Analysis of selected emerging contaminants in sewage sludge

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Pharmaceuticals, personal-care products, steroid sex hormones, illicit drugs, flame retardants and perfluorinated compounds are considered environmental emerging contaminants of particular concern, as many of them display endocrine-disrupting properties. These substances released as consequence of human activities enter the wastewater network after use in households and industry. Due to their physico-chemical properties, they tend to accumulate in sewage sludge during wastewater treatment, so the common practice of spreading sewage sludge over agricultural land can constitute a source of many important xenobiotic compounds.

This article provides an overview of the analytical methodologies available for the quantitative determination and the reported levels of these compounds in sewage sludge.

Also, because surfactants are another group of organic contaminants with tendency to accumulate in sewage sludge, we include them in this work.

Keywords: Brominated flame retardant; Emerging contaminant; Illicit drug; Perfluorinated compound; Personal-care product (PCP); Pharmaceutical; Sewage sludge; Steroid sex hormone; Surfactant; UV filter (sunscreen)

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1. Introduction

One of the greatest challenges in keeping water resources clean and safe is that the mixture of chemicals used by society is continually changing. New studies are revealing the presence in water supplies of drugs, personal-care products (PCPs) and other substances that we use every day at home, at work and on the farm. These compounds are commonly referred to as emerging contaminants.

Steroid sex hormones, pharmaceuticals and PCPs, illicit drugs, flame retardants and perfluorinated compounds (PFCs) [1–6] are considered emerging environmental contaminants of particular concern, as many of them display endocrine-disrupting properties. In this review, we include some of these emerging contaminants, most commonly found in sewage sludge. We also include surfactants due to the high concentrations frequently detected.

The main points of collection and subsequent release of these contaminants into the environment are wastewater-treatment plants (WWTPs), where they enter via domestic and hospital sewages or industrial discharges [1]. WWTPs achieve only partial removal. Unlike excreted conjugated forms (which are less toxic and more polar), free estrogens are more likely to accumulate in sewage sludge, due to their moderate to high hydrophobic properties (log K_{ow} = 3–5) [1]. Some classes of illicit drugs, such as cannabinoids, are highly hydrophobic, with octanol-water partition coefficients of 5–7.6, so, despite their high metabolization before excretion [7] and due to their high consumption, cannabinoids could be found bound to sewage sludge. As regards ultraviolet (UV) filters, due to their high octanol-water partition coefficient (5–8) and their low biodegradability (<1%, according to the US EPA [8]), their sorption onto sludge constitutes an important process for their removal from the water column in WWTPs.

Typically, 25% of surfactants entering a WWTP via influent are removed during primary treatment via primary sludge [9]. Due to restricted metabolic pathways, most common surfactants are not degradable under anaerobic conditions [10], and sludge after the anaerobic digestion process is rich in surfactants.

0165-9936/$ - see front matter © 2009 Published by Elsevier Ltd. doi:10.1016/j.trac.2009.09.003

In this context, we need to increase our knowledge about the occurrence of all these selected contaminants in sewage sludge, with the aim of evaluating and reducing potential sources of these compounds entering the environment (e.g., the common practice of using biosolids as fertilizers in agriculture). The high volume of sewage sludge produced nowadays is partly a consequence of the increase in the number of new WWTPs built to achieve the water-quality standards set by the European Union (EU) (Directives 91/271/EEC and 98/15/EEC).

In general, the EU considers that re-use of sludge should be encouraged, since it represents a long-term solution, provided the quality of the sludge re-used is compatible with public-health and environmental-protection requirements. The current legislation regulates the agricultural use of sewage sludge based only on the concentration of toxic heavy metals and nutrients. However, following the measures that the European Commission (EC) started in 1999, the third draft of a future Sludge Directive contained a proposal for limit values for several organic contaminants [11]. However, subsequent evaluation [12] of the relevance of organic micro-pollutants in sewage sludge proposed the elimination of some compounds from the list. For example, the evaluation concluded that there is no reason to set up limits for linear alkyl benzenesulphonate (LAS), since LAS poses no environmental impact when sludge is applied to land. Nevertheless, for other compounds [e.g., nonylphenol (NP) and NP ethoxylates (NPEOs)], the conclusion of the JRC Provisional report [12] was that restrictions for sewage sludge seem necessary, and 50 mg/kg was proposed as the lower guide value of a greater span taking into account the situation in the different European countries (limit values in the range 50–100 mg/kg d.w.).

2. Analysis of sewage sludge samples

To date, most of the analytical methods reported to determine these selected contaminants in the environment focus on aqueous matrices (e.g., surface water and sewage water). Quite few methodologies have been developed for their analysis in solid matrices, with sediments having been investigated slightly more than sewage sludge, probably because of the complexity of the latter matrix. From an analytical viewpoint, sewage sludge is a challenging matrix because it is not uniform in its composition. The concentrations of pollutants present in samples vary depending on the nature of the inputs to the WWTP. In addition to the pollutants of interest, sewage sludge contains a number of other components that are potential interferences in analyzing the pollutants of interest. Some of these ''co-extracted'' interferences include lipids and other naturally-occurring materials, as well as materials that may be added to the sewage during processing (e.g., surfactants, ferric chloride, polymeric colloids, or lime). These components can manifest themselves as interferences at all stages of the analytical process from sample preparation, so it is critical to remove them from the sample extracts using established clean-up procedures.

Overall, the reported methodologies (Table 1) comprise extraction of the sludge sample, subsequent purification of the extract, and final analysis by either gas or liquid chromatography (GC or LC) coupled mostly to mass spectrometry (MS) or tandem MS (MS^2) detection.

2.1. Sample preparation

2.1.1. Pharmaceutical compounds. At present, there are advanced analytical methods for detecting and quantifying more than 100 different drugs in aqueous samples, but the methodology is not sufficiently developed for analysis of sludge. The existing methods mostly focus on specific therapeutic classes, paying special attention to the antibiotics due to their potential for antibiotic resistance.

In recent years, extraction methods have usually been based on liquid partitioning with ultrasonic extraction (USE) [13,14], microwave-assisted extraction (MAE) [15] or the more advanced pressurized liquid extraction (PLE) [16,17]. Compared to the other extraction techniques, PLE provides good recoveries, and saves time and organic solvents, so it has become currently the preferred technique. The most effective clean up of extracts of sludge samples containing pharmaceutical residues has proved to be solid-phase extraction (SPE) using Oasis HLB, Oasis MCX and Strata-X cartridges.

2.1.2. Estrogens. Kuster et al. [1] and Gabet et al. [18] reviewed the environmental analysis of estrogens in 2004 and 2007, respectively. In the past two years, a few works dealing with the environmental fate of these chemicals have made use of newly developed methodologies, already validated methodologies, or methods validated for sediment and water samples slightly modified to evaluate the presence of estrogens in sewage sludge matrices.

Extraction of the samples was performed using a variety of techniques including tumbling [19], shaking and USE [20], and Soxhlet and PLE [21,22].

Purification of the extracts was carried out by SPE with C18 [19] and polymeric materials [23], preparative LC [19,21] and gel-permeation chromatography (GPC) [23]. Nieto et al. [22] purified the sludge extracts by simple filtration, but the limits of detection (LODs) achieved for the free estrogens estradiol (E2), ethynyl estradiol (EE2) and αE2 (150 μg/kg d.m.) and the conjugated form E2-17-acetate (175 μg/kg d.m.) were the highest reported.