International Journal of Advanced Research in Engineering Technology & Science
ISSN: 2349-2819
Email: editor@ijarets.org Volume-7, Issue-2 February- 2020 www.ijarets.org

CHEMICAL CHARACTERIZATION OF PERSISTENT ORGANIC POLLUTANTS (POPS) IN THE ENVIRONMENT

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ABSTRACT

Persistent Organic Pollutants (POPs) are a group of toxic chemicals that resist degradation and persist in the environment, posing significant risks to ecosystems and human health. This study provides a comprehensive overview of the chemical characterization of POPs, focusing on their identification, monitoring, and impact assessment in various environmental matrices. The research begins by detailing the diverse classes of POPs, including polychlorinated biphenyls (PCBs), organochlorine pesticides, and polybrominated diphenyl ethers (PBDEs). We discuss their sources, pathways, and the factors influencing their distribution and persistence in the environment. The study explores advanced analytical techniques for the identification and quantification of POPs in environmental samples. Gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) methods are among those highlighted. We also examine the use of passive samplers and remote sensing technologies for monitoring POPs over large geographic areas. the research delves into the toxicological and ecological consequences of POP contamination. We assess their bioaccumulation and biomagnification in aquatic and terrestrial food chains, as well as their adverse effects on wildlife and human populations. Special attention is given to the endocrine-disrupting properties of certain POPs. The study emphasizes the importance of international agreements such as the Stockholm Convention in regulating and phasing out the production and use of POPs. We also discuss strategies for managing and remediating POP-contaminated sites and ecosystems. this study offers a comprehensive exploration of the chemical characterization of Persistent Organic Pollutants in the environment. By providing insights into their identification, monitoring, and ecological impact, we contribute to the ongoing efforts to mitigate the global threat posed by POPs and protect both ecosystems and human health.

Keywords: *Chemical, POPs, Environment*

INTRODUCTION

POPs, which stands for "persistent organic pollutants," are organic molecules that, to varied degrees, resist being broken down by photolysis, biological processes, and chemical processes. Because of their low water solubility and high lipid solubility, persistent organic pollutants, or POPs, tend to bioaccumulate in fatty tissues due to the fact that they are frequently halogenated. In addition to this, they have a semi-volatile nature, which allows them to travel great distances in the atmosphere before being deposited there. Although many different forms of POPs may exist, both natural and anthropogenic, POPs which are noted for their persistence and bioaccumulative characteristics include many of the first generation organochlorine insecticides such as dieldrin, DDT, toxaphene and chlordane and several industrial chemical products or byproducts including polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (dioxins) and dibenzo-p-furans (furans). Many of these chemicals have been or are now being used in significant quantities, and as a result of their propensity to remain in the environment, they have the potential to bioaccumulate and biomagnify in living organisms. Some of these chemicals, such as PCBs, have the potential to remain in the environment for extended periods of time and can bioconcentrate to levels as high as 70,000 times their original concentration. POPs are also notable for their semi-volatility, which is a trait of their physico-chemical properties that allows these compounds to exist either in the vapour phase or adsorbed on atmospheric particles, so making it easier for them to be transported over long distances in the atmosphere. This semi-volatility is another characteristic that makes POPs stand out among other air pollutants. Compounds such as PCBs may be found all over the world due to their extraordinary ability to survive for long periods of time and to only partially volatilize, as well as due to the fact that they share other features with other substances. This includes areas in which PCBs have never been utilized. POPs may be found almost anywhere. They have been measured on all of the world's continents, at locations that are intended to be representative of the world's several major climate zones and geographic regions. In these isolated places, such as the open oceans, deserts, the Arctic, and the Antarctic, there are no substantial local sources of the element in question, therefore the only conceivable explanation for their presence is long-distance transit from other parts of the world. There have been reports of PCBs in the air at concentrations as high as 15ng/m3 in all parts of the world; but, in industrialized regions, the amounts may be far higher by several orders of magnitude. There have also been reports of PCBs being found in snow and rain. Two of the most important subgroups of POPs are the polycyclic aromatic hydrocarbons and the halogenated hydrocarbons. POPs also include some of the halogenated hydrocarbons. This latter category consists of several organochlorines that, over history, have shown themselves to be the most resistant to degradation and that have had extensive manufacturing, usage, and release characteristics. Of all the halogenated hydrocarbons, these chlorinated derivatives are often the ones that stick around the longest. In general, it is known that the more highly chlorinated biphenyls have a tendency to accumulate to a higher extent than the less chlorinated PCBs; similarly, metabolism and excretion is also more quick for the less chlorinated PCBs than it is for the highly chlorinated biphenyls. POPs can enter humans' bodies through their food, through occupational mishaps, and through the environment (particularly indoor environments). Acute or chronic exposure to persistent organic pollutants (POPs) has been linked to a broad variety of harmful consequences on human health, including disease and even death.

POPs have been linked to a variety of negative health effects, including endocrine disruption, reproductive and immunological dysfunction, neurobehavioral problems, and cancer, as a result of research conducted in laboratories and environmental impact studies conducted in the wild. More recently, some POPs have been linked to lowered immunity in newborns and children, as well as a rise in concurrent infections, as well as developmental abnormalities, neurobehavioral impairment, and the formation or promotion of cancer or tumors. Some POPs are being looked at as possibly key risk factors in the etiology of human breast cancer by some writers. This is something that has been going on for a while.

PROPERTIES AND ENVIRONMENTAL BEHAVIOUR OF PERSISTENT ORGANIC POLLUTANTS

The chemical and physical qualities of substances, as well as the characteristics of the environment, are what ultimately decide how chemicals behave and what happens to them in the environment. The structure of the molecule and the characteristics of the atoms that are present in the molecule are what define the chemical and physical properties of the molecule. These physical and chemical characteristics can take on a wide variety of values, depending on the structure of the molecule they are attached to. Compounds might have very low persistence, low toxicity, and immobility all at the same time. It is extremely improbable that these substances will pose a threat to either human health or the health of the environment. hazardous and lipophilic POPs are found in a range of the distribution that includes the compounds that are persistent, mobile, and hazardous. This range of the distribution represents the opposite end of the spectrum from the first. The relationship between environmental behavior and exposure is quite strong. Therefore, the danger of exposure to a material will be significantly reduced if the substance is not persistent, and the risk, if any, will be confined to a specific area, unless the substance possesses features that enable it to migrate to sites that are further apart. It is essential to acknowledge that only a modest number of compounds are capable of fulfilling the requirements to be classified as POPs. In point of fact, if the spectrum of these qualities were shown in the form of a distribution, only the compounds at the extreme ends of the distribution would exhibit the level of persistence, mobility, and toxicity necessary to classify them as POPs (Figure 2). Some chemicals may have extraordinarily long half-lives in the environment (t12 values that are longer than six months), making them exceedingly difficult to remove. Clarification is needed about the nature of this persistence, which may be defined as the amount of time the molecule will remain in the environment before being broken down or degraded into other compounds that pose a lower risk. The disappearance of a material is referred to as dissipation, and it is the result of the interaction of at least two processes, namely mobility and deterioration. Because mobility may just result in the substance being carried to other areas where, if critical concentrations are obtained, adverse effects may occur, it is not an acceptable measure of persistence. Mobility may simply result in the substance being transported to other locations. POPs have a number of interesting properties, one of which is that they are semi-volatile. This characteristic provides a degree of mobility in the atmosphere that is adequate to allow relatively large volumes to enter the atmosphere and be carried over long distances. Because of this property's mobility through the atmosphere, it is possible to transport volatile organic compounds over long distances. Due to the substance's modest volatility, it is not possible for it to persist indefinitely in the atmosphere, where it would provide a negligible direct threat to both people and other species in the environment. Therefore, these chemicals have the potential to evaporate in warmer places, but they will condense and have a greater propensity to remain in colder ones. In general, highly halogenated substances, those with a molecular weight in the range of 200 to 500, and a vapour pressure that is lower than 1000 Pa are considered to have this feature. POPs must also have a quality that results in their migration into organisms in order for them to be able to concentrate in the organisms that are found in the environment. This quality is known as lipophilicity, and it refers to the tendency of a substance to dissolve more easily in fats and lipids than in water. Because of the substance's high lipophilicity, it is able to undergo bioconcentration within the organism, moving in from the surrounding medium. Lipophilicity, when combined with other factors like as environmental persistence and resistance to biological degradation, can lead to biomagnification along the food chain. Because of biomagnification, species at the top of the food chain are subjected to significantly higher concentrations of contaminants.

CHEMISTRY AND TOXICOLOGY

POPs are organic molecules that, by definition, cannot be degraded very easily by either biological or photolytic processes or through chemical methods. POPs are frequently halogenated, with chlorination being the most common form. The carbon-chlorine bond is particularly resistant to hydrolysis, and the larger the amount of chlorine substitutions and/or functional groups, the greater the resistance to biological and photolytic degradation. Chlorine is a very reactive element. When compared to chlorine in aliphatic structures, chlorine that is linked to an aromatic ring (such as benzene) is more resistant to hydrolysis. As a direct consequence of this, chlorinated POPs often take the form of ring structures that are composed of a chain or branching chain framework. POPs have a propensity to rapidly pass through the phospholipid structure of biological membranes and accumulate in fat deposits as a result of their high degree of halogenation, which gives them very low water solubility and high lipid solubility. This gives them the ability to pass through biological membranes and accumulate in fat deposits. One of the most significant classes of POPs is called halogenated hydrocarbons, and within this class, the organochlorines are by far the most important class. The compounds known as dioxins and furans, PCBs, hexachlorobenzene, mirex, toxaphene, heptachlor, chlordane, and DDT are all examples of the family of chemicals known as organohalogens. These chemicals have a low solubility in water but a high solubility in lipids. They, like many other persistent organic pollutants (POPs), are known for their ability to remain in the environment, have lengthy half-lives, and have the potential to bioaccumulate and biomagnify in living organisms once they have been released into the environment. Although it is known that certain organochlorines come from natural sources, the vast majority of persistent organic pollutants come almost exclusively from human sources. These sources are mostly related with the production, use, and disposal of specific organic substances. On the other hand, HCB, dioxins, and furans are byproducts of a variety of manufacturing and combustion processes that were not intended to produce them. As was said before, POPs are often molecules that are only semi-volatile, which is a property that makes it easier for these chemicals to be transported over great distances. Because of this, they are able to travel vast distances through the atmosphere. Following the application of POPs that are being employed as pesticides, volatilization may take place from the plant and soil surfaces. Halogenated organic compounds, and chlorinated organic compounds in particular, have become deeply ingrained in today's society. These compounds are utilized by the chemical industry in the production of a wide variety of products, including polyvinyl chloride (millions of tonnes per year), solvents (several hundreds of thousands of tonnes), pesticides (tens of thousands of tonnes), specialty chemicals and pharmaceuticals (thousands of tonnes down to kilogram quantities), and so on. In addition, both anthropogenic and non-anthropogenic sources can contribute to the formation of undesired by-products and emissions, which are frequently distinguished by their ability to persist for long periods of time and resist being broken down (for example, chlorinated dioxins). As was mentioned before, molecules containing organochlorine exhibit a diverse set of physicochemical characteristics. Many different microbiological, chemical, and photochemical reactions can be responsible for the transformation of organochlorines in their natural environments. The physicochemical qualities of the particular molecule as well as the features of the environment in which the compound is to be processed are major factors that determine how effective environmental procedures are. Compounds with molecular weights greater than 236 g/mol that are cyclic, aromatic, cyclodiene-type, and cyclobornane type chlorinated hydrocarbons, such as certain chlorinated pesticides, have been noted for their ability to accumulate in biological tissues, and to particularly concentrate in organisms that occupy positions in the upper trophic levels. It should come as no surprise that these compounds are also known for their persistence in the environment. Some of the early organochlorine pesticides, such as DDT, chlordane, lindane, heptachlor, dieldrin, aldrin, toxaphene, mirex, and chlordecone, are included in this class of compounds, and they typically share many physico-chemical features with one another. This class of compounds also includes chlordecone. On the other hand, the chlorinated hydrocarbons with a lower molecular weight (less than 236 g/mol) can include a number of alkanes and alkenes (dichloromethane, chloropicrin, chloroform), and they are typically associated with little acute toxicity, reversible toxicological effects, and relatively short half-lives in both the environment and in living organisms. That portion of the total concentration of a chemical that is available for uptake by a specific organism is referred to as bioavailability. Bioavailability is controlled by a combination of the chemical properties of the compound, including the surrounding environment, as well as the morphological, biochemical, and physiological characteristics of the organism itself. In most cases, the metabolic transformation of organic contaminants into more polar forms is what makes the process of excreting them easier. POPs are not easily expelled due to their susceptibility to degradation and breakdown, and those pollutants (such as toxaphene, PCBs, and others) that are the most resistant to metabolism and disposition have a tendency to accumulate in organisms and via the food chain. Notably, some organic pollutants may also be transformed to metabolites that are more persistent than the parent substance. One example of this is the metabolic conversion of DDT to DDE, which is a chemical with a longer half-life than DDT. In a similar vein, it is interesting that the metabolic conversion of aldrin to its very environmentally persistent metabolite dieldrin occurs at a fast rate.

METHODS

The collection was carried out by the "Companhia Ambiental do Estado de So Paulo – CETESB" at the Billings dam, where a total of eight points were gathered. The following locations have been designated as collecting points: "1o Linha, 2o Linha, Estoril, Corpo Central, Braco Capivari, Bororé, Elta, and Tahiti." Because of their long histories of chemical contamination, these specific locations were chosen. The samples were collected in amber bottles weighing one kilogram each, kept at a temperature of around four degrees Celsius for conditioning, and labeled with the respective localization, GPS coordinates, and collection date of each sample. The QuEChERS technique was chosen for the extraction of samples because it employs "green chemistry" and requires just a minimal amount of solvent. In this technique of extraction, 10 grams of the sample were weighed, followed by the addition of 20 milliliters of acetonitrile, stirring for twenty minutes, followed by the addition of 4 grams of magnesium sulfate, one gram of sodium chloride, one gram of sodium citrate, and five grams of sodium hydrogencitrate sesquihydrate. After that, it was mixed and centrifuged once more. After removing the supernatant, the sample was placed in a vial with a capacity of 2 milliliters. The material is now prepared to undergo chromatographic examination. The QuEChERS extraction only requires a little amount of solvent and takes a short amount of time (about thirty minutes of extraction time and twenty milliliters of solvent). The purpose of this work is to evaluate the effectiveness of this extraction method in comparison to other methods that have previously been utilized. The gas chromatography with electron capture detector, also known as GC/ECD, generates free electrons by exposing a sample to a tiny amount of radioactive material (63Ni). This process is known as the electron production step. The electrons that are created as a consequence of this process are gathered in the anode, which causes current to be generated. This current is then amplified by an electrometer, which results in the baseline. In the event that the sample possesses an affinity for electrons, it will be able to "capture" these electrons as it travels through the detector. This will result in a reduction in the amount of current that is generated, which will be proportional to the sample's concentration.

METHOD VALIDATION

The validation of a method is a process that starts with the planning of the analytical strategy and continues through its development. The planning of the analytical strategy is the first step in the validation of a method. This should confirm, via experimental tests, that the technique satisfies the requirements of the analytical applications; doing so will guarantee that the results can be trusted. Analytical metrics such as Limit of Detection (LD), Limit of Quantification (LQ), Recovery, Repeatability, and Uncertainty measurements were utilized during the course of this investigation.

RESULTS

In a vial containing 2 milliliters of n-hexane, a calibration curve was constructed with the following concentrations: 1, 2, 3, 10, 15, 20, and 30 micrograms per kilogram. Every single one of the POPs' calibration curves managed to achieve a linearity of at least R = 0.995. The detection limit, often known as the LD, is the point at which the apparatus can detect anything without putting itself in danger. The lowest detectable concentration (LD) of this approach for any and all POPS that were investigated is determined to be 0.1 g kg-1, which is the starting point of the calibration curve. The quantification limit identifies the minimum value that the apparatus is able to quantify in a secure manner. The LQ for this technique is 0.2 micrograms per kilogram, which may be found as the second point on the calibration curve. In order to conduct a recovery analysis, seven separate examples of each component were administered at a concentration of 0.1 micrograms per kilogram. It is expected that the sediment matrix will recover between 40 and 120% of its original volume. The formula for calculating the recovery of the POPS is shown in Table 1.

Table 1: For the POPs that were investigated, the analytical parameter Recovery (%) was calculated.

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

Repeatability is the degree of concordance between the findings of repeated measurements of the same analyte, carried out under the same measurement settings, same measurement process, same analyst, and same instrument used under the same conditions and repeats in short time. Additionally, repeatability requires that the measurements be carried out in a short amount of time. Seven measurements with no analyte present were collected for each level, and then concentrations of the analyte ranging from 1 to 2 levels were added. After the analytical data shown in the repeatability record, it is presented in Table 2.

Table 2: For each of the POPs that were investigated, the analytical parameter known as Repetitivity was computed, where SD stands for the standard deviation and RSD for the relative standard deviation.

Compound	Concentration	Average	SD	RSD
	1	1,097	0,05407	4,92846
Aldrin	2	1,87	0,08793	4,70264
	1	1,061	0,04598	4,33202
Dieldrin	2	2,137	0,03817	1,78614
	1	1,081	0,04561	4,21825
Endrin	2	2,084	0,03207	1,53872
	1	1,069	0,04879	4,56637
DDE	2	2,076	0,06241	3,00676
	1	1,089	0,05398	4,95917
DDD	2	2,081	0,07010	3,36797
	1	1,091	0,05209	4,77345
DDT	2	2,094	0,05472	2,61324
	1	1,079	0,04810	4,46025

Heptachlor	2	2,097	0,04386	2,09147

Uncertainty in a measurement is a metric that is connected with the outcome of a measurement, and it is used to define the spread of values that may be legitimately given to the thing being measured. In order to compute the measurement uncertainties, we utilized the uncertainties from the calibration certificate of the glassware that was used in the analysis. Additionally, we used the uncertainty from the micro syringe, the uncertainty from the standard of analysis, and the uncertainty from the calibration curve. The uncertainty in the measurements is presented in Table 3.

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

Measurement uncertainty	**µg 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 that were taken at the Billings dam for this investigation did not contain any of the POPs that were investigated. Spikes were conducted on four of the eight samples, and recovery of more than eighty percent of the analytes was obtained.

CONCLUSIONS

The qualities of lipophilicity, persistence, and semi-volatility are some of the distinctive features of the POPs that are described in this Assessment Report. Other distinguishing characteristics include toxicity. Because of these features, the environmental durability of these compounds is likely to be fairly high, as is their potential for long-distance transportation. Additionally, due to these properties, the likelihood of their being transported great distances is also high. These substances are also known for their propensity to biomagnify and bioconcentrate in the natural environment, which, if allowed to continue, might result in the attainment of concentrations that are substantial from a toxicological point of view. At least some of the countries are still making use of a sizeable portion of the chemicals that are covered in this study. This is true for at least some of the countries. It has not been possible to accurately determine the quantities of these substances that are still in use, where they are used, the particular crops to which the pesticidal substances are being applied, or the direction that is being taken or the initiatives that are being taken to eliminate these substances all over the world because there is a lack of reliable data regarding use and disposal. This is due to the lack of dependable data on the usage of the product and how it should be disposed of. When data are accessible, they are frequently subject to a variety of limitations, which makes it difficult to develop use profiles that are both comprehensive and accurate. Even though there is compelling evidence for the actual and potential toxic impact of these substances on both human health and the environment, it is imperative that an inventory that is complete, accurate, and trustworthy of the manufacture, use, and disposal of these substances throughout the world be developed in order to facilitate the effective and efficient elimination of these substances everywhere in the world. This will allow for the elimination of these substances in a manner that is both effective and efficient. In order to perfect the process of extracting sediment samples from the Billings dam using CETESB, up to one kilogram of sediment was collected at each of the eight places that had been selected in advance. QuEChERS was able to realize the extraction, which led to the development of a technology for the extraction of POPs analytes from samples taken from the Billings dam. When doing the examination of the samples, GC/ECD and GC/MS chromatographs were utilized, and analytical values of micrograms per kilogram were attained. The QuEChERS technique has been verified by meeting the requirements of INMETRO's criteria, which include repeatability, reproducibility, detection limit, measurement limit, and measurement uncertainty. The limit of detection is determined to be 0.1 g kg-1, whereas the limit of quantification is set at 0.2 g kg-1. The reliability of this validation was established by the acquisition of recovery values ranging from 40% to 120% for the sediment matrix.

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