biology and life sciences forum

MDPI

Proceeding Paper

Evaluating Contaminants in Fish: Plastic Additives and Pesticides in the Context of Food Safety †

Virgínia Cruz Fernandes [1,*], Dylan Boesmans [1,2], Valentina F. Domingues [1] and Cristina Delerue-Matos [1]

[1] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal; dylan.boesmans@student.ucll.be (D.B.); vfd@isep.ipp.pt (V.F.D.); cmm@isep.ipp.pt (C.D.-M.)
[2] UC Leuven–Limburg
* Correspondence: vir@isep.ipp.pt or vcf@isep.ipp.pt
† Presented at the 4th International Electronic Conference on Foods, 15–30 October 2023; Available online: https://foods2023.sciforum.net/.

Abstract: The World Health Organization reports that foodborne illnesses cause millions of cases globally, resulting in approximately 33 million lost healthy years of life. Over the past decade, global awareness of food safety has grown significantly, highlighting various hazards from biological, chemical, and environmental factors in our food supply, including marine sources. Emerging contaminants like pharmaceuticals, personal care products, pesticides, plastic additives, and microplastics are concerning, with some remaining unregulated. Our work focuses on analyzing plastic additives and pesticides in fish from local Oporto supermarkets captured in the Atlantic Ocean. We used QuEChERS extraction and Gas Chromatography for the analysis of Organophosphate Ester compounds in fish samples. Our goal is to ensure safe and healthy seafood, aligning with the principles of the blue economy and sustainable fisheries.

Keywords: ; contaminants; food safety

Citation: Fernandes, V.C.; Boesmans, D.; Domingues, V.F.; Delerue-Matos, C. Evaluating Contaminants in Fish: Plastic Additives and Pesticides in the Context of Food Safety. *Biol. Life Sci. Forum* **2023**, *3*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: date

1. Introduction

In recent years, the World Health Organization has highlighted the alarming global impact of foodborne illnesses, leading to millions of cases worldwide and an estimated loss of around 33 million healthy years of life, which may be an underestimation [1]. This recognition has spurred a significant increase in global awareness of the critical importance of food safety [2].

It has become increasingly evident that our food supply is vulnerable to a range of hazards, spanning biological, chemical, and environmental factors, even including threats from the marine environment. Many emerging contaminants, such as pharmaceuticals, personal care products, pesticides, plastic additives, and microplastics, have been present in our environment for some time [3–5]. However, some of these contaminants have only recently come to our attention, and a concerning number of them remain unregulated.

To address these concerns, researchers have developed advanced analytical methods capable of measuring the concentrations, toxicity, and potential risks associated with various families of contaminants. This ongoing effort is vital for safeguarding public health and ensuring the safety of our food supply in a world where threats to food safety continue to evolve.

The aim of this study was to explore an analytical method for the assessment of contaminants of emerging concern, namely plastic additives and pesticides, in fish samples.

2. Material and Methods

The extraction of 6 organophosphorus pesticides (OPP) and 8 organophosphate esters (OPE) from fish samples was performed using the QuEChERS method and the analysis by gas chromatography with a flame photometric detector. The analytical methodology was optimized and validated based on reported work [4,6]. The fish samples acquired consist of 7 horse mackerel, 7 mackerel and 2 Atlantic chub mackerel and are bought in batches from Portuguese supermarkets. All samples are from wild fish, caught at sea in the Northeast Atlantic Ocean.

3. Results and Discussion

3.1. Method Validation

Method validation experiments were conducted in terms of linearity, limit of detection (LOD) and quantitation (LOQ), repeatability, recoveries, and matrix effect. All the compounds at low spiking levels could be quantified at LOQs higher than 7.9 μg/L. The linearity of the solvent (10–150 μg/L) and matrix-matched calibration curves (1.5–12.4 μg/kg) for each compound presented a coefficient of determination (R2) > 0.991. Satisfactory recovery values of 70–120% with a relative standard deviation of ≤20% are obtained for all compounds in fish samples. A matrix effect between (−87–5%) was observed in 100% of compounds. For repeatability, a sample of 50 μg/L was prepared and measured ninefold on the same day. And with the regressions of the solvent, the concentrations are measured. Then the standard error and relative standard error (RSE) are calculated and the RSE was less than 20% for all the compounds studied. As an example, Table 1 shows the results for tri-propyl phosphate (TPrP). Therefore, according to the guidelines established by SANTE/11312/2021, this analytical method meets most of the requirements and can contribute to OPE and OPP residue analyses of fish samples for routine laboratory testing.

Table 1. Summary injections of TPrP for repeatability study.

				TPrP					
Injection	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Area	**2330779**	**1359183**	**1601568**	**2288192**	**1436445**	**1693913**	**2030356**	**1951238**	**1675209**
Conc (μg/L)	47.9	29.3	33.9	47.1	30.8	35.7	42.1	40.6	35.
Average conc (μg/L)					38.1				
Standard error					6.70				
Relative standard error					18%				

3.2. Application of the Analytical Procedure in Fish Sample Analysis

After validating the methodology, the OPP and OPE compounds were evaluated in the 16 samples under study. As shown in Figure 1 of the complete chromatogram, all the peaks are clearly defined and the compounds are successfully separated. The screening analysis was performed and the comparison between chromatograms of standards and the samples, 2 OPE compounds were observed in 4 Atlantic chub mackerel and 1 horse mackerel samples.

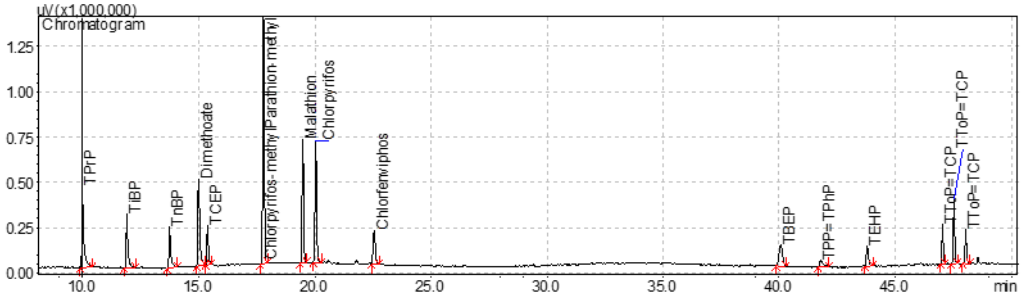

Figure 1. Full gas chromatogram of 6 organophosphorus pesticides and 8 organophosphate esters.

Tri-cresyl phosphate (TCP) was observed in 4 Atlantic chub mackerel samples. Tris (2-butoxyehyl) phosphate (TBEP) was observed in one of the Atlantic chub mackerels and one of the horse mackerels. After the screening analysis, the compounds were quantified using the respective calibration curves and the values obtained were below the detection limits. No OPP were observed in the samples. For this reason, we can see that the samples analyzed are in terms of the selected OPP and OPE compounds safe for human consumption.

There is still not much data in the literature about OPE in fish samples. Indeed there is no regulatory standards concerning (OPEs) maximum residue levels permitted in food. Although we observe the presence of these compounds, the values are below the LOD, however, in the literature, some studies already show the presence of these compounds in low concentrations in edible fish such as sardines, hakes, etc. [7].

4. Conclusions

The sample extraction using QuEChERS demonstrated good performance, as evidenced by the recoveries and matrix effects. The regressions, LOD and LOQ are satisfactory and allow the applicability of the method to the samples, as previously discussed. However, the method can be improved mainly concerning its sensitivity in order to improve the LODe LOQ values.

While plasticizers and flame retardants are indeed detected in numerous samples as a result of widespread environmental pollution stemming from the disposal of plastic waste in our oceans, with plastic forming a substantial portion of this waste, as well as the presence of OPEs which serve as flame retardants and are utilized in various industries, it's worth noting that the concentrations of these target compounds in the fish are below levels of concern for toxicity. As such, consuming these types of fish remains safe. In our research, we encountered a notable gap in regulatory standards concerning (OPEs) maximum residue levels permitted in food. This absence of specific regulations highlights the need for further attention and assessment of OPEs in food safety guidelines to ensure the protection of public health and the environment. Addressing this regulatory void is crucial to establishing comprehensive safety measures for OPEs in our food supply chain.

Author Contributions: Conceptualization, V.F.D. and V.C.F.; methodology, V.F.D. and V.C.F.; validation, V.C.F. and D.B.; formal analysis, V.C.F. and D.B.; investigation V.C.F. and D.B.; resources, C.D.-M.; writing—original draft preparation, V.C.F.; writing—review and editing V.C.F.; visualization; supervision, C.D.-M., V.F.D. and V.C.F.; funding acquisition, C.D.-M. All authors have read and agreed to the published version of the manuscript.

Funding: This work has been developed within the scope "Blue Bioeconomy Innovation Pact" (Project No. C644915664-00000026) funded by NextGenerationEU, under the "Agendas for Business Innovation" incentive line of the Recovery and Resilience Plan (PRR).

Institutional Review Board Statement:

Informed Consent Statement: Not applicable.

Data Availability Statement:

Acknowledgments: This work received support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020.

Conflicts of Interest:

References

1. World Health Organization. Food Safety. Available online: https://www.who.int/news-room/fact-sheets/detail/food-safety (accessed on 5 September 2023).
2. The Lancet Gastroenterology Hepatology. Food safety really is everyone's business. *Lancet Gastroenterol. Hepatol.* **2019**, *4*, 571. https://doi.org/10.1016/s2468-1253(19)30202-x.
3. Lamas, M.; Rodrigues, F.; Amaral, M.H.; Delerue-Matos, C.; Fernandes, V.C. Contaminant Cocktails of High Concern in Honey: Challenges, QuEChERS Extraction and Levels. *Separations* **2023**, *10*, 142.
4. Fernandes, V.C.; Podlasiak, M.; Vieira, E.F.; Rodrigues, F.; Grosso, C.; Moreira, M.M.; Delerue-Matos, C. Multiple Organic Contaminants Determination including Multiclass of Pesticides, Polychlorinated Biphenyls, and Brominated Flame Retardants in Portuguese Kiwano Fruits by Gas Chromatography. *Foods* **2023**, *12*, 993.
5. Vera, J.; Fernandes, V.C.; Correia-Sá, L.; Mansilha, C.; Delerue-Matos, C.; Domingues, V.F. Occurrence of Selected Known or Suspected Endocrine-Disrupting Pesticides in Portuguese Surface Waters Using SPME-GC-IT/MS. *Separations* **2021**, *8*, 81.
6. Dorosh, O.; Fernandes, V.C.; Moreira, M.M.; Delerue-Matos, C. Occurrence of pesticides and environmental contaminants in vineyards: Case study of Portuguese grapevine canes. *Sci. Total Environ.* **2021**, *791*, 148395. https://doi.org/10.1016/j.scitotenv.2021.148395.
7. Sala, B.; Giménez, J.; Fernández-Arribas, J.; Bravo, C.; Lloret-Lloret, E.; Esteban, A.; Bellido, J.M.; Coll, M.; Eljarrat, E. Organophosphate ester plasticizers in edible fish from the Mediterranean Sea: Marine pollution and human exposure. *Environ. Pollut.* **2022**, *292*, 118377. https://doi.org/10.1016/j.envpol.2021.118377.