Science of the Total Environment 520 (2015) 241–252

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Emission factor estimation of ca. 160 emerging organic microcontaminants by inverse modeling in a Mediterranean river basin (Llobregat, NE Spain)

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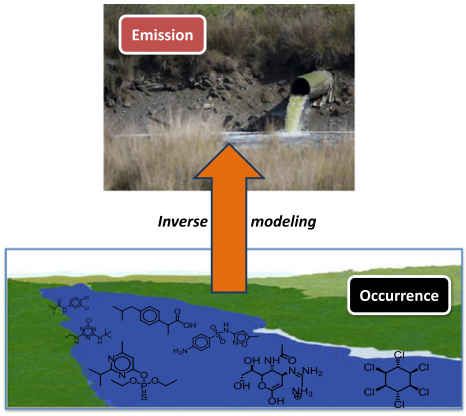
HIGHLIGHTS

- Emission factors of 160 microcontaminants discharged in a river basin are modeled.
- Industrial compounds showed the highest emissions compared to other families.
- In-stream attenuation averaged 60% for all families except Perfluoroalkyls (20%).
- Emission estimation was mainly sensitive to the hydraulic parameters of the model

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 November 2014
Received in revised form 23 February 2015
Accepted 13 March 2015
Available online 25 March 2015

Editor: Eddy Y. Zeng

Keywords:
Inverse modeling
Emission factors
Organic micropollutants
Llobregat river
Sensitivity
Uncertainty analysis

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ABSTRACT

Starting from measured river concentrations, emission factors of 158 organic compounds out of 199 analyzed belonging to different groups of priority and emerging contaminants [pesticides (25), pharmaceuticals and hormones (81), perfluoroalkyl substances (PFASs) (18), industrial compounds (12), drugs of abuse (8) and personal care products (14)] have been estimated by inverse modeling. The Llobregat river was taken as case study representative of Mediterranean rivers. Industrial compounds and pharmaceuticals are the dominant groups (range of 10^4 mg·1000 inhab^{-1}·d^{-1}). Personal care products, pesticides, PFASs and illegal drugs showed a load approximately one order of magnitude smaller. Considered on a single compound basis industrial compounds still dominate (range of ca. 10^3 mg·1000 inhab^{-1}·d^{-1}) over other classes. Generally, the results are within the range when compared to previously published estimations for other river basins. River attenuation expressed as the percentage fraction of microcontaminants eliminated was quantified. On average they were around 60–70% of the amount discharged for all classes, except for PFASs, that are poorly eliminated (ca. 20% on average). Uncertainties associated with the calculated emissions have been estimated by Monte-Carlo methods (15,000 runs) and typically show coefficients of variation of ca. 120%. Sensitivities associated with the various variables involved in the calculations (river discharge, river length, concentration, elimination constant, hydraulic travel

http://dx.doi.org/10.1016/j.scitotenv.2015.03.055

time and river velocity) have been assessed as well. For the intervals chosen for the different variables, all show sensitivities exceeding unity (1.14 to 3.43), tending to amplify the variation of the emission. River velocity and basin length showed the highest sensitivity value. Even considering the limitations of the approach used, inverse modeling can provide a useful tool for management purposes facilitating the quantification of release rates of chemicals into the aquatic environment.

1. Introduction

Developed societies are characterized by a growing use of chemicals in their urban, industry and agriculture activities (Muir and Howard, 2006; Arnot et al., 2006). Depending on their production volumes, mode of use and properties, chemicals may reach the aquatic environment from both point and non-point sources resulting on a potential threat to the water cycle and the aquatic ecosystems (Vörösmarty et al., 2010). Among the hundreds of thousands of different commercially available chemicals, the so called 'emerging contaminants' are of special concern. These are defined as chemicals, whose environmental relevance has been only recently highlighted due to either new scientific findings or because their environmental occurrence has been evidenced owing to the progress achieved by analytical techniques (Barceló and Petrovic, 2007). Pharmaceuticals and personal care products, endocrine disrupting chemicals (ECD), pesticides, illicit drugs, perfluoroalkyl substances (PFASs) and other industrial compounds are just some relevant examples. All these families are characterized by their widespread introduction into the environment, the lack of knowledge as regards their middle or long-term effects in the human health and the ecosystems, as well as the fact that they are generally only poorly covered by existing regulations (Schwarzenbach et al., 2006). Therefore knowledge about their environmental occurrence, fate and inputs discharged are of great relevance.

The emission of pollutants into the environment has been addressed by both sector and environmental legislation, especially in developed countries. For instance, in the European Union the so called REACH regulation (European Commission, 2006a) foresees to regulate ca. 30,000 chemical compounds used in industry and reaching consumer products. The classification criteria taken into consideration are not only their environmental and health effects but also their production volumes (Guillén et al., 2012). As regards emissions of contaminants, the so called European Pollutant Release and Transfer Register (E-PRTR) (European Commission, 2006b) sets the obligation to the operators that carry out certain activities to report specific information on the release of pollutants into the air, water and land and specifically of pollutants into waste water. As far as the aquatic environment is concerned, the Water Framework Directive (WFD) (Directive 2000/60/EC) (European Commission, 2000) is aimed to the achievement of good ecological and chemical status of European water bodies by the year of 2015. The latter is fulfilled by compliance with certain Environmental Quality Standards (EQS) for 45 priority substances and priority hazardous substances (Directive 2013/39/UE) (European Union, 2013). In addition to these, other substances discharged into the water bodies should be also controlled by the responsible authorities (Directive 2008,105, EC) (European Commission, 2008). All these regulatory frameworks require substantial information about both environmental concentrations and emissions of pollutants as well.

Appropriate estimates of such two variables can be obtained by either experimental measurements or modeling (Johnson et al., 2008). While both approaches show their respective pros and cons, there is a growing interest on the latter due to increasing development and affordability of computation and information techniques as compared to costly monitoring campaigns (Johnson et al., 2008; Pistocchi et al., 2012). Modeling efforts have been mostly focused on the prediction of environmental concentrations of pollutants. Existing models include GREAT-ER (Feijtel et al., 1997; Schowanek and Webb, 2002), PhATE (Anderson et al., 2004) and LF2000-WQX (Keller and Young, 2004; Johnson et al., 2007) among others (Pistocchi et al., 2010; Osorio et al., 2012). In contrast, estimations of emissions are much scarcer in the literature. Emissions of chemicals into environmental compartments (e.g., air, water, soil and biota) are usually estimated taking into account the volume produced (Daginnus et al., 2011) and/or their consumption data, if available. As regards the aquatic environment, emission estimations are based on the market (kg of chemical sold/year), basin population (Pistocchi and Loos, 2009; Pistocchi et al., 2012) and WWTP removal rates (Verlicchi et al., 2012, 2014). However, since this information is only available for certain families of contaminants, such approaches are difficult to apply for a large number of chemicals.

An alternative is to consider emissions as the volume of any pollutant actually discharged into the receiving river. This should not be confused with consumption or amount discharged into the sewage system. Within this framework, and taking advantage of the availability of measured environmental concentrations in many European rivers as a result of the existing monitoring efforts carried out during the last years, some authors (Pistocchi et al., 2012; Boxall et al., 2014) recently showed the potential of inverse modeling (that is by back calculation from actually measured concentrations) combined with Geographic Information Systems (GIS). Using such approach the authors were able to estimate quantities like emission factors (Pistocchi et al., 2012) or overall compound removal (Boxall et al., 2014).

The present study aims at estimating the emission of ca. 160 priority and emerging contaminants belonging to different families (pharmaceuticals and hormones, personal care compounds, pesticides, PFASs, illegal drugs, and industrial organic products) in a Mediterranean basin (Llobregat river basin, Sabater et al., 2012) by inverse modeling using the minimal amount of information. To achieve this, we used concentrations in river waters measured during two monitoring campaigns carried out in 2010–2011 as part of an ongoing project (Navarro-Ortega et al., 2012). Then, we estimated emissions using a Monte-Carlo framework to account for the different sources of uncertainty carried by the inverse calculations. This enabled to quantitatively assess their respective contributions. Finally, in-stream removal of pollutants, expressed as the fraction of the total emission which is eliminated by the river for every compound, was quantified and discussed.

2. Materials and methods

2.1. Site description

Llobregat river (Sabater et al., 2012) is situated in North East of the Iberian Peninsula (Fig. 1). The length of the mainstream is 165 km and it has a catchment area of 4957 km^2. Because of its proximity to the city of Barcelona and its metropolitan area, the lowest course of the river receives strong anthropogenic pressures caused by concentration of both population and industry. Consequently urban and industrial wastewaters are increasingly discharged in the low Llobregat. In addition surface run-off coming from both geology and salt mining exploitation occurring in its middle basin (Cardener and Llobregat) increases the river salinity. Diffuse pollution from agriculture is also present. In

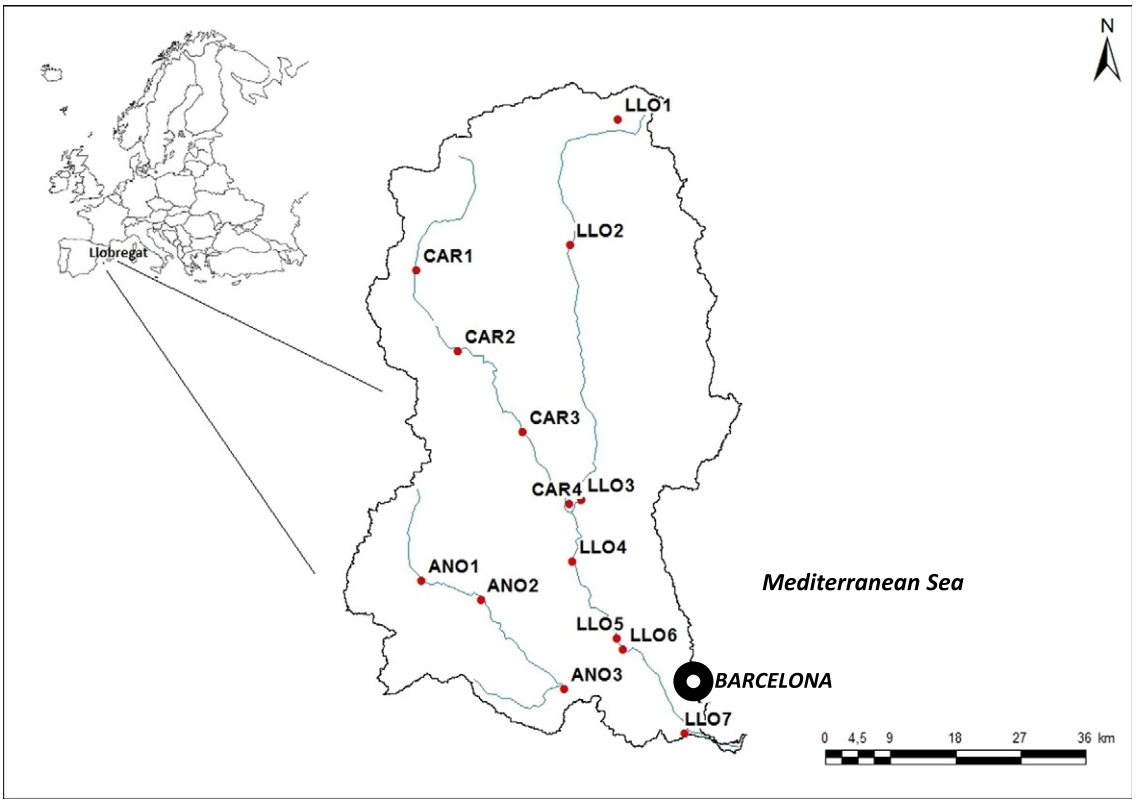

Fig. 1. Llobregat river basin (NE Spain), showing sampling sites.

spite of the severe pressures received, this river constitutes one of the major supply sources of drinking water for Barcelona and surrounding cities (ca. 3 million inhabitants; 545 inhab·km^{-2}). About half of this population (ca. 1.5 million) discharges its treated waste water into the basin, while the remaining is discharged into the Mediterranean sea from the wastewater treatment plant (WWTP) located in Prat de Llobregat. The river is regulated by three reservoirs located in the mid/upper basin. Its mean year precipitation is ca. 650 mm, and the mean river discharge 620 Hm^3 y^{-1}. The average flow measured in the gauging station of Sant Joan Despí for the last 10 years (2004–2014) has been 10.7 m^3 s^{-1}, with minimum and maximum values of 0.75 and 50 m^3 s^{-1}, respectively. This reflects a typical Mediterranean hydrological behavior in which precipitation is not evenly distributed, giving rise to peak flows and drought periods (Supplementary Material, Fig. S1). Flow measurements are continuously recorded on several gauging stations by the local authority (Agència Catalana de l'Aigua, ACA), being publicly available at the ACA website (http://www.gencat.cat/aca/).

2.2. Sampling

River pollutant concentrations were gathered within the Spanish funded research SCARCE-CONSOLIDER project (Navarro-Ortega et al., 2012). Extensive monitoring of water was carried out in two monitoring campaigns (autumn 2010 and autumn 2011). The autumn of 2010 was characterized by intense precipitation which resulted in a high flow, while the autumn 2011 was dry and the river flows were comparatively lower. Grab water samples were collected for chemical characterization at 14 selected sampling sites, located in both the mainstream (7 sites) and the two main tributaries, i.e., the Cardener (4 sites) and the Anoia (3 sites) (Fig. 1).

2.3. Chemical analysis

Organic micropollutants were measured by following previously published analytical methods based on gas chromatography–tandem mass spectrometry and liquid chromatography–tandem and hybrid mass spectrometry (see Table S1, Supporting information). Water phase concentrations of 199 organic compounds belonging to different groups of priority and emerging contaminants: pesticides (39), pharmaceuticals and hormones (89), PFASs (21), industrial organic compounds (14), drugs of abuse (19) and personal care products (17) were included in the monitoring campaigns carried out in the Llobregat basin. Maximum concentrations are reported in Table 1. These correspond to the highest found in the whole basin throughout the two campaigns. Exclusion of those compounds that were never positively detected (i.e., not exceeding their detection limits) resulted on a final set of 158 compounds, namely pesticides (25), pharmaceuticals and hormones (81), PFASs (18), industrial organic compounds (12), drugs of abuse (19), and personal care products (14). Concentration values below their limit of detection were set equal to 0 for calculation purposes.

2.4. Modeling

Our modeling approach aims at estimating the emissions occurring at the basin scale using a minimum of information. Briefly, the observed concentrations available from monitoring campaigns (typically 14 sites × 2 campaigns = 28 measurements per compound) are transformed into mass flows multiplying by the river discharge and related to the emissions occurring upstream by setting a mass-balance. The effect of the distance from the emission source to the observation site is reflected in the corresponding in-stream removal produced

Table 1
Maximum measured basin concentrations, base elimination pseudo first order constant used in Monte-Carlo simulations, emission factors and water purification ecosystem service values corresponding to the studied compounds.

Compound			Emission[b,c] (mg·1000 inhab^{-1}·d^{-1})		River attenuation[c] (% removed)	
	C_{max} ng·L^{-1}[a]	k (h^{-1})	Mean	Std.dev.	Mean	Std.dev.
Industrial organic compounds						
1H-Benzotriazole (BT)	1622.99	5.26E−03	1250.14	1482.48	71.4	21.2
Tolyltriazole (TT)	7017.67	4.52E−03	4791.65	5672.31	68.8	21.5
Bisphenol A (BPA)	649.35	3.55E−03	358.70	429.36	63.6	22.5
Nonylphenol (NP)	116.34	6.18E−03	104.40	126.13	74.1	20.4
Nonylphenol diethoxylate (NP2EO)	287.67	6.50E−03	270.12	324.03	75.2	20.2
Nonylphenol monocarboxylate (NP1EC)	989.53	1.10E−02	1553.67	1939.86	83.3	16.7
Nonylphenol monoethoxylate (NP1EO)	bld	7.37E−03	–	–	–	–
Octylphenol (OP)	84.73	6.40E−03	79.00	94.67	75.0	20.1
Octylphenol diethoxylate (OP2EO)	32.84	2.83E−03	14.99	17.32	58.0	22.9
Octylphenol monocarboxylate (OP1EC)	1.25	4.80E−03	0.88	1.01	69.7	21.6
Octylphenol monoethoxylate (OP1EO)	bld	7.63E−03	–	–	–	–
Tris(2-chloroethyl) phosphate (TCEP)	232.40	4.62E−03	160.78	190.02	69.2	21.8
Tris(butoxyethyl) phosphate (TBEP)	315.08	2.20E−02	971.04	1211.16	90.3	12.2
Tris(chloroisopropyl) phosphate (TCCP)	1117.27	4.02E−03	685.51	820.44	66.1	22.2
Pesticides						
3-Hydroxycarbofuran	bld	5.99E−03	–	–	–	–
Acetochlor	bld	3.38E−03	–	–	–	–
Alachlor	bld	3.38E−03	–	–	–	–
Atrazine	6.44	1.96E−03	4.3	5.0	50.2	22.2
Azinphos ethyl	3.43	6.67E−03	6.1	7.2	76.0	19.6
Azinphos methyl	8.69	7.15E−03	16.3	19.6	76.9	19.6
Burpofezin	4.38	2.58E−03	3.5	4.1	56.3	22.7
Carbofuran	6.75	4.45E−03	8.2	9.6	68.1	21.7
Chlorfenvinphos	3.48	3.09E−03	3.1	3.6	60.6	22.6
Chlorpyriphos	13.65	2.74E−03	11.2	13.1	57.7	22.6
Deisopropylatrazine	bld	2.18E−03	–	–	–	–
Desethylatrazine	bld	2.10E−03	–	–	–	–
Diazinon	35.77	5.84E−03	56.8	68.8	73.3	20.8
Dichlofenthion	bld	4.09E−03	–	–	–	–
Dimethoate	71.91	1.26E−02	229.6	282.6	84.9	16.0
Diuron	159.53	2.26E−03	116.3	136.4	53.5	22.4
Ethion	7.10	1.34E−02	24.7	30.9	85.6	15.5
Fenitrothion	47.39	5.83E−03	73.7	89.0	73.3	20.7
Fenoxon	bld	7.28E−03	–	–	–	–
Fenoxon sulfone	1.76	6.73E−03	3.1	3.6	75.7	20.0
Fenoxon Sulfoxide	bld	7.00E−03	–	–	–	–
Hexythiazox	24.00	2.23E−03	17.1	19.8	52.7	22.6
Imazalil	6.33	1.90E−03	4.1	4.8	49.3	22.1
Imidacloprid	66.53	2.75E−03	55.8	63.7	58.2	22.4
Isoproturon	9.60	3.78E−03	10.3	12.1	64.9	22.1
Malathion	9.13	1.51E−02	34.8	41.9	86.7	14.9
Methiocarb	3.23	4.46E−03	4.0	4.7	68.2	21.9
Metolachlor	12.96	3.27E−03	12.2	14.2	61.7	22.5
Molinate	bld	6.19E−03	–	–	–	–
Ometoate	bld	1.31E−02	–	–	–	–
Parathion-ethyl	bld	6.33E−03	–	–	–	–
Parathion-methyl	bld	6.79E−03	–	–	–	–
Prochloraz	9.87	1.37E−03	5.4	6.5	41.4	20.8
Propanil	bld	3.33E−03	–	–	–	–
Propazine	8.77	1.90E−03	5.7	6.8	49.1	22.2
Pyriproxyfen	1.72	4.64E−03	2.2	2.5	69.1	21.7
Simazine	45.77	2.03E−03	30.6	35.2	50.8	22.2
Terbutryn	23.37	1.88E−03	14.9	17.1	49.1	22.1
Tolclophos-methyl	bld	3.77E−03	–	–	–	–
Pharmaceuticals & hormones						
Phenazone	9.53	4.48E−03	11.8	13.9	68.5	21.7
Propyphenazone	24.40	4.04E−03	27.3	32.5	66.0	22.1
Oxycodone	4.35	1.31E−03	2.3	2.7	40.7	20.7
Codeine	44.07	2.30E−03	31.9	37.2	53.8	22.6
Hydrocodone	3.56	1.48E−03	2.0	2.3	43.2	21.3
Acetaminophen	142.89	5.18E−03	200.6	240.7	71.3	21.0
Ibuprofen	179.31	6.49E−03	306.8	371.4	75.4	20.0
Indomethacin	63.72	3.85E−03	69.2	81.2	65.2	22.1
Diclofenac	280.00	2.77E−03	231.5	268.3	57.8	22.5
Ketoprofen	153.09	6.29E−03	257.9	308.5	74.8	20.1
Naproxen	90.53	7.84E−03	185.1	226.5	78.3	19.1
Piroxicam	4.32	5.35E−03	6.2	7.4	71.6	21.2
Meloxicam	1.58	4.68E−03	2.0	2.4	69.2	21.5
Tenoxicam	bld	2.97E−03	–	–	–	–
Erythromycin	12.66	8.22E−04	5.6	6.7	30.2	17.5

Table 1 (*continued*)

Compound			Emission[b,c] (mg·1000 inhab^{-1}·d^{-1})		River attenuation[c] (% removed)	
	C_{max} ng·L^{-1}[a]	k (h^{-1})	Mean	Std.dev.	Mean	Std.dev.
Pharmaceuticals & hormones						
Azithromycin	12.20	5.04E−04	4.7	6.0	21.2	13.6
Clarithromycin	28.33	7.81E−04	12.1	14.5	29.4	17.2
Tetracycline	17.01	1.88E−03	10.9	12.7	48.8	22.1
Sulfamethoxazole	41.91	2.80E−03	35.2	41.2	57.8	22.9
Trimethoprim	150.43	3.15E−03	136.1	158.9	60.7	22.7
Metronidazole	10.07	4.27E−03	12.0	14.2	67.3	21.8
Metronidazole-OH	6.20	4.95E−03	8.3	9.9	70.3	21.4
Ofloxacin	43.55	1.44E−03	24.3	28.4	42.8	21.2
Ciprofloxacin	20.00	2.39E−03	14.9	17.2	54.5	22.5
Cephalexin	5.08	1.27E−02	16.8	20.7	85.2	15.5
Bezafibrate	24.55	4.68E−03	31.6	37.1	69.2	21.6
Gemfibrozil	302.67	5.11E−03	421.6	511.6	71.1	21.2
Pravastatin	7.82	1.37E−02	27.6	34.5	85.8	15.4
Fluvastatin	3.90	7.87E−03	8.2	9.8	78.6	19.0
Atorvastatin	5.75	7.04E−03	10.7	12.9	76.9	19.4
Loratidine	4.29	2.21E−03	3.0	3.4	53.1	22.5
Desloratadine	10.27	2.05E−03	6.9	8.0	50.9	22.4
Ranitidine	18.44	2.31E−03	13.5	15.6	53.8	22.7
Famotidine	bld	3.08E−03	–	–	–	–
Cimetidine	19.42	3.37E−03	19.0	22.0	62.2	22.3
Atenolol	331.58	7.08E−03	622.8	760.8	76.8	19.5
Sotalol	223.81	4.85E−03	295.5	360.5	69.6	21.5
Metoprolol	295.56	4.90E−03	397.6	477.1	70.1	21.4
Propanolol	12.41	5.71E−03	19.1	22.8	72.9	20.8
Nadolol	4.82	4.78E−03	6.3	7.3	69.7	21.3
Enalapril	10.22	1.09E−02	29.0	36.2	83.2	16.8
Enalaprilat	91.20	1.53E−02	357.9	438.5	87.2	14.3
Diltiazem	31.80	3.73E−03	33.7	39.7	64.6	22.3
Irbesartan	141.10	4.25E−03	165.3	196.5	67.4	21.9
Losartan	126.88	2.16E−03	88.0	101.7	52.0	22.6
Valsartan	698.90	1.05E−02	1906.1	2328.7	82.4	17.4
Torasemide	9.43	2.15E−03	6.5	7.3	52.0	22.5
Fluoxetine	9.46	2.56E−03	7.4	8.5	56.4	22.6
Norfluoxetine	4.42	2.65E−03	3.6	4.2	56.9	22.7
Paroxetine	12.46	4.56E−03	15.4	18.0	69.1	21.7
Diazepam	35.51	3.78E−03	36.6	42.3	64.7	22.2
Lorazepam	187.87	3.23E−03	177.3	204.2	61.5	22.4
Alprazolam	4.98	2.23E−03	3.5	4.1	53.0	22.5
Carbamazepine	64.04	3.95E−03	71.2	84.1	65.7	22.2
Sertraline	144.87	1.81E−03	89.5	103.4	47.8	22.1
Citalopram	31.83	1.35E−03	16.6	19.4	41.0	20.7
Venlafaxine	127.62	1.71E−03	77.9	91.3	46.9	21.7
Olanzapine	20.19	1.48E−03	11.4	13.6	43.2	21.4
Trazodone	34.27	7.99E−04	14.8	17.8	29.7	17.3
Albendazol	5.11	5.11E−03	7.0	8.4	70.8	21.3
Thiabendazole	12.92	4.30E−03	15.2	18.2	67.3	22.1
Levamisol	37.85	4.30E−03	44.6	51.9	67.6	22.0
Dimetridazole	18.39	3.69E−03	19.2	22.4	64.5	22.3
Ronidazole	bld	4.99E−03	–	–	–	–
Xylazine	1.10	2.70E−03	0.9	1.0	57.6	22.6
Carazolol	6.43	5.18E−03	9.0	10.8	71.1	21.2
Azaperone	7.18	1.13E−03	3.5	4.1	37.2	19.7
Azaperol	2.19	1.45E−03	1.2	1.5	42.8	21.2
Dexamethasone	4.85	1.36E−03	2.6	2.9	41.4	20.8
Hydrochlorothiazide	793.33	2.13E−03	552.3	631.4	52.1	22.4
Furosemide	296.47	1.99E−03	200.0	229.9	50.5	22.3
Glibenclamide	4.61	2.27E−03	3.3	3.9	53.4	22.4
Warfarin	1.20	5.26E−03	1.7	2.0	71.5	21.0
Acridone	42.73	3.49E−03	42.6	49.9	63.0	22.4
Tamsulosin	0.67	3.67E−03	0.7	0.8	63.8	22.6
Salbutamol	16.82	5.40E−03	24.3	29.1	71.9	20.8
Amlodipine	23.52	4.31E−03	27.9	33.0	67.6	21.8
Clopidogrel	17.98	1.94E−03	11.6	13.3	49.7	22.3
Iopromide	1370.37	3.58E−03	1388.8	1624.7	64.0	22.3
Diethylstilbestrol (DES)	bld	4.17E−03	–	–	–	–
Estradiol (E2)	2.17	2.94E−03	1.9	2.3	59.2	22.6
Estradiol 17-glucuronide (E2-17G)	bld	5.52E−03	–	–	–	–
Estriol (E3)	5.69	3.52E−03	5.7	6.6	63.3	22.5
Estriol 16-glucuronide (E3-16G)	bld	8.95E−03	–	–	–	–
Estriol 3-sulfate (E3-3S)	12.78	2.70E−03	10.4	11.9	57.2	22.8
Estrone (E1)	6.21	2.28E−03	4.5	5.2	53.6	22.6
Estrone 3-glucuronide (E1-3G)	4.03	4.67E−03	5.1	6.0	69.1	21.7

(*continued on next page*)

Table 1 (*continued*)

Compound	C_{max} ng·L^{-1}[a]	k (h^{-1})	Emission[b,c] (mg·1000 inhab^{-1}·d^{-1})		River attenuation[c] (% removed)	
			Mean	Std.dev.	Mean	Std.dev.
Pharmaceuticals & hormones						
Estrone 3-sulfate (E1-3S)	bld	1.75E−03	–	–	–	–
Ethinyl estradiol (EE2)	bld	1.71E−03	–	–	–	–
Caffeine	1220.90	4.38E−03	1472.8	1696.0	67.7	22.0
Perfluoroalkyl substances (PFASs)						
L-PFOS	2708.71	2.80E−04	961.4	1217.0	13.2	9.3
L-PFHxS	33.18	6.04E−04	13.2	16.5	24.3	15.1
PFBA	111.17	2.99E−03	98.5	112.5	59.7	22.5
PFPeA	5.26	2.03E−03	3.5	4.1	50.7	22.4
PFHxA	25.15	1.38E−03	13.6	15.4	41.8	20.7
PFHpA	30.93	9.42E−04	14.3	17.4	33.1	18.4
PFOA	146.40	6.41E−04	60.7	81.3	25.6	15.7
PFNA	52.36	4.36E−04	19.5	24.3	18.9	12.4
i,p-PFNA	0.19	3.55E−04	0.1	0.1	16.0	10.9
PFDA	54.31	2.97E−04	19.0	23.6	13.9	9.7
PFUdA	3.65	2.02E−04	1.3	1.7	9.9	7.2
PFDoA	7.92	1.38E−04	2.6	3.3	7.0	5.2
PFTrDA	9.75	9.37E−05	3.2	4.3	4.9	3.8
PFTeDA	7.59	6.38E−05	2.5	3.2	3.4	2.6
PFHxDA	4.25	2.96E−05	1.4	1.9	1.6	1.2
PFODA	0.00	1.37E−05	–	–	–	–
L-PFBS	25.69	1.30E−03	13.7	16.5	40.1	20.7
L-PFHpS	bld	4.11E−04	–	–	–	–
L-pPFNS	12.00	1.06E−04	3.9	5.4	5.5	4.2
L-PFDS	0.82	1.30E−04	0.3	0.3	6.6	4.9
PFOSA	bld	2.08E−04	–	–	–	–
Personal care products						
2,2′-Dihydroxy-4-methoxybenzophenone (DHMB)	bld	4.86E−03	–	–	–	–
4,4′-Dihydroxybenzophenone (4DHB)	153.00	4.59E−03	191.2	223.0	68.6	21.9
4-Hydroxybenzophenone (4HB)	1.70	4.50E−03	2.1	2.5	68.6	21.7
4-Methylbenzylidene camphor (4MBC)	9.30	1.92E−03	6.0	7.0	49.6	22.2
Benzophenone-1 (BP1)	15.40	4.63E−03	19.5	23.1	69.0	21.5
Benzophenone-2 (BP2)	bld	4.86E−03	–	–	–	–
Benzophenone-3 (BP3)	44.10	4.77E−03	57.0	67.3	69.5	21.6
Ethyl 4-aminobenzoate (Et-PABA)	bld	5.77E−03	–	–	–	–
Ethylhexyl dimethyl PABA (OD-PABA)	2.10	5.10E−03	2.9	3.6	70.5	21.3
Ethylhexyl methoxycinnamate (EHMC)	41.00	9.21E−03	99.0	122.8	80.8	17.8
Octocrylene (OC)	27.00	6.17E−03	44.2	52.2	74.6	20.1
Triclorocaraban	bld	1.39E−03	–	–	–	–
Triclosan	13.63	1.81E−03	8.4	9.6	48.2	21.9
Propylparaben	20.21	7.16E−03	38.0	45.7	76.7	19.7
Benzylparaben	6.69	6.42E−03	11.4	13.9	75.1	20.3
Ethylparaben	40.69	7.41E−03	79.8	97.0	77.6	19.2
Methylparaben	50.94	7.67E−03	101.3	122.2	78.1	18.9
Illicit drugs						
(−)-9-THC	bld	3.83E−03	–	–	–	–
(±)-11-hydroxy-THC	bld	4.59E−03	–	–	–	–
(±)-11-nor-9-carboxy-9-THC	bld	6.86E−03	–	–	–	–
Cannabidiol	bld	4.67E−03	–	–	–	–
Cannabinol	bld	3.87E−03	–	–	–	–
(±)-Amphetamine	bld	4.89E−03	–	–	–	–
(±)-Methamphetamine	0.38	4.72E−03	0.5	0.6	69.3	21.6
(±)-MDMA	56.80	5.46E−03	83.0	101.4	72.0	21.1
(±)-EDDP perchlorate	49.50	1.71E−03	30.0	34.5	46.9	21.9
(±)-Methadone hydrochloride	20.00	3.23E−03	18.7	21.9	61.1	22.5
1S,2R (+)-Ephedrine	88.60	6.36E−03	147.5	179.0	75.0	20.0
Cocaine	23.80	4.51E−03	28.8	33.9	68.2	21.7
Cocaethylene	bld	4.35E−03	–	–	–	–
Benzoylecgonine	44.00	6.09E−03	71.0	84.1	74.1	20.3
Heroin	bld	2.97E−03	–	–	–	–
Morphine	3.02	2.23E−03	2.2	2.5	53.4	22.4
6-Acetylmorphine	bld	2.38E−03	–	–	–	–
LSD	bld	2.46E−03	–	–	–	–
2-Oxo-3-hydroxy LSD	bld	2.93E−03	–	–	–	–

[a] bld: below limit of detection.
[b] Emissions calculated assuming 1,500,000 inhabitants in the basin.
[c] Mean and standard deviation obtained after application of Monte-Carlo method (15,000 runs).

during the travel time, which can be expressed as a first order exponential decay. Since many of the compounds might have both point and non-point emission sources, these were assumed to be evenly distributed throughout the whole basin upstream a given site and the variable travel distances are approximated by an integral. The second feature of the model refers to the uncertainty implicit in most of the parameters

taking place in the calculations (concentrations, flow, river distance, elimination constants, etc.), which is conveniently handled using a Monte-Carlo simulation framework. Output emissions are thus given as statistical distributions (characterized by a mean and a standard deviation) rather than as a single estimate.

2.4.1. Emissions

Let us consider a site in the basin that it is in principle affected by all the emissions occurring upstream. The observed mass flow Φ_i of compound i at this point is given by:

$$\Phi_i = C_i \times Q \tag{1}$$

where C_i is the concentration of compound i and Q is the river flow.

In turn, the mass-flow Φ_i of compound i at the observation site depends on the emissions produced anywhere in the basin at distance ξ upstream to that point, corrected by the decay produced during the travel time along such distance. Since ξ may vary depending on where the point is located it can be represented by the following integral extended along the whole basin:

$$\Phi_i = \int_0^L E_i(\xi) \cdot \exp\left(\frac{-k_i \cdot \xi}{v_\xi}\right) d\xi \tag{2}$$

where $E_i(\xi)$ is the emission of contaminant i at distance ξ upstream from the sampling site, k_i is an overall pseudo-first order elimination constant of compound i (see Section 3 for details), and v_ξ is the average water linear velocity between the sampling point and the point at distance ξ. The integral is extended along the distance of influence in the basin. That is from 0 to L, being the latter an appropriate measure of the basin length. Here we used the basin equivalent diameter d, i.e., $d = 2 \times (\text{basin area} / \pi)^{1/2}$. Other alternatives, such as the mainstream length, are obviously possible.

In order to handle the above integral with minimal information, the following assumptions are taken: 1) for a given flow Q the velocity v_ξ is supposed constant along the whole river (denoted v hereafter) (this assumption is later relaxed in the Monte-Carlo uncertainty analysis) and 2) the emissions are supposed uniformly distributed along the river path, and therefore can be averaged as constant $\left(\overline{E}_i = \frac{\mathbf{E_i}}{L}\right)$. Eq. (2) thus becomes:

$$\Phi_i = \overline{E}_i \cdot \int_0^L \exp\left(\frac{-k_i \cdot \xi}{v}\right) d\xi. \tag{3}$$

Those assumptions are obviously not exact although they may be accepted as a first approximation to model a large number of compounds in non-ideal situations in terms of information availability, particularly about the exact location and magnitude of point and non-point source emissions.

Solving the integral:

$$\Phi_i = \overline{E}_i \cdot \frac{v}{-k_i}\left(e^{-k_i \cdot L/v} - 1\right). \tag{4}$$

Note that the ratio L/v in Eq. (4) corresponds to the travel (or hydraulic retention) time τ of the river basin concerned:

$$\Phi_i = \overline{E}_i \cdot \frac{v}{-k_i}\left(e^{-k_i \cdot \tau} - 1\right). \tag{5}$$

From Eqs. (1) and (4), the emission per length unit of compound i is readily obtained:

$$\overline{E}_i = \frac{C_i \cdot Q \cdot k_i}{v \cdot \left(1 - e^{-k_i \cdot \tau}\right)}. \tag{6}$$

The total emission of compound i across the whole basin $\mathbf{E_i}$ is

$$\mathbf{E_i} = \overline{E}_i \times L. \tag{7}$$

The percentage of load of compound i eliminated by in-stream processes river can be calculated as follows:

$$ES_i(\%) = 100 \times \left(1 - \frac{\Phi_i}{\mathbf{E_i}}\right). \tag{8}$$

2.4.2. Water velocity

Advection velocity of river water v is related to the flow by means of a Manning type equation parameterized according Pistocchi and Pennington (2006) for European rivers:

$$v = 0.37 \cdot Q^{0.4}. \tag{9}$$

Such relationship is maintained throughout the Monte-Carlo simulation as explained below, so that velocities are always calculated from flow discharges Q.

2.4.3. Attenuation constants

The overall depletion constant for each contaminant i referred to as k_i is supposed to follow pseudo-first order kinetics. They involve any biotic and abiotic elimination processes, including biodegradation, hydrolysis, photolysis, sorption to particulate material and volatilization, among others. Values reported in the literature show in general a broad variation and often they do not clearly specify which processes they encompass. Field studies are also inconclusive as pointed out by Kunkel and Radke (2011). In general, it seems that they are specific to each river site. Here, we used the estimated values obtained from BIOWIN 4 (Boethling et al., 1994) (see Tables 1 and 2) as base-line (minimum) values since they only reflect biodegradation. BIOWIN provides ranges of classes (i.e., five classes, namely, class 5 degradable in hours; class 4 degradable in days; class 3 degradable in weeks; class 2 degradable in months and 1 degradable in years), so that half-life values $H_{1/2}$ (h) obtained from BIOWIN 4 were subsequently converted to elimination constants k (h^{-1}) by interpolation using the suggested default values proposed by Aronson et al. (2006) (Table 2). It must be emphasized that k_i values for a few compounds, estimated by regression using direct concentration measurements at different flow regimes in the same river (Osorio et al., 2012), were significantly higher, typically exceeding by one or two orders of magnitude those obtained from BIOWIN 4 shown in Table 1. It suggests that in addition to biodegradation the contribution of other depletion processes like absorption/desorption onto particulate material and sediments or photodegradation cannot be disregarded. Such variation has been taken into consideration on setting the bounds of k_i in the Monte-Carlo step, as explained below.

2.4.4. Uncertainty estimation

The overall variation in $\mathbf{E_i}$ was estimated for all compounds showing non-zero concentration (158) using a Monte-Carlo approach. This allows

Table 2
Ranges of compound classes according BIOWIN, with half-lives and attenuation constants.

BIOWIN class range		Half-life	Attenuation constant
From	To	$H_{1/2}$ (h)	k_i (h^{-1})
4.25	4.75	30	2.31E−02
3.75	4.25	55.92	1.24E−02
3.25	3.75	208.08	3.33E−03
2.75	3.25	360	1.93E−03
2.25	2.75	900	7.70E−04
1.75	2.25	2880	2.41E−04
1.25	1.75	5760	1.20E−04
0	1.25	17,280	4.01E−05

Table 3
Variable distribution used in the Monte Carlo sensitivity analysis.

Variable	Symbol	Units	Distribution[a]	Remarks
Concentration	C	ng L^{-1}	U(C_{max}, C_{min})	C_{max} = max concentration measured; C_{min} = 0
Discharge	Q	m^3 s^{-1}	LN(2.01, 0.86)	Q measured (last 10 years)
Attenuation constant	k	h^{-1}	U(k_{max}, k_{min})	k_{max} = 50 · k; k_{min} = k estimated from BIOWIN
Length	L	km	U(159.8, 79.4)	Max = 2 · basin diameter; Min = 1/2 · basin diameter

LN(m, sd) denotes lognormal distribution with mean m and standard deviation sd.
[a] U(a,b) denotes uniform distribution between a = max and b = min.

varying simultaneously all the parameters involved, namely C_i, Q, L, k_i, and the secondary (calculated) parameters τ and v between certain bounds (Table 3). C_i was varied between its maximum and minimum values obtained from monitoring in the whole basin (typically these included 28 measurements) and Q was publicly available from measured values recorded by the water authority Agència Catalana de l'Aigua (ACA) in existing gauge stations. Primary parameters C_i, L and k_i were allowed to randomly vary between a *max* and *min* bounds using uniform distributions, whereas Q was varied using a log-normal distribution (Ritzema, 1994) characterized by *mean* and *standard deviation* obtained from log-transformed monthly flow values recorded for the last 10 years (February 2004–February 2014). L was varied between $2d$ and $d/2$ (d: basin diameter); it should be noted that for the Llobregat catchment mainstream length approximately equals $2d$. k_i was estimated as explained above and allowed to vary according to a uniform distribution using $k_{i\ (BIOWIN)}$ value as minimum and $50\times k_{i\ (BIOWIN)}$ as maximum. Choice of this factor was supported on our previous studies in the same river, as explained in the previous section (Osorio et al., 2012). Variation bounds for secondary parameters v and τ were derived accordingly from Eqs. (5) and (9) by introducing variability in the corresponding primary variables (Q and L) used in their computation. The Monte-Carlo calculation was run 15,000 times. Values for the emission $\mathbf{E_i}$ and river attenuation (%) are given in Table 1 and correspond to the mean and standard deviation of the distributions obtained after the Monte-Carlo calculations. Both are stable to <5% of variation. The relative sensitivity S_{E_iX} of the different parameters X ($X = C_i$, k_i, Q, L, τ and v) to the overall variation of $\mathbf{E_i}$ was calculated by using the following equation (MacLeod et al., 2002; Osorio et al., 2012):

$$S_{E_iX} = \frac{\sigma_{E_i}}{\sigma_X} \cdot \frac{\mu_X}{\mu_{E_i}} \tag{10}$$

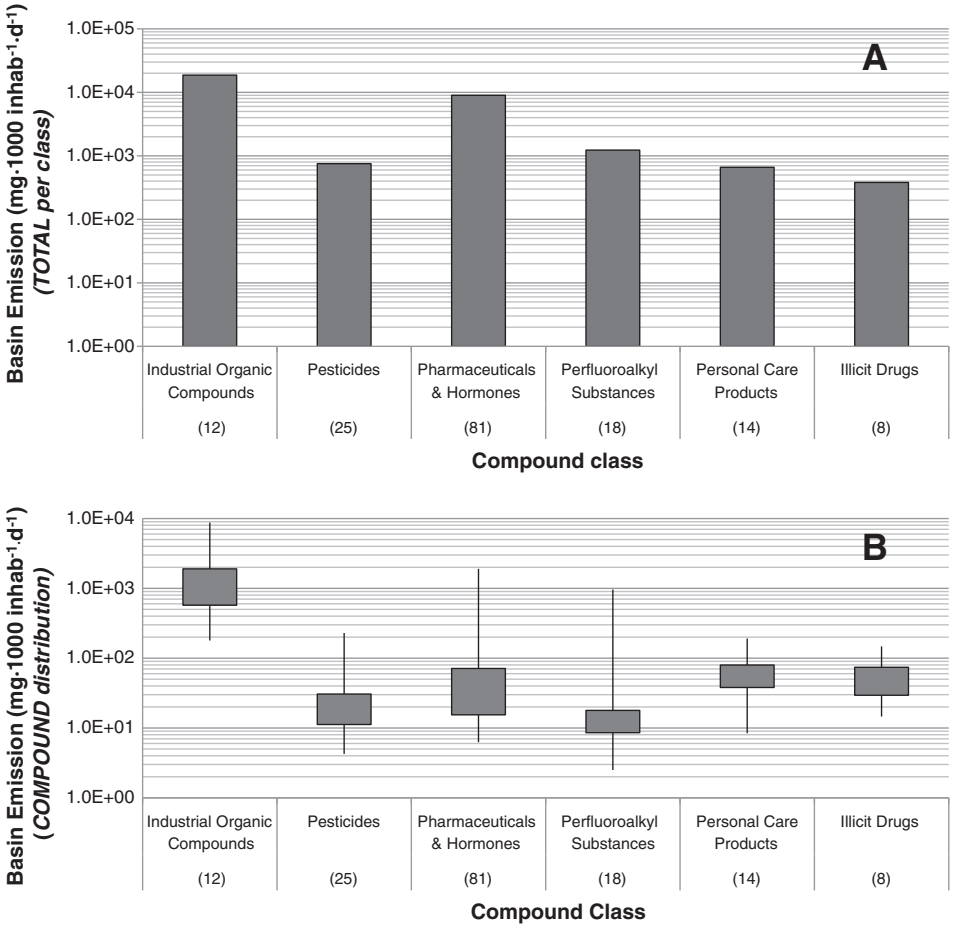

Fig. 2. Emission loads for the different compound classes. Number of compounds on each class is indicated in parentheses. (A) Aggregated basin emissions (mg 1000 $inhab^{-1}\cdot d^{-1}$) for each compound class. (B) Range of basin emissions (mg 1000 $inhab^{-1}\cdot d^{-1}$) per single compound within each class. Boxes correspond to quartiles 50 and 75 and whiskers to quartiles 25 and 100.

where σ and μ are the standard deviations and averages of subscript variables, respectively.

3. Results and discussion

3.1. Emission factors

The average emission factors expressed in mg·1000 inhab^{-1}·d^{-1} for the organic contaminants studied showed substantial variability as expressed by the standard deviation of the distribution obtained after the Monte-Carlo analysis (Table 1). In terms of sums of all compound in the different classes considered, emissions were dominated by industrial compounds and pharmaceuticals (Table 1, Fig. 2A), both in the range of 10^4 mg·1000 inhab^{-1}·d^{-1}, roughly exceeding those of the other remaining groups (personal care products, pesticides, PFASs and illegal drugs) by one order of magnitude. However these figures are somehow misleading since they are strongly dependent on the total number of compounds analyzed for each class. A slightly different picture is obtained if one considers the distribution ranges per compounds within each class (Fig. 2B). Industrial compounds are still dominant (range of ca. 10^3 mg·1000 inhab^{-1}·d^{-1}) over the other classes, being pharmaceuticals, PCPs and drugs about one order of magnitude less, and pesticides and PFASs occupying the last positions. Despite its apparent large contribution as a group, pharmaceuticals and hormones, if considered on a single compound basis, are closer to the other groups. This is due to the fact that they are represented by 81 compounds in our monitoring campaign, which is significantly higher than the number of compounds included in the other classes (12 industrial compounds, 25 pesticides, 18 PFASs, 14 personal care products and 19 illegal drugs).

Industrial compounds (Table 1) are dominated by triazoles (benzotriazole and tolyltriazole) used as anticorrosion agents, both showing estimated emissions in the range of 10^3 to 10^4 mg·1000 inhab^{-1}·d^{-1}. They were followed by bisphenol A and some flame retardants belonging to the trialkyl phosphates family, and by the group of alkylphenols (nonylphenol and octylphenol) together with some ethoxylated derivatives. These result from the biodegradation of the corresponding polyethoxylated compounds used as tensioactives in industry (range 10^2 to 10^3 mg·1000 inhab^{-1}·d^{-1}). Nonylphenol monocarboxylate (NP1EC) is the dominating compound in that class (2.8×10^3 mg·1000 inhab^{-1}·d^{-1}). It is worth noting that two compounds in the latter class (i.e., nonylphenol and octylphenol) are included in the list of priority compounds related to the WFD (Directive 2013/39/UE) (European Union, 2013).

Eighty-one pharmaceuticals and hormones out of the 89 analyzed belonging to different therapeutical classes have been positively detected in the Llobregat river basin, being their corresponding emissions in the range of 1 to 2×10^3 mg·1000 inhab^{-1}·d^{-1} (Fig. 2B). Compounds showing higher emissions were the diuretic hydrochlorotriazide, the antiinflammatories ibuprofen, diclofenac and ketoprofen, followed by the antilipidemic agent gemfibrozil, the antihypertensive valsartan, and the contrasting agent iopromide. Other antiinflammatories such as acetaminophen, naproxen and codeine, the antilipidemic bezafibrate, the beta blockers atenolol, sotalol, metoprolol, nadolol or the ACE inhibitor enalaprilat, the antibiotics ofloxacin and trimethoprim or psychiatric drugs carbamazepine and lorazepam show relevant emission values as well. Emission of estrogenic hormones such as estradiol (E2), estriol (E3) and its sulfate conjugate and estrone are estimated in the range of 2 to 10 mg·1000 inhab^{-1}·d^{-1}.

PFASs are hazardous compounds (Fàbrega et al., 2013) largely used both in the industry and consumer products (Pérez et al., 2013). Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most relevant, being the former recently included in the list of priority compounds of the WFD (Directive 2013/39/UE) (European Union, 2013). Among the 18 PFCs studied, PFOS and PFOA are the most relevant, showing emissions of ca. 960 and 60 mg·1000 inhab^{-1}·d^{-1}, respectively. Their emissions have been correlated to the amount of population living in the basin (Pistocchi and Loos, 2009). Using the models developed by these authors for European basins (E_{PFOS} (kg·y^{-1}) $= 9.6 \times 10^{-6} \times$ Pop$^{1.0115}$; E_{PFOA} (kg·y^{-1}) $= 1.4 \times 10^{-7} \times$ Pop$^{1.2841}$ with Pop = basin population), the emissions predicted are 30 and 22 mg·1000 inhab^{-1}·d^{-1} for PFOS and PFOA respectively. These estimations are lower than those found here, remarkably for PFOA. This can be possibly attributed to the substantial contribution of industrial effluents in the Llobregat River, particularly in the lowest part of the basin close to Barcelona. This is in agreement with the findings of Pistocchi and Loos (2009), who already highlighted the role of industrial effluents at European level.

As far as pesticides are concerned, 25 out of the 39 compounds analyzed were positively identified in the Llobregat basin. Even though in terms of overall emission, it is not a relevant group (ca. 750 mg·1000 inhab^{-1}·d^{-1}), from an environmental point of view pesticides are likely the group causing more risk to the aquatic ecosystems (Köch-Schumeyer et al., 2012; Kuzmanovic et al., 2015). Individual compounds' emissions are typically in the range of 10 to 10^2 mg·1000 inhab^{-1}·d^{-1}, being the most relevant the herbicides diuron and simazine (both included in the WFD priority list) as well as the insecticides diazinon, dimethoate and malathion.

Personal care products (17 compounds) included UV-filters (11), disinfectants (2) and antioxidants (parabens) (4). Overall emissions are ca. 660 mg·1000 inhab^{-1}·d^{-1} (Fig. 2A). Top compounds are methyl and propylparabens, triclosan (disinfectant) and UV filters benzophenone-3, 4,4′-dihydroxybenzophenone (4DHB) and ethyl hexylmethoxycinamate (EHMC), all of them in the range of ca. 50 to 200 mg·1000 inhab^{-1}·d^{-1}.

Drugs of abuse monitored included 19 compounds belonging to several subfamilies such as cannabinoids, lysergic acid derivatives, cocainics, amphetaminics and opioids. Overall emissions were ca. 380 mg·1000 inhab^{-1}·d^{-1} (Fig. 2A). Among the 8 compounds detected, the most relevant compounds were amphetaminics EDDP, MDMA (ecstasy) and ephedrine (used also as pharmaceutical), methadone, cocaine and its metabolite benzoylecgonine, with emission factors between 30 and 150 mg·1000 inhab^{-1}·d^{-1}. Results obtained are consistent with estimations of consumptions in other Spanish basins, according to data from WWTP outlets measurements (Thomas et al., 2012).

It is worth mentioning the specific case of caffeine, which is not included in any of the above families. This compound, commonly discharged from WWTPs, is originated by the population consumption of coffee, tea and soft drinks, being a well known tracer of urban pollution (Buerge et al., 2003; Zarrelli et al., 2014). Although it is not expected to cause acute effects in ecosystem, it is detected in 93% of the samples in concentrations up to 1.2 μg·L^{-1}. Its emission in the Llobregat basin has been estimated in 1400 mg·1000 inhab^{-1}·d^{-1}.

Finally, for the sake of comparison, emission factors calculated by other authors for some selected compounds are presented in Table 4. Values compared include those obtained by Pistocchi et al. (2012) using two sets of elimination constants (k = 0, i.e., no decay and k = $2.88 \cdot 10^{-2}$ h^{-1} corresponding to an average half-life of 24 h) and those presented by the same author based on his literature survey. First of all, it must be stressed that for all compounds considered emission estimates cover a broad range of values, usually exceeding one order of magnitude thus underlining the uncertainty involved in those calculations. In general, our results are within the low side of the range particularly for some pharmaceuticals like carbamazepine, bezafibrate and sulfamethoxazole. Overall, this justifies the need of performing an uncertainty analysis as presented in Section 3.3.

3.2. River removal of contaminants

In-stream removal of pollutants may be seen as a 'detoxification' process provided by the aquatic environment, and in that sense it could be truly qualified as an ecosystem service related to water purification. Elimination of organic micropollutants in the river encompasses several biotic and abiotic processes such as biodegradation, sorption by

Table 4
Comparison of emission factors obtained in this work with previously reported values for some selected compounds.

Compound	Reported emission factors (collected by Pistocchi et al., 2012) (mg·1000 inhab^{-1}·d^{-1})		Emission estimation by inverse modeling (Pistocchi et al., 2012) (a) (mg·1000 inhab^{-1}·d^{-1})		Emission estimation by inverse modeling (this work) (mg·1000 inhab^{-1}·d^{-1})
	Min	Max	$k = 0$ (no decay)	$k = 2.88 \cdot 10^{-2}$ h^{-1} (b)	
Benzotriazole	927	4113	233.28	4579.2	2283.4
Nonylphenol	28	2531	8.64	241.92	190.7
NPE1C	200	1356	69.12	1503.36	2837.8
Octylphenol	0.7	18.8	4.32	34.56	144.3
Bisphenol A	21.9	2542	129.6	561.6	655.2
Caffeine	60	3429	190.08	2229.12	1472.8
Estrone	0.43	5	1.728	8.64	9.5
Naproxen	25	2310	8.64	103.68	185.1
Ketoprofen	6.3	136	6.91	103.68	257.9
Bezafibrate	87	800	17.28	345.6	31.6
Ibuprofen	32	2510	34.56	285.12	306.8
Diclofenac	75	629	17.28	302.4	231.5
Gemfibrozil	91	589	8.64	103.68	421.6
Carbamazepine	42	580	190.08	1321.92	71.2
Sulfamethoxazole	24	160	25.92	596.16	35.2

(a) Linear model.
(b) It corresponds to a half-life of 24 h.

sediments and suspended particulate material, photolysis, hydrolysis, volatilization, etc. Most of these processes depend on the physical-chemical properties of the compounds involved, but also on the environmental conditions as well. For instance, sorption onto sediments or suspended solids is characterized by the partition coefficient of the compound (K_d), but more specifically it depends both on the lipophilicity of the compound itself and the organic carbon content of the sediments. For weakly acidic or basic compounds water pH influences its dissociation equilibrium (pK) and hence its sorption actual behavior. Furthermore effects of temperature changes on kinetic and equilibrium processes cannot be neglected. Overall, this results on a complex set of processes specific for every compound and highly variable on space and time along the river, whose detailed modeling may be an almost unbearable task (in any case it falls far beyond the scope of the present article) (Johnson et al., 2000, 2008; Jürgens et al., 2002). For a given pollutant the joint effect of the foresaid processes typically leads to its depletion as it separates in time and space from its emission source. Therefore, as first approach, it is accepted that it can be reasonably captured as a pseudo-first order decay process.

On the other hand hydrological conditions (i.e., river flow and water velocity) (Johnson, 2010) have direct effects on the concentration of pollutants. Besides the most obvious dilution effect, high flow may influence sediment re-suspension and re-dissolution of contaminants. Other less evident effects associated with high flows are reduction of hydraulic travel time (and consequently reduction of reaction time) and increase of turbidity in the water column thus decreasing light penetration and the associated photolytic reactions. Previous studies support the evidence that in-stream attenuation is highly variable and strongly dependent on the local environmental conditions (Kunkel and Radke, 2011; Johnson et al., 2008; Boxall et al., 2014). The complexities embodied in all these processes require a suitable and explicit handling of uncertainties thus justifying further the Monte-Carlo approach chosen here.

The percentage of the original emissions that has been depleted by in-stream processes for the different compounds showed an average of 58%, although huge variability was apparent in terms of both the different compounds and the dispersion showed by the individual compounds (Table 1). Percent elimination ranged from 1.6% to 90%, and the standard deviation of the distributions after the Monte-Carlo analysis showed an average of 19% with respect to the mean elimination. As for the different classes, the rates of elimination were, on average, around 60 to 70% for all classes (Fig. 3), except for PFASs, which were poorly eliminated ca. 20% on average and can be therefore considered as persistent (i.e., *quasi* conservative).

Although the attenuation constant was variable up to a factor of 50 during Monte-Carlo computations, the average percent elimination of the different contaminants is still strongly related to the original value from BIOWIN (Kendall's tau = 0.99, $p < 0.0001$, $n = 158$). Therefore,

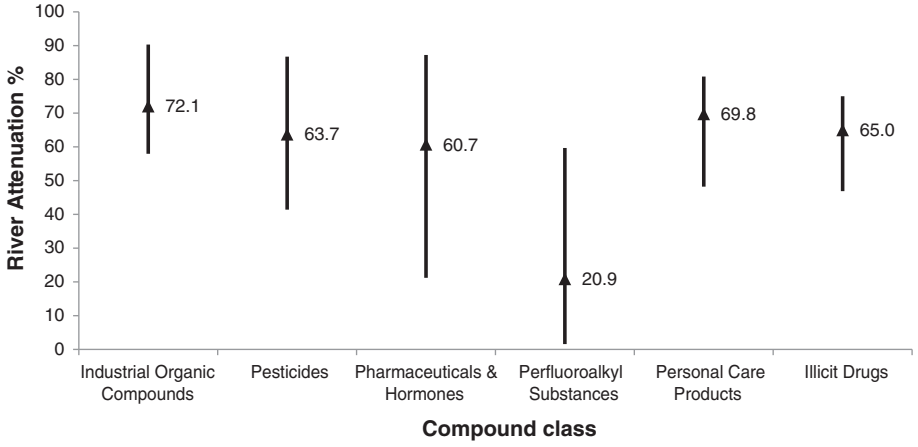

Fig. 3. Ranges of river attenuation (%) per single compound within each class. Mean value is indicated by a black triangle (▲).

our results may show the potential uncertainty associated with these values and the overall effect on contaminant retention in rivers, but should not be considered as an independent estimation of attenuation rates. This means that if we have to consider BIOWIN estimates as very rough approximations to attenuation rates for particular compounds, this limitation also applies for our study.

In any case, our results strongly suggest that in-stream biotic and abiotic processes have a major role on the fate of pollutants, and more research is needed to constrain the still uncertain mechanisms behind their elimination and the overall decay rates. This is particularly true for pharmaceuticals, which showed the widest ranges in percent river attenuation (Fig. 3). This fact can be explained by the broad variety of chemical structures encompassed in this group and the corresponding differences on their physical–chemical properties.

3.3. Uncertainty and sensitivity analysis

Uncertainties associated with the emissions of the different compounds are given in the form of standard deviations in Table 1. In general, they show coefficients of variation (CV%) of c.a. 120% (CV% = 100 × std.dev./average) thus reflecting the propagation effect of the corresponding uncertainties of the different variables involved in the calculations and evidenced after the Monte-Carlo process.

In order to have some insight in the role played by the different variables involved in the emission estimation, i.e., the primary variables (C, Q, k and L) as well as the secondary variables τ and v, the respective sensitivities have been calculated for the compounds positively identified in the catchment (158) using Eq. (10). Results are depicted in Fig. 4. For the intervals chosen for the different variables, all show sensitivities exceeding 1 (between 1.1 and 3.5). This means that all tend to amplify the variation of the emission, with river velocity (v) and basin length (L) showing the highest sensitivity value (about 3.5), followed by residence time (τ) (sensitivities about 2.35), attenuation constant k (2.2) and concentration (2.1). Discharge Q exhibited the lowest values (slightly over 1). However Q is involved in the calculation of the secondary variables v and τ.

3.4. Limitations of the approach

As seen in the preceding sections, our emission estimation based on inverse modeling seems to yield lower values than those based on direct emission. The only exceptions were those compounds characterized by low degradation rates and thus behaving as conservative (notably this is the case of some PFASs). Such a general trend is particularly evident for those families of compounds associated with population and industry like pharmaceuticals, personal care products, industrial compounds and illicit drugs.

Considering the different sources of uncertainty as described in the previous section, one of the main reasons of such underestimation is likely due to the assumption of uniform distribution of emissions upstream to the site which obviously is just an approximation. Population and industry are not evenly distributed throughout the entire basin. Instead, they are concentrated in the lowest area surrounding Barcelona. In our model this would directly affect the choice of L, possibly requiring a lower value in order to reflect more realistically the distribution of population and industry in the basin. Since L (and consequently also the residence time τ) was shown to be one of the most sensitive parameters this seems a relevant factor to be taken into consideration. In that respect, the GIS-based approaches (Feijtel et al., 1997; Anderson et al., 2004; Williams et al., 2009; Pistocchi et al., 2012; Boxall et al., 2014), which explicitly consider the catchment emission proportional to population distribution, could be advantageous, at least for substances associated with urban emission point sources (domestic and industrial origin). In turn, the uniform emission assumption would be more suitable for those substances associated with diffuse pollution sources such as pesticides. In contrast GIS based catchment models require a larger quantity of data (Johnson et al., 2008) as compared to the approach presented here, and may be unfeasible for certain applications at very large scales and regions lacking data.

4. Conclusions

Along the present contribution, the possibilities of applying inverse modeling have been explored to assess the emission to river of some organic micropollutants belonging to different families. The method is based on simple conceptual assumptions making it easy to apply. The use of Monte-Carlo simulation enables to quantify the uncertainty of the result on the basis of that of the parameters used. In spite of some limitations, overall the estimation of emissions by inverse modeling as presented here is simple and can provide a useful tool for management purposes in order to classify and quantify release rates of chemicals into the environment and providing support to managers in the implementation of regulations such as REACH, WFD or E-PRTR as well.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.03.055.

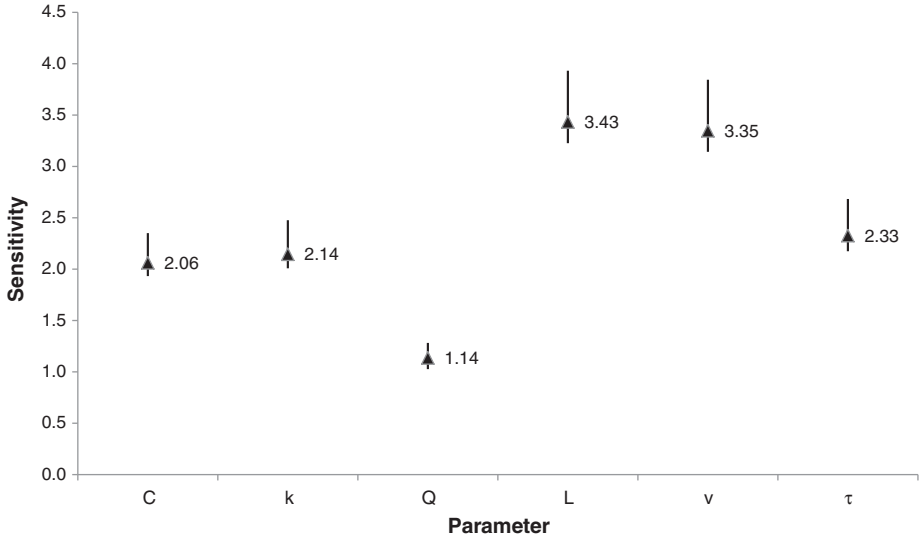

Fig. 4. Sensitivity of the emission values respect to the different variables calculated using Eq. (10) after application of Monte-Carlo simulation (15,000 runs) to the 158 compounds positively identified in the basin. Bars indicate maximum and minimum values; mean value is indicated by a black triangle (▲).

Acknowledgments

This study has been financially supported by the EU through the FP7 project GLOBAQUA (Grant Agreement No. 603629), by the Spanish Ministry of Economy and Competitiveness [project Consolider-Ingenio 2010 SCARCE CSD2009-00065] and by the Generalitat de Catalunya (Consolidated Research Groups: 2014 SGR 418—Water and Soil Quality Unit and 2014 SGR 291—ICRA). It reflects only the author's views. The Community is not liable for any use that may be made of the information contained therein. MK acknowledges an AGAUR fellowship from the Generalitat de Catalunya (Spain).

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