

Analytes Extraction and Quantification for Organochlorine Pollutant Residues in Water and Sediments of River Elbe

Muhammad Jamil Khan

Department of Soil & Environmental Sciences, Gomal University, DIKhan, 29050, Pakistan
shahmir3rd@yahoo.com

Abstract. During the comparison of various organic pollutant extraction methods soxhlet extraction method was considered erroneous due to the time consumption and quantity of solvents. The step of evaporation is also considered a cause to erroneous readings. While the extraction done by supercritical method (SFE) is thought to be fast, requiring low solvent volumes but selective. This extraction method is very challenging because of the presence of polarity and numerous other materials present in the residues. Therefore, the criteria for extraction should be thoroughly examined before the method's selection. Accelerated Solvent Extraction (ASE) is the method of extraction using high temperature and heavy pressure to get maximum results of the extraction process. It is commonly used as extraction method for the pollutants due to its time efficiency, accuracy and environment friendly nature. The MASE (Microwave Assisted Solvent Extraction) takes less time as compared to other conventional methods of sample extraction. It has also got a plus point that high grade pure water can also be used as solvent in place of organic solvents, which are most environments friendly. It is therefore concluded that Accelerated Solvent Extraction (ASE) is the most suitable and efficient procedure for analytes extraction in combination with quantification by GC-MS.

Keywords: Analytes Extraction, Organochlorine, Water, Soil, Elbe

1. Introduction

Organochlorines belong to the group of Persistent Organic Pollutants (POPs) which mostly contain organic compounds of anthropogenic origin from agriculture and industry. They are highly resistant to chemical or biological degradation and exist in the environment (soil sediments and water) even for decades and are readily accumulated in the organic tissues and also contaminate different food items. Due to their long life POPs can travel from one continent to other and contaminate the area where the residues make their way through rivers, oceans and other means (WHO 2003). These organic pollutants are highly dangerous for human life and the environment on earth.

The German River named Elbe is 1100 km long and has got about 65 % of its catchment's area in Germany, 34 % in Czech Republic and a small portion in Poland and Austria (A.L.P.C.N., 2001), is the contaminated due to its flood water getting back to the river from the flood plains. This water brings suspended organic pollutants and pesticide residues into the river and its pollution level increases after each flood season (Gorte et al., 2005) which is substantially higher than the level fixed as a limit in the Federal Soil Protection and Contaminated Site Ordinance (from 12.07.1999). These organic pollutants not only deteriorate the water quality temporarily but also cause a permanent danger to the human health and marine life. This is also evident by the fact that a wide range of soils are contaminated along the entire bank of German river Elbe (Krüger and Gröngröft, 2003).

Due to the high volatile nature of organochlorines the selection of methods of analytes extraction has got primary importance. Soxhlet extraction is one of the old techniques where the analytes are extracted in a process called cleaning process followed by solid phase extraction (SPE). Supercritical fluid extraction

(SFE), accelerated solvent extraction (ASE) and microwave assisted solvent extraction (MASE) are some of the most recently developed techniques used for the sample preparation for GC-ECD/FID/MS analysis.

Therefore, the present work is outlined as a review report to summarize important previous research work published and unpublished on the status of Organochlorine Pesticides in river Elbe. Along with the residues determination, the paper will not only concentrate on comparison among the existing methods of sediments/water extract (analytes) preparation like soxhlet extraction, supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and microwave assisted solvent extraction (MASE) for GC-ECD/FID/MS but will also endure to conclude for the most suitable technique of extraction which gives the most accurate and minute quantity detections of the compounds in the samples.

2. Pesticides used in Germany and Czech Republic: The region which contribute mostly as the catchment's area to River Elbe.

The present data on the pesticides used in Germany was collected from various sources publishing pollutants residue data of surface water, groundwater and edibles from 1997 to 2001. The knowledge on pesticide use and their pollution of natural resources in Germany is very thin. Therefore the above mentioned sources were considered as a main source of information on pesticide used on different crops and their residues (Pesticide Action Network, Germany, 2002). Names of more than 50 pesticides were published in the contaminants detection list including the five most dangerous pesticides (dimethoate, chlorpyrifos, cypermethrin, cyfluthrin and lambda-cyhalothrin). This data was obtained from the studies carried out on various crops. The study has found following pesticide residues, which indicate that they have been or being used in Germany.

2.1. List of Various Pesticides Detected in Germany

Organochlorines: DDT, DDD, DDE, HCB, HCH, BHC, Azinphos-methyl, Endosulfan, Lindane,.

Organophosphate Group: Chlorfenvinphos, Dimethoate, Bromophos, Azinphos-methyl, Chlorpyrifos, Diazinon, Dioxathion, Disulfoton, Ethion, Etrifos, Fenamiphos, Fenchlorphos, Fenitrothion, Fenthion, Malathion, Methamidophos, Methyl Parathion, Mevinphos, Omethoate, Parathion, Phosalone, Quinalphos.

N-Methyl Carbamate: Carbofuran, Carbaryl, Pirimicarb.

Pyrethroids: Cyfluthrin, Cypermethrin, Deltamethrin, Lambda Cyhalothrin, Permethrin.

3. A brief review of literature on organochlorines in River Elbe, methods of analytes extraction, quantification and their limits of detection

The detailed comparison of different methods used for Elbe sediments and water analytes extraction and quantification along with the limits of detection for different organochlorines residues is given in Table 1 and 2. Table 1 contains the reviews for sediment samples analysis and Table 2 shows the water samples analysis. Most of the reviews are about River Elbe but few from other countries like Czech Republic, which contributes to the catchment's area of River Elbe, are also included. One each from Belgium, Pakistan and India is also included for comparison of different methods used for extraction and analysis.

Thorough study of literature showed no significant effect by different analytes extraction methods like soxhlet extraction, SFE, ASE and MASE on the limit of detection (LoD) of different organochlorine compounds while the quantification technique GC/MS has in certain cases given better results as compared to GC/ECD and GC/FID (Nuzhat et al. 2004; Umlauf et al. 2005 and Watanabe et al. 2005).

4. Different Methods of Sample/Analytes Extraction from Sediments and Water

Presently most of the Organochlorine Pesticides residues are determined by GC-MS/NPD/ECD/FID. And the most abundantly used technique is GC-MS. Due to the highly volatile nature of the Organochlorine Pesticides the selection of methods for analytes extraction is also the basic important step to determine the minute quantities and avoid any erroneous results. The most common old and new methods used for the analytes extraction from marine sediments (solid particles) are the soxhlet extraction, supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and microwave assisted solvent extraction (MASE) for GC-MS/NPD/ECD/FID. Some of these procedures are well established for a long time and some are

quite new. Here we will also concentrate on different methods in detail and will compare them with each other. At the end we may be able to recommend any one of them which should be more accurate and more efficient depending upon the length of time, kind and quantity of solvent or solvents required for sample extraction and their efficiency in detection.

These different procedures are discussed in detail as follows:

4.1. Soxhlet Extraction Method (USEPA methods 3540-41)

During the Soxhlet extraction method, two common procedures are followed:

1. The sample is mixed with desiccant mixture in glass or paper thimble and is placed for leaching with the warm solvent/ mixture of solvents. The leaching time varies from 5 upto 12 hours. The solvents most commonly used are diethyl ether, acetone, DCM and hexane, alone and in mixtures (EPA 3540).

2. During automated Soxhlet e.g. "Soxtec" Extraction the paper thimble is kept dipped for about one hour in the boiling solvent after which extraction is carried out. Solvent (same as in EPA 3540) can also be evaporated (EPA 3541) (Camel, V. 1998). After extraction the analyte is then subjected to a clean up process.

4.2. Supercritical Fluid Extraction (SFE)

This process of extraction involves four-steps: First of all the target compound is desorbed or separated from the matrix and subsequently defused into the matrix; Secondly the desired analyte is dissolved by the supercritical fluid; which is removed from the extraction cell by the fluid in the third step; In the fourth step the solutes are then collected by trapping as a result of depressurization of the fluid. The Sample is usually desiccated and then placed in the cartridge and carbon dioxide chambers where pressure is kept at 150-450 atm and the temperature is 50-150°C. Before collection the analyte is depressurized and finally collected in solvent trap comprised of hexane alone or hexane+DCM (EPA 3560-3562). High speed blending is also useful but only for those samples which contain high amount of water such as plant tissues and other parts. The samples are then homogenized with sodium chloride and acetone (Specht et al. 1995).

4.3. Accelerated Solvent Extraction (ASE)

ASE (Dionex ASE 200, Salt Lake City, UT) is the analytes extraction procedure where solvents of organic nature are added at high temperatures under a specific degree of pressure. During this process sample is mixed with the solvents in a steel cell and is heated with automatic heaters supplemented by pumps which are operated by the autofed programs. Following steps are involved in the process; 1) Loading of cell containing sample, 2) Application of solvent to samples under a specific pressure, 3) Heating of the cell containing sample under a constant pressure, 4) Static extraction, 5) Removal of extract from the cell and collecting it in a sealed glass vial which is washed with fresh solvent 6) Nitrogen purge of cell, and 7) Reloading of new sample for extraction (Brumley 1998).

The process of extraction starts from loading soil sample into the vessel which is extracted with a 1:1 mixture of methylene chloride-acetone / sodium acetate, acetic acid in menthol (1:1) at the temperature of 150°C and a pressure of 1500 psi (10 Mpa). The time duration is kept for 5 minutes which is the static time (DIONEX, Application Note, 339, 2001).

It is in practice that the volume of solvent used for extraction is brought upto 15 ml at the end. After the analyte extraction their concentration is brought to the acceptable lower range and even exchanged if necessary. The solvent used should be compatible with the cleanup process and method determination carried out to get the results. This final volume of sample (15 ml) is further brought down to near dryness and made up to one ml by adding methylene chloride (and acetone to get the complete dissolution) for subsequent HPGPC fractionation.

4.4. Microwave Assisted Solvent Extraction (MASE)

A sediment sample in the range of 1-10 gm is weighed and placed in the microwave oven for heating. Approximately 8 ml of organic solvents like acetone, hexane: acetone (mixture) and methanol/ (methylene chloride-acetone mixture (50:50 v/v)) / water at 600 W are added (Basheer et al. 2005) and heated for 20 minutes per extraction. Later the extract is stored into a 10 ml capacity volumetric flask. A small amount of solvent is again taken for rinsing the sediments and transferred to the same 10 ml volumetric flask. The

rinsing process is then followed by enrichment and extraction to get the final analyte for injection into the GC-MS.

5. Discussion

It is evident from the literature that Soxhlet Extraction method consumes more time and quantity of solvents. The step of evaporation is also considered a cause to erroneous readings (Brumley et al. 1998).

Literature also shows that the supercritical fluid extraction (SFE) method has gained popularity from the last couple of years due to its consumption of fewer amounts of solvents, selectivity, swiftness and accuracy of results in comparison to the established traditional liquid solvent extraction method. Due these plus points this method was widely used for the organochlorine residues determination. It is also evident from the literature that this extraction technique was particularly used for the determination of pesticide residues in complex matrices of clay soil separates, canals and river sediments and surface and underground water samples. The technique was also very useful for food, plants and animals tissues analysis for pesticide residues if supplemented with the solid-phase extraction. But inspite of all these advantages the SFE method has still got certain serious limitations like that of demonstrating polarity which hinders the complete dissolution of the residues bound to various matrices. That's why SFE method cannot be used freely without serious considerations which need a lot of home work during its selection.

During the Accelerated Solvent Extraction (ASE) method the increased pressure and high temperatures are used in combination to get the maximum analyte dissolution and enhance the performance and accuracy of the method. Due to its accurate results and environment friendly operation the method is widely used in environment industrial laboratories and research organizations. Literature shows that ASE has replaced the traditional extraction methods (sonication and Soxhlet) because time effectiveness and environment friendly feature of creating less pollution due to lower amount of solvents used. The problem of polarity and bonding effects of the matrices for a number of compounds is also affectively overcome by the ASE method. Accurate results and maximum recoveries are therefore reported as compared to other methods. Korner et al (2002) also concluded during their experiments that ASE generally yielded higher levels of certain PCBs and PCDD/PCDF than soxhlet extraction.

The MASE takes less time as compared to other conventional methods of sample extraction.

It has also got a plus point that high grade pure water can also be used as solvent in place of organic solvents, which are most environments friendly. This method can be confidently used for rapid quantification and determination of minor traces of POP's (Basheer et al. 2005).

6. Conclusion

From the above discussion it can be concluded that Accelerated Solvent Extraction (ASE) is the most suitable and efficient procedure for analytes extraction. It extracts the accurate and minute quantities of persistent organochlorine compounds present in the sample. For quantification GC-MS can be relied upon as a good technique.

7. Acknowledgements

This program was funded by Higher Education Commission of Pakistan and was carried out with the cooperation of DAAD, Germany. The author is extremely thankful to HEC, Pakistan and DAAD, Germany.

8. References

- [1] Basheer, C. Obbard, J. P and Hian, K. L. 2005. Analysis of persistent organic pollutants in marine sediments using a novel microwave assisted solvent extraction and liquid-phase microextraction technique. *Journal of Chromatography A*, 1068: 221–228.
- [2] Brumley, W.C., Latorre, E., Kelliher, V., Marcus, A., Knowles D.E., 1998. Determination of chlordane in soil by LC/GC/ECD and LC/GC/EC NIMS with comparison of ASE, SFE, and Soxhlet extraction. *Journal of Liquid Chromatography and Related Technologies*. 21, 1199-1216.

- [3] Camel, V. 1998. Institut National Agronomique Paris-Grignon, Laboratoire de Chimie Analytique, 16 rue Claude Bernard, 75231 Paris Cedex 05, France. ANALYSIS MAGAZINE, 26, N° 6.
- [4] Gorte, M. et al., 2005. Ecotoxicological profiling of Transect River Elbe Sediments. *Acta hydrochim. hydrobiol.* 33: 555-569.
- [5] Krüger, F and Gröngröft, A. 2003. The difficult assessment of heavy metal contamination of soils and plants in Elbe River flood-plains. *Acta Hydrochim. Hydrobiol.* 31: 436-443.
- [6] Nuzhat, K. Inam, A. Jochen F. Mueller, Herrmann, T and Paepke, O. 2004. Determination of Dioxins, dioxin-like PCBs and Flame Retardants (PBDEs) in Sediments Collected in Pakistan. *ORGANOHALOGEN COMPOUNDS.* 66: 1420-1425
- [7] Specht, W. Pelz, S and Gilsbach, W. 1995. Gas chromatographic determination of pesticide residues after clean-up by gel-permeation chromatography and minisilica column chromatography. *Fres. J. Anal. Chem.* 353: 183-190.
- [8] Svobodova, Z. Zlabek, V. Randak, T. Machova, J. Kolaova, J. Hajslova, J and Suchan, P. Brno, A. V. 2003. Profiles of Persistent Organochlorine Pollutants (POPs) in Tissues of Marketable Common Carp and in Bottom Sediments of Selected Ponds of South and West Bohemia. *72: 295-309.*
- [9] The Elbe - Contribution of the IKSE and of several research programmes to the protection of an unique riverscape. *Bulletin Permanent International Association of Navigation Congresses (P.I.A.N.C.) – Association Internationale Permanente des Congrès de Navigation (A.I.P.C.N.)* No. 106, 2001, 35-47.
- [10] Theobald, N., Wilfried Lange, Winfried Gihlert, Florian Renner (1995) Mass spectrometric investigations of water extracts of the river Elbe for the determination of potential inputs of pollutants into the North Sea Fresenius. *J. Anal. Chem.* 353:50 56.
- [11] Umlauf, G. et al., 2005. The situation of PCDD/Fs and Dioxin-like PCBs after the Flooding of River Elbe and Mulde in 2002. *Acta hydrochim. hydrobiol.* 33: 543-554.
- [12] Watanabe, E., Watanabe Eiki, Heesoo, E. Koji, B. Tadashi, S. Tomohito, A and Shozo, E. 2004. 1PCDD/Fs and dioxin-like PCBs in the Tone River, Japan. *LEVELS IN SOIL AND WATER. ORGANOHALOGEN COMPOUNDS*, 66, pp : 1414-1417
- [13] WHO. 2003. Health risks of persistent organic pollutants from long-range transboundary air pollution. Drukkerij Wilco, Netherlands.