

## Chapter 2

# Detection of Transformation Products of Emerging Contaminants

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**Abstract** Environmental research nowadays is focusing more and more on different categories of emerging contaminants, because of their increasing release into the environment, the lack of information regarding the occurrence and health effects of the parent compounds, and, even more, of their transformation products, and the need for the development and optimisation of analytical methods for their determination in environmental samples. Emerging contaminants and transformation products are detected by advanced analytical methods such as liquid chromatography (LC) or gas chromatography (GC) combined with tandem mass spectrometric (MS/MS) detection. The rapid development and improvement of these methods during the last few years provides the opportunity not only to determine trace levels of emerging pollutants in environmental samples, but also to identify and detect their transformation products. This is a particularly important step towards safeguarding environmental quality and human health.

**Keywords** Emerging pollutants • Transformation products • Pharmaceuticals • Personal care products • Environmental samples • LC–MS • GC–MS

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## 2.1 Introduction

Emerging contaminants are increasingly being released into the environment, raising concerns for environmental quality and human health. These compounds, belonging to several categories, have not been regulated yet. The reason can be either the lack of information regarding their occurrence and environmental effects, or the lack of appropriate analytical methods for their determination in complex environmental samples, or both. Many emerging contaminants are produced and used in major sectors of human life, such as industry, agriculture, consumer goods. Others are unintentionally formed as by-products of industrial processes, advanced oxidation processes, degradation and transformation processes of the original compounds in general. The latter category is gaining more and more scientific interest, as very little is known about these compounds. With the analytical techniques available some years ago, they could not even be identified or detected in environmental samples. However nowadays this has become technically feasible, and therefore much relevant research is being carried out, in order to obtain knowledge about them, and, if necessary, take the required measures to protect the environment and human life.

Emerging contaminants are currently not subject to routine monitoring and may be candidates for future regulation, depending on research on their toxicity and potential health effects. Their inclusion in routine monitoring programs requires analytical methods for their determination in environmental samples to be developed, evaluated and optimised. This can be a difficult task, especially for pollutants occurring in trace levels in environmental samples rich in organic compounds that can interfere during analysis.

The main categories of emerging contaminants are pharmaceuticals, steroid estrogens and personal care products. More categories as well as more compounds and transformation products are being detected in trace levels in the environment, with the help of newly available technology enabling analysts to accurately identify and quantify them in environmental samples. Obtaining information on the sources, occurrence, fate, risk assessment and ecotoxicological data of emerging pollutants is the aim of many investigations worldwide. For this purpose, development and validation of analytical methods appropriate for the determination of these categories of pollutants is a fundamental issue, and the subject of many relevant publications nowadays [1, 2].

The present chapter provides an overview of the recent research findings regarding the determination of the main categories of emerging contaminants and their transformation products in environmental samples.

## 2.2 Detection of Emerging Contaminants and Their Transformation Products in Environmental Samples

### 2.2.1 *Pharmaceuticals and Transformation Products*

Pharmaceuticals consist one of the largest and most important categories of emerging pollutants. During the recent years, several analytical methods have been

**Table 2.1** Transformation products of pharmaceuticals identified in environmental samples

Pharmaceuticals	Transformation products	References
Sulfamethoxazole	Hydroxylamine	[3]
Paracetamol	N-4-hydroxyphenyl-acetamide 2-[(2,6-dichlorophenyl)-amino]- 5-hydroxyphenylacetic acid 2,5-dihydroxyphenylacetic acid	[4, 5]
Sulfadiazine	4-methyl-2-amino-pyrimidine	[6, 7]
Sulfamethoxine	2,6-dimethoxy-4-aminopyrimidine 2-aminothiazole	[6, 7]
Sulfathiazole	2,6-dimethoxy-4-aminopyrimidine 2-aminothiazole	[6, 7]
Sulfamerazine	4-methyl-2-aminopyrimidine	[6, 7]
Busperidone	Hydroxybusperidone Dihydroxybusperidone Dipyrimidinylbusperidone 1-pyrimidinyl piperazine	[6, 7]
Carbamazepine	1-(2-benzaldehyde)-4-hydro(1H,3H)quinazoline-2-one 1-(2-benzaldehyde)-(1H,3H)quinazoline-2,4-dione 1-(2-benzoic acid)-(1H,3H)quinazoline-2,4-dione Acridine, salicylic acid, catechol, anthranilic acid	[8, 9]
Iopromide	Primary alcohols Carboxylates	[10]
Acetyl salicylic acid	Salicylic acid	[10]
Clofibrate	Clofibric acid	[10]
Fluoxetine	Norfluoxetine	[10]

developed for the analysis of different groups of pharmaceuticals, because of their different properties. The trend nowadays is to achieve the development and application of “multi-residue” methods for the simultaneous analysis of a large number of pharmaceuticals belonging to different categories [11, 12]. Multi-residue methods have the advantage of providing data on the occurrence of pharmaceuticals in the environment with less time and effort spent. However, the simultaneous analysis of compounds with different physico-chemical properties requires a compromise in regard to the experimental conditions of the analytical method, to accurately determine all analytes in a single run. The same methods used for the determination of the parent compounds are being applied in order to identify and quantify the transformation products of pharmaceuticals as well, based on the MS techniques (Table 2.1).

### 2.2.2 Detection Methods

During the application of the multi-residue methods, simultaneous extraction of all target analytes from the sample is performed, typically in one single solid phase extraction (SPE) step [13, 14]. Combination of two SPE materials can be

performed either in series or classifying the analytes into two or more groups, according to their physico-chemical properties. The most commonly used cartridges for this purpose are Oasis HLB or C18. The value of pH can be very important for this step. For example, for the Oasis HLB neutral sample pH is advisable, whereas for C18 sample pH adjustment prior to extraction is required depending on the acidic, neutral or basic nature of the analytes. Other cartridges used are Lichrolut ENV+ , Oasis MCX and StrataX [2]. The elution is performed with pure organic solvents, mostly methanol or acetonitrile [14–16]. Other extraction methods include Molecularly Imprinted Polymers (MIPs) and immuno-sorbents. They provide high selectivity for target analytes when performing single group analysis, for this reason they have been widely employed to selectively isolate clenbuterol, aniline  $\beta$ -agonists, tetracycline and sulphonamide antibiotics,  $\beta$ -agonists and  $\beta$ -antagonists from biological samples. Some applications also in environmental samples have been reported [17, 18].

After extraction, a purification step is required in order to avoid matrix effects, especially in complex environmental samples. Purification (cleanup) is generally performed by SPE, using the same cartridges and conditions as the analysis of pharmaceuticals in water samples. Sample extracts are therefore diluted with an appropriate volume of MilliQ water, until the organic solvent content is below 10%, in order to avoid losses of target compounds during SPE [19].

LC-MS/MS is the preferable analysis method, due to its versatility, specificity and selectivity, gradually replacing GC-MS and LC-MS. GC-MS can still be successfully applied in some cases, especially for nonpolar and volatile pharmaceutical compounds, however it still requires a time-consuming derivatization step, during which there are risks of analyte losses [20, 21]. Among LCMS/MS techniques, triple quadrupole (QqQ) and ion trap (IT) instruments are in common use, and they permit the detection of pharmaceuticals at the ng/L range. More recent approaches in LC-MS/MS are linear ion traps (LITs), new generation triple quadrupoles and hybrid instruments, such as quadrupole-time of flight (QqTOF) and quadrupole-linear ion trap (QqLIT) [22]. QqTOF instruments have been used for the elucidation of structures proposed for transformation products [23–25]. They are also used for confirmation purposes. QqLIT methods have also been developed, for the determination of diclofenac, carbamazepine and iodinated X-ray contrast media [26], and for determination of  $\beta$ -blockers in wastewater [27]. Reversed-phase LC is mainly used, with C18 columns. For acidic drugs, ionpair reversed-phase LC with a Phenyl-Hexyl column has also been used [28]. The mobile phases mostly used are acetonitrile, methanol or mixtures. The sensitivity of the method can be improved with use of mobile phase modifiers, buffers and acids, usually ammonium acetate, tri-*n*-butylamine (TrBA), formic acid and acetic acid [13].

LC-MS/MS methods have been recently used for the determination of the occurrence of illicit drugs and metabolites in water and wastewater with interesting results. Cocainics, amphetamine-like compounds, opiates, cannabinoids and lysergics have been determined [14, 29, 30]. The highest levels were reported for cocaine and its main metabolite benzoylecgonine (BE), sometimes reaching the  $\mu\text{g/L}$  [14].

Another product of cocaine, cocaethylene (CE), was detected. CE is a transesterification product formed when cocaine is consumed together with ethanol. CE transforms rapidly into metabolites not studied yet in WWTPs, such as norcocaethylene and ecgonine ethyl ester. The cocaine metabolites norcocaine and norbenzoylecgonine, have been determined at two WWTPs in Italy with maximum concentration 40 ng/L. Morphine has been found in some WWTPs at high ng/L levels and heroine at very low concentrations due to its low consumption and its also rapid hydrolysis to morphine and 6-acetylmorphine (heroine is quite unstable in blood serum). Research in WWTPs in Italy and in Switzerland reported that methadone was detected at lower ng/L levels than its pharmacologic inactive metabolite 2-ethylidine-1,5-dimethyl-3,3-diphenylpyrrolidine perchlorate (EDDP). Lysergic acid diethylamide (LSD) and its metabolites nor-LSD and nor-iso LSD (nor-LSD) and 2-oxo-3-hydroxy-LSD (O-H-LSD), have been detected at very low concentrations [14]. Phenylethylamine ephedrine, 3,4-methylenedioxymetamphetamine hydrochloride (MDMA or “ecstasy”), methylenedioxyethylamphetamine (MDE, MDEA or “Eve”) and 3,4-methylenedioxyamphetamine (MDA or “Love pills”, and metabolite of both MDE and MDMA), have been detected frequently at the ng/L level. 11-nor-9 carboxy THC (nor-THC) and 11-hydroxy-THC (OH-THC), both metabolites of  $\Delta^9$ -tetrahydrocannabinol (THC), which is the most psychologically active constituent of Cannabis have also been detected [30, 31].

## 2.3 Steroid Estrogens and Transformation Products

Steroid estrogens (hormones and contraceptives) include free estrogens, both natural (estradiol, estrone and estriol) and synthetic (basically ethynyl estradiol, mestranol and diethylstilberol). These compounds have been investigated in environmental samples more than conjugated estrogens and halogenated derivatives recently identified, again by advanced LC–MS and GC–MS techniques [32–35] (Table 2.2).

### 2.3.1 Detection Methods

SPE is the preferable method for the extraction of estrogens from water samples using mostly cartridges, C18-bonded silica, polymeric graphitized carbon black (GCB) and Oasis HLB [36]. On-line SPE has also been used [37]. Methanol is mainly used for the elution. Use of MIPs for the extraction has also been reported [38], as well as SPME (fibre and in-tube SPME), in combination with either LC or GC instruments [39, 40].

GC–MS and GC–MS/MS have been applied for the determination of estrogens, but their disadvantage is the need for derivatization prior to analysis [39]. Moreover, these methodologies are mainly based on the determination of free estrogens,

**Table 2.2** Transformation products of steroid estrogens identified in environmental samples

Steroid estrogens	Transformation products	References
17 $\beta$ -estradiol	Estrone	[32]
	Estriol	[34]
Testosterone	Androstenedione	[34]
Ethinylestradiol (EE2)	2-Cl-EE2	[33]
	2-Br-EE2	[35]
	4-Cl-EE2	
	4-Br-EE2	
	2,4-diCl-EE2	
	2,4-diBr-EE2	

unless intermediate hydrolysis steps are performed [41]. Therefore, LCMS and especially LC–MS/MS are mostly being used [42], which allow the determination of both conjugated and free estrogens without derivatization and hydrolysis. In the case of GC–MS, derivatization is generally carried out in the –OH groups of the steroid ring, performed by silylation with reagents such as N,O-bis(trimethylsilyl)-acetamide (BSA), N-methyl-N trimethylsilyltrifluoroacetamide (MSTFA), NO-bis(trimethylsilyl)-trifluoroacetamide (BSTFA), or N-(tert-butyldimethylsilyl)-N methyltrifluoroacetamide (MTBSTFA), which lead to the formation of trimethylsilyl (TMS) and tert-butyldimethylsilyl (TBS) derivatives [43]. In the case of LC, octadecyl silica stationary phases are used, with mobile phases consisting of mixtures of water/methanol and, more frequently, water/acetonitrile, sometimes with added modifiers such as 0.1% acetic acid, 0.2% formic acid or 20 mM ammonium acetate. Single and triple quadrupole analysers have been the most widely used for the analysis of estrogens, and application of Q-TOF has been reported as well [44].

Estrogens are mainly excreted as their less active sulphate, glucuronide and sulfo-glucuronide conjugates. However, in the environment, these conjugates may suffer deconjugation and act as precursors of the corresponding free steroids [45]. Thus, an appropriate evaluation of their occurrence and impact requires the analysis of both free and conjugated estrogens. Concentrations reported in wastewater have been most usually in the ng/L range. Estradiol (E2) and estrone (E1) have been the free estrogens most frequently found, whereas estriol (E3) has been studied and detected only sporadically. However, E3 concentrations, when detected, have been usually higher than those of E2 and E1. In general, estrogens concentrations decrease in the order  $E3 > E1 > E2$  [45, 46]. The most studied synthetic estrogen, ethinylestradiol (EE2), has been either not detected [47] or detected at concentrations in general much lower than the other estrogens [48]. Conjugated estrogen derivatives have been less investigated than free ones [49]. Sulphates and glucuronides of E1, E2 and E3 have been determined at similar levels as the free estrogens. Derivatives of the synthetic estrogen EE2 were studied, but they were not detected [50]. From the Di-conjugated E2 derivatives, high levels of the disulphate and moderately high levels of the sulphate-glucuronide derivative were reported [51].

## 2.4 Personal Care Products and Transformation Products

Personal Care Products (PCPs) are a group of emerging pollutants of particular environmental interest as they are used daily and released into the environment. Synthetic musk fragrances (nitro and polycyclic musk fragrances), antimicrobials (triclosan and its metabolites and triclocarban), sunscreen agents (ultraviolet filters), insect repellents (N,N diethyl-m-toluamide, known as DEET) and parabens (p-hydroxybenzoic esters), which are basically substances used in soaps, shampoos, deodorants, lotions, toothpaste and other PCPs are some of the major substances of this group. The nitro musk fragrances were the first to be produced and include musk xylene, ketone, ambrette, moskene and tibetene. In the environment, the nitro substituents can be reduced to form amino metabolites of these compounds. The polycyclic musk fragrances, which are used in higher quantities than nitro musks, include 1,2,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- $\gamma$ -2-benzopyrane (HHCB), 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN), 4-acetyl-1,1-dimethyl-6-tert-butylindane (ADBI), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane (ATII) and 6,7-dihydro-1,1,2,3,3-pentamethyl-4-(5H)-indanone (DPMI). Parabens are the most common preservatives used in personal care products and in pharmaceuticals and food products. This group of substances includes methylparaben, propylparaben, ethylparaben, butylparaben and benzylparaben. Transformation products of PCPs have also been detected in environmental samples (Table 2.3).

### 2.4.1 Detection Methods

PCPs and transformation products are extracted from the matrix by liquid–liquid extraction (LLE) [52], continuous liquid–liquid extraction (CLLE), SPE [53] and SPME [54]. LLE and CLLE have been applied with various organic solvents such as dichloromethane, pentane, hexane, toluene, cyclohexane and petroleum ether, or mixtures of them. For SPE, sorbents commonly used are C18, Isolute ENV+, OasisMAX, SDB-XC, XAD-2, and XAD-4/XAD-8. Several organic solvents have been used for the elution, such as acetone, methanol, toluene, hexane, ethyl acetate and their mixtures. Cleanup is performed with SPE with silica and alumina [53].

The analysis of PCPs is performed mainly by GC–MS techniques, in particular by GC–EI–MS or GC–NCI–MS. The latter is more sensitive for the category of nitro musk fragrances. These compounds have also been analysed by GC–FID, GC–ECD, and high-resolution and ion trap tandem mass spectrometry (MS/MS). Triclosan and its chlorinated metabolites are also determined by GC–EI–MS with and without derivatization, LC–MS and LC–MS/MS. When derivatizing, N,N-diethyltrimethylamine (TMS-DEA), (BSTFA), pentafluorinated triclosan and tert-butyldimethylsilyl triclosan are the ether derivatives generated after reaction with methyl chloroformate (MCF), pentafluoropropionic acid anhydride (PFA) and

**Table 2.3** Transformation products of PCPs identified in environmental samples

PCPs	Transformation products	References
Paraben	4-hydroxybenzoic acid Phenol	[55]
Triclosan	Methyl-triclosan	[56]
Nitroaromatic musks	Aniline transformation products	[57]
HHCB	HHCB lactone	[57]

Ntert-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA), respectively. UV filters and insect repellants are determined mainly with GC–MS analysis. Almost all UV filters are amenable to GC except octyl triazone, avobenzene, 4-isopropylidibenzoylmethane and 2-phenylbenzimidazole-5-sulphonic acid, that can be determined by HPLC–UV. Parabens are analysed by LC–MS/MS methods [37].

## 2.5 Concluding Remarks

The determination of emerging contaminants and of their transformation products in complex environmental samples is a challenging task. These compounds occur in the environment in trace concentrations, however due to their continuous release they can have adverse effects of aquatic organisms and the trophic chain. Moreover, their oxidation/degradation products and metabolites have not yet been fully documented, but with advanced analytical techniques currently available they can be identified and quantified, providing more insight to the occurrence, formation, properties and environmental pathways of these pollutants.

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