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**Assessment of non-steroidal anti-inflammatory and analgesic pharmaceuticals in
seawaters of North of Portugal: occurrence and environmental risk**

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Table S1 - Geographical location (GPS) of seawater sampling points and WWTPs in the study area

		Points number	Geographical location	
Seawater	Frente Urbana – Vila do Conde	1	41°21'29.84"N	8°45'25.59"W
	Mindelo – Vila do Conde	2	41°18'32.32"N	8°44'26.39"W
	Angeiras Norte – Matosinhos	3	41°16'4.74"N	8°43'39.65"W
	Azul Conchinha – Matosinhos	4	41°12'14.82"N	8°42'55.06"W
	Leça da Palmeira – Matosinhos	5	41°11'24.38"N	8°41'40.86"W
	Matosinhos – Matosinhos	6	41°10'34.09"N	8°41'40.86"W
	Castelo do Queijo – Porto	7	41°10'3.04"N	8°41'25.83"W
	Foz – Porto	8	41° 9'1.54"N	8°40'38.66"W
	Lavadores – Vila Nova de Gaia	9	41°7'40.30"N	8°40'5.48"W
	Miramar – Vila Nova de Gaia	10	41°4'0.63"N	8°39'27.71"W
	São Félix da Marinha – Vila Nova de Gaia	11	41°1'58.45"N	8°38'48.88"W
	Seca – Espinho	12	41°0'52.00"N	8°38'49.78"W
	Frente Azul – Espinho	13	41°0'41.96"N	8°38'49.78"W
	Espinho-Baía – Espinho	14	41°0'31.35"N	8°38'51.33"W
WWTPs	WWTP Parada, Maia	15	41°12'17.00"N	8°35'40.00"W
	WWTP Ponte Moreira, Maia	16	41°14'14.00"N	8°38'37.00"W
	WWTP Cambado, Maia	17	41°15'32.00"N	8°40'34.00"W
	WWTP Sobreiras, Porto	18	41° 8'52.82"N	8°39'29.24"W
	WWTP Freixo, Porto	19	41° 8'54.02"N	8°34'41.02"W
	WWTP Leça da Palmeira, Porto	20	41°12'42.92"N	8°42'49.37"W
	WWTP Gaia Litoral, Vila Nova de Gaia	21	41° 6'43.03"N	8°39'14.45"W
	WWTP Lever, Vila Nova de Gaia	22	41° 3'38.00"N	8°29'10.85"W
	WWTP Crestuma, Vila Nova de Gaia	23	41° 4'5.41"N	8°30'13.42"W
	WWTP Areinho, Vila Nova de Gaia	24	41° 8'7.19"N	8°35'12.40"W
	WWTP Febros, Vila Nova de Gaia	25	41° 7'5.08"N	8°34'15.76"W
	WWTP Ave, Vila do Conde	26	41°22'3.80"N	8°42'23.22"W
	WWTP Paramos, Espinho	27	40°58'28.00"N	8°38'52.00"W

Table S2- Informations on the beaches studied and their water quality (adapted from www.apambiente.pt).

City	Beach	Water quality classification*	River basin:	Bathing water description	Short term pollution (for less than 72 hours)	Potential microbiological pollution sources to bathing water	Potential for proliferation		
							Cyanobacteria	Macroalgae	Phytoplankton
Espinho	Espinho - Baía	Excellent	Coastal waters between Douro and Vouga	Urban beach with an extensive sand strip and rocky outcrops.	Unlikely	-	Unlikely	Likely	Unlikely
Espinho	Frente Azul	Good	Coastal waters between Douro and Vouga	Urban beach, with an extensive sand strip, bordered by an urban waterfront.	Unlikely, but may occur due to excessive flow of the tributary in rainfall situations, which leads to entrainment of the microbiological load.	Faecal contamination, which may originate mainly from the Mocho stream that empties near the beach.	Unlikely	Likely	Unlikely
Espinho	Seca	Sufficient	Coastal waters between Douro and Vouga	Urban beach with an extensive sand strip bordered by urban waterfront.	Unlikely, but may occur due to excessive flow of the tributary in rainfall situations, which leads to entrainment of the microbiological load. May also occur due to contamination of the rainwater network or from the discharge of untreated effluents, in the event of malfunction in the wastewater pumping station.	Faecal contamination which may originate mainly from the local sewerage and rainwater drainage networks or from the waterline (Mocho stream) that empties near the beach.	Unlikely	Likely	Unlikely
Matosinhos	Angeiras Norte	Good	Coastal waters between Ave and Leça	Rural beach with a small sand strip and rocky outcrops	Likely. May occur due to excessive flow of the tributary in rainfall situations, which leads to entrainment of the microbiological load. May also occur due to discharges of untreated effluents, in the event of malfunction in the WWTP.	Faecal contamination which may originate mainly from the local wastewater drainage network and the tributary to the beach (Onda river).	Unlikely	Likely	Unlikely
Matosinhos	Matosinhos	Good	Coastal waters between Ave and Leça	Urban beach with an extensive sand strip bordered by an urban waterfront.	Unlikely, but may occur due to excessive surface flow of the tributaries during rainfall situations, which leads to entrainment of the microbiological load. May also occur due the contamination of the rainwater and sewerage networks. May also happen due to the proximity of the Leixões harbour (fishing and mooring of cargo and passenger ships)	Faecal contamination which mainly originates from the rainwater network, from the tributaries (Leça river and Riguinha stream) that empty near the bathing water, from malfunction in the WWTP and from nearby vessels.	Unlikely	Likely	Unlikely
Matosinhos	Azul (Conchinha)	Sufficient	Coastal waters between Ave and Leça	Small urban beach surrounded by rocky outcrops, forming a small cove with specific characteristics	Unlikely, but may occur due to excessive surface flow of the tributary during rainfall situations, which leads to entrainment of the microbiological load. May also occur due to the discharge of untreated effluents in case of malfunction in the WWTP	Faecal contamination which may originate mainly from the local wastewater network and the from Boa Nova stream, that empties near the	Unlikely	Likely	Unlikely

City	Beach	Water quality classification*	River basin:	Bathing water description	Short term pollution (for less than 72 hours)	Potential microbiological pollution sources to bathing water	Potential for proliferation		
							Unlikely	Likely	Unlikely
Matosinhos	Leça da Palmeira	Excellent	Coastal waters between Ave and Leça	Urban beach with an extensive sand strip and rocky clusters	Unlikely, but may occur due to excessive surface flow of the tributaries during rainfall situations, which leads to entrainment of the microbiological load. May also occur due to the contamination of the rainwater and sewerage networks. May also happen due to the proximity of the Leixões harbour (fishing and mooring of cargo and passenger ships).	Faecal contamination which mainly originates from the rainwater network, from the tributaries rivers that empty near the bathing water (Leça river and (Sardoal stream)), from malfunctions in the WWTP and from nearby vessels.	Unlikely	Likely	Unlikely
Porto	Castelo do Queijo	Sufficient	Coastal waters between Douro and Vouga	Wide sand strip bordered by an urban waterfront	Likely, may occur due to excessive flow of the tributaries in rainfall situations, which leads to entrainment of the microbiological load. May also occur due to discharges of untreated effluents, in the event of malfunction in the WWTP, or due to contamination of the rainwater or even from vessel contaminations.	Faecal contamination which may originate mainly from the tributary (Riguinha stream), from the local rainwater drainage and sewerage networks and from Leixões harbour. May eventually originate from the Leça and Douro rivers	Unlikely	Likely	Unlikely
Porto	Foz	Excellent	Coastal waters between Douro and Vouga	Urban beach with wide sand strip and rocky outcrops bordered by an urban waterfront	Unlikely, but may occur due to excessive flow of the tributaries in rainfall situations, which leads to entrainment of the microbiological load. May also occur due to discharges of untreated effluents, in the event of malfunction in the WWTP, or due to contamination of the rainwater network or from vessel contaminations	Faecal contamination which may originate mainly from the local rainwater drainage and sewerage networks and from Leixões harbour. May eventually originate from the Douro river	Unlikely	Likely	Unlikely
Vila do Conde	Frente Urbana	Excellent	Coastal waters between Cávado and Ave	Urban beach, with an extensive sand strip, bordered by an urban waterfront	Unlikely, but may occur due to excessive flow of the tributary in rainfall situations, which leads to entrainment of the microbiological load. May also occur due to contamination of the rainwater network or from ship spills.	Faecal contamination, which may originate mainly from the Ave river, from the rainwater network or from the fishing harbour	Unlikely	Likely	Unlikely
Vila do Conde	Mindelo	Excellent	Coastal waters between Cávado and Ave	Urban beach with an extensive sand strip bordered by a well consolidated dune system	Unlikely	—	Unlikely	Likely	Unlikely
Vila Nova de Gaia	Lavadores	Excellent	Coastal waters between Douro	Urban beach with a small sand strip,	Unlikely, but may occur due to excessive flow of the tributaries in rainfall	Faecal contamination which may originate	Unlikely	Likely	Unlikely

City	Beach	Water quality classification*	River basin:	Bathing water description	Short term pollution (for less than 72 hours)	Potential microbiological pollution sources to	Potential for proliferation		
			and Vouga	bordered by a concrete wall	situations, which leads to entrainment of the microbiological load. May also occur due to discharge of untreated effluents in the event of malfunction in the WWTP	mainly from the local sewerage network, but also from the tributary to the beach (Ralo stream) and Douro river			
Vila Nova de Gaia	Miramar	Excellent	Coastal waters between Douro and Vouga	Urban beach with an extensive sand strip and rocky outcrops. Beach bordered by a line of dunes	Unlikely, but may occur due to excessive surface flow of the drainage network and tributaries, in rainfall situations, which lead to the entrainment of the microbiological load. It may also occur due to eventual malfunctions in the wastewater lift station	Faecal contamination which may originate from the local sanitation network but also from the tributary to the beach (Espírito Santo stream)	Unlikely	Likely	Unlikely
Vila Nova de Gaia	São Félix da Marinha	Good	Coastal waters between Douro and Vouga	Urban beach with an extensive sand strip, bordered by a line of dunes	Unlikely, but may occur due to excessive surface flow of the drainage network and tributaries, in rainfall situations, which lead to the entrainment of the microbiological load. It may also occur due to eventual malfunctions in the WWTP	Faecal contamination which may originate from the local sanitation network but also from the tributary to the beach (Prego stream)	Unlikely	Likely	Unlikely

* Classification in 2012, to comply with Directive 2006/7/EC of the European Parliament and of the Council of 15 February 2006 concerning the management of bathing water quality and repealing Directive 76/160/EEC.

Table S3 – Optimized UHPLC-ESI-MS/MS conditions for the selected pharmaceuticals

Compound	Rt (min)	Precursor ion (m/z)	Product ion (Quantifier)				Product ion (Qualifier)				Ion ratio (\pm SD) (n = 6)
			Q1		Q3		Q1		Q3		
			Q3	Pre Bias (V)	CE (V)	Pre Bias (V)	Q3	Pre Bias (V)	CE (V)	Pre Bias (V)	
Acetylsalicylic acid	1.51	179	137	22	10	29	93	22	22	19	1.87 \pm 0.03
Acetaminophen	1.56	150	107	14	18	21	—	—	—	—	—
Carboxybupropfen*	2.68	235	191	12	8	14	73	12	17	15	1.39 \pm 0.02
Hydroxybupropfen*	2.72	221	177	11	8	21	—	—	—	—	—
Ketoprofen	3.90	253	209	13	8	23	—	—	—	—	—
Naproxen	3.96	229	170	10	17	19	169	10	35	18	1.01 \pm 0.01
Nimesulide	4.11	307	229	10	18	16	79	10	29	16	7.63 \pm 0.05
Diclofenac	4.34	294	250	14	12	18	35	14	24	13	13.04 \pm 0.04
Ibuprofen-d3	4.46	208	164	13	10	18	—	—	—	—	—
Ibuprofen	4.48	205	161	13	10	18	—	—	—	—	—

*Metabolite; CE – Collision energy

Table S4 – Ecotoxicological data (EC₅₀ or LC₅₀) reported in literature used to calculate PNEC for algae, daphnids and fish for the detected pharmaceuticals in seawaters

Compound	Fish	Daphnid	Algae	Reference
	EC ₅₀ or LC ₅₀ (mg L ⁻¹)	EC ₅₀ or LC ₅₀ (mg L ⁻¹)	EC ₅₀ or LC ₅₀ (mg L ⁻¹)	
Acetaminophen	378	2.04	134	(Dave and Herger, 2012; Henschel et al., 1997)
Acetylsalicylic acid	274.6	88.1	106.7	(Cleuvers, 2004; Praskova et al., 2012)
Diclofenac	0.09	18	7.5	(Cleuvers, 2003; Haap et al., 2008; Huschek et al., 2004)
Ibuprofen	>0.68	5.7	2.3	(Dave and Herger, 2012; Harada et al., 2008; Overturf et al., 2012)
Naproxen	52	37	3.7	(Harada et al., 2008; Straub and Stewart, 2007)
Ketoprofen	6.44	2.3	2.0	(Harada et al., 2008; Praskova et al., 2011)

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1 **Table S5** – Concentrations of pharmaceuticals (expressed in ng L⁻¹) for the different sampling campaigns in Vila do Conde seawaters

Frente Urbana beach				
	03/06/13	01/07/13	29/07/13	26/08/13
Acetaminophen	62.7	66.2	76.9	61.7
AAS	n.d.	n.d.	n.d.	n.d.
Carboxyibuprofen	n.d.	n.d.	n.d.	n.d.
Diclofenac	n.d.	n.d.	27.0	2.20
Hydroxyibuprofen	37.7	43.2	30.6	27.9
Ibuprofen	23.2	26.0	28.4	15.0
Naproxen	17.8	n.d.	30.9	17.4
Nimesulide	1.21	n.d.	n.d.	n.d.
Ketoprofen	15.4	14.6	14.4	14.3
Mindelo beach				
Acetaminophen	61.3	60.0	70.6	71.37
AAS	n.d.	n.d.	n.d.	n.d.
Carboxyibuprofen	n.d.	n.d.	n.d.	n.d.
Diclofenac	n.d.	n.d.	n.d.	n.d.
Hydroxyibuprofen	35.1	31.6	37.0	30.7
Ibuprofen	18.9	19.9	19.7	15.7
Naproxen	20.1	18.6	20.6	17.7
Nimesulide	1.76	n.d.	0.63	n.d.
Ketoprofen	19.5	13.7	16.3	12.3

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3 **Table S6** – Concentrations of pharmaceuticals (expressed in ng L⁻¹) for the different sampling campaigns in Matosinhos seawaters

Leça da Palmeira beach														
	04/06/13	18/06/13	25/06/13	02/07/13	09/07/13	16/07/13	23/07/13	30/07/13	06/08/13	13/08/13	20/08/13	27/08/13	03/09/13	10/09/13
Acetaminophen	62.3	—	—	54.2	—	—	—	57.7	—	—	—	62.0	—	—
AAS	n.d.	—	—	n.d.	—	—	—	n.d.	—	—	—	n.d.	—	—
Carboxyibuprofen	n.d.	—	—	n.d.	—	—	—	n.d.	—	—	—	n.d.	—	—
Diclofenac	n.d.	—	—	n.d.	—	—	—	2.88	—	—	—	4.17	—	—
Hydroxyibuprofen	31.5	—	—	26.7	—	—	—	29.4	—	—	—	27.8	—	—
Ibuprofen	18.7	—	—	9.54	—	—	—	14.3	—	—	—	15.9	—	—
Naproxen	18.7	—	—	n.d.	—	—	—	n.d.	—	—	—	20.4	—	—
Nimesulide	n.d.	—	—	0.46	—	—	—	n.d.	—	—	—	2.49	—	—
Ketoprofen	12.1	—	—	11.4	—	—	—	12.6	—	—	—	13.3	—	—
Angeiras Norte beach														
Acetaminophen	67.8	97.7	—	62.8	—	62.4	—	55.9	—	55.4	—	229	—	51.2
AAS	n.d.	n.d.	—	4.56	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Carboxyibuprofen	n.d.	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Diclofenac	n.d.	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Hydroxyibuprofen	35.6	32.0	—	31.1	—	29.3	—	28.5	—	26.7	—	28.4	—	27.6
Ibuprofen	27.6	12.9	—	16.4	—	16.9	—	16.4	—	8.21	—	10.6	—	10.4
Naproxen	18.4	18.6	—	n.d.	—	18.4	—	n.d.	—	17.4	—	n.d.	—	18.3
Nimesulide	n.d.	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Ketoprofen	12.3	51.0	—	11.9	—	16.2	—	13.0	—	11.4	—	15.9	—	12.1
Matosinhos beach														
Acetaminophen	65.8	70.7	—	58.1	—	85.6	—	62.5	—	80.4	—	67.2	—	69.3
AAS	n.d.	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.

Carboxyibuprofen	n.d.	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Diclofenac	n.d.	n.d.	—	n.d.	—	n.d.	—	n.d.	—	18.3	—	15.5	—	n.d.
Hydroxyibuprofen	60.2	34.8	—	26.1	—	36.9	—	28.4	—	29.6	—	26.9	—	28.3
Ibuprofen	53.1	25.4	—	39.6	—	29.4	—	6.21	—	5.91	—	24.3	—	21.8
Naproxen	25.2	21.9	—	n.d.	—	18.5	—	n.d.	—	25.4	—	n.d.	—	18.7
Nimesulide	n.d.	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Ketoprofen	27.2	12.9	—	17.4	—	12.3	—	11.5	—	14.6	—	12.4	—	13.2
Azul (Conchinha) beach														
Acetaminophen	104	78.3	69.6	56.3	276	58.2	60.0	89.6	123	110	303	178	464	65.6
AAS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Carboxyibuprofen	n.d.	n.d.	n.d.	n.d.	600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	356	n.d.	n.d.
Diclofenac	3.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	33.0	17.6	20.6	8.33	217	n.d.	n.d.
Hydroxyibuprofen	25.3	26.9	24.6	22.6	191	23.6	30.8	125	22.4	27.0	25.5	131	26.4	34.9
Ibuprofen	7.30	7.20	3.06	5.45	75.8	50.0	40.3	108	110	16.7	25.9	29.5	18.8	20.5
Naproxen	n.d.	18.2	n.d.	n.d.	n.d.	n.d.	17.9	58.8	17.4	24.5	n.d.	56.6	18.1	18.8
Nimesulide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.48	n.d.	n.d.	n.d.	n.d.
Ketoprofen	13.7	14.1	18.2	11.9	15.6	11.0	11.7	13.4	11.3	13.7	14.1	12.0	14.3	11.5

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6 **Table S7** – Concentrations of pharmaceuticals (expressed in ng L⁻¹) for the different sampling campaigns in Porto seawaters

Foz beach														
	04/06/13	18/06/13	25/06/13	02/07/13	09/07/13	16/07/13	23/07/13	30/07/13	06/08/13	13/08/13	20/08/13	27/08/13	03/09/13	10/09/13
Acetaminophen	58.8	—	—	61.1	—	—	—	56.4	—	—	—	225	—	—
AAS	n.d.	—	—	n.d.	—	—	—	n.d.	—	—	—	n.d.	—	—
Carboxyibuprofen	47.6	—	—	n.d.	—	—	—	n.d.	—	—	—	n.d.	—	—
Diclofenac	n.d.	—	—	n.d.	—	—	—	n.d.	—	—	—	n.d.	—	—
Hydroxyibuprofen	32.4	—	—	29.8	—	—	—	27.4	—	—	—	29.0	—	—
Ibuprofen	14.7	—	—	24.8	—	—	—	15.4	—	—	—	27.6	—	—
Naproxen	20.5	—	—	18.5	—	—	—	18.0	—	—	—	17.5	—	—
Nimesulide	n.d.	—	—	n.d.	—	—	—	n.d.	—	—	—	5.24	—	—
Ketoprofen	13.9	—	—	12.1	—	—	—	10.9	—	—	—	11.3	—	—
Castelo do Queijo beach														
Acetaminophen	58.6	144	103	86.59	66.8	62.5	72.0	58.9	112	181	559	584	58.0	270
AAS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Carboxyibuprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1227	n.d.	n.d.	63.4	270
Diclofenac	n.d.	n.d.	13.7	n.d.	n.d.	5.73	1.14	n.d.	16.4	32.5	45.7	36.0	n.d.	3.99
Hydroxyibuprofen	24.2	74.3	24.8	24.35	61.8	25.5	27.7	23.6	28.7	287	28.4	37.3	26.8	98.9
Ibuprofen	21.9	39.5	22.7	44.03	28.9	26.4	17.0	12.2	118	222	6.87	9.75	20.2	40.6
Naproxen	22.4	46.9	37.0	17.65	113	17.8	22.9	20.6	n.d.	20.3	91.3	102	n.d.	178
Nimesulide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ketoprofen	22.1	31.	16.8	11.57	15.6	11.8	12.0	10.6	11.1	13.4	12.6	13.8	11.9	12.9

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8

9 **Table S8** – Concentrations of pharmaceuticals (expressed in ng L⁻¹) for the different sampling campaigns in Vila Nova de Gaia seawaters

Lavadores beach								
	05/06/13	19/06/13	03/07/13	17/07/13	31/07/13	15/08/13	28/08/13	11/09/13
Acetaminophen	55.0	—	60.3	—	53.8	—	108	—
AAS	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Carboxyibuprofen	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Diclofenac	n.d.	—	n.d.	—	n.d.	—	241	—
Hydroxyibuprofen	34.4	—	26.6	—	26.7	—	116	—
Ibuprofen	12.3	—	28.6	—	14.3	—	30.1	—
Naproxen	n.d.	—	n.d.	—	19.4	—	71.3	—
Nimesulide	n.d.	—	n.d.	—	n.d.	—	0.69	—
Ketoprofen	13.2	—	10.9	—	10.8	—	13.7	—
Miramar beach								
Acetaminophen	64.4	—	98.6	—	53.2	—	55.0	—
AAS	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Carboxyibuprofen	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Diclofenac	3.53	—	n.d.	—	n.d.	—	n.d.	—
Hydroxyibuprofen	28.2	—	30.8	—	27.1	—	29.3	—
Ibuprofen	19.1	—	23.8	—	44.9	—	17.7	—
Naproxen	n.d.	—	n.d.	—	n.d.	—	n.d.	—
Nimesulide	n.d.	—	n.d.	—	n.d.	—	0.61	—
Ketoprofen	18.0	—	17.7	—	10.6	—	11.2	—
São Félix da Marinha beach								

Acetaminophen	61.4	75.7	55.4	57.5	53.3	56.0	61.7	55.4
AAS	n.d.	n.d.	5.34	n.d.	n.d.	n.d.	n.d.	n.d.
Carboxyibuprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diclofenac	n.d.	n.d.	n.d.	n.d.	2.36	n.d.	n.d.	n.d.
Hydroxyibuprofen	27.2	26.6	28.7	27.2	27.3	27.2	61.1	27.3
Ibuprofen	13.1	20.7	14.9	10.1	32.7	14.4	19.8	20.6
Naproxen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	17.7	n.d.
Nimesulide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.38
Ketoprofen	11.5	12.0	11.9	11.6	11.2	11.8	12.2	11.1

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12 **Table S9** – Concentrations of pharmaceuticals (expressed in ng L⁻¹) for the different sampling campaigns in Espinho seawaters

Espinho Baía beach														
	04/06/13	18/06/13	25/06/13	02/07/13	09/07/13	16/07/13	23/07/13	30/07/13	06/08/13	13/08/13	20/08/13	27/08/13	03/09/13	10/09/13
Acetaminophen	68.5	—	—	57.7	—	—	—	57.1	—	—	—	69.0	—	—
AAS	n.d.	—	—	n.d.	—	—	—	n.d.	—	—	—	n.d.	—	—
Carboxyibuprofen	n.d.	—	—	n.d.	—	—	—	236	—	—	—	n.d.	—	—
Diclofenac	n.d.	—	—	n.d.	—	—	—	39.4	—	—	—	n.d.	—	—
Hydroxyibuprofen	28.7	—	—	35.0	—	—	—	78.0	—	—	—	28.9	—	—
Ibuprofen	22.7	—	—	16.8	—	—	—	24.7	—	—	—	20.9	—	—
Naproxen	n.d.	—	—	n.d.	—	—	—	n.d.	—	—	—	n.d.	—	—
Nimesulide	n.d.	—	—	n.d.	—	—	—	n.d.	—	—	—	n.d.	—	—
Ketoprofen	89.7	—	—	37.0	—	—	—	11.5	—	—	—	13.9	—	—
Frente Azul beach														
Acetaminophen	156	78.8	—	—	—	54.5	—	64.6	—	58.1	—	58.5	—	52.0
AAS	5.12	n.d.	—	—	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Carboxyibuprofen	n.d.	n.d.	—	—	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Diclofenac	n.d.	n.d.	—	—	—	n.d.	—	n.d.	—	n.d.	—	n.d.	—	n.d.
Hydroxyibuprofen	30.3	40.3	—	—	—	27.6	—	28.6	—	24.6	—	23.	—	29.5
Ibuprofen	33.6	14.4	—	—	—	3.20	—	4.67	—	8.00	—	9.89	—	n.d.
Naproxen	n.d.	18.7	—	—	—	n.d.	—	27.3	—	n.d.	—	n.d.	—	n.d.
Nimesulide	n.d.	n.d.	—	—	—	n.d.	—	n.d.	—	0.20	—	n.d.	—	n.d.
Ketoprofen	11.9	12.4	—	—	—	12.9	—	11.7	—	11.8	—	11.6	—	11.3
Seca beach														
Acetaminophen	129	61.4	68.3	65.5	64.6	59.4	56.2	53.5	64.1	53.8	53.0	124	52.0	51.8
AAS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Carboxyibuprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diclofenac	n.d.	n.d.	n.d.	n.d.	0.46	n.d.	n.d.	4.73	9.67	n.d.	n.d.	1.25	n.d.	n.d.
Hydroxyibuprofen	44.5	35.7	25.6	38.6	57.6	27.6	23.8	39.8	25.3	24.7	23.0	23.5	23.5	24.6
Ibuprofen	22.1	7.24	14.5	9.12	9.72	9.44	3.36	16.7	13.6	4.76	4.93	n.d.	67.5	22.2
Naproxen	29.1	n.d.	n.d.	n.d.	92.7	17.4	n.d.	28.3	27.8	n.d.	n.d.	n.d.	n.d.	n.d.
Nimesulide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.33	n.d.	n.d.	n.d.	n.d.	n.d.
Ketoprofen	12.9	13.5	12.9	15.9	13.6	12.3	10.5	12.0	12.0	12.1	11.0	12.8	10.3	11.2

