Application of POCIS for the monitoring of pesticides, pharmaceuticals and alkylphenols in marine water.

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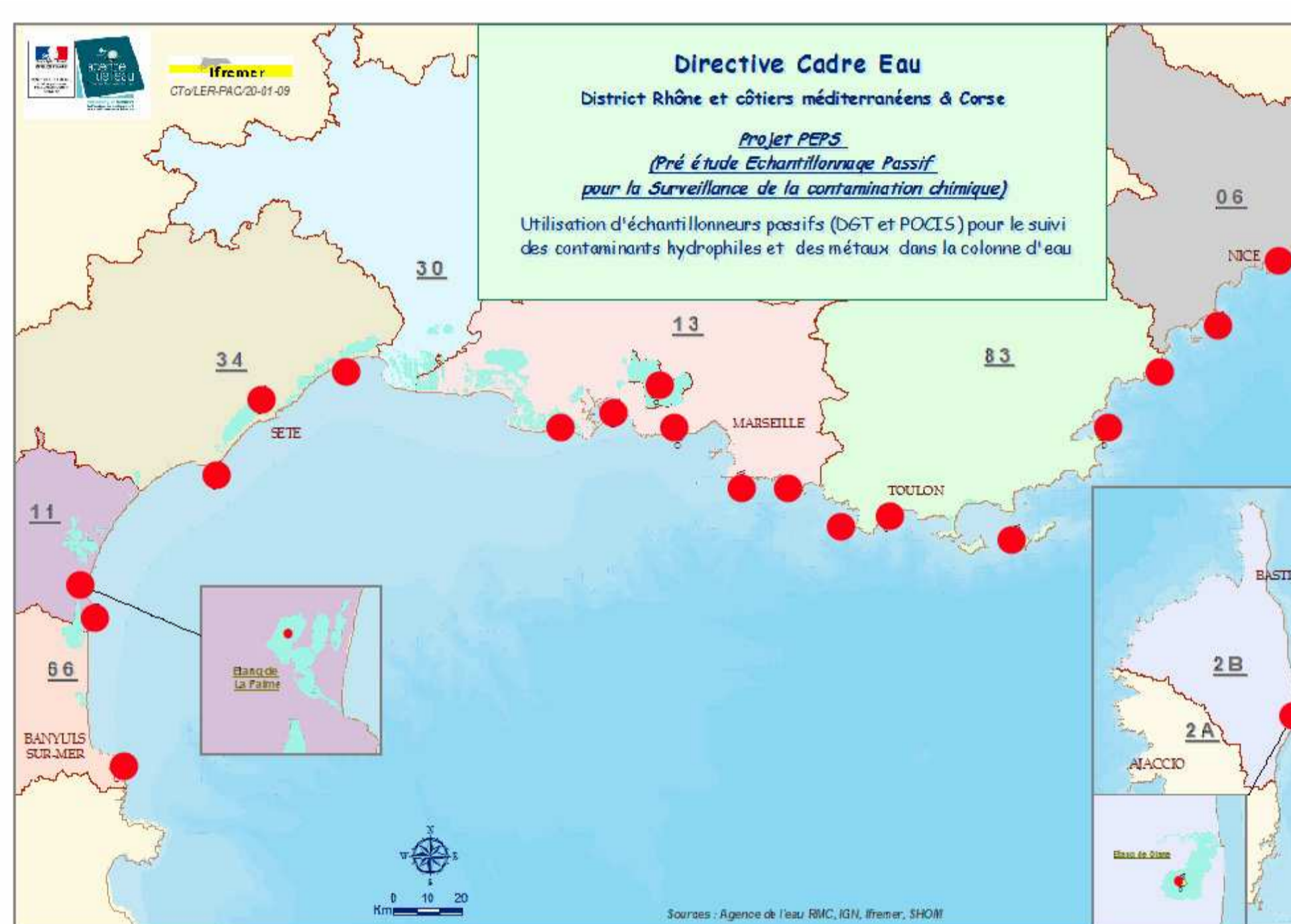3. IFREMER, Département Biogéochimie et Ecotoxicologie, La Seyne/mer, France

Introduction

With the new European legislation (the Water Framework Directive, 2000/60/EC), the decision makers responsible for the assessment of the environmental contamination require simple monitoring tools. Passive sampling methods seem to be promising tools for the sampling of polar organic compounds in water, especially in marine waters where important dilutions and low concentrations are usual. They are taking into account the temporal variability and integrating the contamination over period of time. This work presents a study, on a large scale, of the contamination of French Mediterranean coastal waters realized in partnership with the Water Agency Rhône Méditerranée Corse (AERMC), and Coastal Water Quality Offices (CQEL)).
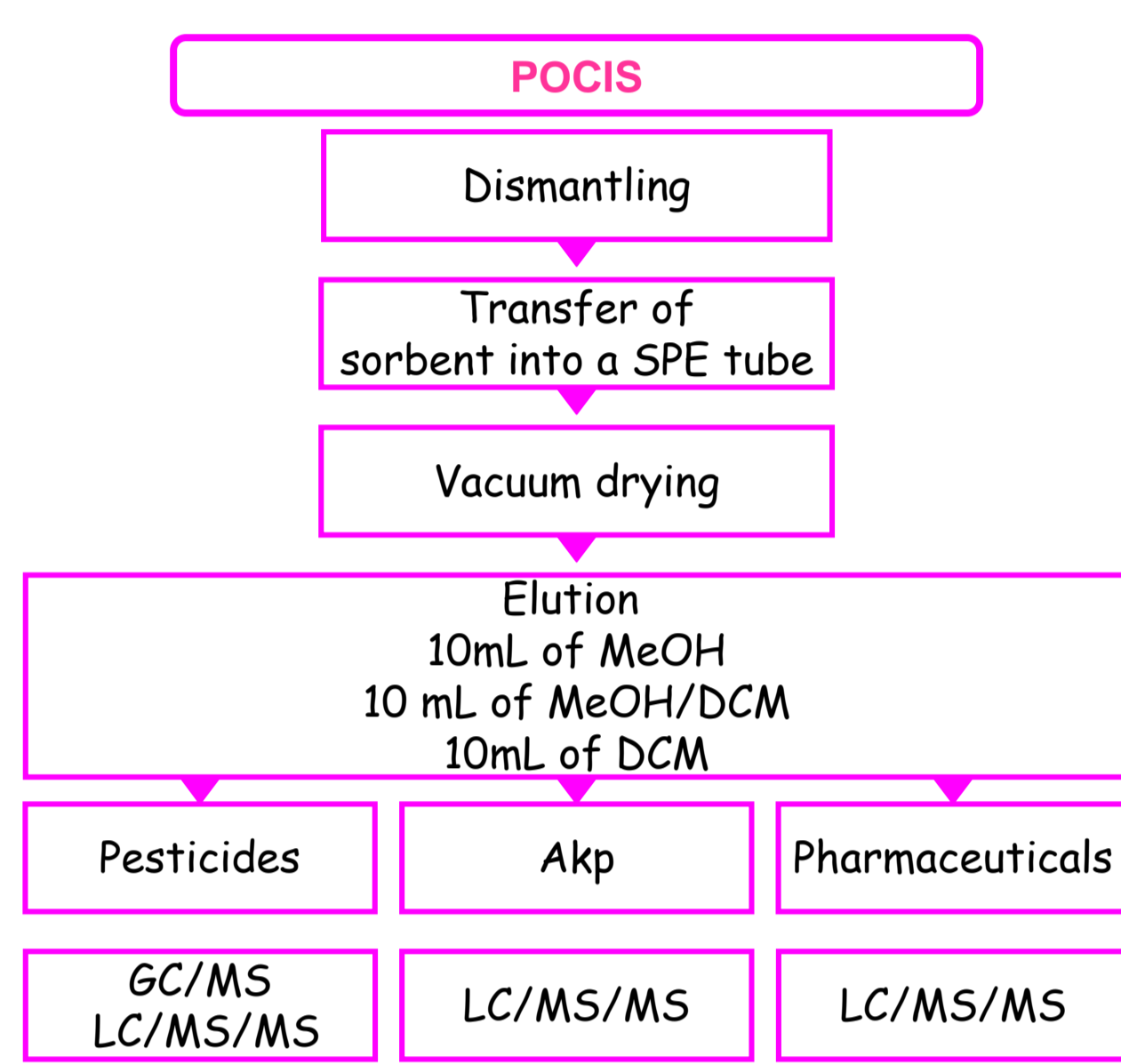
Materials and Methods

Sampling sites

Polar Organic Chemical Integrative Samplers (POCIS) were deployed in Mediterranean Sea along the French coast. Pharmaceutical POCIS were exposed in surface water in 20 specific Mediterranean water bodies to sample Pharmaceuticals (bromazepam, clenbuterol, nordiazepam, salbutamol, carbamazépine, terbutaline, cafeine, theophylline, fluoxetine, paracetamol, alprazolam, diazepam, imipramine, doxepine, amitriptiline, aspirine, ibuprofene, naproxene, gemfibrozil, ketoprofene, diclofenac), Alkylphenols (NP1EO, NP2EO, NP1EC, BPA, 4-NP, OP) and Pesticides (DEA, DIA, Simazine, Atrazine, Cyromazine, Propazine, Terbuthylazine, Promethryn, Terbuthryn, Cyanazine, Irgarol, Pymethrozine, Propachlor, Dimethachlor, Acetochlor, Alachlore, S-Metolachlor, Metazachlor, Nicosulfuron, DCPU, Chlorsulfuron, Linuron, Diuron, Metoxuron, DCPMU, Chlorotoluron, Isoproturon). Passive samplers were deployed by the CQEL' s operators in July 2008 for 3 weeks. After field exposure, they were frozen, and then sent to the laboratory for analysis. The POCIS's phase was eluted by a mixture of DCM/MeOH. The Pharmaceuticals and the Alkylphenols were analyzed by LC/MS/MS and pesticides by GC/MS and LC/MS/MS.

Extraction protocols

POCIS → Dismantling → Transfer of sorbent into a SPE tube → Vacuum drying → Elution 10mL of MeOH / 10 mL of MeOH/DCM / 10mL of DCM

- Pesticides → GC/MS LC/MS/MS
- Akp → LC/MS/MS
- Pharmaceuticals → LC/MS/MS

Results and Discussion

Thirteen POCIS out of the twenty exposed were recovered. 7 POCIS were lost during the exposure time (about 21 days) because of accidental (or intentional) catch.

Results obtained after POCIS extraction and analysis are shown below. The results are expressed in ng.g^{-1} of POCIS sorbent. These results show that for pesticides and pharmaceuticals, the most impacted area are the Berre and the Thau lagoon. For alkylphenols the maximum level are found in the area of Fos sur Mer and Antibes.

	Dia ng.g^{-1}	Agd ng.g^{-1}	Tha ng.g^{-1}	Leu ng.g^{-1}	Em ng.g^{-1}	Sol ng.g^{-1}	Ber ng.g^{-1}	Fos ng.g^{-1}	Rou ng.g^{-1}	Pla ng.g^{-1}	Man ng.g^{-1}	Ant ng.g^{-1}	Por ng.g^{-1}
NP1EO	85	37	nd	72	59	50	134	249	81	277	191	273	124
NP2EO	21	22	15	16	33	39	36	99	17	37	41	35	24
NP1EC	nd	6	4	54	16	2	nd	11	35	2	1	14	2
BPA	nd	8	nd	150	38	61	nd	65	nd	48	nd	nd	nd
4-NP	91	41	75	97	205	29	241	393	73	129	150	170	195
OP	14	14	9	191	28	20	50	131	77	17	32	45	15
bromazepam	nd	nd	nd	nd	nd	nd	8	1	nd	nd	nd	nd	nd
nordiazepam	nd	nd	nd	nd	nd	nd	23	nd	1	nd	nd	nd	nd
carbamazépine	2	10	45	11	24	5	487	9	5	3	nd	10	7
terbutaline	2	0	3	1	1	1	2	1	0	2	4	1	2
cafeine	88	109	178	117	68	133	237	123	108	121	97	128	63
théophylline	17	10	26	13	13	nd	35	9	10	23	36	7	16
fluoxetine	nd	nd	nd	nd	nd	nd	1	nd	nd	nd	nd	nd	nd
diazepam	nd	2	nd	nd	4	8	nd	nd	4	8	5	nd	nd
amitriptiline	nd	nd	nd	1	nd	nd	nd	nd	nd	nd	nd	nd	nd
naproxene	nd	nd	nd	6	nd	nd	nd	nd	nd	nd	nd	nd	nd
gemfibrozil	nd	nd	nd	2	nd	27	nd	nd	nd	nd	2	1	
ketoprofene	17	nd	12	nd	109	nd	nd	nd	nd	nd	31	nd	23
diclofenac	nd	nd	1	nd	nd	nd	9	21	2	nd	nd	nd	nd
DIA	nd	nd	nd	nd	nd	242	nd	nd	nd	nd	nd	nd	nd
DEA	nd	8	nd	nd	nd	44	nd	10	nd	nd	nd	nd	nd
simazine	nd	5	nd	nd	nd	24	9	17	15	nd	nd	nd	nd
atrazine	nd	20	nd	9	nd	7	54	27	35	43	20	5	nd
propazine	nd	nd	24	nd	nd	nd	27	nd	6	nd	75	nd	nd
terbuthylazine	18	13	55	13	24	19	40	23	15	15	nd	18	15
terbuthryn	nd	10	nd	nd	nd	nd	21	nd	nd	nd	nd	nd	nd
irgarol	nd	nd	43	nd	nd	nd	13	nd	nd	nd	nd	nd	nd
dimethachlor	nd	nd	nd	12	nd	nd	nd	nd	nd	nd	nd	nd	nd
acetochlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
alachlore	19	nd	nd	nd	nd	nd	nd	nd	nd	8	nd	nd	nd
s-metolachlor	nd	31	nd	17	nd	11	159	37	50	27	11	nd	nd
diuron	1	6	100	4	4	2	162	13	8	7	41	3	5
DCPMU	1	nd	6	nd	nd	nd	17	nd	nd	nd	nd	nd	nd
chlorotoluron	nd	1	nd	1	nd	2	1	1	1	nd	nd	nd	nd
isoproturon	nd	1	1	nd	nd	nd	18	1	1	1	nd	nd	nd

The water concentration were determined by using sampling rate (Rs) for some compounds (Togola et Budzinski 2007, Arditsoglou et Voutsa 2008, Mazzella et al 2007, Alvarez et al 2007). The results expressed in ng.L^{-1} are shown in the right side of the poster.

Pesticides

Alkylphenols

Pharmaceuticals
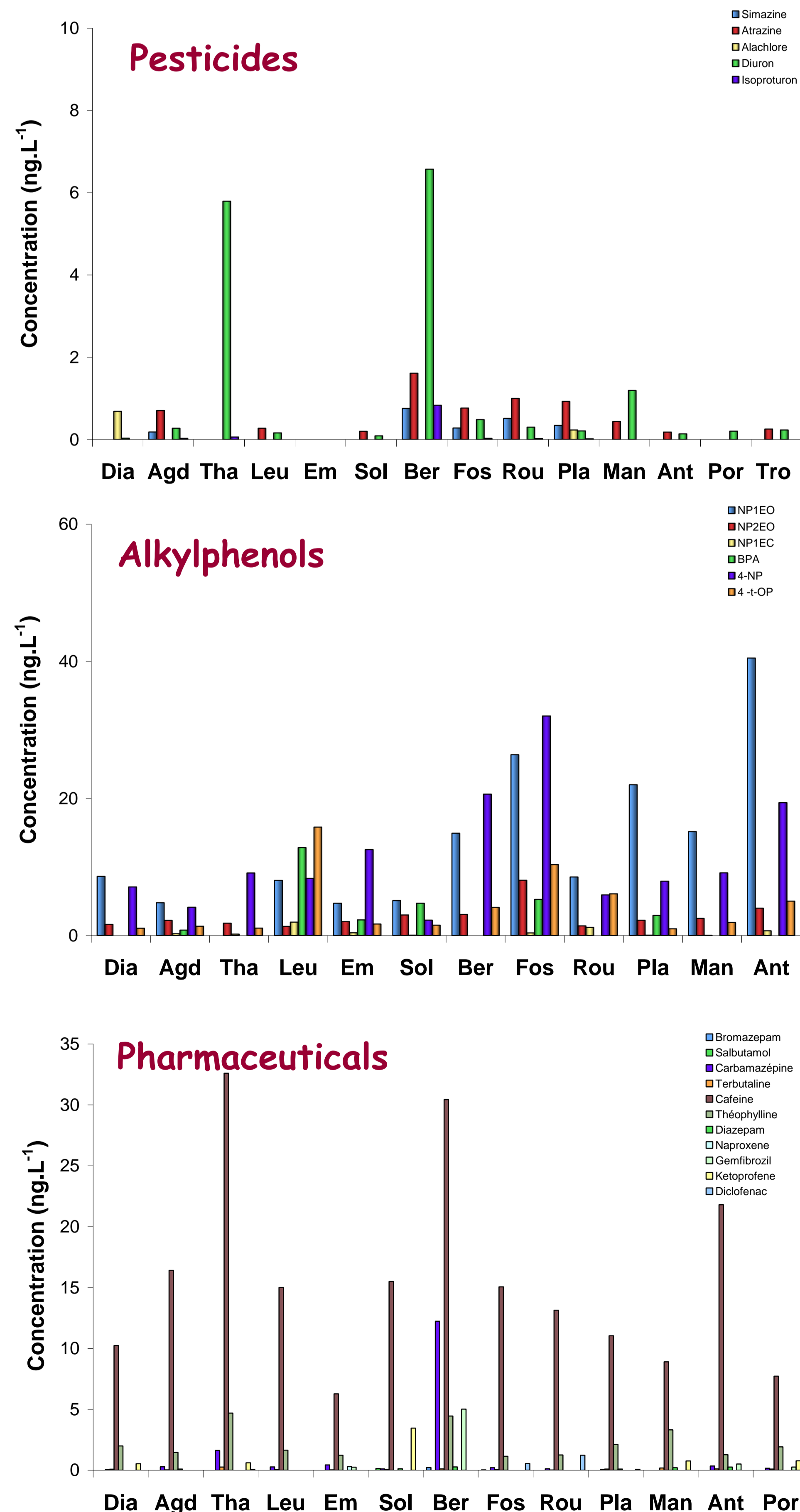
Conclusion

This study has allowed to conduct a first assessment of the contamination of the French Mediterranean coast for a wide range of contaminants including emerging pollutants and has allowed to estimate the applicability of POCIS to be used for environmental screening in the case of marine water. In conclusion POCIS are applicable in marine, but the quantitative aspect should be improve with a better determination of Rs in marine water and with the developement of some performance reference compounds (PRCs) to avoid the problem of biofouling.