



Thermal Effect on Recovery Levels of Some Selected Organochlorine Pesticides (OCPs) and Triazine Herbicides During Preparatory Analysis

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Organochlorine pesticides and triazine herbicides are synthetic pesticides widely used in agriculture all over the world to control pests. They have been linked with human, environmental and health hazards, from short-term impacts to chronic impacts. This research work presents a methodology to reduce the time taken to dry and recover organochlorine pesticides and triazine herbicides samples from 40 hours to 9 hours by proposing the use of oven drying technique over the traditional air drying method. The results obtained were found to be promising. Recovery efficiency is an important factor when it relates to analytical methods being evaluated. The calculated percentage analyte recoveries were in the range of 53-107% for OCPs and 75-108% for triazines. This showed excellent recovery was found (>75%) with exception to the low recoveries found in isodrin (53-58%) and Aldrin (55-61%), although both percentage recovery falls within the acceptable analysis range (>50%), Isodrin and Aldrin analysis using this method will be considered qualitative analysis and not quantitative according to International norm. c-HCH was found to have the highest percentage recovery 100-107% using this methodology. In conclusion, the use of oven to dry samples of organochlorine pesticides and triazine herbicides for analysis is an effective method, except for isodrin and Aldrin. The major advantage of the proposed method of oven-drying is the short time required for sample preparation (9 hours), the low cost, and ready availability in any standard laboratory.

1. INTRODUCTION

Pesticides are chemical substances and biological agents that are used in agriculture to control pests. Pests include any insects that feed on and damage agricultural crops and produce.

The Food and Agriculture Organization (FAO) defines pesticide as any substance or combination of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or

animals, causing harm during or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feed, or substances that may be administered to animals for the control of insects, arachnids, or other pests in or on their bodies (FAO, 1978).

Due to their persistent nature, pesticides are the main cause for concern when it comes to water pollution. Pesticide contamination of river and lake waters from agricultural use is

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a problem of worldwide concern (Azab *et al.*, 2013). There are different chemically related pesticides, which may be grouped into organophosphate, carbamate, organochlorine pesticides, pyrethroid, sulfonyleurea herbicides, and biopesticides. Among these, organochlorine pesticides and triazines are of more concern in the environmental research field as it has been proven to have the most detrimental effects on human health as well as the environment because of their persistent nature.

Organochlorine pesticides and triazine herbicides are synthetic pesticides widely used all over the world. They are environmental contaminants belonging to the group of chlorinated hydrocarbon derivatives, which have vast application in the chemical industry and in agriculture. High toxicity, slow breakdown, and bioaccumulation are all characteristics of these substances (Jayaraj *et al.*, 2016).

Organochlorine pesticides and triazines belong to a category classified as persistent organic pollutants and even endocrine disrupting chemicals since they resist biological and chemical degradation. Even after many years of application, pesticides have a greater risk of contaminating the air, water, and soil due to their high lipophilicity, bioaccumulation, long half-life, and capacity for long distance transport (Jayaraj *et al.*, 2016).

This means that in as much as they are effective in controlling insects and insect-borne diseases, they can become persistent in the environment, transporting between phase media moving long distances in surface runoff and groundwater, and accumulating to various levels entering air, water, sediments, and even our food chains, implying that they could pose a risk of causing adverse effects to human health and the environment (National Center for Environmental Health 2005; Jadwiga *et al.*, 2012).

Generally, Pesticides have been linked with

human health hazards, from short-term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm. However, because of their stability and persistence, the most hazardous pesticides are organochlorines and atrazines (Azab *et al.*, 2013). Exposure to organochlorine pesticides and triazines over a short period may lead to convulsions, headache, dizziness, nausea, vomiting, tremors, confusion, muscle weakness, slurred speech, salivation and sweating. Triazines can cause irritation to skin and eyes. Long-term exposure to organochlorine pesticides and triazines may damage the liver, kidney, central nervous system, thyroid and bladder. Organochlorine insecticides may also cause cancer in humans, according to some studies. Additionally, the majority of triazines have been classified as human carcinogens (Jiang, 2006). Atrazine can impose serious effects on the central nervous system, immune system, and the endocrine system; it is a potential carcinogen and teratogen for humans (Sun *et al.*, 2019; Pooja *et al.*, 2020).

For these reasons, organochlorine pesticides and triazines have been banned in many countries, and efforts are being made over the years to recover them from the environment (Public Health Service 1974; FAO/WHO 1978; Osibanjo, 2003; Kelderman *et al.* 2005; Karl *et al.* 2010; Azab *et al.*, 2013; Jayaraj *et al.*, 2016). In the process of recovery of organochlorine pesticides and triazines from environmental samples, the samples collected are usually air dried in the laboratory for about 40 hours before they can be analyzed.

This research work aims to reduce the time taken to dry and recover organochlorine pesticides and triazine herbicides samples by proposing the use of oven drying technique instead.

1.1. Background to the research

1.1.1. What are Organochlorines Pesticides?

Organochlorines (OC) are a group of chlorinated compounds frequently used as pesticides. Example of organochlorine pesticides include HCH derivatives, benzene hexachloride (chloro-benzol), heptachlor, aldrin, Isodrin, Methoxychlor Aldrin, chlordane, dichloro-diphenyl-trichloroethane, dieldrin, endrin, Endosufan, DDT derivatives, DDD derivatives, methoxychlor, mirex, PCB 209, etc. These substances fall under the category of persistent organic pollutants (POPs) with a high level of environmental persistence. Due to their low cost and their effectiveness against various pests, organochlorine insecticides such as DDT, hexachlorocyclohexane (HCH), aldrin and dieldrin are among the most widely used pesticides in developing countries (Lallas, 2001; Jayaraj *et al.*, 2016). OCPs are a diverse set of chemicals, and there are differences in their toxicity, ability to accumulate in tissues, and persistence.

1.1.2. What are Triazines?

Triazines are selective herbicides widely used to control weeds and broadleaved weeds (Valera *et al.*, 2007). They can be sprayed on farmland plants before plants begin to grow and emerge from the soil (Singh *et al.*, 2013). Most triazines are derived from s-triazine, a six-atom heterocyclic compound characterized by the presence of nitrogen atoms symmetrically arranged in the 1, 3, and 5 positions and various substituents in the 2, 4, and 6 positions. As shown by many studies, triazine herbicides are among the most often detected xenobiotics in aquatic environments because they are very soluble in water and can thus leach into ground waters or be washed into surface waters (Klementova and Keltnerova, 2015).

The compounds that fall under this category are herbicidal pesticides. They include ATR – atrazine, DEA – desethyl atrazine, Simazine, Atrazine, Propazine, Terbutylatrazine, prometryn, and Bromacin, etc. It is recognized that these compounds could be used as insect chemosterilants. Higher concentrations of these herbicides were found to inhibit plant catabolism pathway (Evan *et al.*, 2007; Jayaraj *et al.*, 2016).

1.1.3. Where Are They Found in the Environment?

Organochlorine pesticides and triazine herbicides are used in agriculture to control pests. Soil, water, and air pollution have all increased because of the growing usage of pesticides for high agricultural productivity. Traces of organochlorine pesticides and triazines can be found in water and complex matrices such as soil and in a wide range of vegetation samples—different plants and plant materials. (Wang *et al.*, 2020; Jayaraj *et al.*, 2016). Researchers have made efforts to study pesticide pollution in water, sediment, aquatic weeds, and fish (Azab *et al.*, 2013). Organochlorine pesticides and triazines are washed into the aquatic ecosystem by water runoff and soil erosion. They can also drift during application and contaminate aquatic systems samples (Mansour *et al.*, 2001; Shukla *et al.*, 2002; Osibanjo 2003; National Center for Environmental Health 2005; Jadwiga *et al.*, 2012; Azab *et al.*, 2013). They can cause severe water pollution because of their high persistence in the environment and accumulation in the soil (Vidal *et al.*, 2008). Persistent organochlorines can accumulate in food chains; for example, shrimp and fish can concentrate some pesticides as much as 1,000 to 10,000-fold (El-Kady *et al.*, 2007; Azab *et al.*, 2013; Jayaraj *et al.*, 2016). Wild birds and mammals are damaged and destroyed by pesticides and these animals make excellent “bio-indicator species” (Pimentel 2005; Akhtar *et al.*, 2009).

1.1.4. Common Method of Drying Soil Samples

Soil samples must be dried to eliminate moisture content before organochlorine pesticides and triazines contaminants can be extracted for analysis. The common method of drying soil samples for the recovery analysis of organochlorine pesticides and triazines contaminants is by air drying. Soil samples are air-dried at room temperature for about 40-48 hours, pulverized and passed through a sieve or filter paper before they are extracted (Wang *et al.*, 2020). For sediments, water is removed in situ from sediment samples collected at a depth of 5cm of sediment surface by decantation before they are transferred to the laboratory where they are totally air dried for 48 hours before analysis (Azab *et al.*, 2013).

Cost-effective, user-friendly, and easy to operate procedures are needed to detect pesticides (Shenoy *et al.*, 2018). The first step in reducing organochlorine pesticides and triazine herbicides widespread distribution is using low-cost and rapid monitoring procedures for its determination (Roueinfar *et al.*, 2019). This research work aims to assess and present the use of the oven drying method for drying soil samples in the recovery analysis of organochlorine pesticides and triazines as an alternative to air drying for a low-cost and faster analysis.

1.1.5. Extraction of Organochlorine pesticides and Triazines

Sample preparation involves modifying the physical form of the sample so that the pesticides can be extracted efficiently (EPA, 2007). Target organochlorine pesticides and triazine herbicides are directly extracted from water samples while soil samples are first dried before extraction. This is known as analyte preconcentration enrichment. For the enrichment of organochlorine pesticides and triazine residues, several sample preparation

methods available have been developed. During sample preparation, soil samples are usually air-dried at room temperature, pulverized and sieved or filtered (Wang *et al.*, 2020). In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place and it typically takes several stages to analyze trace amounts of organic contaminants in complex matrices like soil and sediment (EPA, 2007). Prior to the chromatographic analysis, the extract is cleaned up after an extraction stage. Because these hydrophobic chemicals are so tightly sorbed to the soil material, extraction is a crucial step in the sample preparation process for the detection of OCPs in soil samples. The typical technique for extracting OCPs from soils are shaking flask (Nawab *et al.*, 2003; Ozcan *et al.*, 2011) and soxhlet extraction (Sporring *et al.*, 2005; Ozcan *et al.*, 2011), however, they are time-consuming and requiring a significant amount of organic solvents (Ozcan *et al.*, 2011). Therefore, alternative extraction techniques that can be used for the extraction of target compounds from soil samples such as sonication (Gonçalves & Alpendurada, 2005; Ozcan *et al.*, 2011), microwave-assisted solvent extraction (MASE) (Cheng *et al.*, 2007; Ozcan *et al.*, 2011), super critical fluid extraction (SFE) (Sporring *et al.*, 2005), pressured liquid extraction (Lundstedt *et al.*, 2000; Björklund *et al.*, 2000), accelerated solvent extraction (ASE) (Richter, 2000; Sparring *et al.*, 2005), and ultrasound-assisted emulsification microextraction (Wu *et al.*, 2010), etc have been developed in order to shorten the extraction process, reduce the amount of solvent needed, and increase the amount of sample extracted (Sporring *et al.*, 2005; Ozcan *et al.*, 2011). They all have their own pros and cons. However, the time and money required for some of these alternative techniques such as SFE and ASE are relatively significant

(Ozcan *et al.*, 2011). Therefore, the effectiveness, recovery, reproducibility, little solvent use, simplicity, and convenience of use of each technique are the major factors that determine which one is preferred.

1.1.6. Method of Analysis of Organochlorine pesticides and Triazines

Different analytical methods, such as gas chromatography (GC) (Djozan, and Ebrahimi, 2008), gas chromatography-mass spectrometry (GC-MS) (Bagheri and Khalilian, 2005), high-performance liquid chromatography (HPLC) (Zhou *et al.*, 2009), and capillary electrophoresis (Carabias-Martinez *et al.*, 2006), and others have been introduced and developed to obtain sensitive and accurate analysis of these hazardous compounds. Gas chromatography (GC) and high-performance liquid chromatography (HPLC) coupled to different detectors, and in combination with different sample extraction methods, are most widely used for analysis of organochlorine pesticides and triazine herbicides in different environmental samples. High-performance liquid chromatography (HPLC) has been used these last few years because of its ability to analyze both polar and non-polar thermo-degradable compounds without the need for a derivatization step (Hennion, 2000).

2. EXPERIMENTAL METHOD

The aim of this work is to show that using oven-drying technique during the analysis of organochlorine pesticides and triazines (herbicides) soil samples is a better alternative to the traditional air-drying of the samples. For this study, six (6) different triazines were analyzed in this trial namely; Desethyl, Simazin, Athrazin, Propazin, Terbutylazin, and Bromacin, while twenty-five (25) different pesticides were tested in this trial which include benzene hexachloride (chloro-benzol), heptachlor, aldrin, Isodrin,

Methoxychloro Aldrin, chlordane, dichloro-diphenyl-trichloroethane, dieldrin, endrin, Endosufan, methoxychlor, mirex, and derivatives of HCH, DDT, and DDD.

2.1. Materials and Instruments

- Gas chromatograph (GC) Thermo TRACE 1310 with 25 µl PTV - LVI injector
- Mass spectrometer (MS) Thermo TSQ 9000
- Software Thermo Chromeleon
- TriPlus RSH Autosampler Thermo Autosampler
- Additional Accessories:
 - Pre-column 1m Fused Silica Tubing deactivated, 0.32mm I.D. e.g. BGB P/N TSP-320450-D-10
 - Capillary separation column CP-Sil 8 CB Low Bleed/MS, 30m x 0.25mm, 0.25µm film, Agilent P/N CP5860, or similar.
 - Liner/Septum Thermo Baffle Liner Siltek Deactivated
 - P/N 453T2120 or similar inert.
 - Septum used is "Septum with Center Guide" pkg. of 50 Brechbuehler P/N (31303233)
 - GC Syringe Thermo 100µl SYR RSH 57mm, 26s Ga, Cone P/N 365H2161
 - Carrier gas Helium with at least quality 5.0 (He) with Gas Clean Filters (e.g.: Thermo Gas Specific Triple Filter Helium P/N 60180-825)
 - Collision gas Argon 5.0
 - Extraction apparatus 250ml Erlenmeyer flask

- Glass-coated magnetic rod with magnetic stirrer
- Pipettes Variable piston-stroke pipette 10 - 100 μ l
- Variable piston-stroke pipette 100 - 1000 μ l
- Consumables 4ml amber glass vials with screw cap e.g. BGB P/N 130401 with 13mm cap 130800 and 12mm Septa Silicone/PTFE 120201-1.5
- Vials for auto sampler, e.g. 1.5ml Crimp Neck Vial 32 x 11.6mm (amber), BGB 11BW
- Vial lid, e.g. 11mm Crimp Cap (silver), Septa Silicon/PTFE, BGB 11030101

2.2 Chemicals and Reagents

- 1,11-Dibromundecane \geq 98 % Sigma Aldrich ISTD
- Acetone \geq 99.8 % Honeywell Analytics AG
- Common salt, NaCl 99.8 % Salzdepot Zürich AG
- 48996-U EPA 8151 Herbicide Mix Supelco
- QC: Pesticide-Kit Mix 24 SL 2084-KIT/Mix 24 LGC
- QC: Pesticide-Kit Mix 2 SL 2084-KIT/Mix 2 LGC
- Pesticide-Mix 56 (Herbicide) Dr Ehrensdorfer
- Pesticide-Mix 29 (Herbicide) Dr Ehrensdorfer
- Sodium sulfate anhydrous \geq 99 % Merck
- 46861-Acid Herbicide Mix Supelco

- Cyclohexane \geq 99.8 % Carlo Erba Reagenti SPA
- Phosphoric acid 85 % Sigma Aldrich Preservative
- Acid Extractables Mixture-3 5 μ g/ μ l LGC Surrogate
- Acetic anhydride $>$ 99 % Romil (Thommen-Furler AG)
- NaOH Cookie $>$ 97 % Sigma Aldrich For 40% solution.

2.3 Experimental Procedure

1. Prepare solvent solutions containing all six (6) Triazine (Sol. 22) and another containing all twenty-five (25) organochlorine pesticides (Sol. 26).

Note: For the Triazine mix, Solution. 22 contain six (6) triazines namely; Desethyl, Simazin, Athrazin, Propazin, Terbutylazin, and Bromacin, while for the organochlorine pesticides mix, Solution 26 contains twenty-five (25) OCPs namely: a-HCH, 6CL-Benzol, b-HCH, c-HCH, e-HCH, Heptachlor, Aldrin, Isodrin, c-Heptachlor, Oxychlordan, t-Heptachlor, c-Chordan, o,p-DDE, a-Endosulfan, t-Chlordan, p,p-DDE, Dieldrin, o,p-DDD, Endrin, b-Endosulfan, p,p-DDD, o,p-DDT, p,p-DDT, Methoxychlor, and Mirex, and (PCB 209) as a control/surrogate. Note that most of these twenty-six OCPs and six Triazines have been confirmed by researchers to be endocrine disruptors (Jayaraj *et al.*, 2016; Sun *et al.*, 2019; Pooja *et al.*, 2020).

2. Filter papers are spiked with the analyte solutions and left to dry for nine (9) hours in the oven.
3. The dried filters are then treated with acetone to extract the triazines and organochlorine pesticides still left in the filters after drying.
4. The Triazine and organochlorine pesticides extracts are then quantified using a GC-MS analytical instrument.
5. The values will then be analyzed using Excel plots and Histogram.

2.3.1. Samples Treatments and Labelling

- *Sample TE-A + TE-B* were spiked with 20 µl of the Triazine/OCPs mix (solution.22+26) applied to the filter then left to dry in the drying oven for 9 hours and then extracted with 20 ml acetone.
- *Sample TE-D* was spiked with 20 µl of the Triazine/OCPs mix (solution.22+26) added directly to 1 ml of acetone.

Note: Sample TE-D was the reference and was analysed directly.

- *Sample TE-E* was spiked with 20 µl of the Triazine/OCPs mix (sol.22+26) applied to the filter then left to air-dry for 40 hours (without being dried in the oven) and then extracted with 20 ml acetone

2.4. Instrumentation Setup

The extract is separated using gas chromatography and detected by MS/MS.

- *Identification:* Retention time and MS/MS transitions.
- *Quantification:* Peak area with internal standard calibration.

- *Quality Assurance:* Surrogates, blank controls, positive control.

2.5 Samples Injection

The analytes in the extract were separated by means of capillary gas chromatography using temperature programming. The chromatographically separated triazines and OCPs are detected with Mass Spectrometer and quantified using Thermo Scientific Chromeleon Software. This process is made possible by large volume injection injection (LVI) technique used to introduce 25µl of the sample solvent extract at a rate of approx. 5.6µl/sec into the PTV injector. The injector is kept at a suitable temperature of above 200°C to enable complete volatilisation of solvent into the analytical column. Oven initial temperature is kept at 70°C and on injection rises to 300°C at different rates of the temperature program.

3. RESULTS AND DISCUSSION

Recovery efficiency is an important factor when it relates to analytical methods being evaluated. Figure 1 and 2 presents the differences in recovery found during the extraction process of organochlorine pesticides and triazines respectively when using oven-drying of soil samples compared to the traditional open air drying that takes days to accomplish. The use of oven-drying in the initial preparation step of the analytes in our test, when compared to the traditional air drying techniques used in the analytical industry today showed an interesting and effective analyte recovery. The graphical percentage recoveries in the organochlorine and triazine test samples are presented below in figure 1 and 2 respectively. From the results, the percentage recovery rate of all 25 organochlorine pesticides analyzed using the oven dry method were in the range of 53-107% for TE-A and 58-100% for TE-B

samples while that of the 6 triazine herbicides analyzed ranged from between 75-105% for TE-A and 75-108% for TE-B samples. Furthermore, the percentage recovery rate of all 25 organochlorine pesticides analyzed using the air-dry method were in the range of 59-110% for TE-E samples while that of the 6 triazine herbicides analyzed ranged from between 80-107% for TE-E samples.

Since the aim of this experiment is to propose that using oven-drying technique during the analysis of organochlorine pesticides and triazines (herbicides) soil samples is a better alternative to the traditional air-drying of the samples, we will compare the percentage recovery obtained from the use of oven-drying the soil samples (TE-A and TE-B) with that gotten from air-drying (TE-E). The values obtained from direct extraction without drying (i.e. TE-D) will therefore not be considered in the graphical representation because its values are only needed to determine the percentage recovery of TE-A, TE-B, and TE-E.

From the results, the percentage recovery rate of the OCPs and triazine samples when air dried at room temperature for 40 hours before extraction (i.e. TE-E samples) were in the range of 59-110% for the OCPs and 80-107% for the triazines. When compared with the percentage recovery rate for the duplicate samples dried using oven at 30°C (i.e. 53-107% for TE-A and 58-100% for TE-B for the organochlorine pesticides samples, and, 75-105% for TE-A and 75-108% for TE-B for the triazine samples), it can be seen that the difference in the analyte recovery is negligible; this is to say that the recovery range for the oven-dried method is proportionate to that of the traditional air-dried method. This shows that use of the oven-drying technique for OCPs and triazine samples is equally as effective as the traditional air-drying technique. The oven-drying technique however becomes a better

alternative to air-drying technique because of its advantaged time efficiency as it gives room for a faster analysis; thereby saving hours of time that will have otherwise be needed in the sample preparation step as in the case of the air-drying technique.

Furthermore, focusing on the samples extracted by means of oven-drying, c-HCH was found to have the highest percentage recovery (107% in TE-A and 100% in TE-B) while isodrin and Aldrin were found to have the lowest recovery (53% and 55% in TE-A and 58% and 61% in TE-B respectively) among the OCPs analyzed, and Simazin was found to have the highest percentage recovery (105% in TE-A and 108% in TE-B) while Bromacin was found to have the lowest recovery 75% in TE-A and 83% in TE-B) among the Triazines analyzed.

From the analysis, the samples with >75% recovery represents excellent analysis, >50% represents acceptable, while <50% represents poor or inadequate analysis. There can be several reasons for low recovery during sample preparations. Results with <50% can be as a result of impurities, poorly prepared samples, reference or blank samples, or loss of sample content during preparation, or any other unknown factor like the sample matrix. For the OCPs, excellent recovery was found (>75%) with exception to the low recoveries found in isodrin (53% in TE-A and 58% in TE-B) and Aldrin (55% in TE-A and 61% in TE-B), although both percentage recovery falls within the range considered as acceptable analysis (>50%). For the triazines, an excellent recovery rate was also found (>75%), even in Bromacin which was found to have the lowest recovery rate (75% in TE-A and 83% in TE-B) but still falls within the range considered as excellent analysis.

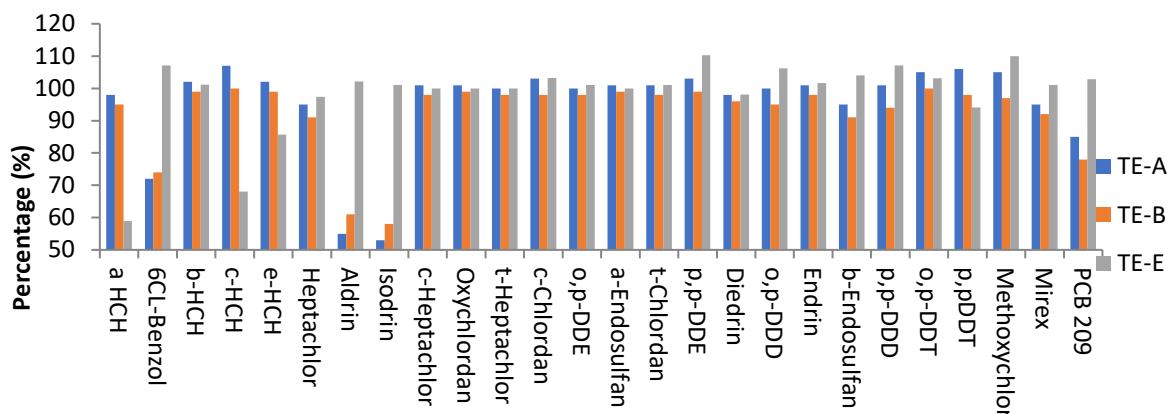


Fig. 1. Percentage recovery of OCPs after oven drying. *TE-A* and *TE-B* are test samples spiked with 20ul of the organochlorines mix (solutions.26) applied to the filter, then oven-dried for 9 hours and then extracted with 20ml acetone. *TE-E* are test samples spiked with 20ul of the organochlorines mix (solutions.26) applied to the filter, then air-dried for 40 hours and then extracted with 20ml acetone.

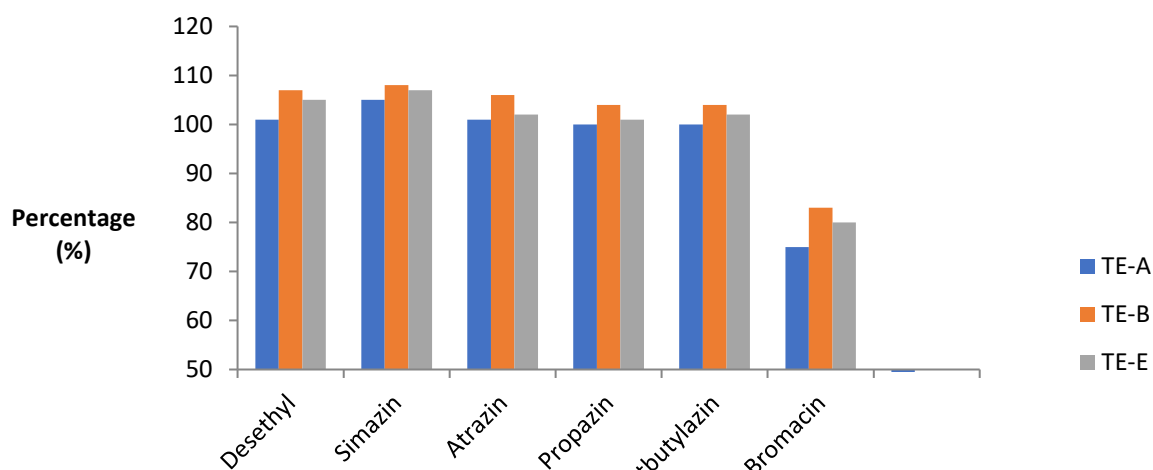


Fig. 2. Percentage recovery of triazines herbicides after oven drying. *TE-A* and *TE-B* are test samples spiked with 20ul of the triazine mix (soluton.22) applied to the filter, then oven-dried for 9 hours and then extracted with 20ml acetone. *TE-E* are test samples spiked with 20ul of the triazine mix (soluton.22) applied to the filter, then air-dried for 40 hours and then extracted with 20ml acetone.

4. CONCLUSION

From the results, it can be seen that the oven drying method was effective in all the OCPs analyzed excluding isodrin and Aldrin which had low recovery but still fell in the range considered as acceptable analysis. However, according to international analytical standards and norms, the analysis

of isodrin and Aldrin using this method of oven-drying will be considered qualitative analysis and not quantitative. The oven drying method was also very effective in all the Triazine mixtures with excellent recovery rate, even for Bromacin which had a <75% recovery rate in either duplicate. It is then my considered opinion that the use of an oven to dry samples of organochlorine

pesticides and triazine herbicides for analysis is an effective method, except for isodrin and Aldrin. The major advantage of the proposed method of oven-drying is the short time required for sample preparation (approximately Nine hours). The use of oven-drying technique is also low-cost as ovens are readily available for use in any laboratory and require low-cost maintenance and energy for heating.

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