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Review

Nanomaterials for products and application in agriculture, feed and food

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ABSTRACT

Background: Nanotechnology applications can be found in agricultural production, animal feed, food processing, food additives and food contact materials (hereinafter referred to as agri/feed/food). A great diversity of nanomaterials is reported to be currently used in various applications, while new nanomaterials and applications are reported to be in development.
Scope and approach: It is expected that applications of nanomaterials in agri/feed/food will increase in the future and thereby increase the human and environmental exposure to such materials. To gain up-to-date knowledge we explored and reviewed the already marketed and in-development applications of nanomaterials in the agri/feed/food sectors upon the request of the European Food Safety Authority (EFSA). In this paper the results of the project are highlighted and discussed in more detail.
Key findings and conclusions: The majority of the applications of nanomaterials that we identified concerned application in food as food additives and food contact materials, while much fewer applications seem to be developed for agriculture and feed. Nano-encapsulates, silver, titanium dioxide and silica are the most often mentioned nanomaterials in the literature. About half of the identified applications are claimed to be already in use. In-development applications are found for nano-encapsulates and nanocomposites in novel foods, food and feed additives, biocides, pesticides and food contact materials.

1. Introduction

Nanotechnology is one of the six key enabling technologies (KETs) for Europe (European Commission, 2016) as it offers substantial prospects for the development of innovative products and applications in several industrial sectors including the primary agricultural production, animal feed, food processing, novel foods, food additives and food contact materials (hereinafter referred to as agri/feed/food) (Chaudhry et al., 2008; Joseph & Morrison, 2006; Kah, Beulke, Tiede, & Hofmann, 2013; Kah & Hofmann, 2014; Sekhon, 2010; Singh Sekhon, 2014). Countries and regions that fully exploit KETs will be at the forefront of creating advanced and sustainable economies. Nanotechnology involves working with manufacturing, characterisation and manipulation of materials which have a size range at the nanometer scale. Reduction of the size of the material to the nano scale may change the physico-chemical properties compared to the same material at larger-size scales, e.g. much larger surface to mass ratio, enhanced surface reactivity or increased ion release.

Nanomaterials (NM) used in agri/feed/food may be of natural origin (i.e. naturally occurring/formed in the final product) or intentionally added. Intentionally added NM may be developed

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using natural components or engineered components. Several formal definitions of the term "nanomaterial" have been proposed by different international and national bodies (European Commission, 2011a; ISO, 2010) and most of them aim to identify substances within a specific size range (reviewed by Amenta et al., 2015; Lövestam et al., 2010; Rauscher et al., 2014). Notably, the only common feature between all NM is that they have at least one dimension in the nanoscale (Lövestam et al., 2010). In the EU, engineered NM in food products have been defined as *"any intentionally produced material that has one or more dimensions of the order of 100 nm or less or that is composed of discrete functional parts, either internally or at the surface, many of which have one or more dimensions of the order of 100 nm or less, including structures, agglomerates or aggregates, which may have a size above the order of 100 nm but retain properties that are characteristic of the nanoscale"* (European Parliament and Council, 2015). In contrast, the European Commission's Recommendation on a definition of NM, which was drafted independently from any specific legislation and thus is broadly applicable across regulatory sectors, defines NM regardless of their origin and thereby includes also natural and incidental NM (European Commission, 2011a,b). The upper size limit of 100 nm used in most definitions is fairly arbitrary and does not directly correspond to any particular change in physico-chemical properties. Neither is there a direct link between this threshold and any potential increase in risk for human health or for the environment. Some countries (e.g. USA) therefore consider a definition based solely on size as inappropriate and have not introduced any legal definitions. Instead they have drafted flexible guidance to identify when potential implications should be considered for regulatory status, safety, effectiveness, or public health impact that may arise with the application of nanotechnology (FDA, 2011). This guidance also provides rules for certain chemical substances when they are manufactured or processed at the nanoscale (US-EPA, 2015).

Engineered NM used in agri/feed/food can roughly be divided into inorganic, organic and combined materials such as surface modified clays. Inorganic NM include metals, metal oxides, salts, full carbon-based materials such as carbon nanotubes, fullerenes, carbon black and clay (see Fig. 1). Some of these materials have been used in food-related applications for several decades, and consist of primary particles or contain fractions of particles in the nanosize range. Silicon dioxide, for example, has been used in food processing as anti-caking agent for years in a form called synthetic amorphous silica (SAS) and it is registered in the EU as food additive E551 (Peters et al., 2012). Some metals are available as nano-sized particles in food or health supplements. These include nano-selenium (Xu et al. 2007) and colloidal suspensions of e.g. gold, platinum and silver (Park, Li, & Kricka, 2006).

Food naturally contains nanostructured organic ingredients such as proteins, carbohydrates and fats, which usually self-assemble into higher-order structures. The same materials can also serve to build food-grade polymers or nano-encapsulates and nano-emulsions (Graveland-Bikker & de Kruif, 2006; Luykx, Peters, Van Ruth, & Bouwmeester, 2008; Mozafari et al., 2006). Nano-encapsulates consist of an organic shell and a core containing the (bio)active ingredient. (Phospho-)Lipid-based NM, including micelles and liposomes, are among the most applied organic NM due to their wide solubility range (hydrophilic or lipophilic surface), i.e. they can be "tuned" to an application. Protein-based NM are often built from molecules capable of self-assembly, e.g. micelle-like structures. Polysaccharides are naturally occurring compounds in plants (e.g. pectin, guar gum), animals (e.g. chitosan, chondroitin sulphate), algae (e.g. alginates) and micro-organisms (e.g. dextran). Nano-encapsulation serves to increase the stability, delivery and bioavailability of nutrients (vitamins, minerals), agrochemicals or pharmaceuticals (Anu Puri et al., 2009). The modified optical characteristics of nano-encapsulated materials are important for their application in clear beverages. Inorganic NM such as clays are often surface modified (functionalised) with an organic coating to improve their dispersion in polymer matrices thus forming a nanocomposite (de Paiva, Morales, & Diaz, 2008). Modified nanoclays (e.g. montmorillonite) incorporated in food packaging enhance mechanical strength and/or form a barrier against gases (e.g. oxygen), volatile components (such as flavours) or moisture (Jorda-Beneyto et al., 2014). According to the revised European Novel Food Regulation (European Parliament and Council, 2015), these NM can be regarded as engineered NM and this should be taken into consideration when evaluating their prospective applications in agri/feed/food.

The potential risk that these newly applied NM in agri/food/feed products might pose to human health (and the environment) needs to be taken into account during the safety evaluation of such products. The work herein presented focussed on gaining more up-to date information on the exposure potential to NM due to its application in agri/feed/food products. In particular, we explored, upon a request by the European Food Safety Authority, the currently used (i.e. already on the market) and in-development applications of NM in the agricultural, feed and food sectors. This included systematic bibliographic database searches and ad-hoc searches in the Internet and at company websites (initial and refined searches were performed between April and August 2013 and updated through a recent literature search in 2016 using the same search strategy) (the search strategy is provided as supplementary file 1). In addition, a questionnaire was sent to research institutes, government agencies and companies active in agri/feed/food (Peters et al., 2014).

This paper presents the overall trends, application domains, and diversity of NM applied in the agri/feed/food sector. This is followed by a more detailed description per application domain, complemented with examples. Finally the current claims for marketed nanoproducts and potential future developments are critically

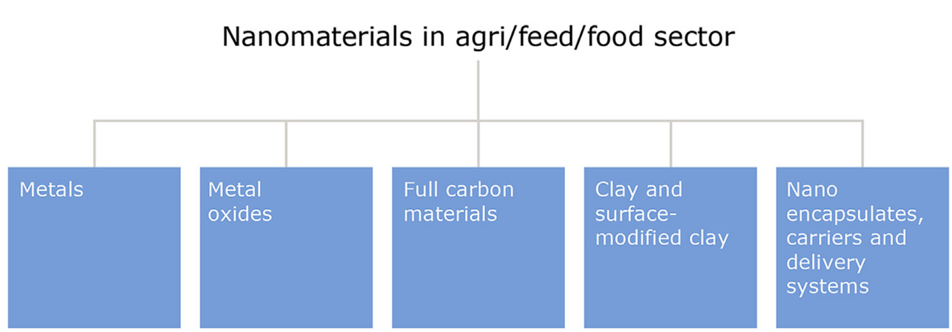

Fig. 1. Overview of engineered nanomaterial types applied in agriculture, feed and food sectors.