CHEMICAL CHARACTERIZATION OF PERSISTENT ORGANIC POLLUTANTS (POPs) AND DEVELOPMENT OF ITS DECOMPOSITION IN AN INDUSTRIAL AREA OF SÃO PAULO, BRAZIL

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Introduction

In compliance with the Treaty of Stockholm[1], hosted by the United Nations and financially supported by the Global Enabling Facility (GEF), which provides for a bank of at least 26 Persistent Organic Pollutants - POPs, in which Brazil is one of the 179 countries which ratified the Stockholm Convention, this work aims to contribute positively to this environmental issue. The study aimed to develop and validate a method to identify and quantify persistent organic pollutants, known as POPs, in soil of industrial regions Caieiras and Franco da Rocha municipalities, São Paulo, Brazil, by Gas Chromatography coupled with Mass Spectrometry (GC/MS) and Electron Capture Detector (GC/ECD). The GC/MS does the qualitative analysis of the POPs and the GC/ECD does the quantitative analysis of the respective POPs[2]. These compounds are highly toxic and stable in the environment and living organisms, among which are addressed in the work as chlordane cis/trans ($C_{10}H_6Cl_8$), heptachlor ($C_{10}H_5Cl_7$), heptachlor epoxide cis/trans ($C_{10}H_5Cl_7$) and the isomers α, β, γ and δ benzene hexachloride BHC (C_6Cl_6). To ensure reliability of the analysis carried out, the method was validated based on the guidelines of INMETRO[3]. The samples analyzed were contaminated by compounds hexachlorobenzene α, β, γ and δ, many of which are above the maximum allowable in accordance with national legislation and international law[4].

Besides the development of characterization methods, IPEN has also developed advanced processes for safe decomposition of POPs. The molten salt oxidation is a process which promotes a more complete and safer decomposition of wastes considered critical, such as POPs. This paper presents the activities of construction and development of a molten salt reactor for decomposition of hazardous wastes, as well as some results from the decomposition of pesticides[5].

Materials and methods

The following materials and methods were employed for the analysis of POPs. The second part of the work describes the development process for safe decomposition of the following POPs.

Extraction methodology

The extraction employed was the QuEChERS method (Quick, Easy, Cheap, Effective, Rugged, and Safe), achieving recovery in the range 70 to 120% for the most of compounds, acceptable for complex matrices[6]. The limits of detection and quantification of the method comprises the range of 0.0002 and 0.01 $\mu g.g^{-1}$, respectively[7]. Figure 1 shows detail of the QuEChERS method, these are the follow: a) 10 g sample in a 50 mL Falcon tube within 20 mL acetonitrile, b) shake during one minute, c) add 4 g of $MgSO_4$, 1g of NaCl, 1g trisodium citrate and 0.5 g of sodium hydrogencitrate sesquihydrate, d) shake for one minute, e) centrifugation for 5 min at 3000 RPM, f) transfer 10 mL aliquot to a 20 mL Falcon tube, g) add 0.95 g of $MgSO_4$ and 0.15 g of Bondesil PSA, h) centrifugation for 5 min at 3000 RPM and inject to GC analyzer.

FIGURE 1 – Extraction of the POPs by QuEChERS method from the industrial region soil.

Chemicals and standards

The chemical standards: chlordane cis/trans ($C_{10}H_6Cl_8$), heptachlor ($C_{10}H_5Cl_7$), heptachlor epoxide the cis/trans ($C_{10}H_5Cl_7$) and the isomers α, β, γ and δ BHC (C_6Cl_6) were obtained from Sigma-Aldrich (Steinheim, Germany). Magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), sodium citrate ($C_6H_5Na_3O_7$), sodium hydrogencitrate sesquihydrate ($C_6H_6Na_2O_7$ 1,5H_2O), absorbent Bondesil PSA, acetonitrile and iso-octane (HPLC-grade) were purchased from Tedia, Brazil.

Gas chromatograph and mass spectrometry

The experiments were performed using two gas chromatographs. One is a gas chromatograph coupled with mass spectrometry GC/MS Shimadzu QP-5000 and the other is a gas chromatography with electron capture detector GC/ECD Shimadzu GC-17A. Both gas chromatographs were equipped with 30 m DB-5 capillary column (J&W Scientific, Folsom, CA.) with internal diameter of 0.25 mm and 0.25 µm film thickness. Helium was used as carried gas with column head pressure of 12 p.s.i. (1 p.s.i. = 6894.76 Pa) and average flux of 1 mL min^{-1}. The temperature program for the GC column consisted of one minute hold at 80 °C, a 25 °C min^{-1} ramp to 210 °C, an isothermal at 210 °C during 7 min, a 35 °C min^{-1} ramp to 290 °C and one min hold at 290 °C. The injector, transfer line and MS temperature were set at 250 °C, 290 °C and 170 °C, respectively. The mass range used was m/z 65 to 400 with a scan time of 500 ms in the electron impact mode with electrons of 70 eV. The electron multiplier voltage was set as 1500 V. The Selected Ion Monitoring (SIM), which is a resonant ejection mode, was used. This technique consist of an application of multi-frequency waveforms imposed to quadrupoles bars so that undesired ions are ejected and characteristic selected ions are monitored[8]. For this purpose, a waveform was built in order to monitoring γ- BHC ions at m/z 109, 181, 183, 217 and 219. Pentachlorophenol was monitored by ions at m/z 165, 167, 264, 266 and 268. Heptachlor ($C_{10}H_5Cl_7$) was monitored by ions at m/z 65,

100, 270, 272 and 274. Heptachlor epoxide was monitoring by ions at m/z 81, 351, 353, 355 and 357. Chlordane cis/trans was monitored by ions at m/z 237, 371, 373, 375 and 377.

Results and discussion:

Results for the Caieras site are presented on Figure 2. The x-axis relates to the sampling site and the y-axis to the concentration in $\mu g.g^{-1}$. Samples from 1 to 7 were collected on a landfill site and from 8 to 15 were collected on an irregularly occupied area close by (Figure 3). The α isomer of BHC showed higher concentration, mostly above the EPA limit for industrial sites (0.27 $\mu g.g^{-1}$), being the highest concentration of 66 $\mu g.g^{-1}$.

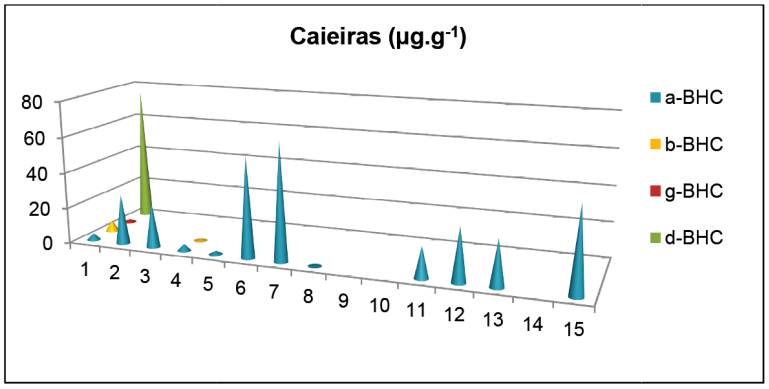

FIGURE 2 – Results from the Caieras sampling site

FIGURE 3 – Sampling sites of Caieras, São Paulo. The numbers represent the sites in figure 2.

Results for the Franco da Rocha sampling site are presented on Figure 4. This area is unpopulated and comprehends only the landfill (Figure 5). Results from all isomers of BHC were higher than the previous location, Caieras, and the α isomer presents the highest concentration, ranging from 0.2 to 70 $\mu g.g^{-1}$.

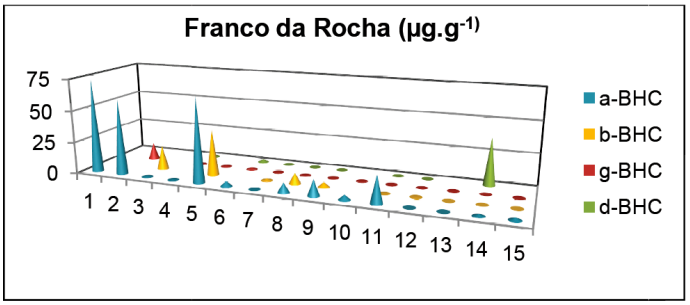

FIGURE 4 – Results from the Franco da Rocha sampling site.

FIGURE 5 – Sampling sites of Franco da Rocha, São Paulo. The numbers represent the sites in figure 4.

Conclusions

Among the major POPs could be cited pesticides, dioxins and PCBs that represent, according to the United Nations Industrial Development Organization - UNIDO, one of the most serious and urgent problems to be faced, because on the one hand, its wide dissemination in environment and, secondly, because of its properties and characteristics, which determine its persistence in soil and water. The technology developed at IPEN is applicable for intrinsically safe disposal of hazardous organic wastes, particularly the organochloride, whose degradation has presented problems when using the most common methods, such as incineration. The molten salt oxidation is a process which promotes a more complete and safer decomposition of wastes considered critical, such as POPs. This process is developing and promoting in the IPEN laboratories with the objective to eliminate the serious contamination in São Paulo areas.

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