SiO_2		50-nm-thick silicon oxide (SiO2) layer deposited on top of a 300-nm-thick PMMA film embedded with 3.8nm CdSe/ZnS nanoparticles
Sensor technologies in packaging				TiO_2, nanoporous SiO_2		Fullerenes, nanocrystals of urethane-substituted polydiacetylenes
RFID tags and tracking				SnO_2, ZnO	Ag, Au, Cu	

4. Summary and Conclusions

The key nanoparticles identified as carrying exposure potential across the agrifood technology sector are outlined in the table 1 within section 3.

Nanoclays are the most commonly utilised type of nanomaterials in agricultural production, with gold nanoparticles and carbon nanotubes being used predominantly in food processing, and titanium and silver used in particular in food packaging. The nanoparticles with the broadest use within the total sector were nanoclays, followed, by silver, gold, carbon nanotubes and titanium dioxide (see Table).

The use of nanostructured materials may result in higher stability of the formulation, increased solubility, decreased degradation, and therefore greater bioavailability. The higher efficacy of this type of formulations shows that toxicity testing should be performed with the nanoformulation, because use of the data for the conventional formulation is not sufficient.

In agricultural production exposure to nanomaterials in humans is mainly via the oral route, as (residues of) these nanomaterials will be present in crops, meat and milk for consumption. In food processing procedures related to quality control, exposure is predicted to be via skin and inhalation, but for processing technology and functional foods oral exposure is most significant. Exposure to nanomaterials from food packaging will mainly be dermal (via handling).

The environment is mainly exposed via surface water (effluent of sewage treatment plants) and soil, although in the disposal phase air also becomes an important route if waste is incinerated. Human exposure in the disposal phase will be limited.

Currently, only a limited number of nanotechnology applications within the Agrifood sector are on the market (nano-emulsions in pesticides, equipment coatings for disinfection, and delivery systems for nutrients), and it can be expected that at present these are the applications where exposure potential is highest. In addition, the applications in food additives (in edible coatings, or to enhance ‘mouth feel’) have by nature high exposure potential, especially for consumers.

5. References

Aitken R, Aschberger K, Baun A, Christensen F, Fernandes T, Foss Hansen S, Hankin S, Hartmann NB, Hutchinson G, Johnston H, Micheletti C, Peters S, Ross B, Sokull-Kluettgen B, Stark D, Stone V, and Tran L (2009a), Engineered Nanoparticles: Review of Health and Environmental Safety (ENRHES). Report on EC FP7 CSA #218433, Edinburgh Napier University, Edinburgh, UK.

Aitken RJ, Hankin SM, Ross B, Tran CL, Stone V, Fernandes TF, Donaldson K, Duffin R, Chaudhry Q, Wilkins TA, Wilkins SA, Levy LS, Rocks SA, and Maynard A (2009b), EMERGNANO: A review of completed and near completed environment, health and safety research on nanomaterials and nanotechnology. Report TM/09/01, Institute of Occupational Medicine (IOM), Edinburgh, UK.

Basavaraja S, Balaji SD, Lagashetty A, Rajasab AH, and Venkataraman A (2008), Extracellular biosynthesis of silver nanoparticles using the fungus Fusarium semitectum. Mater. Res. Bull. 43: 1164-1170.

Bouwmeester H, Dekkers S, Noordam MY, Hagens WI, Bulder AS, de Heer C, ten Voorde SECG, Wijnhoven SWP, Marvin HJP, and Sips AJAM (2009), Review of health safety aspects of nanotechnologies in food production. Regul. Toxicol. Pharmacol. 53: 52-62.

Chen H, Zuo X, Su S, Tang Z, Wu A, Song S, Zhang D, and Fan C (2008a), An electrochemical sensor for pesticide assays based on carbon nanotube-enhanced acetycholinesterase activity. Analyst 133: 1182-1186.

Chen SH, Wu VCH, Chuang YC, and Lin CS (2008b), Using oligonucleotide-functionalized Au nanoparticles to rapidly detect foodborne pathogens on a piezoelectric biosensor. J. Microbiol. Meth. 73: 7-17.

Cheng J, Flahaut E, and Shuk HC (2007), Effect of carbon nanotubes on developing zebrafish (Danio rerio) embryos. Environ. Toxicol. Chem. 26: 708-716.

Eranna G, Joshi BC, Runthala DP, and Gupta RP (2004), Oxide materials for development of integrated gas sensors - A comprehensive review. Crit. Rev. Sol. State 29: 111-188.

ETP (2008), European Technology Platform "Food for Life". Available at: http://etp.ciaa.be/.

Geertsma RE (2007), Nanotechnology and medical technology: risk management and regulatory consequences. Oral presentation at Investing in Medical Nanotechnologies II, London, United Kingdom.

Griffitt RJ, Luo J, Gao J, Bonzongo JC, and Barber DS (2008), Effects of particle composition and species on toxicity of metallic nanomaterials in aquatic organisms. Environ. Toxicol. Chem. 27: 1972-1978.

GRUB S UP (2009), Recycling and upgrading wastes from food production for use within the food chain. EU FP6 Project Reference: 514049. Available at: http://cordis.europa.eu/fetch?CALLER=FP6_PROJ&ACTION=D&DOC=2&CAT=PROJ&QUERY=0128b58a5c5b:36d9:5f49d307&RCN=75729.

Ivanov D, Sokolov B, and Kaeschel J (2010), A multi-structural framework for adaptive supply chain planning and operations control with structure dynamics considerations. Eur. J. Oper. Res. 200: 409-420.

Johnston JH, Grindrod JE, Dodds M, and Schimitschek K (2008), Composite nano-structured calcium silicate phase change materials for thermal buffering in food packaging. Curr. Appl. Phys. 8: 508-511.

Joshi KA, Tang J, Haddon R, Wang J, Chen W, and Mulchandani A (2005), A disposable biosensor for organophosphorus nerve agents based on carbon nanotubes modified thick film strip electrode. Electroanalysis 17: 54-58.

Lee SK, Sheridan M, and Mills A (2005), Novel UV-activated colorimetric oxygen indicator. Chem. Mater. 17: 2744-2751.

Lee WM, An YJ, Yoon H, and Kweon HS (2008), Toxicity and bioavailability of copper nanoparticles to the terrestrial plants mung bean (Phaseolus radiatus) and wheat (Triticum aestivum): Plant agar test for water-insoluble nanoparticles. Environ. Toxicol. Chem. 27: 1915-1921.

McMurray TA, Dunlop PSM, and Byrne JA (2006), The photocatalytic degradation of atrazine on nanoparticulate TiO_2 films. J. Photochem. Photobiol. A 182: 43-51.

Mills A, Doyle G, Peiro AM, and Durrant J (2006), Demonstration of a novel, flexible, photocatalytic oxygen-scavenging polymer film. J. Photochem. Photobiol. A 177: 328-331.

Mukherjee P, Roy M, Mandal BP, Dey GK, Mukherjee PK, Ghatak J, Tyagi AK, and Kale SP (2008), Green synthesis of highly stabilized nanocrystalline silver particles by a non-pathogenic and agriculturally important fungus T. asperellum. Nanotechnology 19.

Poland CA, Duffin R, Kinloch I, Maynard A, Wallace WAH, Seaton A, Stone V, Brown S, MacNee W, and Donaldson K (2008), Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. Nat. Nanotechnol. 3: 423-428.

Ross BL, Aitken RJ, Heugens EHW, Wijnhoven SWP, Fontanelle S, and Nowak B (2009), Baseline Studies v1.1. Observatory NANO, EC.

Royal Society & Royal Academy of Engineering (2004), Nanoscience and nanotechnologies: opportunities and uncertainties. Latimer Trend Ltd, Plymouth, UK.

Saikhwan P, Geddert T, Augustin W, Scholl S, Paterson WR, and Wilson DI (2006), Effect of surface treatment on cleaning of a model food soil. Surf. Coat. Tech. 201: 943-951.

Seaton A, Tran L, Aitken R, and Donaldson K (2009), Nanoparticles, human health hazard and regulation. J. R. Soc. Interface 7: S119-S129.

Subramanian V, Fréchet JMJ, Chang PC, Huang DC, Lee JB, Molesa SE, Murphy AR, Redinger DR, and Volkman SK (2005), Progress toward development of all-printed RFID tags: Materials, processes, and devices. Proc. IEEE 93: 1330-1338.

Sygenta (2010), Karate® Insecticide. Available at: www.syngenta.com/en/products_brands/karate_page.html.

Van Zijverden MSips AJAM (2009), Nanotechnology in perspective. Risks to man and the environment. RIVM Report 601785003/2009, National Institute of Public Health and Environmental Protection (RIVM), Bilthoven, The Netherlands.

Viswanathan S, Wu LC, Huang MR, and Ho JAA (2006), Electrochemical immunosensor for cholera toxin using liposomes and poly(3,4-ethylenedioxythiophene)-coated carbon nanotubes. Anal. Chem. 78: 1115-1121.

VWA (2010), Nanodeeltjes in consumentenproducten. Factsheet ND09231G, Voedsel en Waren Autoriteit (VWA), Regionale dienst Noord, Groningen, The Netherlands.

Yonzon CR, Jeoung E, Zou S, Schatz GC, Mrksich M, and Van Duyne RP (2004), A comparative analysis of localized and propagating surface plasmon resonance sensors: The binding of Concanavalin A to a monosaccharide functionalized self-assembled monolayer. J. Am. Chem. Soc. 126: 12669-12676.