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Assignment: Literature Assignment

Course: CHEM 3140

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Article Title: Persistent Organic Pollutants (POPs) in Sardine (Sardinella brasiliensis): Biomonitoring and Potential Human Health Effects

Article Authors: Carlos German Massone, Allan Amendola dos Santos, Pedro Gonçalves Ferreira and Renato da Silva Carreira.

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Goal of the Research

To investigate the composition profile, bioaccumulation potential, and human risks associated with organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs).

Analytical question

What are the concentrations of organochlorine pesticides (OCPs) and polychlorinated biphenyl (PCB) in the muscle tissue of sardine samples (Sardinella brasiliensis) sampled off the south-east Brazilian shelf?

Analyte

In this analytical method, two groups of persistent organic analytes were investigated: organochlorine (OCPs) and polychlorinated biphenyls (PCBs). I will be focusing on the organochlorine pesticides (OCPs). OCPs are chlorinated hydrocarbons and are an organic compound containing at least one covalently bonded chlorine. OCPs are commonly used in the chemical industry and can be found in some pesticides. These compounds are known for their high toxicity, slow degradation, and bioaccumulation. OCP's have varying volatilities as it depends on the molecule, but all have low solubility in water which causes them to bioaccumulate.

Analytical Method Steps:

Sampling

1. Sardine samples were taken through active and passive strategies. The active sampling strategy involved a cruise which navigated along the coast of southern brazil.

Purpose: This was judgmental sampling since research was done which showed the best sampling areas along the coast of southern brazil, and each sample was a grab sample. This step was one of the sampling strategy and types to collect the sardine samples.

2. The passive sampling strategy consisted of collecting samples from four different landing stations.

Purpose: The passive strategy was random sampling and convenience sampling since the fish were chosen based on the availability at each landing station. Each sample was a grab sample. Since there was no information regarding the specific positions where the sardines were caught, these samples were considered to represent the sardine fishery in southern brazil. This step was one of the sampling strategy and types to collect the sardine samples (along with step 1).

Sample Preparation

3. Overall, the fish were sampled from five sampling areas (one cruise and the four landing stations). Ten fish were randomly selected between the first and third quartiles of the size distribution from each of the five sampling areas.

Purpose: This step was a form of sub sampling and the goal was to reduce the number of samples. This is also judgmental sampling since background research was conducted as to which size of fish would have the highest concentrations of OCPs.

4. Muscle samples were taken from these 50 fish (10 samples from each of the five samplings). Muscle samples were sub-sampled from the lower portion of the dorsal fin.

Purpose: This was judgmental sampling as research suggested this area of the sardine would have the highest concentration of organochlorine pesticide, and each sample was a grab sample.

5. These sub-samples were then freeze dried and ground to make it homogenous.

Purpose: Since these are biological samples, freeze drying is used to make the grinding easier. The samples are now homogenous meaning that after this step is when the sample preparation for analysis begins.

Analysis

6. Dry mass extraction was conducted. The extraction was performed using dichloromethane.

Purpose: Dry mass extraction was chosen due to high precision and accuracy. Dichloromethane was chosen as the solvent since it is not miscible with water, is highly effective, and is a suitable solvent for GC-MS/MS.

Quality Control and Quantification

7. The EPA3545 protocol was applied for an in-cell clean-up approach to remove the lipids.

Purpose: The EPA3454 protocol includes a clean-up to remove lipids. This protocol uses high temperature and pressure which requires less solvent and time than traditional methods. Lipids would give interference and would impact the analytical results of the research.

8. Surrogate standards and a certified material were used for analytical control.

Purpose: The surrogate standards were used to see the potential loss or gain of analyte during the extraction process. The addition of a surrogate standard and certified material were a part of quality control. Two surrogate standards were used (PCD-103 and PCB-198) and the certified material (IAEA-459).

9. The concentrated extracts were applied to liquid chromatography fractionation on a silica/alumina column.

Purpose: This is a clean-up method meant to remove interferences from the solution. This step will remove any leftover lipids and macromolecules.

10. A deuterated polycyclic aromatic hydrocarbon (PAH) mixture was used as an internal standard for quantification.

Purpose: The addition of an internal standard is used for calibration. The deuterated PAH mixture was used since it is similar to the analyte but is not the analyte. Internal standards can be used to compensate for fluctuation in flow rates (relative retention time).

11. The organochlorine pesticides were analyzed by gas chromatography coupled with tandem mass spectrometry (GC-MS/MS).

Purpose: GC-MS/MS was chosen because it gives high sensitivity, fast results, and enhanced sample identification. The tandem mas spectrometry gives a better signal to noise ration than a single mass spectrometer.

12. Eighteen OCPs were analyzed from this method.

Critique

The analytical question for this paper was: what are the concentrations of organochlorine pesticides (OCP) and polychlorinated biphenyl (PCB) in the muscle tissue of sardine samples (Sardinella brasiliensis) sampled off the south-east Brazilian shelf? This paper did not successfully answer this question. The results show that in 94.4% of the samples, the concentration of organochlorine pesticides was below the limit of quantification meaning the concentrations were not accurately quanitified. The detected compounds were not representative as they were poorly distributed among the locations and 31 samples. These detected compounds ranged from 0.70 to 55.8 ng/g. This method included some quality control steps such as a recovery standard and certified material but there was no discussion of blanks. Also, there was no information about the transportation and storage of the samples to the laboratory. In addition, this paper often used the word “random” without discussing the randomization steps which made that specific step random. This method did include some green analytical chemistry principals specifically the in-cell clean-up approach for lipid removal which used high temperature, high pressure, and less solvent. Also, dichloromethane was used to replace chloroform which has many health risks.

References

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