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1. Introduction

Bisphenol A is a typical endocrine-disrupting chemical. In the 1950s, it was observed that BPA could be polymerized to make polycarbonate plastic. BPA rapidly became one of the most produced and used chemicals worldwide, even though it was a recognized synthetic estrogen. About 70% of BPA production (3.4 million tons per year) is used to produce polycarbonate plastics used in a variety of common products. About 20% of BPA is used as an essential component of epoxy resins that are mainly used to coat the inner surface of metallic cans [1]. Finally, BPA is used as antioxidant or inhibitor of polymerization in some plasticizers, polyvinyl chloride, and thermal cash register paper. Consequently, during sampling operation in river, if the operator uses a plastic bucket, a risk of sample precontamination can be observed. This study will give some warnings on the cleaning steps and on which material needs to be used during water sampling for environmental monitoring of bisphenols. AQUAREF is performing this type of investigation since 2013, especially on emerging compounds: parabens [2] and plasticisers [3].

2. Materials and methods

Material testing and on-field sampling were performed by INERIS. 5 different sampling methods were used on a reference site and in laboratory: direct sampling in the river; indirect with a plastic bucket, a horizontal PFTE bucket, a telescopic rod and vial and a new bucket (uncleaned). Two types of tests were performed on these 4 types of sampling material :

- A) different rinsing process of bucket/bottles before sampling in laboratory. The cleaning procedure includes a first step with tap water, followed by a hot water rinsing with an alcalin detergent. Then the sampling material was rinsed with dilute acetic acid and demineralised water. For the PTFE bottle, an extra ultapure acetone + demineralised water (3 times) cleaning was performed. After another cleaning with tap plus hot water, the sampling material was washed again with an alcalin solution (dissolved in hot water) and an acidified water. The second and final rinsing was performed three times with demineralised water. This process was repeated twice and samples were analysed after the 1st and after the 2nd process
- B) on-site sampling with the cleaning process validated during the 1st test in laboratory. A new with plastic bucket (used immediately after buying and without cleaning) was also tested.

Analyses were carried out at NILU on 20 bisphenols (Bisphénol A, Bisphénol S, Tetrabromobisphenol A, 4,4'-Bisphénol F, 2,2'-bisphenol F, 2,4-bisphenol F, Bisphénol FL, Bisphénol AF, Bisphénol AP, Bisphénol B, Bisphénol BP, Bisphénol C, Bisphénol C II, Bisphénol G, Bisphénol M, Bisphénol P, Bisphénol PH, Bisphénol TMC, Bisphénol Z, Tetrabromobisphenol S).

500 ml of unfiltered water samples that were stabilized with 2% methanol and 1% acetic acid were subjected to a solid phase extraction procedure with Oasis® HLB column (500mg, 6cc) that were conditioned with ethyl acetate, methanol and 2% acetic acid in MillQ water. Ater loading the samples, cartridges were washed with water and 5% methanol in water and dried under vacuum. Bisphenols were eluted with a solution containing ethyl acetate and methanol (85:15). Then the samples were upconcentrated and analysed with Agilent 1290 ultra high performance liquid chromatograph coupled with Agilent 6550 high resolution quadrupole – time of flight mass spectrometer with Dual Jet Stream electrospray source operating in a negative mode. Analytes were separated with Phenomenex Luna C18 (150 x 2.1 mm) with water and methanol as mobile phases.

Since contamination with bisphenol A is known to occur when using plastic equipment and very little is known about the other new bisphenols besides several procedural blanks also instrumental blanks were analyzed with the samples. Especially the ubiquity of BPA made not possible to obtain all procedural blanks completely free of this product therefore the background level was calculated for every batch of the extracted samples and then if needed subtructed from the BPA concentration on the analysed samples.

3. Results and discussion

3.1. Experiment A - Laboratory cleaning procedures

9 substances out of 20 were quantified in the blank laboratory samples. Sampling materials display different level of precontamination and different compound-specificity (Bisphenol TMC only quantified in on type of sampling, the rod + transfert in a glass vial)(figure 1).

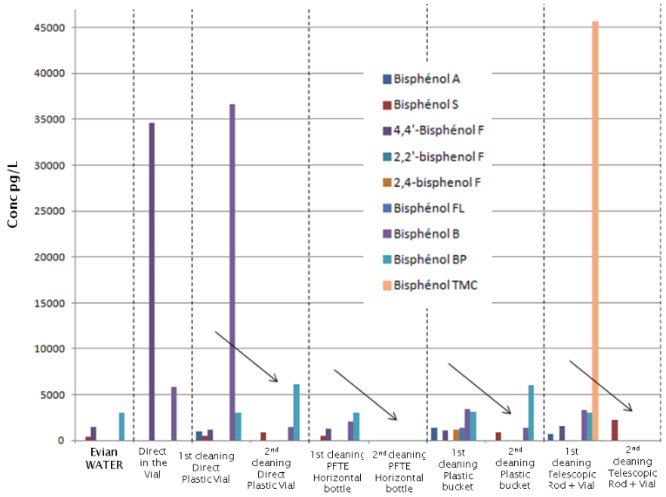

Figure 1: Impact of cleaning procedure on BPs concentrations with 4 different sampling materials

The overall results display that repetition of 2 strong cleaning procedures (as described in *§Materials and methods*) can be extremely impactant on the over-estimation of bisphenols concentrations. For exemple, contaminated samples collected with an Horizontal bottle or a rod vial, are almost “uncontaminated” after a 2nd round of cleaning. These results permitted to define the cleaning procedure to adopt for the on-site sampling. Finally, two cleaning steps were adopted before the on-site sampling (Experiment B).

3.2. Experiment B - Sampling on surveillance conditions (river samples)

6 bisphenols were quantified during the field sampling. Highest concentrations were observed for bisphenol A using a new plastic bucket to sample in the river (not cleaned in laboratory). Concentration in the final samples were above 6 ng/l in 4 out of 4 replicates. 2,2'-bisphenol F was sistematically quantified in all river samples.It has to be noticed that Bisphenol S, frequently found in samples during *experiment A*, was never quantified in the river samples. TBBPA was observed only in samples collected with plastic bucket.

4. Conclusions

Firstly, this study displays a risk of precontamination not for all bisphenols, but for 9 out of 20 (essentially Bisphenol A and bisphenol BP). This study suggests a potential contamination of the sample by bisphenol if the sampling operator do not apply a multiple and correct cleaning procedure on the laboratory before field operations. Authors also observed that samples collected with a non-rinsed plastic bucket were highly contaminated, especially for bisphenol A. Hovewer, in this study concentrations were very low (high sensibility of analytical method) but still very far from PNEC threshold (0,2 µg/L for Bisphenol A).In conclusion, AQUAREF reccomends a strict cleaning procedure and few field blanks before to collect field sample for bisphenols investigations.

5. References

[1] Eladak S. et al (2015). A new chapter in the bisphenol A story: bisphenol S and bisphenol F are not safe alternatives to this compound, Fertility and Sterility, Volume 103, Issue 1, January 2015, Pages 11-21, ISSN 0015-0282.

[2] Botta F. et al. (2016). Measuring parabens in surface water: the impact of the field operator. NIVA-NORMAN Workshop on “Trends and advancements in the sampling and preservation of samples for the identification of contaminants of emerging concern”, 2-3 March 2016, Oslo, Norway.

[3] Lepot B. et al (2015). Assessment of the contamination from sampling materials and procedures for substances of urban/industrial origins : phthalates and perfluoroalkyl substances (PFAS). SETAC Europe annual meeting "Science across bridges, borders and boundaries", Mai 2015, Barcelone, Spain.

Acknowledgement - The authors thank ONEMA for financial support.