

Emerging Organic Contaminants and Nanomaterials in Food

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Abstract Governments all over the world are intensifying their efforts to improve food safety. These efforts come as a response to an increasing number of food safety problems and rising consumer concerns. In addition, the variety of toxicant residues in food is continuously increasing as a consequence of industry development, new agricultural practices, environmental pollution, and climate change. This paper reviews the major groups of emerging contaminants in food, as well as, the levels of concentrations reported and the analytical approaches presented for their detection with special emphasis on more fast and cost-efficient methods of detection.

The four main groups of emerging food contaminants that are discussed here are:

1. Industrial organic pollutants: Perfluorinated compounds (PFCs), polybrominated diphenylethers (PBDEs), new pesticides, and nanomaterials.
2. Pharmaceutical residues: Antibiotics and coccidiostats
3. Biotoxins: Emerging groups of marine biotoxins

Keywords Biotoxins, Coccidiostats, Food contaminants, LC-MS/MS, Nanomaterials antibiotics, Perfluorinated compounds, Pesticides, Polybrominated diphenylethers

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1 Introduction

Contaminants are substances that have not been intentionally added to food. These substances may be present in food as a result of the various stages of its production, packaging, transport, or holding. They also might result from environmental contamination. Since contamination generally has a negative impact on the quality of food and may imply a risk to human health, the EU has taken measures to minimize contaminants in foodstuffs.

There are many thousands of chemical substances in food; most of them being of natural origin. A number, however, are man-made and arise from the use of agrochemicals, or due to pollution of water, soil and air, or occur during food preparation/processing. In addition, food may contain biological contaminants. A range of additives may also be added for a variety of purposes (e.g., to enhance the flavor, color, improve stability).

Therefore, while consumers expect the food that they eat to be safe, as a consequence of industrial development, pollution, and climate change, the variety of food contaminants are increased. Currently, one of the great challenges in food safety is controlling the risks associated with mixtures of contaminants, which continuously are changing.

Among the most prominent groups of emerging food contaminants can be considered industrial origin contaminants as perfluorinated compounds (PFCs), polybrominated biphenyls (PBBs), the new generation of pesticides, nanomaterials, and emerging groups of marine biotoxins (such as palytoxins and spirolides). Many of them are of particular concern because they can cause severe damages in human health; for example, some of them are suspected to be cancer promoters. Other selected compounds have been related to endocrine disruptor effects or can be accumulated and biomagnified through the food chain.

In this review, we have been selected the most relevant groups of emerging food contaminants. We also included some groups of pharmaceuticals of special concern such as antibiotics which can create bacterial resistances and which are illegally used as growth promoters. The main sources of the selected groups of contaminants will be discussed together with their toxicological data and concentrations reported during the last few years. The strategies for their analysis including sample preparation, separation, and detection will be presented.

2 Sources of Food Contamination, Properties and Toxicological Properties

2.1 Industrial Origin Compounds

Since the industrial revolution in the nineteenth century, the knowledge on chemistry was developed rapidly, together with several industries. Currently, under the REACH legislation more than 100,000 compounds have been pre-registered for use within the European Union. Chemicals are present in all kinds of industrial applications and consumer products. However, some of these compounds or their degradation products can cause damage to the environment and human health.

Food safety, have to face the possible contamination produced during the whole process, including those from environmental contamination or used directly related to the food production (pesticides, veterinary drugs, contamination associated with cooking, processing, packaging, and conservation, among others).

In addition, some compounds are classified as persistent organic pollutants (POPs), because of their resistance to degradation and can be bioaccumulated, show long-range transportation, and are toxic. Most POPs are lipophilic and their uptake rates in organisms are higher than the rate of depuration. This results in an accumulation in aquatic, terrestrial organisms and in humans. Further transfer-up in the food chain can lead to elevated levels in top predators (biomagnification). Their toxic properties can cause serious health damages such as the development of certain types of cancer, metabolic dysfunctions, and endocrine disruption. Initially, 12 chlorinated compounds were classified as POPs and following the ratification of the Stockholm Convention, parties took action in order to reduce the emissions of the 12 POPs. The production and use of POPs was substantially decreased (such as p,p'-DDT), and almost completely stopped for some compounds in most countries. However, some groups of compounds largely used and produced during the last decades meet the definition of POP. Examples of these new POPs are perfluorinated compounds (PFCs), brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecane (HBCD). The restriction and replacement of some of these compounds should be carefully evaluated. Also, the possible alternative compounds that have to be taken into account include

effectiveness, persistence, bioaccumulative effects, toxicological properties, economic feasibility of their production, and human and environmental risk assessment.

On the other hand, during recent years, nanotechnology has emerged, presenting a great variety of new materials, allowing new applications for all industrial sectors including food industry. Nevertheless, while nanotechnology is successfully introduced in the industry, their possible risk to the environment and human health is not well understood and assessed. In addition, food industry has developed a variety of applications based on engineered NPs and nanomaterials, such as high loadings of vitamins and health benefits active in food, new methods for flavor stabilization, as well as, natural food-coloring dispersions can be developed. But NPs and NMs also appear as a new group of possible food contaminants, whereas their detection and characterization in food is poorly developed, and the potential risks of the application or associated contamination in food need to be understood.

In this section, emerging food contaminants with industrial origin, including perfluorinated compounds, polybrominated compounds, new pesticides, and nanomaterials will be discussed.

2.1.1 Perfluorinated Compounds

PFCs comprise a large group of compounds characterized by a fully fluorinated hydrophobic linear carbon chain attached to one or more hydrophilic head. PFCs repel both water and oil, and are therefore ideal chemicals for surface treatments. These compounds have been used for many industrial applications including stain repellents (such as Teflon), textile, paints, waxes, polishes, electronics, adhesives, and food packaging [1].

Usage and disposal of PFCs has led to the widespread distribution of these chemicals in the environment. Furthermore, PFOS and PFOA, as well as other perfluorocarboxylic acids (PFCAs) are stable degradation products and/or metabolites of neutral PFCs like fluorotelomers alcohols (PFTOHs), perfluorinated sulfonamides (PFASAs), and perfluorinated sulfonamide ethanols (PFASEs) [2]. PFCs are bioaccumulative attached to proteins and, these compounds have been detected in different water matrices [3, 4], wildlife [5, 6], fish [6], and humans [7]. In addition, PFCs are biomagnified in the food chains [5, 8], leading to increased levels in animal-derived foods. Main sources of human exposure to PFCs have been identified through: drinking water, food, and dust inhalation. Bioaccumulation in fish has been shown to be one of the main influences of PFCs in dietary exposure. Food preparation is another relevant source of food contamination [9], but preliminary data on the influence of domestic cookware on levels of PFCs in the preparation of food indicated no elevated levels for a limited number of experiments [10]. Packaging may also introduce PFCs used in greaseproof packaging for fast foods and special packaging. In these situations, PFCs enter into food via migration from the food package [9].

2.1.2 Polybrominated Flame Retardants

Polybrominated biphenyl (PBBs) and polybrominated diphenyl ethers (PBDEs) are classes of additive congeners that were used in a wide range of products, including paints, plastics, textiles, and electronics to reduce their flammability. Electrical and electronic equipment waste (WEEE) is generated on the order of millions of tons annually, bringing significant risk to human health and the environment [11]. The problem connected with the use of brominated flame retardants PBB and PBDE in polymers is the recycling of wastes containing these chemicals, resistance to biodegradation, and the potential for long-range transport and bioaccumulation in the lipid compartments of biota. During the last decade the production and usage of PBBs were discontinued because of their harmful effects, mainly in disturbing steroid hormone secretion. Due to their persistence and long-range transport, both PBBs and PBDES have been detected in many places and populations on Earth [12]. Photochemical transformation studies conducted by the same authors proved that PBBs have a great ability to debrominate higher brominated isomers, leading to identified and unidentified structures of lower brominated PBBs which are believed to be environmentally relevant since they can be formed by natural sunlight and reach the marine food chain [13]. The most probable route for exposure of the general human population to PBBs and PBDEs is through diet, but very little is known about PBB and PBDEs concentrations in fish, which are at the basic level of the food chain. Comparing both groups of brominated compounds, PBBs showed an even higher biomagnification potential than PBDEs, although PBB concentrations were in general lower than those of PBDEs [14, 15]. In a recent study, the contamination level of PBBs in fish from the North and Baltic Sea, freshwater fish from Poland, and cod liver oils from two different Polish manufacturers were assessed. PBB concentrations were also measured in foodstuff samples from Poland, like pork fat, beef meat, and butter. The main conclusion of this study was that almost all fish classes and fish products were contaminated [16].

2.1.3 Pesticides

The largest groups of food pollutants are pesticides. Pesticide testing in foodstuffs is a challenging application involving the simultaneous trace analysis of a wide range of agrochemicals possessing a wide range of physicochemical properties, effects, and toxicities. Considering the number of registered compounds (currently more than 1,000), the continuous introduction of new compounds in the market, and the possible presence of trace amounts of these compounds and their degradation products in food, pesticide monitoring is one of the highest interest fields in food safety. For this reason, numerous regulations such as the European Union directives have set maximum residue limits (MRLs) for pesticides in food [17].

During the last decades a vast literature has reported new methods for analysis, as well as, the levels encountered in foodstuffs. In parallel, many reviews [18–23]

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