

# ANALYSIS OF PERSISTENT ORGANIC POLLUTANTS (POPs) IN SEDIMENTS BY GC/ECD GENERATED BY NUCLIDE $^{63}\text{Ni}$

Katia A. Mesquita<sup>1</sup>, Priscila O. Amaral<sup>1</sup> and José O. V. Bustillos<sup>1</sup>

<sup>1</sup>Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)  
Av. Professor Lineu Prestes 2242  
05508-000 São Paulo, SP  
[ovega@ipen.br](mailto:ovega@ipen.br)

## ABSTRACT

Persistent Organic Pollutants (POPs) are toxic organic compounds resistant to environmental degradation. Besides, POPs bioaccumulate with potential significant impacts on human health and the environment. The Global Monitoring Plan (GMP) under the Stockholm Convention on POPs is a program that enables collection of comparable monitoring data from all regions of the world to assess the effectiveness in minimizing human and environmental exposure to POPs. The scope of this work is to develop and validate a method for the extraction and determination of POPs in sediments collected at Billings dam locate in São Paulo Metropolitan City. The compounds studied in this work are: Aldrin ( $\text{C}_{12}\text{H}_8\text{Cl}_6$ ), DDD ( $\text{C}_{14}\text{H}_{10}\text{Cl}_4$ ), DDE ( $\text{C}_{14}\text{H}_8\text{Cl}_4$ ), DDT ( $\text{C}_{14}\text{H}_9\text{Cl}_5$ ), Dieldrin ( $\text{C}_{12}\text{H}_8\text{Cl}_6\text{O}$ ), Endrin ( $\text{C}_{12}\text{H}_8\text{Cl}_6\text{O}$ ) and Heptachlor ( $\text{C}_{10}\text{H}_5\text{Cl}_7$ ). This work use the QuEChERS extraction method (Quick, Easy, Cheap, Effective, Rugged, and Safe) for sediment samples and the analysis of the compounds were carried out by gas chromatography with the electron capture detector (GC/ECD). The ECD detector ionizes the analytes by the beta particles from the nuclide sources  $^{63}\text{Ni}$  within carrier gas  $\text{N}_2$ . The electrons produced in this process are collected, create an amplified current, and generating the chromatographic peak. The recovery of this method obtained values between 57% and 65% and the Relative Standard Deviation (RSD) values are between 1 and 4%. Details of the analytical method beside quantitative analyses data are presented in this work.

## 1. INTRODUCTION

Persistent Organic Pollutants (POPs) are highly stable compounds that persist in the environment, resisting chemical, photolytic and biological degradation. The Stockholm Convention, sponsored by the United Nations, provides to be banned at least twelve of these POPs. In compliance with the Stockholm Convention, which Brazil is one of the 179 countries that ratified the Convention; this work aims to contribute positively to this environmental issue. POPs can bioaccumulate in living beings organisms and act negatively as a disruptor of the reproductive, immune and endocrine systems, besides, some of they are considered carcinogenic. The determination of POPs in sediments collected at Billings dam locate in São Paulo Metropolitan City, is important for monitoring the sewer that has been release into the dam by metropolitan population and is critical due to reuse of this water by these population.

## 2. OBJECTIVE

The purpose of the present work is to develop a methodology for the analysis of POPs in sediments of the Billings dam using the QuEChERS extraction technique and gas chromatography with electron capture detector (GC/ECD) for the quantification of these analytes.

### 3. METHODS

The collection was performed at the Billings dam by the “Companhia Ambiental do Estado de São Paulo – CETESB”, where eight points were collected. This collection points are: “1° Linha, 2° Linha, Estoril, Corpo Central, Braço Capivari, Bororé, Elta e Tahiti”. These points were chosen because of the history of pesticide contamination.

Samples were collected in one kilogram amber bottle and conditioned at a temperature around 4°C, identified with their respective localization, their GPS coordinates and the date of collection. Samples were extracted using QuEChERS because this method uses the green Chemistry and minimum solvent. In this extraction method, 10 g of sample was weighed, then 20 ml of acetonitrile was added, stirred for 20 minutes, 4 g of magnesium sulfate, 1 g of sodium chloride, 1 g of sodium citrate, 5 g of sodium hydrogencitrate sesquihydrate. It was again stirred and centrifuged. The supernatant was removed and the sample is transfer to a 2 mL vial. The sample is ready for chromatography analysis. The QuEChERS extraction takes place in a few minutes and with very little solvent (about 30 minutes of extraction and 20 mL of solvent). This work uses this technique to measure the advantages of this extraction compared to other techniques already used.

The gas chromatography with electron capture detector (GC/ECD) consists on the generation of free electrons by exposing the sample to the small source of radioactive material ( $^{63}\text{Ni}$ ). The electrons produced in this process are collected in the anode, generating current, which is amplified by an electrometer, resulting in the baseline. If the sample has affinity for electrons, when passing through the detector, it can "capture" these electrons, causing a decrease in the current produced and generating a signal proportional to its concentration.

### 4. METHOD VALIDATION

The validation of a method is a process that begins in the planning of the analytical strategy and continues through its development. This should ensure by experimental studies that the method meets the requirements of the analytical applications, ensuring the reliability of the results. In this work, we used the analytical parameters: Limit of Detection (LD), Limit of Quantification (LQ), Recovery, Repeatability and Uncertainty measurements.

### 5. RESULTS

A calibration curve was performed with the concentrations of 1, 2, 3, 10, 15, 20, 30  $\mu\text{g kg}^{-1}$  using n-hexane solvent in a 2 mL vial. All calibration curves of the POPs obtained a linearity of at least  $R = 0.995$ .

The detection limit (LD) indicates the lowest point the equipment safely detects. The calibration curve has 0.1  $\mu\text{g kg}^{-1}$  as the first point of the calibration curve, this being the LD of this method for all POPS studied.

The quantification limit indicates the lowest point the equipment can quantify safely. The calibration curve has as a second point 0.2  $\mu\text{g kg}^{-1}$ , which is the LQ of this method. Seven samples of each compound were injected at a concentration of 0.1  $\mu\text{g kg}^{-1}$  for recovery

evaluation. The sediment matrix should recover between 40 and 120%. Table 1 illustrates the calculation of recovery of the POPs.

Table 1: The analytical parameter Recovery (%) calculates for the studied POPs.

<b>Compounds</b>	<b>Recovery (%)</b>
Aldrin	60
Dieldrin	61
Endrin	61
DDE	59
DDD	65
DDT	57
Heptachlor	57

Repeatability is the degree of concordance between the results of successive measurements of the same analyte, carried out under the same measurement conditions, same measurement procedure, same analyst, same instrument used under the same conditions and repetitions in short time. Seven blanks readings were taken for each level, with addition of concentrations at 1 to 2 levels of the analyte. In Table 2, it follows the analytical data of the repeatability record.

Table 2: The analytical parameter Repetitivy calculates for the studied POPs, where SD is the standard deviation and RSD is the relative standard deviation.

<b>Compound</b>	<b>Concentration</b>	<b>Average</b>	<b>SD</b>	<b>RSD</b>
Aldrin	1	1,097	0,05407	4,92846
	2	1,87	0,08793	4,70264
Dieldrin	1	1,061	0,04598	4,33202
	2	2,137	0,03817	1,78614
Endrin	1	1,081	0,04561	4,21825
	2	2,084	0,03207	1,53872
DDE	1	1,069	0,04879	4,56637
	2	2,076	0,06241	3,00676
DDD	1	1,089	0,05398	4,95917
	2	2,081	0,07010	3,36797
DDT	1	1,091	0,05209	4,77345
	2	2,094	0,05472	2,61324

	1	1,079	0,04810	4,46025
Heptachlor	2	2,097	0,04386	2,09147

The measurement uncertainty is a parameter associated with the result of a measurement, which characterizes the dispersion of values that can be reasonably assigned to the measured. In order to calculate the uncertainties of measurement, the uncertainties of the calibration certificate of the glassware used in the analysis were used, as well as the uncertainty of the micro syringe and the standard of analysis and the calibration curve. Table 3 presents the measurement uncertainty.

Table 3: The Measurement uncertainty calculates for the studied POPs.

Measurement uncertainty	$\mu\text{g kg}^{-1}$
Aldrin	0.2938
Dieldrin	0.5424
Endrin	0.4118
DDE	0.5424
DDT	0.3497
DDD	0.2945
Heptachlor	0.2977

The eight samples collected at the Billings dam did not present the POPs studied in this study. Spikes were performed from 4 of the 8 samples, obtaining recovery above 80% of the analytes.

## 6. CONCLUSIONS

The following conclusions can be enumerated from this work:

1 - The methodology of extraction for sediment samples from the Billings dam with CETESB was optimized by collecting up to 1 kg of sediment in the eight previously chosen points.

2 - The methodology of extraction for POPs analytes of the samples from the Billings dam was reached realizing the extraction by QuEChERS. The analysis of the samples was performed on GC / ECD and GC / MS chromatographs reaching analytical concentrations of  $\mu\text{g kg}^{-1}$ .

3 - The QuEChERS method was validated through parameters required by INMETRO, such as Repeatability, Reproducibility, Detection Limit, Quantification Limit and Measurement Uncertainty. The value for detection limit is  $0.1 \mu\text{g kg}^{-1}$ , and the limit of quantification is

0.2  $\mu\text{g kg}^{-1}$ . The effectiveness of this validation was verified obtaining recovery values between 40 and 120% for the sediment matrix.

## ACKNOWLEDGMENTS

This template was adapted from the template for the American Nuclear Society Topical Meeting in Mathematics & Computations, Gatlinburg, TN, 2003 posted on the Internet. Acknowledge the help of colleagues, and sources of funding, if you wish.

## REFERENCES

1. Declaration on the elimination of Persistent Organic Polluants (POPs). Stockholm Declaration. Stockholm, Sweden, 2001.
2. CAMPOS, M. J. A., NAKANO, V., Poluentes Orgânicos Persistentes, POPs e Metais Tóxicos. São Paulo, 2010.
3. MALLIAROS, C.; GUITONAS, A., Pré-treatment and elimination systems of toxic industrial waste and sludges. The case study of the department of Attika. **Wat. Sci. Tech**, v.36, p. 91-100, 1997.
4. MARONI, M.; COLSIO, C.; FERIOLI, A; FAIT, A. Introduction. **Toxicology**, v. 143, p. 5-8, 2000.
5. Companhia Ambiental do Estado de São Paulo, CETESB, Stockholm Convention. Acedido em 24/08/2014. Disponível em, <http://www.cetesb.sp.gov.br/institucional/>
6. PINTO, C.G.; LAESPADA, M. E. F.; MARTÍN, S.H.; FERREIRA, A. M. C.; PAVÓN, J. L.; CORDERO, B. M. Simplified QuEChERS approach for the extraction of chlorinated compounds from soil samples. *Talanta*, v. 81, 385-391,2010.
7. Standard Methods for the Examination of Water and Wastewater. 2005. 21<sup>st</sup> edition – métodos 1060A, B e C, 9060A e B e 9060 A
8. Guia Nacional de coleta e preservação - Agência Nacional de Águas, Brasília, 2011
9. Guia de coleta e preservação de amostras de água, CETESB, 2011;
10. ANASTESSIADES, M.; SCHERBAUM, E.; TASDELEN, B.; STAJNBAHER, D.; Crop protection health, environmental safety. Wiley-VCH, 2007.
11. SKOOG, D. A.; et al. *Fundamentos de química analítica*, 8<sup>o</sup>ed, Ed. Thomson,São Paulo, SP, 2006.
12. COLLINS, C. H. (Org.); BRAGA, G. L. (Org.); BONATO, P. S. (Org). *Fundamentos de Cromatografia*. 1a.ed. Campinas: Editora UNICAMP, 2006. V. 1. 453p.
13. BUSTILLOS, O.V., SASSINE, A., MARCH, R., *A espectrometria de massas quadrupolar*, Ed. Scortecci, 2003.
14. Agência Nacional de Vigilância Sanitária (ANVISA); *Resolução RE n°899*, de 29/05/2003.
15. Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO); *Orientações sobre Validação de Métodos de Ensaio Químicos*, DOQ-CGCRE-008, 2011.

16. THOMPSON, M.; ELLISON, S. L. R.; WOOD, R.; *Pure Appl. Chem.* 2002, 74, 835.
17. International Standard Organization; *General Requirements for the Competence of Testing and Calibration Laboratories*, ISO/IEC 17025, 1999.
18. International Conference on Harmonisation (ICH); *Validation of Analytical. Procedures: Methodology*, Q2B (CPMP/ICH/281/95), 1995.
19. United States Food and Drug Administration, Center for Drug Evaluation
20. Associação Grupo de Analistas de Resíduos de Pesticidas (GARP); *Manual de Resíduos de Pesticidas em Alimentos* (apostila), 1999.
21. BOX, G. E. P.; HUNTER, W. G.; HUNTER, J. S.; *Statistics for Experimenters*, Wiley: New York, 1987.
22. SNYDER, L. R. ; KIRKLAND, J. J.; GLAJCH, J. L.; *Practical HPLC Method Development*, 2 a ed., Wiley: New York, 1997, cap. 15.
23. LEITE, F.; *Validação em Análise Química*, 4 a ed., Editora Átomo: Campinas, 2002
24. GUIMARÃES, G, A, R.; RUBINI, C, P, L.; SCLOGEL, E, M.; FUGMAN, H, A, J.; PINHEIRO, L, I., *Pesticidas - métodos de análise & informações técnicas*, vol 1, Paraná, 1988.
25. SILVERSTEIN, R, M.; WEBSTER, F, X.; KIEMLE, D, J.; *Identificação espectrométrica de compostos orgânicos*, Rio de Janeiro, LTC, 2007.
- 26 MILLER, J. C.; MILLER, J. N.; *Statistics for Analytical Chemistry*, 2ª ed., Ellis Horwood: Chichester, 1988.
27. DEAN, J. R.; XIONG, G. Extration of organic pollutants from environmental matrices: selection of extraction technique. *Trends in analytical chemistry*, v. 19, n. 9, 2000.
28. BRAULT, E, K; GOEBEL, M, E; GEISZ, H, N; CANUEL, E, A; DICKHUT, R, N, Inter-annual variation of Persistent Organic Pullutants (POPs) in a Antartic Top Predator *Arctocephalus gazell*. **Environmental Science & Technology**. 2013.
29. KOELMANS, A, A; BESSELING, E; WEGNER, A; FOEKEMA, E, M; Plastic as a Carrier of POPto aquatic organisms: A model analysis. **Environmental Science & Technology**. 2013.
30. TOLEDO, H. H. B.; INOMATA, O. N. K.; LEMES, V. R. R. Curso Análise de Resíduos de Pesticidas. Instituto Adolfo Lutz, São Paulo, 1997.