ORGANIC MATTER TRANSFORMATIONS INCLUDING TRACE ORGANICS DURING ROTARY DRUM COMPOSTING

A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY

by

MUNTJEER ALI

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247 667 (INDIA)
MARCH, 2012

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **ORGANIC MATTER TRANSFORMATIONS INCLUDING TRACE ORGANICS DURING ROTARY DRUM COMPOSTING** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Chemistry of Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from January 2009 to March 2012 under the supervision of Dr. Naseem Ahmed, Assistant Professor, Department of Chemistry and Dr. A. A. Kazmi, Associate Professor, Department of Civil Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree in this or any other Institute.

Muntjeer Ali.

(MUNTJEER ALI)

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

(A. A. Kazmi)
Supervisor

(Naseem Ahmed)
Supervisor

Date:

The Ph.D Viva-Voce examination of **Mr. Muntjeer Ali**, Research Scholar, has been held on 05th July 2012

Supervisor

Chairman SRC 5/7/12

External Examiner

Head of the Department/Chairman ODC

ACKNOWLEDGEMENT

I would like to express my sincere gratitudes to Dr. Naseem Ahmed, Assistant Professor, Department of Chemistry and Dr. A. A. Kazmi, Associate professor, Environmental Engineering Section, Department of Civil Engineering, who is always available for discussion as a teacher, guardian and as a friend. He contributed a great deal to my understanding the research area through valuable discussions, ideas and useful comments, which were a great source of inspiration.

I take the opportunity to express the gratitude to my Student Research Council members Dr. Kaushik Ghosh, Department of Chemistry, Prof. M. R. Maurya, Department of Chemistry, Prof. (Ms) Indu Mehrotra, Department of Civil Engineering, for extending me all possible help along with valuable suggestions during the course of my study.

I am thankful to Mr. Abdul Haque, Mr. Zaheer Ahmad, Mr. Lal Singh, Mr. Naresh and all the staff of Department of Chemistry and Environmental Engineering section, Department of Civil Engineering, who were ever willing to give a helping hand to me on all the occasions.

I take this opportunity to thanks Head, Department of Chemistry, Head, Department of Civil Engineering, and Head Department of Institute Instrumentation Center for giving me the permission to carry out the experiments related to my study.

I wish to put on record my gratitude to the Editors and Reviewers of my all manuscript published in the respective journals and Conference proceedings for their valuable comments to upgrading my research study.

Thanks are also to the All India Council for Technical Education (AICTE) for awarding me the generous National Doctoral Fellowship (NDF) to peruse my doctoral studies, in addition to the Department of Science and Technology (DST) for making available the financial support to carry out the experiments for this study.

I offer my warm thanks to all my seniors and colleagues (Dr. Ajay S. Kalamdhad, Mr. Anwar Khursheed, Dr. Abid Khan, Ms. Rubia Zahid Gaur, Ms. Akansha Bhatia, Ms Mina Mr. Mohd. Azfar, Mr. Ajay Nagpure, Mr. Tarun Kumar, Dr. Gaurav Jindal, Mr. Anand Kumar, Mr. Laxmi Das) master's and Ph.D students. Mr. Amit kumar, Mr. Shekh Arshad, Mr. Thapyal, and Mr. Jaypal who ever directly or indirectly involved at various stages of my present work.

I am very grateful to my parents, brothers and my sisters (Mustakeem Ahmed, Mohd. Javed, Hush Jahan Mehnaz and Tabassum Jahan Mehnaz) for their ever willing support and encouragement.

Over and above all, I am thankful to almighty GOD, for HIS mercy and grace bestowed upon me carrying out this work.

MUNTJEER ALI

ABSTRACT

During the transformation of organic waste in composting process, different groups of carbohydrate such as OH, CH_2, CH_3 converted into carboxylic (COOH), C=O conjugated, esters (COOC) and C=C groups of aromatic acids. Similarly, in the protein transformation, amide ($CONH_2$) and carboxylate (C=O) groups converted to nitrogenous compounds such as NH_3, NO_3^-. Aliphatic compounds in organic waste get converted to aromatic acids (humic and fulvic acid) by microorganism in a series of steps. The rate kinetics of the transformation of these compounds during composting can be significantly increased by proper mixing, oxygen transfer and enhancing microbial diversity in an enclosed vessel. The degradation time can be reduced to 1/3 to 1/5 compared to conventional techniques without causing environmental nuisance such as odor, leachate generation and ground water pollution.

The high rate composting technology not only stabilized aggregate organic matter in the waste material, but also detoxify emerging hazardous organic compounds such as trace hazardous organochlorine pesticides by co-metabolism. Highly available substrate, fast reaction kinetics and microbial diversity during composting can also lead to co-metabolism of trace hazardous organochlorine pesticides.

In recent years, spectroscopic techniques such as FT-IR, thermal methods (TG, DTG & DTA) have been used as characterization tools for studying the transformation of organic matter and along with evaluating the maturity of the compost during conventional windrows composting (Chen, 2003; Inbar *et al*; 1989; Hsu and Lo, 1999). Information on organic matter transformation in high rate composting such as rotary drum composting is rather limited. In addition, considerable studies have been conducted on transformation of trace hazardous organochlorine pesticides in soil, water and a few in conventional windrows composting, however, studies on rotary drum composting is rather limited.

Hence, the present work comprises of studies on organic matter transformation including trace hazardous organochlorine pesticides in household batch, full-scale continuous rotary drum and conventional windrow piles using mainly vegetable market waste. Further, the effects of seasonal variations on degradation of trace hazardous organochlorine pesticides were also investigated.

The study is summarized into six chapters with a brief discussion is presented herewith;

CHAPTER ONE: Background Information & objectives

Provides the background on organic matter (functional groups) transformation including trace hazardous organochlorine pesticides and their degradation. The chapter also includes problem identification, objectives, scope of the work and thesis organization. The study objectives are as follows;

1. Performance evaluation and fate of aggregate organic matter transformation by the application of advanced chemical techniques like FT-IR and thermal methods (TG, DTG & DTA) during full scale continuous rotary drum composting.
2. To study the fate and kinetics of hazardous trace organochlorine-pesticides (Aldrin, Endosulfan α, Endosulfan β and Lindane) in household batch and full-scale continuous rotary drum composting and their comparison with conventional windrows composting.
3. To study the effects of seasonal variation on degradation of trace hazardous organochlorine pesticides (Aldrin, Endosulfan α, Endosulfan β and Lindane) in full-scale continuous rotary drum composting.

CHAPTER TWO: Comprises of experimental methodologies such as composting material characterization, composter configuration, experimental design and analytical methods.

CHAPTER THREE: Part A: Performance evaluation of full-scale continuous rotary drum composter using herbal industry solid waste.

- It was found out that composting of herbal waste and cattle manure in 3:1 (w/w) ratio can be successfully conducted in 7-8 days detention period.
- Favorable composting conditions were obtained at once a day rotation, during which the inlet zone temperature increased to 70°C leading to higher degradation. Increase in rotation to twice a day couldn't improve the quality. Conversely, it resulted in lowering of thermophilic temperature to 60°C which results in slow degradation, and unstable compost compared to one rotation.
- Co-composting of herbal and vegetable wastes gave better quality compost in terms of temperature, moisture, nitrogen, solvita maturity index and aerobic environment due to high moisture content of vegetable waste and bulking agent of herbal waste.

- FT-IR also revealed that trial-1 (one rotation) to trial-4 (Co-composting herbal & vegetable waste) gave quality compost in terms presence of high intensity peak at the aromatic region and less intense peaks were found in aliphatic region in trial 1 & 4 compared to trial-2 (two rotation) and trial-3 (inocula addition).

Part B: **Fate of aggregate organic matter transformation (functional groups) and thermal stability during full-scale continuous rotary drum composting.**

- It was found out that there is increase in molecular complexity of compost by the decrease in aliphatic and polysaccharide components.
- New peaks and their intensity in FT-IR bands at 778, 722, and 560 cm^{-1} are due to aromatic ring, halogen-compounds and some metal-halogen bonds.
- A higher degree of maturity was achieved in spring and summer seasons in terms of mass loss (TG), rate of mass loss (DTG), enthalpy change (DTA) compared to winter season.
- Correlation between temperature and CO_2 emission rate follows Andrews–Kambhu–Haug model compared to the Ratkowsky model because optimum temperature (62.1°C) was obtained due to rapid microbial growth temperature while the later model gave 66.4°C as optimum temperature which is unfavorable for microbial growth.

CHAPTER FOUR: Part A: **Study on fate and degradation kinetics of organo-chlorine pesticides in household batch-scale rotary drum and conventional windrows type composting.**

- It was found out that about 70% removal of organochlorine pesticides can be achieved within 20-24 days by household batch-scale rotary drum composting. While, in conventional windrows, the removal of pesticides is possible only 50-60% in 30-36 days in which 40-45% removal of pesticides due to leachate generation.
- Aldrin after diol formation converted to 1-hydroxychlordene in four days at 55-60 °C, followed by 4, 7-methanoisobenzofuran in eight days at 45-50°C temperature. Finally, it was converted to 4,5,6,7,8,8-hexachloro-1,3,3a,4,7,7a-hexahydro- in twelve days at 35-40°C due to oxidation and reduction reactions. However, in conventional windrows, after aldrin epoxidation to toxic dieldrin it was further converted to aldrindiol.

- Endosulfan α first changed to endosulfan β and subsequently converted to endosulfan sulfate by oxidation process. Librating SO_3 gas, it was further converted to endosulfan ether in four days at 55-60°C, followed by chlorendic acid and chlorendic anhydride in eight days at 45-50°C. Finally, it was converted to 4,5,6,7-tetrachloro-3-hydroxy-3H-isobenzofuran-1-one in twelve days at 35-40 °C in household batch-scale rotary drum composter. While in conventional windrows, Endosulfan α converted to endosulfan sulfate followed by Endosulfan ether by removal of SO_3 gas.

- Lindane gave some oxidative and reductive products, formed in both composting techniques under partially aerobic and anaerobic conditions.

- Half life is reduced to 12-20 days from 1095 days, 9-17 days from 160 days, 11-30 days from 60 days and 9-11 days from 270 days in Aldrin, Endosulfan α, Endosulfan β, and Lindane respectively in household batch-scale rotary drum composting. Similarly, half life is reduced to 15-26 days from 1095 days, 13-25 days from 160 days, 13-59 days from 60 days and 95 days from 270 days in Aldrin, Endosulfan α, Endosulfan β, and Lindane respectively in conventional windrows composting.

Part B- Study on fate and degradation kinetics of organo-chlorine pesticides in full-scale continuous rotary drum composter

- It was found out that removal efficiency of Aldrin, Endosulfan α, Endosulfan β and Lindane was calculated as 85.67, 84.95, 83.20 & 81.36% respectively in full-scale continuous rotary drum composting.

- First order degradation kinetics of pesticides was observed during full-scale continuous rotary drum composting. Half life of the pesticides, Aldrin, Endosulfan α, Endosulfan β and Lindane was reduced to 25.54, 18.43, 18.43, and 27.43 days from 1095 days, 60 days, 270 days and 160 days respectively.

- Aldrin converted to Aldrin diol by the hydroxylation reaction in inlet zone. After four days, materials moved to middle zone aldrin diol liberated ethylene molecule to give 1-hydroxychlordene and its isomer. 1-Hydroxychlordene further oxidized to acidic and aldehydic compounds. Finally, aldehydic compounds of aldrin converted to 4,7-methanoisobenzofuran and 4,5,6,7,8,8-hexachloro-1,3,3a,4,7,7a-hexahydro-by the elimination of H_2O during next four days in the outlet zone.

- Endosulfan isomerized to the endosulfan β, followed by conversion to endosulfan sulfate, But, it was converted to endosulfan ether in the middle zone of rotary drum composting by liberating SO_3 gas in next four days. Finally, materials moved to outlet zone where Endosulfan converted to chlorendic anhydride by hydration and dehydration process. Followed by converted to the 4, 5, 6, 7-tetrachloro-3-hydroxy-3H-isobenzofuran-1-one and 4, 5, 6, 7-tetrachloro-3-hydroxy-3H-isobenzofuran-1-one.

- Lindane was converted to β-Lindane in inlet zone of rotary drum composter, which is most persistent in environment. However, β-Lindane on dehydrohelogenation and dehalogenation reactions converted to pentachlorocychlohexene (PeCCh) and tetrachlorocychlohexene (TeCCh) respectively. Materials reached to the middle zone where PeCCh converted to pentachlorocychlohexanone, followed by 1,2,3,5-tetrachlorocychlohexanone and 1,2,3 trichlorocychlohexenone due to dehalogenation and dehydrogenation respectively. Finally, in next four days materials moved to outlet zone where TeCCh converted to 1, 3, 5-trichloro-1,4-dihydroxybenzene. 1,2,3-Trichlorocychlohexenone and 1,3,5-trichloro-1,4-dihydroxybenzene.

CHAPTER FIVE: Effect of seasonal variations on organochlorine pesticides degradation in full-scale continuous rotary drum composter.

- Removal efficiency of Aldrin, Endosulfan α, Endosulfan β and Lindane was found out to be 85.67, 84.95, 83.20 and 81.36% respectively during summer season and found higher than the winter and spring seasons i.e. 69.31, 65.03, 69.84 and 71.94% and 64.33, 65.61, 63.28 and 68.23% respectively due to optimum temperature, moisture and pH conditions, which helped in developing microbial activity during depletion of dissolved pesticides in summer season.

- In winter season, a part of pesticides (30-35%) removed through leachate generation (1-2L/day).

- Higher concentration of pesticides was found in feedstock during winter season composting compared to spring and summer season full-scale rotary drum composting due to lowering ambient temperature (10-15°C), leads to less volatilization, less microbial degradation and more accumulations.

CHAPTER SIX: In toto, a summary of our work done is reported in this chapter. Our observations in contrast of performance of rotary drum, fate of aggregate organic matter transformation during full-scale continuous rotary drum composting, fate and degradation kinetics of organochlorine pesticides during household batch & full-scale continuous rotary drum composting and effects of seasonal variations on degradation of organochlorine pesticides during full-scale continuous rotary drum composting is the best suited technique to check the performance, removal efficiency and fate of trace hazardous pollutants of full-scale composting plants in different seasons and the factors affecting the composting of various kinds of waste.

CONTENTS

LIST OF FIGURES

Chapter 3 (Part B)

Chapter 4 (Part A)

Chapter 5

Chapter 6

Appendix

LIST OF TABLES

Chapter-2

Chapter-3

Chapter 4

Chapter-5

Appendix

ABBREVIATIONS

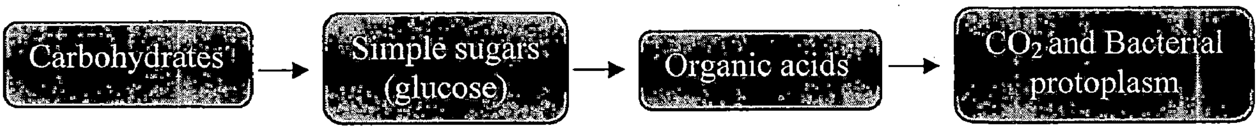
MSW	Municipal Solid Waste
C/N	Carbon/Nitrogen
L	Liter
d	day
h	hour
kg	Kilogram
EC	Electrical Conductivity
TOC	Total Organic Content
TN	Total Nitrogen
NH_4-N	Ammonical Nitrogen
NO_3-N	Nitrate
FTIR	Fourier-Transform Infrared
IR	Infrared
TG	Thermogravimetry
DTG	Derivatives Thermogravimetry
DTA	Differential Thermal Analysis
APHA	American Public Health Association
VS	Volatile Solids
NH_3	Ammonia
GC-MS	Gas chromatography Mass spectroscopy
CHNS	Carbon Hydrogen Nitrogen Sulfur
RDC	Rotary Drum Composter
Dia	Diameter
RD	Rotary Drum
W	Windrows

Chapter 1
Introduction

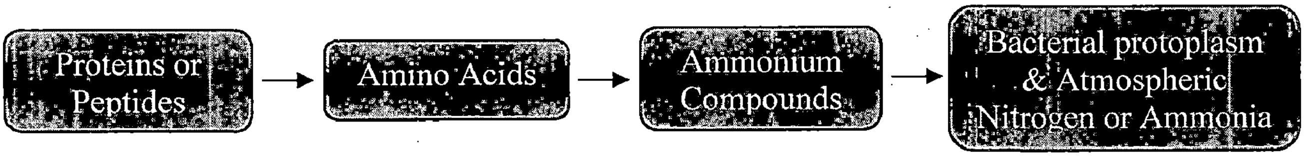
This chapter presents the background of the study and our search objectives based on the problem identification. Followed by, the scope of this work and the description on the organization of the thesis is presented.

1.1 BACKGROUND

During the transformation of organic waste in composting process, the population of microorganisms such as bacteria, fungi and protozoa are relying upon organic matter concentration in the waste material to obtain energy necessary for their metabolic processes. They take the carbohydrates and proteins of organic matter as primary energy sources into their cytoplasm during a complex metabolic process.



Carbohydrates Decomposition Pathway Overview



Proteins Decomposition Pathway Overview

During the transformations or breakdown of carbohydrates, different moieties like OH, CH_2, CH_3, etc. results in the formation of carboxylic (COOH), kitonic conjugated (C=O), esters (COOC) and ethylene (C=C) groups in aromatic acids (Pietro, *et al*, 2004). Similarly, reduction of amide ($CONH_2$) and carboxylate (C=O) groups in peptides of proteins results in the formation of nitrogenous compounds (NH_3, NO_3^-). Some inorganic products such as, CO_2, H_2O, NH_3 gases or NO_3^- (nitrate), sulphates and carbonates of Ca, Mg and K and oxides and phosphates (PO_4^{-3}) of Fe and Mn, also produced. Some of these compounds are removed as gaseous products (CO_2, H_2O, NH_3), and some as solutes in leachate generation (NO_3^-, SO_4^{--}, carbonates of K and Mg) while remaining precipitated or adsorbed (NH_4^+, K^+, Ca^{++}, Mg^{++}, and PO_4^{-3}) in the compost (Saad, 2001). Hence, compounds having aliphatic in nature get converted to aromatic acids (humic and fulvic acid) by a series of steps during transformation of organic waste by microorganism. However, conversion rate of the organic waste material greatly depends on the type of substrate, environmental conditions and type of microorganisms. The rate of composting significantly increased by providing mixing and oxygen transfer in enclosed vessel and degradation time can be reduced to 1/3 to 1/5 without causing any environmental nuisance such as leachate generation and ground water, soil and air pollution.

The composting technology not only stabilized aggregate organic matter in the organic waste, but also detoxification of emerging trace hazardous organic compounds such as trace organochlorine pesticides by co-metabolism. High levels of substrate and microbiological population and fast reaction kinetics in composts can also lead to co-metabolism of trace hazardous organochlorine pesticides (Buyuksonmez, *et al,* 1999; Williams, *et al*, 1993; Rao, *et al*, 1996 & 1996;).

Recently, it was observed that most of the agricultural residues, vegetable waste, food waste, etc. in India contains trace hazardous organochlorine pesticides due to their non-judicious use. About 51% of food commodities in India are contaminated with pesticide residues of which 20% have above the upper residue level of trace hazardous organochlorine pesticides on a worldwide basis (Gupta; 2005).

Composting could be a promising technique for the bioremediation of these pesticides. One of the promising type could be a high rate enclosed in-vessel composting technique is rotary drum composter. It is an excellent concept for smaller communities for recycling and reuse of biodegrading organic solid waste. The function and advantages of rotary drum composter are given in Fig.1.1 and 1.2 respectively.

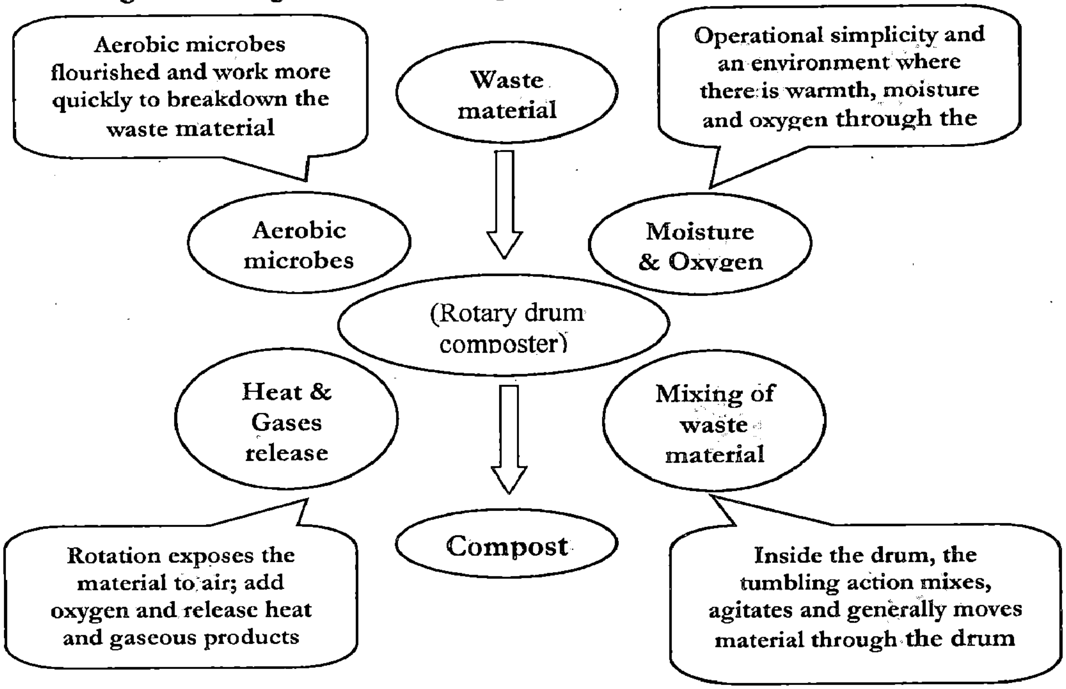


Fig.1.1. Functions of rotary drum composter

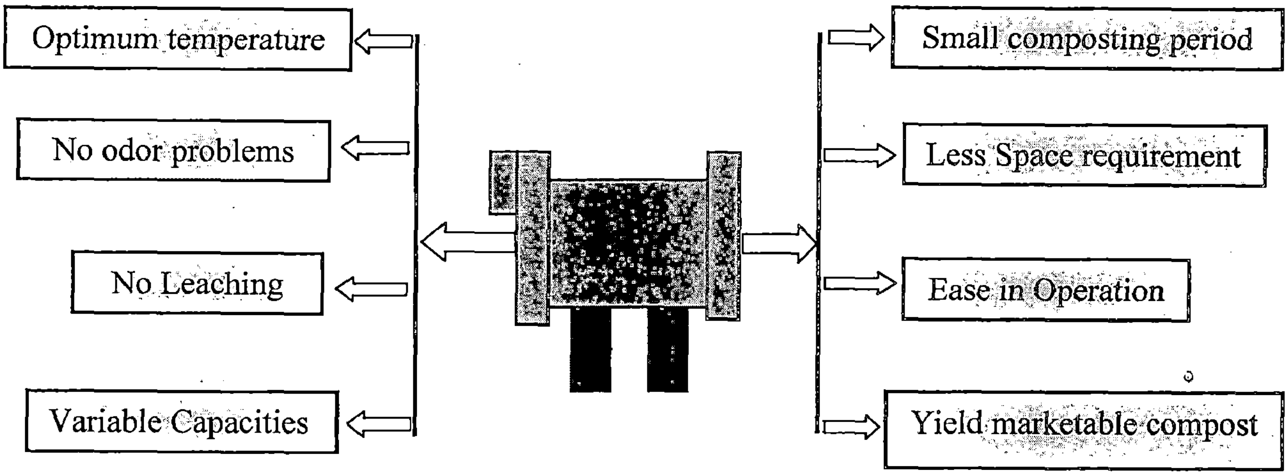


Fig.1.2. Advantages of rotary drum composter

Studies by Kalamdhad and Kazmi (2007-2008) ensured the performance of the household batch and full-scale continuous rotary drum composter based on various kinds of organic waste including MSW (Municipal Solid Waste). Further, they were studied the stability and maturity based on FT-IR and thermal methods (TG, DTG and DTA) by means of MSW with different CN ratios (16, 18, 22 and 26) for household batch-scale rotary drum composting and suggested that waste with CN ratio 22 gave better quality compost in terms of stability and maturity of compost. Kalamdhad and Kazmi (2009) have also been studied long term monitoring (150 days) of institutional vegetable waste and tree leaves during full-scale continuous rotary drum composter and suggested that institutional organic waste composting were composted successfully within 7 days period. About 60–70°C temperature were maintained even in cold weather conditions (around 6°C). A steep temperature gradient existed horizontally in inlet, middle and outlet zones of the full-scale continuous rotary drum composter. Sustained higher temperature at inlet zone has transformed the quality of waste material immediately after feeding into the drum. One rotation caused 60–70% previously added waste material at inlet degraded and continues to move forward in the drum while remaining material is mixed with the incoming new waste material. This remaining material could possibly serve as inoculums for the incoming material resulting in higher degradation. Instead of classical mesophilic phase, the incoming material directly enters into thermophilic phase, resulting in rapid decrease in organic matter.

1.2 PROBLEM IDENTIFICATION

Aggregate organic matter transformation during composting has been endorsed to the use of basic parameters such as: (i) physical parameters: temperature variation, odor emission, color change, particle size reduction (Garcia, *et al*; 1992); (ii) chemical parameters: pH variation, oxidation of carbon of organic matter to CO_2, nitrogen transformation to ammonia and nitrate, CN ratio reduction, alteration in elemental concentration and humification indices (Hsu and Lo, 1999; Jimenez and Garcia, 1992); (iii) biochemical parameters: oxygen consumption and CO_2 respiration (Iannotti, *et al*; 1994). These parameters were successfully applied to study the compost dynamics, however, doesn't provide adequate information on transformation of organic matter.

In recent years, spectroscopic techniques such as FT-IR, thermal methods (TG, DTG & DTA) have been used as characterization tools for studying the transformation of organic matter along with evaluating the maturity of the compost during conventional windrows composting (Chen, 2003; Inbar *et al*; 1993; Hsu and Lo, 1999). Information of organic matter transformation for full-scale continuous rotary drum composting is rather limited.

Therefore, one of the objectives of our study is the performance evaluation of rotary drum composter and fate of aggregate organic matter transformation based on advanced chemical techniques like FT-IR and thermal methods (TG, DTG & DTA) during full scale continuous rotary drum composting.

In addition, the majority of the pesticides detected in waste material or composts were organochlorine insecticides, which were resistant to biodegradation (Buyuksonmez, *et al*, 1999). The destruction of theses pesticides in food, vegetable and agricultural farm waste may be accelerated during composting process (Buyuksonmez, *et al*, 1999; Williams, *et al*, 199; Rao, *et al*, 1995 & 1996). During these processes high levels of substrate and microbiological population in composting can also lead to co-metabolism of trace organic pesticides. The co-metabilism is significantly depends on the composting conditions and time, microbial communities and nature of the trace organic pesticides. In fact, the most reported microbial transformations are aldrin epoxidation to the more persistent dieldrin (Lichtenstein and Schultz, 1960; Tu, *et al*, 1968). The often reported metabolites of these two pesticides are: trans-aldrindiol and photodieldrin (Patil, *et al*, 1970 & 1972). The latter being more toxic than the parent compounds aldrin and dieldrin (Georgacakis and Khan, 1971). A full microbial conversion of any of these cyclodiene pesticides has not been demonstrated yet. There was only one indication of such possibility by Jagnow and Haider

(1972), who reported a $^{14}CO_2$ formation from labeled dieldrin. However, this process occurred almost at trace level less than 1% was converted in several weeks. Endosulfan transformed during microbial degradation into Endosulfan sulfate is more toxic than the parent compound. Other moieties formed are Endosulfan ether, Endosulfan diol, Endosulfan hydroxyl carboxylic acid and Endosulfan hydroxyl ether. All these compounds have six chlorine atoms and are toxic in nature. Lindane also converted to other moieties under anaerobic conditions to tetrachlorocychlohexene (TeCCH), dichrocychlohezene (DCCH), chlorobenzene (CB) and benzene (Peter, *et al*; 1996). Considerable studies have been done on transformation of trace hazardous organochlorine pesticides in soil, water and few in conventional windrows composting. However, studies on house hold batch and full-scale rotary drum composting is rather limited. Hence, other objective of the study is to understand the fate and degradation kinetics of hazardous organochlorine pesticides (Aldrin, Endosulfan α, Endosulfan β and Lindane) during household batch- and full-scale continuous rotary drum composting. In addition, the results shall be compared with conventional windrows composting system.

Since, seasonal variations are not only affects composting process but also background concentration of trace hazardous organics in waste material due to variation in spray timings, humidity, ambient temperature (Kalamdhad and Kazmi, 2009, Esaac and Matsumura, 1980) and might be microbial activity. However, studies are limited to the effect of seasonal variations on the degradation of hazardous organochlorine pesticides during full-scale continuous rotary drum composting. Therefore, the last objective is to study effects of seasonal variations on the degradation of trace hazardous organochlorine pesticides during full-scale continuous rotary drum composting.

1.3 RESEARCH OBJECTIVES

1. To study the performance evaluation of rotary drum and fate of aggregate organic matter transformation by the application of advanced chemical techniques like FT-IR and thermal methods (TG, DTG & DTA) during full scale continuous rotary drum composting.
2. To study the fate and kinetics of hazardous trace organochlorine-pesticides (Aldrin, Endosulfan α, Endosulfan β and Lindane) in household batch and full-scale continuous rotary drum composting and their comparison with conventional windrows composting.
3. To study the effects of seasonal variation on degradation of trace hazardous organochlorine pesticides (Aldrin, Endosulfan α, Endosulfan β and Lindane) in full-scale continuous rotary drum composting.

1.4 THE SCOPE OF THE WORK

To achieve the above mentioned objectives, 3.5 m^3 full-scale continuous-feed rotary drum, 250 L household-scale batch feed rotary drum and 2.10m×0.25m×0.35m conventional windrows feed were performed in parallel during the composting studies. Their performance in terms of aggregate organic matter transformation, stability and maturity were the main scope of this study using advanced techniques like FT-IR and thermal studies i.e. TG, DTG, DTA. Similarly, the fate and degradation kinetics of trace hazardous organic pollutants such as organochlorine pesticides and the effects of seasonal variations on their degradation using GC-MS technique were further scope of our study. In the first attempt, the performance evaluation of rotary drum and the fate of aggregate organic matter transformations were conducted in different seasons during full scale continuous rotary drum composting using Fourier transform-infrared (FT-IR) and thermal studies (TG, DTG & DTA). In the second attempt, we focused on understanding the fate and degradation kinetics of trace hazardous organochlorine pesticides during household batch-scale as well as full-scale continuous rotary drum composting and their comparisons with windrows composting. Finally, we observed the degradation of pesticides under full-scale continuous rotary drum composting with seasonal variations. A large afford of the work was collection of waste material of various sites, feeding, taking samples from the reactors and maintenance of the reactors during the execution of the experiments, followed by the collection, handling and analysis of data including daily visual observations of the waste material and compost in the reactors.

1.5 THESIS ORGANIZATION

The organization of the chapters in the thesis is presented below in the flow chart (Fig. 1

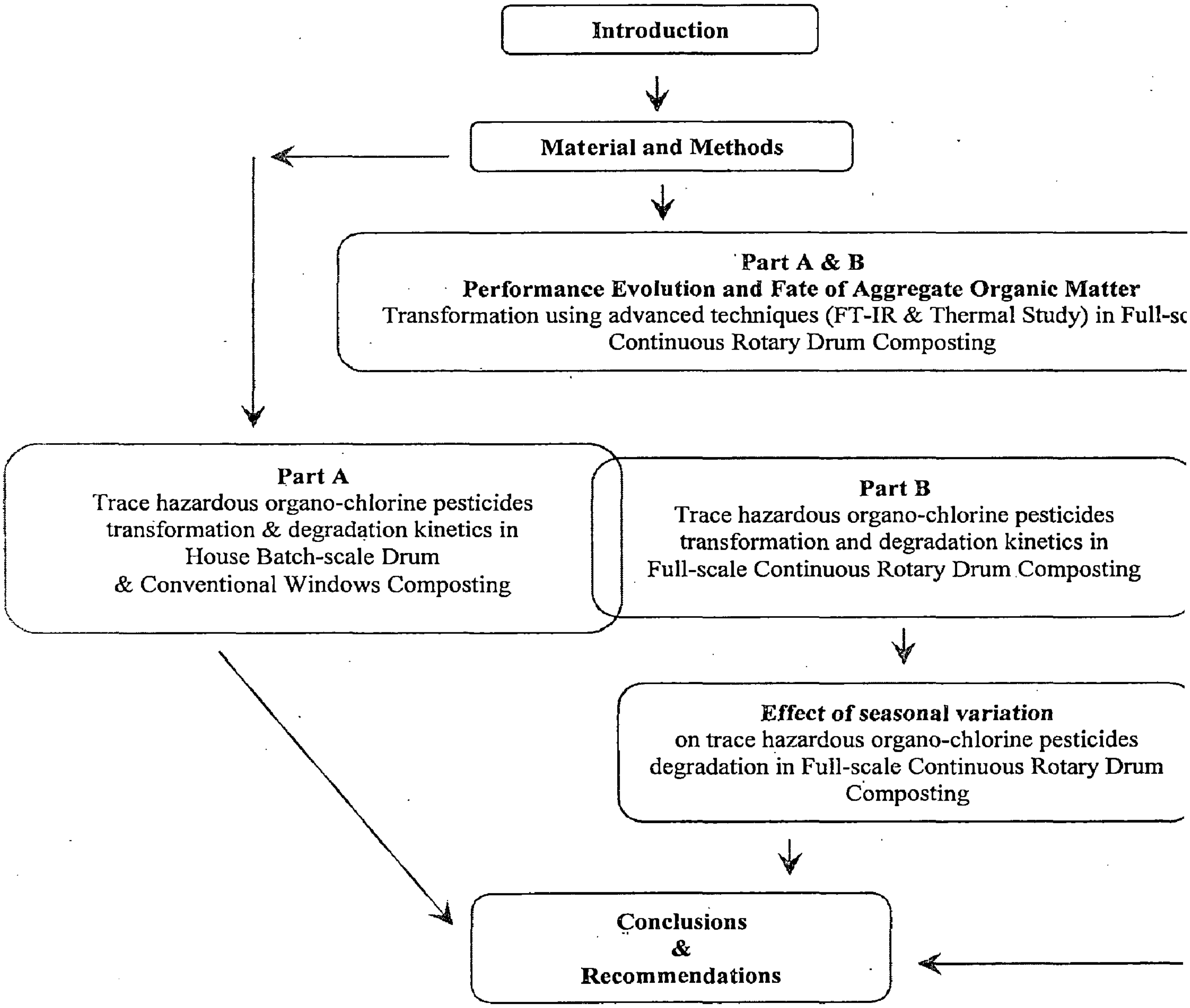


Fig.1.3.Thesis organizations with different studies

Chapter 2

Materials and Methods

Different experimental approaches were applied to accomplish the stipulated objectives. This research was carried out into different parts using vegetable waste materials. A detailed methodology is demonstrated in this chapter.

2.1 THE COMPOST MATERIAL

Cattle (Buffalo) manure, mixed vegetable market wastes (uncooked), dry tree leaves and saw dust were used for preparation of waste mixtures based on various C/N ratio. Cattle manure (C/N=20) was obtained from Tyagi dairy near the campus. Mixed vegetable wastes (C/N=18) collected from vegetable market (Sabzi mandi) of Roorkee city and student hostels including Jawahar, Sarojini, Ravindra, Govind and Azad Bhavans (student hostels) of institute campus, herbal waste (C/N=20) collected from nearby herbal industry of Haridwar city, dry tree leaves (C/N=120) and sawdust (C/N=540) was purchased from nearby saw mill. The waste components used for the study are given in Fig.2.1. The waste material was prepared with different proportioning of waste composition as described in experimental design. After manual sorting of plastics and other non-compostable materials waste was ready for composting. Prior to composting, the maximum particle size of the mixed waste was restricted to approximately 1 cm in order to provide better aeration and moisture control. The material is rendered more susceptible to bacterial invasion through exposing a greater surface area to attack and destroy the natural resistance of vegetation to microbial invasion (Gotaas, 1956).

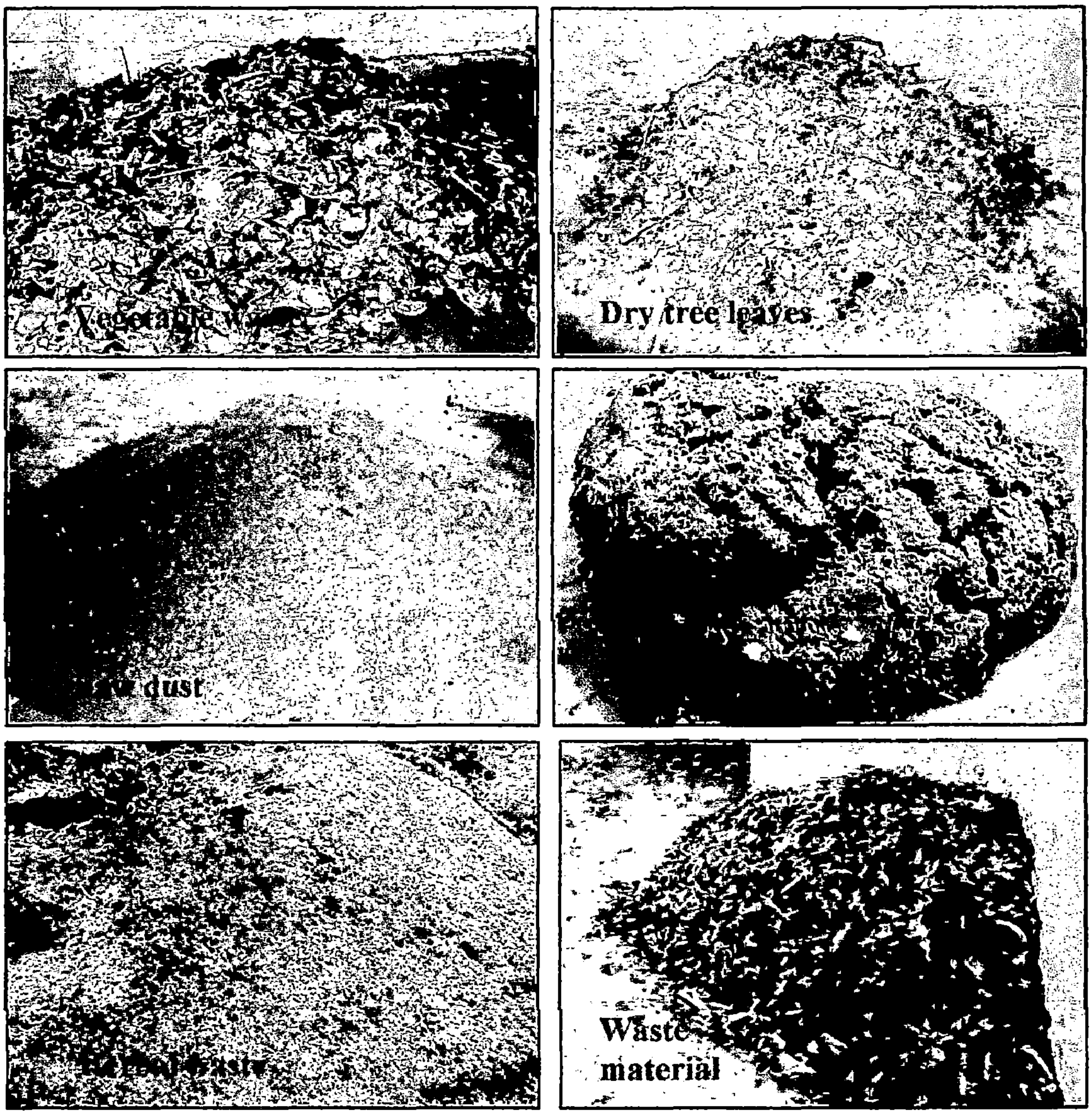


Fig.2.1. Waste material and their components during composting

2.2 THE COMPOSTING REACTORS

2.2.1 BATCH OPERATION

Fig. 2.2 and 2.3 show a schematic diagram and pictorial view of a pilot-scale rotary drum composter of 250 L capacity used for batch operation. The main unit of the composter, i.e. the drum is of 0.92 m in length and 0.9 m in diameter made up of a 4 mm thick metal sheet. The inner side of the drum is covered with anti-corrosive coating. The drum is mounted on four rubber rollers, attached to metal stand and the drum is rotated manually. In order to provide appropriate mixing of waste, 40 mm long angles are welded longitudinally inside the drum. In addition, two adjacent holes are made on top of the drum to drain excess water. Clockwise turning was carried out manually by handle, which ensures proper mixing and aeration. Thereafter, aerobic condition was maintained by opening half side doors. 2-3 rotations at a time were made to ensure that the material on the top portion moved to the central portion, where it was subjected to high temperature.

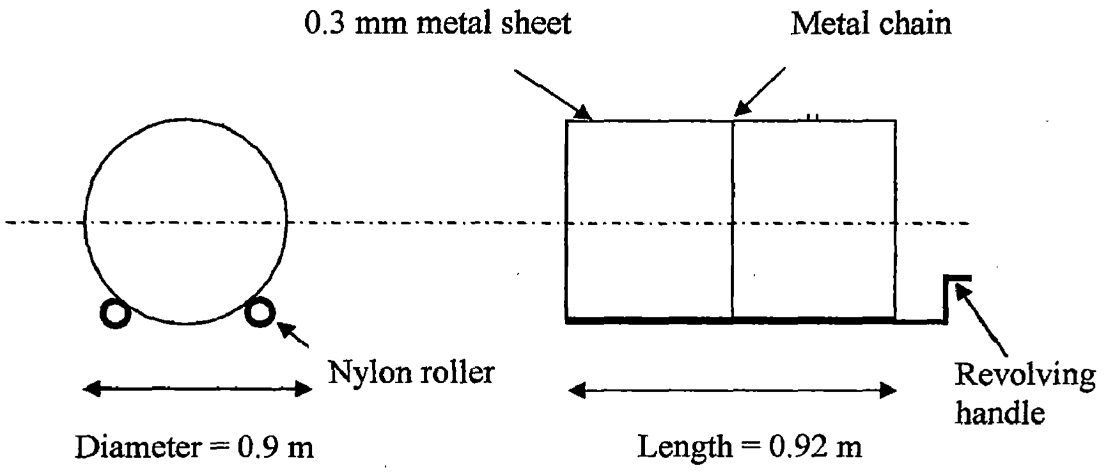


Fig.2.2. Schematic diagram of rotary drum composter for batch operation

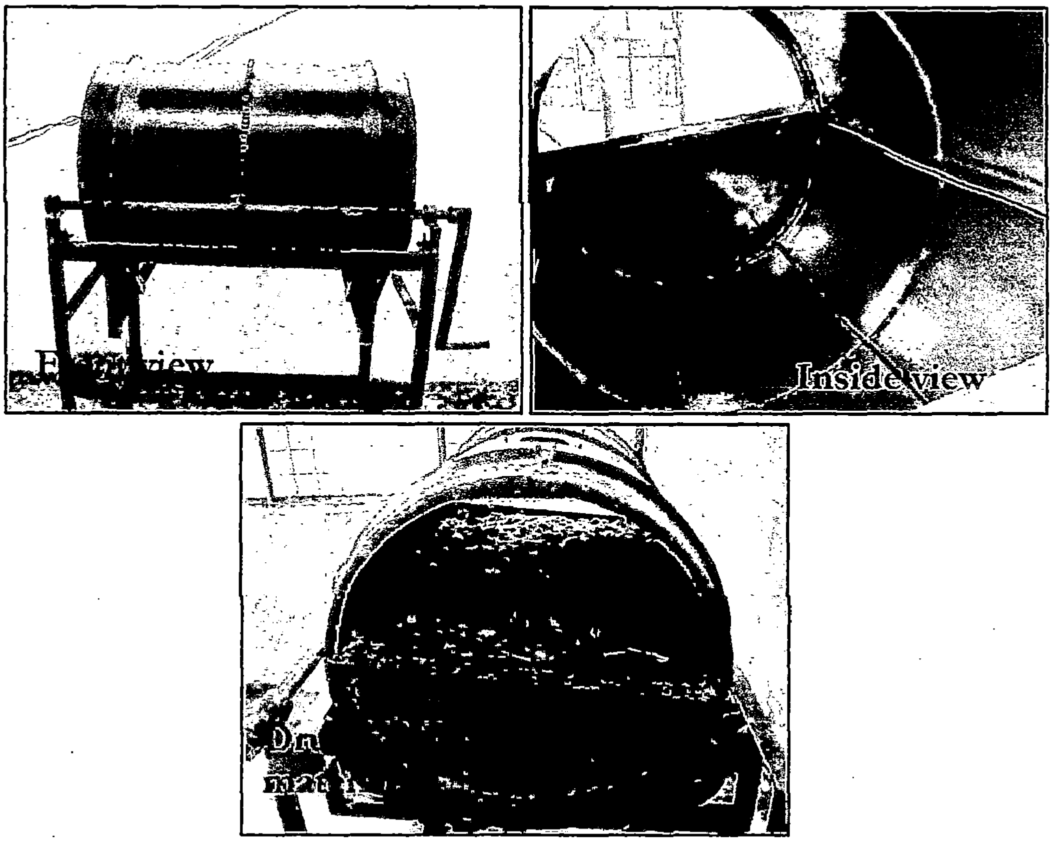


Fig.2.3. Pictorial views of pilot-scale rotary drum composter

2.2.2 FULL-SCALE CONTINUOUS OPERATION

In order to continuous composting process study, a full-scale rotary drum composter of 3.5 m^3 capacity was installed in institute campus (Fig. 2.4 and 2.5). The main unit of the composter, i.e. the drum of 3.7 m in length and 1.1 m in diameter, made up of a 4 mm thick metal sheet. The inner side of the drum was painted with anti-corrosive coating. The drum is mounted on four metal rollers attached to metal stand. A 7.5 kW motor with gear reducer is used to turn the drum in clockwise direction at a speed of 2 rpm. In order to provide the appropriate mixing and agitation, 400 mm long angles with 4 mm width and 150 mm height were welded longitudinally. These angles provided tumbling action and help to move the waste material along the drum. With regards to the composting process, the main function of rotation is to expose the material to air, add oxygen and release the heat and gaseous products of decomposition. Two main openings are provided at both ends for waste inlet and compost outlet. A 2.5 kW air blower fixed at the inlet end was used to suck the air from outlet end for aeration. It also promotes the escape of water vapors and foul gases generated during composting. Two ports are provided at the middle and outlet zone of drum to drain possible excess water and to collect compost samples. The shredded mixed organic waste is loaded into the drum by means of plastic container on daily basis. To reach the stabilization phase, the retention time was kept as 8 days. Two rotations at a time on daily basis were made to ensure that the material on the top portion moved to the central portion, where it will be subjected to higher temperature. Thereafter, aerobic condition was maintained by opening the air blower.

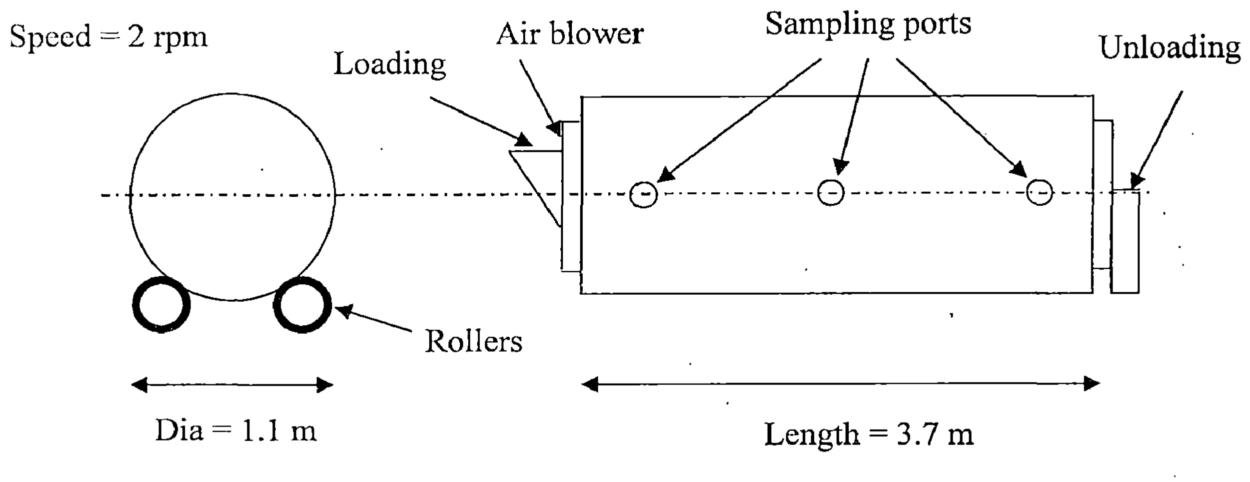


Fig.2.4. Schematic diagram of rotary drum composter for continuous operation

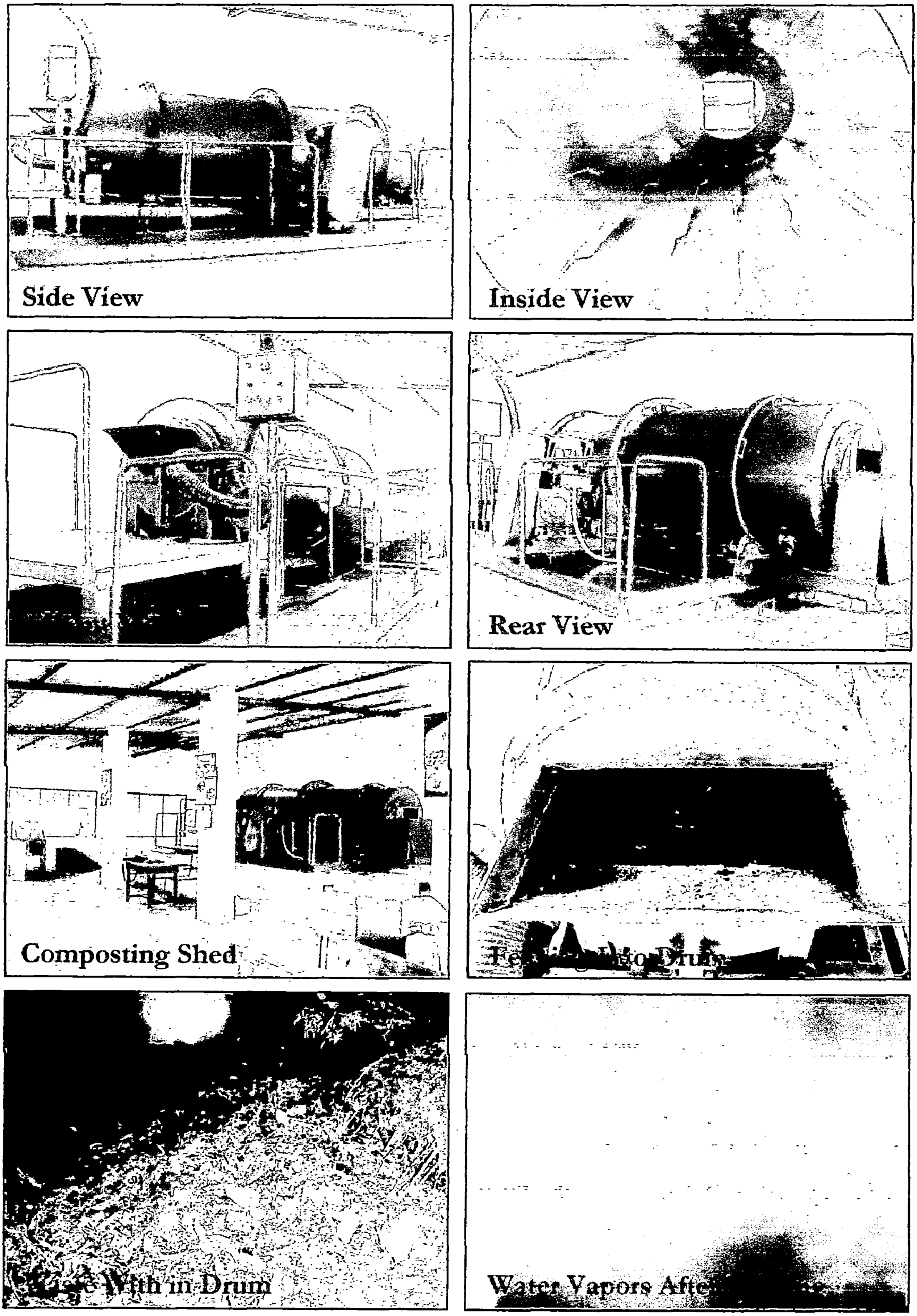


Fig.2.5. Pictorial views of full-scale continuous rotary drum composter

2.2.3 CONVENTIONAL WINDROWS COMPOSTING SYSTEM

In the conventional windrows method waste material was formed into trapezoidal piles (length 2100 mm, base width 350 mm, top width 100 mm and height 250 mm, having length to base width (L/W) ratio of 6. Windrow contained approximately 70 kg of waste material (Fig. 2.6).

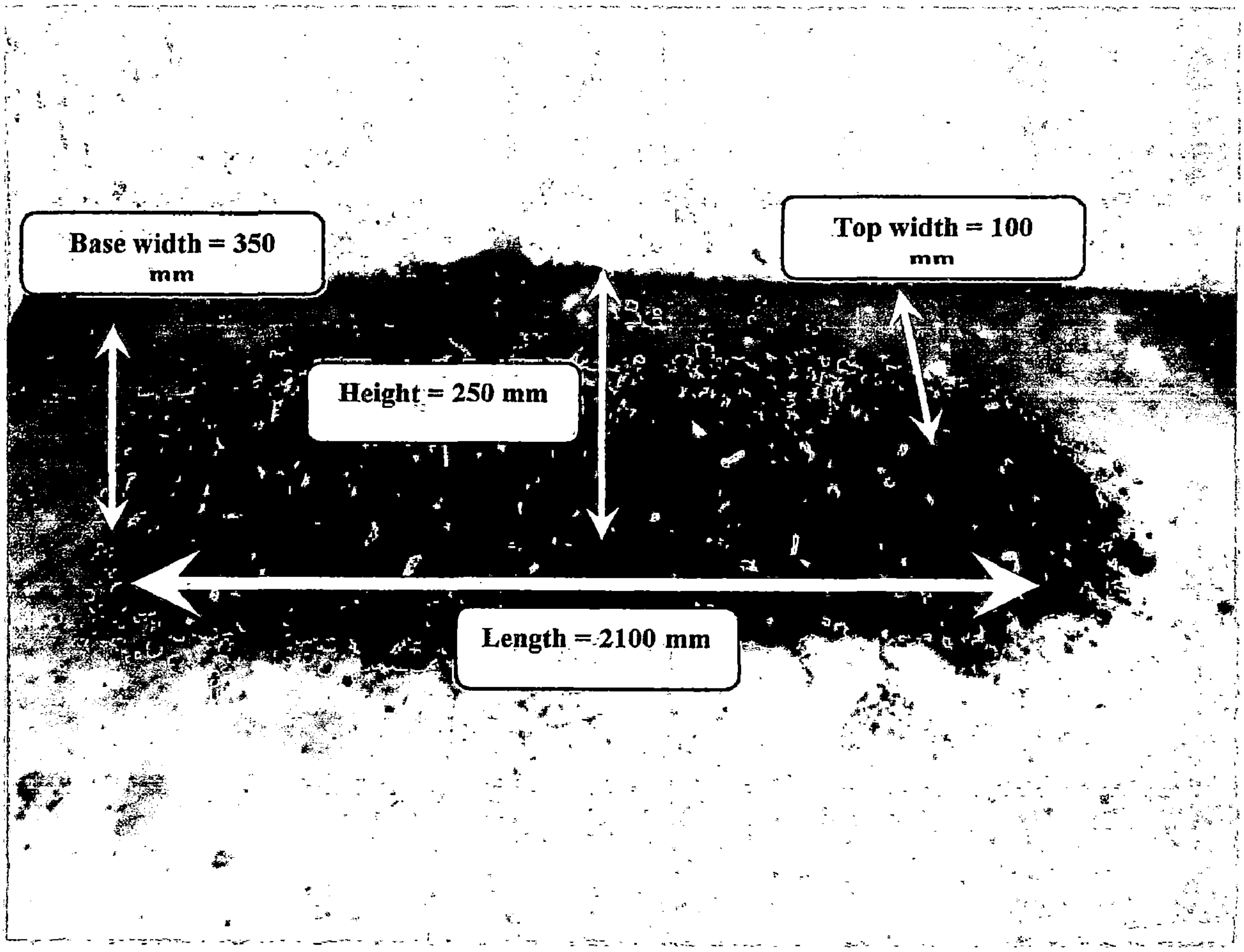


Fig.2.6 Windrow (W) with waste material of the configuration L/W=6

2.3 EXPERIMENTAL DESIGN

In order to accomplish our objectives, the research was carried out in two attempts i.e. Household batch composter and full-scale continuous operated composter. Each attempt was divided into different phases as summarized in Fig. 2.7.

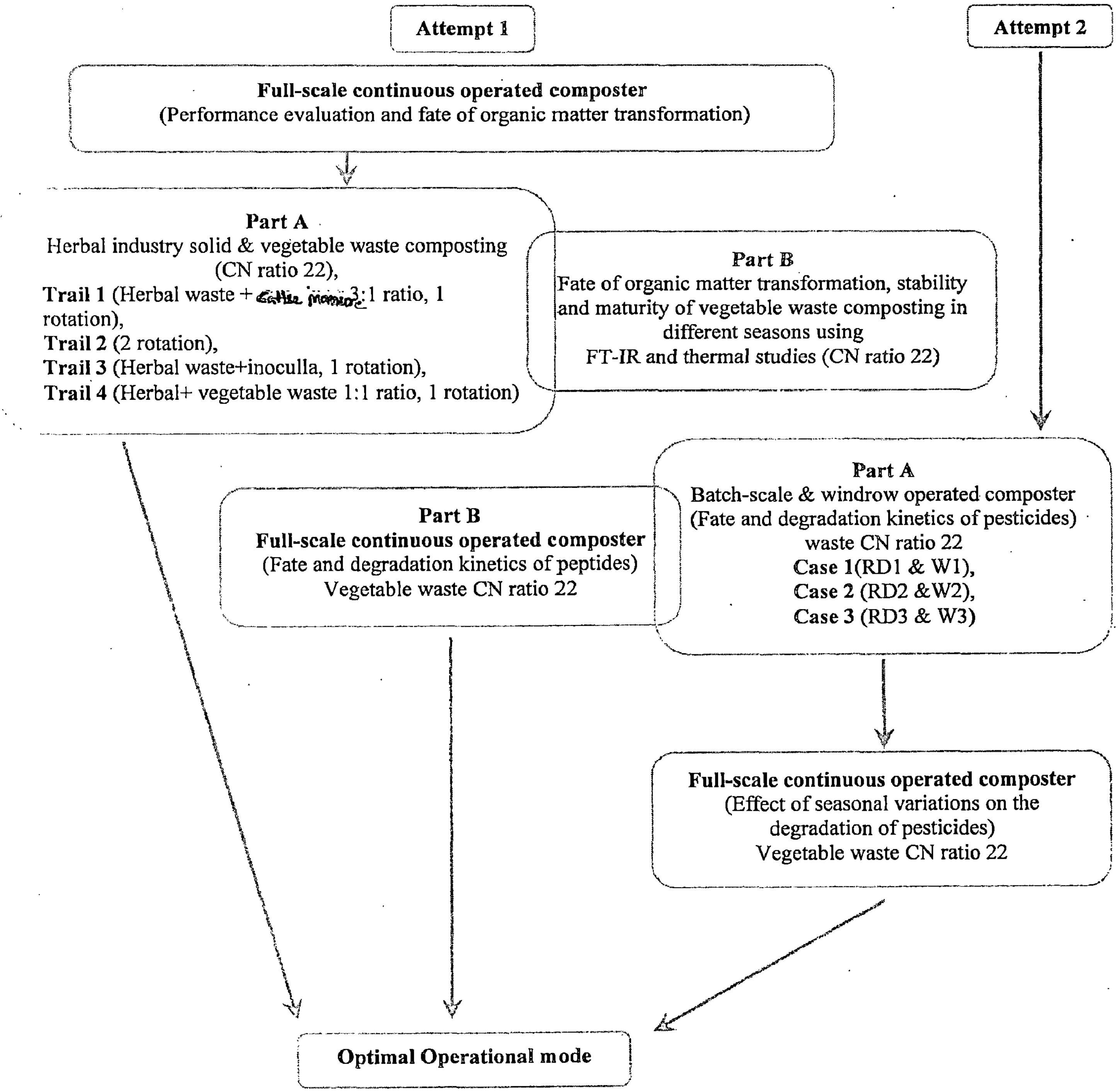


Fig.2.7. Experimental design of the research work

Table.2.1. Initial characterization of herbal waste, cattle manure and vegetable waste

Descriptions	**Herbal waste**	**Cattle manure**	**Vegetable waste**
Moisture content (%)	64 ±0.71	83 ±0.43	93 ±0.31
pH	5.70 ±0.10	7.02 ±0.10	5.3 ±0.12
EC (µS/cm)	0.73 ±0.20	3.33 ±0.14	2.04 ±0.12
Ash content (%)	15.1 ±0.34	12.9 ±0.23	10.8 ±0.27
TOC (%)	47.17 ±0.41	48.4 ±0.27	49.5 ±0.31
Total nitrogen (%)	2.40 ±0.13	2.20 ±0.18	2.0 ±0.20
NH_3-N (%)	0.56 ±0.21	0.38 ±0.12	0.65 ±0.13
C/N ratio	19.65 ±0.42	22.0 ±0.40	24.7 ±0.51

Table.2.2. Waste proportion and physico-chemical characteristics

S. No.	**Feedstock material**	**Weight (kg)**	**Percentage (%)**
1.	Cattle manure	30.00	34.48
2.	Mixed vegetable waste	50.00	57.47
3.	Saw dust	7.00	8.04
4.	Total weight of mixture	87.00	100.00
5.	Initial Moisture content	66.99	77.21
6.	Total solids	20.01	23.00
7.	Initial ash content	11.41	57.23
8.	Initial total organic carbon	7.00	35.36
9.	Initial total nitrogen	0.27	1.37

Table 2.3.Waste characterization with physicochemical parameters used for composting including vegetable waste components

Components	Moisture (%)	pH	EC (mS/cm)	PO_4^{-3} (%)	Total Nitrogen (%)	Total Carbon (%)	Hydrogen (%)	Oxygen (%)	TOC (%)
Mix vegetable waste	90.12±0.32	5.64±0.38	5.31±0.54	1.22±0.20	3.18±0.38	39.06±0.26	8.27±0.29	49.49±0.25	34.12±0.15
Cow dung	76.23±0.05	5.72±0.06	4.23±0.73	0.81±0.19	1.75±0.15	36.48±0.38	5.63±0.22	56.14±0.33	32.24±0.12
Onion	92.50±0.30	5.34±0.42	3.21±0.05	0.02±0.17	1.98±0.23	44.78±0.18	12.37±0.25	40.87±0.35	40.32±0.07
Cauliflower	89.88±0.15	5.68±0.16	5.47±0.31	0.63±0.07	3.12±0.07	43.29±0.40	13.97±0.22	39.62±0.82	39.27±0.20
Reddish	91.80±0.22	5.65±0.25	9.02±0.31	0.51±0.15	3.88±0.20	36.62±0.05	9.97±0.27	49.53±0.29	33.22±0.22
Tomato	96.29±0.06	5.00±0.08	5.77±0.31	1.02±0.44	2.93±0.18	46.42±0.24	11.63±0.20	39.02±0.23	43.72±0.18
Cabbage	93.12±0.18	4.63±0.22	5.30±0.05	0.45±0.05	3.14±0.19	42.26±0.29	9.44±0.28	45.16±0.37	38.27±0.15
Cucumber	97.12±0.16	5.73±0.20	6.32±0.35	0.73±0.27	2.56±0.07	43.24±0.20	12.35±0.48	41.85±0.20	40.43±0.20
Carrot	93.10±0.16	6.56±0.20	3.59±0.15	0.42±0.27	0.67±0.16	49.68±0.18	12.55±0.24	37.10±0.08	40.61±0.25
Bringle	94.50±0.06	5.45±0.08	5.26±0.23	0.50±0.34	0.54±0.50	30.78±0.18	10.89±0.26	57.79±0.17	28.32±0.05
Potato	89.18±0.13	5.44±0.17	4.78±0.06	1.20±0.05	2.52±0.27	38.72±0.24	14.81±0.20	43.95±0.19	34.24±0.24

Table2.4. Pesticides concentration in vegetable waste, cow dung and raw individual vegetables

Components	**Aldrin (µg/kg)**	**Endosulfan α (µg/kg)**	**Endosulfan β (µg/kg)**	**Lindane (µg/kg)**
Mix vegetable waste	438.21±20.72	1229.46±6.64	487.32±4.16	288.66±4.88
Cow dung	74.431±14.28	712.321±10.61	472.39±18.86	127.71±6.73
Vegetable waste	--	--	--	--
Onion	ND*	ND*	485.34±7.35	ND*
Cauliflower	328.52±14.15	1020.69±14.19	732.432±8.91	314.31±7.33
Reddish	382.75±16.31	951.1237±4.00	424.32±7.56	315.95±2.63
Tomato	400.82±21.92	984.23±21.26	502.42±1.21	ND
Cabbage	371.32±4.48	ND*	ND*	389.41±15.15
Cucumber	ND*	889.27±14.15	706.34±7.01	391.07±10.58
Carrot	493.77±15.56	1068.52±14.18	ND*	ND*
Bringel	543.57±7.01	919.33±5.38	499.44±14.14	395.70±9.00
Potato	ND*	1007.72±10.63	532.93±2.21	374.57±8.21

*ND= Not detected

Table.2.5. Pesticides concentration in vegetable waste, cow dung and raw individual vegetables during winter season

Components	**Aldrin (mg/kg)**	**Endosulfan α (mg/kg)**	**Endosulfan β (mg/kg)**	**Lindane (mg/kg)**
Mix vegetable waste	1.8930±0.21	7.1930±3	4.4800±0.21	2.0423±1.06
Cow dung	ND*	0.4467±0.28	0.5800±0.26	ND*
Vegetable waste	--	--	--	--
Onion	0.9718±0.91	0.9600±0.37	1.0700±0.32	0.6332±0.94
Cauliflower	ND*	ND*	0.3800±0.33	0.0489±0.92
Reddish	0.8215±0.30	0.9900±0.23	0.8100±0.22	ND*
Tomato	0.9671±0.23	0.1073±0.25	0.5700±0.34	0.5921±0.91
Cabbage	0.8966±0.9	0.6967±0.28	0.2600±0.84	0.2723±0.43
Cucumber	ND*	0.6000±0.16	0.5600±0.89	0.1841±0.33
Carrot	0.9398±0.92	0.3933±0.24	0.3700±1.2	ND*
Bringel	0.1296±1.06	1.4400±0.24	0.8001±0.91	0.3821±0.42
Potato	ND*	0.6267±0.31	0.2203±1.2	0.0119±0.93

*ND= Not detected

Table.2.6. Pesticides concentration in vegetable waste, cow dung and raw individual vegetables during spring season

Components	**Aldrin (µg/kg)**	**Endosulfan α (µg/kg)**	**Endosulfan β (µg/kg)**	**Lindane (µg/kg)**
Mix vegetable waste	438.00±2.54	1441.80±2.46	607.50±2.62	458.26±2.60
Cow dung	ND*	475.52±2.91	119.55±0.98	ND*
Vegetable waste	--	--	--	--
Onion	71.78±2.87	445.78±2.81	134.60±1.64	ND*
Cauliflower	ND*	407.40±2.78	203.80±2.78	256.33±2.70
Reddish	482.15±2.91	ND*	302.37±2.39	147.14±2.89
Tomato	100.12±1.09	725.52±2.74	427.30±1.64	275.55±2.54
Cabbage	ND*	197.41±3.22	192.62±2.98	178.49±2.33
Cucumber	195.44±0.97	726.63±2.76	107.85±2.45	ND*
Carrot	239.77±2.47	ND*	29.97±2.37	74.63±2.74
Bringel	ND*	309.96±3.09	118.63±2.95	192.96±0.98
Potato	274.74±3.01	224.20±2.75	138.60±1.09	95.63±0.97

*ND= Not detected

Table.2.7. Pesticides concentration in vegetable waste, cow dung and raw individual vegetables during summer season

Components	**Aldrin (µg/kg)**	**Endosulfan α (µg/kg)**	**Endosulfan β (µg/kg)**	**Lindane (µg/kg)**
Mix vegetable waste	738.00±0.98	841.80±0.99	407.50±0.98	328.26±2.38
Cow dung	141.78±0.914	775.52±0.98	119.55±2.48	108.26±2.27
Vegetable waste	--	--	--	--
Onion	92.78±2.78	245.78±1.06	134.60±0.97	ND*
Cauliflower	ND*	321.40±	203.80±0.98	156.33±2.19
Reddish	392.15±2.87	ND*	302.37±0.91	47.14±1.80
Tomato	110.12±2.85	825.52±1.2	427.30±2.68	175.55±1.51
Cabbage	ND*	997.41±2.81	192.62±1.00	134.49±2.16
Cucumber	325.44±2.78	426.63±2,73	107.85±0.94	ND*
Carrot	232.77±1.89	ND*	29.97±0.97	98.63±2.21
Bringel	ND*	729.96±1.89	118.63±1.99	202.96±2.25
Potato	74.74±2.78	134.20±0.71	138.60±2.05	105.63±0.98

*ND= Not detected

2.4. EXPERIMENTALS

Different waste combination of MSW and vegetable waste studies was shown by Kalamdhad and Kazmi (2008-2009) during household batch and full scale rotary drum composting. The remaining studies regarding performance of full scale continuous rotary drum composter in combination of herbal industry solid and vegetable waste and fate of organic matter transformation, their stability and maturity on the basis of seasonal variations was continued here using advanced techniques such as FT-IR and thermal studies (TG, DTA & DTG). Fate and degradation kinetics of trace hazardous organochlorine pesticides during household batch-scale, conventional windrows and full-scale continuous rotary drum composting was also continued using GC-MS. As per the objectives of this thesis, the first attempt divided into two parts.

Part A: Performance of a full-scale rotary drum for continuous operation in combination of herbal industry solid and vegetable waste:

In order to study the performance of full scale rotary drum composter (3.5 m^3 capacity) in combination of herbal industry solid and vegetable waste after loading of feedstock into inlet zone, it took four days to reach middle zone and subsequently enter into the outlet zone in next four days. A mixture of herbal pharmaceutical industry solid waste collected from a nearby industry/pharmacy of Haridwar India, containing solid waste from the extract of plant mainly; *Winthania Somnifera, Raurffia Serpentina, Embelica Officinalis, Asperagus Ralenousus, Ascorus Calamus, Labidium Sativum, Ancicoclus Pirethrum* and *Cassia Angustijalis* and cattle (Buffalo) manure collected from nearby places of institute campus was selected as the mixed organic waste to be used in a ratio of 3:1 (total weight, 100 kg). One rotation (Trial 1) and two rotation (Trial 2) in a day during rotary drum composting was chosen to study the effect of turning frequency on composting system. In trial 3, 100 mL highly concentrated blend of enzymes, probiotics and with organic catalyst inocula (OXYDOL, an AGRANCO CORPO, USA product) was added to 100 kg of herbal waste under one rotation condition on daily basis. About 40-50 kg herbal and vegetable market waste each in 1:1 ratio was used in trial 4 at one turns per day frequency as used in trial 1. In each trial, C/N ratio of waste material was 22 calculated by cornell composting site. Changes in physico-chemical parameters and FT-IR spectroscopic were analyzed for 30 days of loading period for each trails. Initial physico-chemical properties of herbal wastes, cattle manure and vegetable wastes are detailed in table 2.1.

Part B: Fate of organic matter transformation, their stability and maturity on the basis of seasonal variations was continued using advanced techniques such as FT-IR and thermal studies (TG, DTA & DTG). The size of reactor as explained earlier was decided on the basis of the amount of wastes required (maximum 120 kg/day) which can be easily collected from various sources. Initially, one rotation at the rate of 2 rpm and 10 min aeration were decided before and after the feeding of wastes into drum.

Mixed vegetable waste, cattle dung (C/N=20) and saw dust (C/N=540) were collected from institute campus. Prior to composting, the maximum particle size of the mixed waste was restricted to approximately 1.0-2.0 cm in order to provide better aeration and moisture control. The shredded mixed organic waste (table.2.2) is loaded into the drum by means of plastic container on daily basis. To reach the stabilization phase, the retention time was kept as 8 days. One rotation at a time on daily basis was made to ensure that the material on the top portion moved to the central portion, where it will be subjected to higher temperature. Thereafter, aerobic conditions were maintained by opening the air blower. Cattle manure was used as inlet for the growth and enhancement of the microbial activities. Temperature and moisture content were observed on daily basis along with changes in physico-chemical and biological parameters on alternate day based on different seasons including winter (0-70 days), spring (70-120 days) and summer (120-150 days). FT-IR spectroscopic and thermal study parameters were also analyzed during different seasons. The results of our study would be useful in defining operational guidelines, start-up conditions, stability and maturity of waste materials of industrial-scale rotary drum composter dealing with different kind of organic waste.

The second attempt study was further divided into two parts:

Part A: Fate and degradation kinetics of organochlorine pesticides i.e., Aldrin, Endosulfan α, Endosulfan β and Lindane during house hold batch-scale rotary drum and conventional windrow composting using vegetable waste. Here, a hold batch-scale rotary drum composter (RD) of 250 L capacity and a windrows composting system L/W=6 was used. The mixed organic vegetable waste was collected from vegetable market and shredded, cow manure from nearby dairy and saw dust from saw mill, Roorkee city (India) following the proper mixing on weight basis to achieve optimum range of C/N ratio of 22. Thereafter, different cases of degradation of pesticides were studies. In case 1 (RD1 and W1): around 2.2.4120±0.23 mg/kg cumulative concentration of all pesticides actually available in vegetable waste, Case 2 (RD2 and W2): 20.2310±0.12 to 21.1702±0.31 mg/kg cumulative enhancement to three time of actual and Case 3 (RD3 and W3) 42.0210±0.13 to 43.3778±0.20 mg/kg cumulative enhancement six time of actual concentration. The physico-chemical properties and actual pesticides concentration in vegetable waste, cow dung and in different vegetables are given in table 2.3 & 2.4. The composting was carried out in 30-36 days, physico-chemical and pesticides concentration during composting was analyzed on alternate day basis.

Results of this study would be useful in defining removal of organic pollutants like pesticides and their fate from waste materials of industrial-scale rotary drum composter dealing with different kind of organic waste.

Part B: Fate and degradation kinetics of organochlorine pesticides i.e., Aldrin, Endosulfan-α, Endosulfan-β and Lindane during Full-scale continuous rotary drum composting using vegetable waste. After successful study of Fate and degradation kinetics of organochlorine pesticides during house hold batch-scale rotary drum composting, performance of full-scale continuous rotary drum composting on fate and degradation kinetics of pesticides was continued. During this study the waste composition was used same as in previous house hold batch-scale rotary drum composting. The size of reactor as explained earlier was decided on the basis of the amount of wastes required (maximum 120 kg/day) which can be easily collected from various sources. Initially one rotation at the rate of 2 rpm and 10 min aeration were decided before and after the feeding of wastes into rotary drum. Feeded waste materials reached in middle from inlet zone after four days. Then, it moved to the outlet zone in another four days by complete degradation therefore, the drum composting was assumed to be complete in eight days. The physico-chemical properties and actual pesticides concentration in vegetable waste, cow dung and in different vegetables are given in table 2.3 & 2.4.

Furthermore a study was also carried out on effect of seasonal variations on the degradation of pesticides i.e., Aldrin, Endosulfan α, Endosulfan β and Lindane during Full-scale continuous rotary drum composting. The size of the reactor as explained earlier was decided on the basis of the amount of wastes required (maximum 120 kg/day). Initially, one rotation at the rate of 2 rpm and 10 min aeration were decided before and after the feeding of wastes into drum. This study was carried in three different seasons namely winter (0-60 days), spring (60-120 days) and summer season (120-180 days). Temperature was observed on daily basis along with changes in physico-chemical, biological parameters and pesticides concentration after every four day basis in different seasons including winter (0-60 days), spring (60-120 days) and summer (120-180 days). The vegetable waste material was used same (CN ratio 22) as used in pervious study. The physico-chemical properties and pesticides concentration in vegetable waste, cow dung and in different vegetables in different seasons are given in table 2.3, 2.5, 2.6 & 2.7.

Our results in this study would be useful in defining operational guidelines and start-up conditions of industrial-scale rotary drum composter for the removal of organic components and effects of seasonal variations on the performance of composters. Seasonal study further deals with what variations of organic pollutants are possible in different waste materials.

2.5. METHODS

Different experimental methods were used in the study to accomplish the stipulated objectives. Physico-chemical, biological and pesticides analysis of the samples collected from the composters were carried out in different departments/centres of I.I.T. Roorkee, namely Instrumentation laboratory (Chemistry Department) Environmental Engineering laboratory (Civil Engineering Departments), TG laboratory (Institute Instrumentation Centre). The flow chart demonstrates the patterns of physico-chemical, biological and pesticides analysis of collected samples (Fig. 2.8).

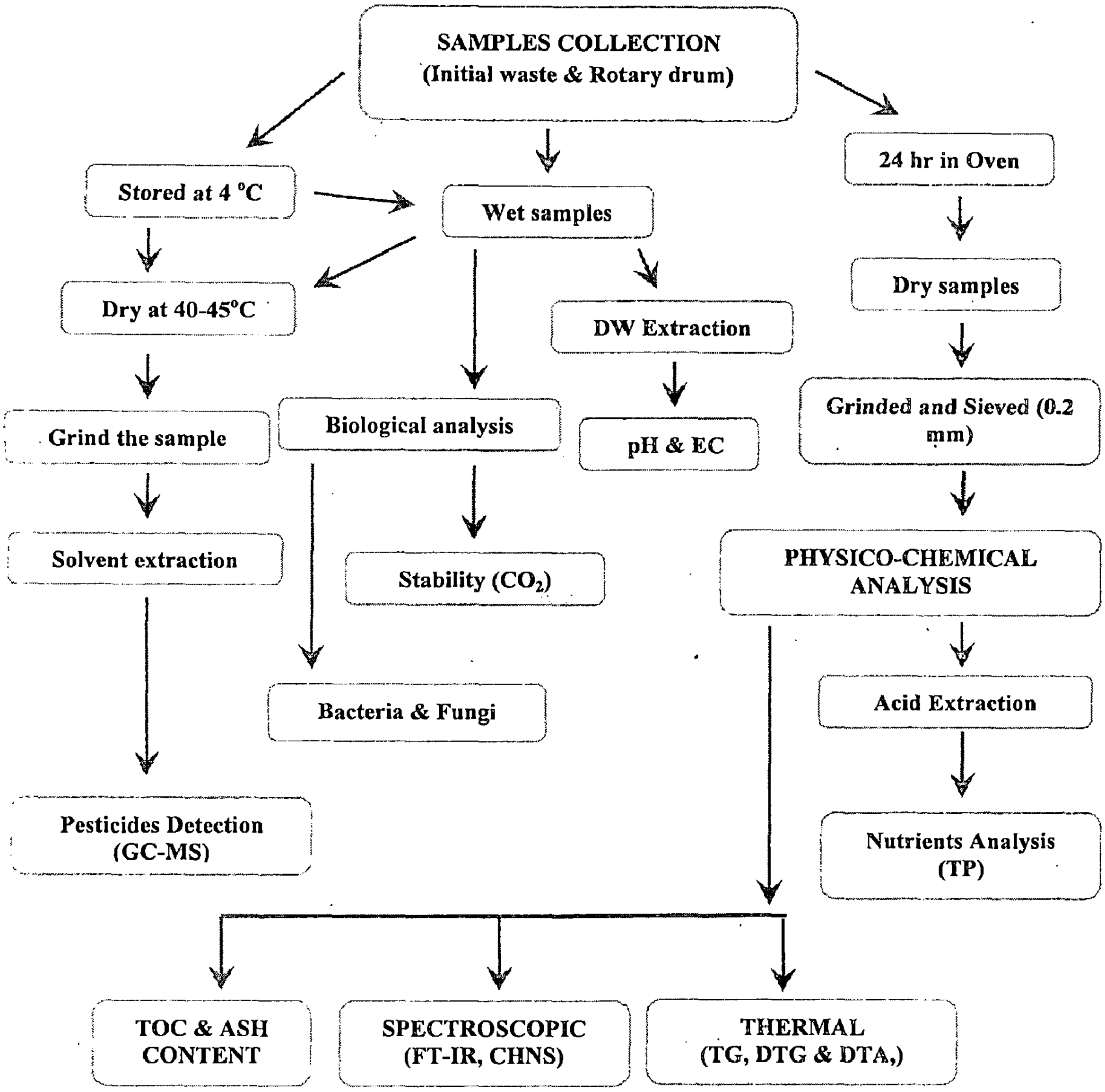


Fig.2.8. Pattern of physico-chemical biological and pesticides analysis of samples

2.6. SAMPLING

About 500 g of each grab samples were collected from six different locations, mostly at the mid span and end terminals of the house hold batch-scale rotary drum composter and conventional windrows by compost sampler without disturbing the adjacent materials. Finally all the grab samples were mixed together and considered as homogenized sample. Samples were collected on day 0, 2, 4, 6, 8, 12, 10, 12 till 36 days of the composting process. Triplicates homogenized samples were collected and stored for maximum 2 days at 4°C immediately for biological and pesticides analysis. Three grab samples from inlet, middle and outlet ports were collected from full-scale rotary drum composter after every four days. Wet samples were used for biological analysis pH, EC and pesticides analysis after properly mixing. Sub-samples were oven dried immediately, ground to pass through 0.2 mm sieve and stored for further analysis. Each sub-sample was analyzed for the physico-chemical parameters spectroscopic (FT-IR, TG, DTG & DTA and CHNS).

2.6.1 PHYSICO-CHEMICAL ANALYSIS

- ***Temperature***

Temperature was monitored on the basis of 24 hour time interval using a digital thermometer throughout the composting period within pilot-scale rotary drum composter. During full-scale continuous rotary drum composting, temperature readings were taken directly using handheld analog thermometer, inserted into the composting mass in three different locations at 24 hour time interval.

- ***Moisture content***

Moisture content was determined by weight loss of compost sample (105°C for 24 hour) using the gravimetric method (BIS, 1982).

- ***pH and electrical conductivity (EC)***

Stirred 5 g of the wet sample in 50 ml distilled water and pH was measured using a pH meter with a glass electrode, previously calibrated and corrected for temperature (BIS, 1982). Filtrate of the above mixture by Watman filter paper No. 42 and was used to measure the EC using a conductivity meter.

- ***Total Carbon, Total Organic Carbon (TOC) and Ash content***

About 5-10mg sub sample was used for the determination of total carbon by CHNS analyzer. 25-100 mg of sub-sample used for determination of TOC by Shimadzu (TOC-V_{CSN}) Solid Sample Module (SSM-5000A). Ash content was measured by the ignition method (550°C for 2 hour in muffle furnace) (BIS, 1982). Decomposition (Dec) was calculated according to the following formula (Jouraiphy et al., 2005):

Dec (%) = $100 \times [(A_f - A_i)/A_f \times (100 - C_i)] \times 100$, Where A_f is final ash content (in fraction), A_i is initial ash content (in fraction) and C_i is initial TOC (in fraction).

- ***Total nitrogen (TN), ammonical nitrogen (NH_4-N) and Nitrate (NO_3-N)***

5-10 mg samples were prepared for analyzing TN using CHNS analyzer. KCl (30 ml of 0.2 M KCl) extraction of 3 g of each sub-sample was used for the analysis of NH_4-N and NO_3-N using standard methods (Tiquia, 2000; APHA, 1995).

- ***Fourier-transform infrared (FTIR) spectroscopy***

FT-IR spectra were obtained on wave number range of 400-4000 cm^{-1} on a Perkin Elmer GX FT-IR system equipped with OMNIC software. The sub-samples (four samples from each trial and three samples from each season) were prepared for analysis by mixing 1 g of dried KBr with approximately 2-5mg of sub-sample and compressing the mixture to pellets.

- ***Thermal analysis***

Three samples (from each season) were selected from a sample set of 9 samples collected during the composting process for thermal analysis. Thermogravimetry (TG) and Derivatives thermogravimetry (DTG) were carried out with a Mettler TG20 Termobalance, TA 3000 system. A calibration with trafoperm, nickel and isotherm contemporarily, followed by a check with nickel, was performed before the analysis. The following conditions were adopted for all TG and DTG analyses: heating rate of 10°C/min from 25 to 800°C, oxidizing atmosphere for static air, and sub-samples weights of about 10 mg. Differential thermal analyses (DTA) was carried out with a Mettler TA-STAR 821. A total calibration with indium/zinc, followed by a check DTA exo-indium, was performed before the analysis. The following conditions were adopted for DTA analyses: heating rate of 5°C/min from 45 to 550°C, oxidizing atmosphere for static air, and sub-samples weights of about 10 mg. Measurements were repeated at least three times.

2.6.2. PESTICIDES ANALYSIS

- ***Reagents and chemicals***

All organochlorine pesticide (OCPs) standards (Aldrin, Lindane, Endosulfan-α and Endosulfan-β) were purchased from Sigma Aldrich (USA). Standard solutions were prepared in n-hexane at a concentration of 100μg/mL and diluted with n-hexane when necessary. Organic solvents (n-hexane, acetone, ethyl acetate, methanol, acetonitrile, and dichloromethane) were of HPLC grade and supplied by J.T. Baker (USA). Anhydrous sodium sulfate, copper powder and silica gel was obtained from Sigma Aldrich (USA) and sodium sulfate used after baking at 400 °C for 12 hours. All glassware was cleaned with laboratory detergents, sequentially rinsed with distilled water of milli-Q system.

- ***Preparation of samples for pesticides analysis***

Samples were collected during all the cases from house hold batch-scale rotary drum composter (RD1, RD2 and RD3) conventional windrow (W1, W2, and W3) and full scale continuous rotary composter for the determination of selected four organochlorine pesticides Aldrin, Lindane, Endosulfan α and Endosulfan β and dried at room temperature for 24 hours. The dried sample ground with a mixture grinder and homogenized stored at - 4°C until use.

- ***Sample Extraction and Clean-up from waste material and compost samples***

Organochlorine pesticides (OCPs) were extracted from 10 gram of raw material and compost samples by ultrasonic agitation in 30 mL of a mixed solvent composed of dichloromethane: acetone (5:2 v/v) for 30 minutes (Kim, *et al,* 2008) extraction was repeated three times. To remove sulfur compounds, active copper powder was added to the extract. To prepare the activated copper powder, copper powder washed with 6M HCl and rinsed with distilled water in three or more interactions. It was then sequentially rinsed three times with methanol, acetone, and n-hexane. The resulting extract was filtered through filter paper containing 5g of sodium sulfate to remove traces of water and was then concentrated to approximately 1 mL using a rotary evaporator. For the clean-up of extract sample, the extract was transferred on the top of glass chromatographic column (35 cm length 1 cm, i.d.) packed with 2.0 g of silica gel. Then elution was processed with 40 mL of dichloromethane: acetone (1:1, v/v) at 2 mL min. Eluate was collected in a 100 mL round bottom flask and evaporated to less than 1 mL in a rotary vacuum evaporator at 30^0C. The volume of extract was adjusted to 2 mL with n-hexane and the final volume was used for the pesticides analysis through GC-MS. The calibration curve and R^2 value of pesticides concentration Vs peak area is given in Fig.2.9. & table 2.8.

- ***Sample Extraction and Clean-up from leaachate samples***

Take 100 ml leachate sample and add 50 mL of a mixed solvent composed of dichloromethane: acetone (5:2 v/v) then extraction was carried out using ultrasonic agitation for 30 minutes. Extraction was repeated three times. The resulting extract was filtered through filter paper containing 5g of sodium sulfate to remove traces of water and was then concentrated to approximately 1 mL using a rotary evaporator. For the clean-up of extract sample, the extract was transferred on the top of glass chromatographic column (35 cm length 1 cm, i.d.) packed with 2.0 g of silica gel. Then elution was processed with 40 mL of dichloromethane: acetone (1:1, v/v) at 2 mL min. Eluate was collected in a 100 mL round bottom flask and evaporated to less than 1 mL in a rotary vacuum evaporator at 30^0C. The volume of extract was adjusted to 2 mL with n-hexane and the final volume was used for the pesticides analysis through GC-MS. GC spectra of waste material and compost in household batch and full-scale continuous rotary drum composting is given in appendix (Fig. A1, A2, A3, A4, A5, A6, A7, A8 and A9).

- ***GC–MS conditions***

Mass spectrometric analyses were carried out with a Varian GC-MS instrument (Germany) equipped with a VF-5MS fused-silica capillary column (30 m x 0.25mm, I.D. film thickness 0.25 μm). Helium was used as the carrier gas at a flow rate of 1.0 mL/min. A 1μL sample was introduced by split mode injection (split ratio 10:1). Both the GC injection port and the MS system were held at 280 °C. After sample injection, the oven temperature was held at 80 °C for 1 minute, raised to 240 °C at 20 °C/min and held for 5 min, raised to 280 °C at 5 °C /min, and held for 5 min.

- ***Calibration curve***

For each pesticides determination by CG-MS, the range of concentration was appropriated to the level usually found in waste material and compost samples. In standard solutions used, the concentration of the compounds ranged between 100 to 700μg/L and this range corresponds to 1, 2, 3, 4, 5, 6, 7mg/kg of waste material respectively. The calibration technique is the external standard multipoint calibration using seven concentration levels (Fig.2.9).

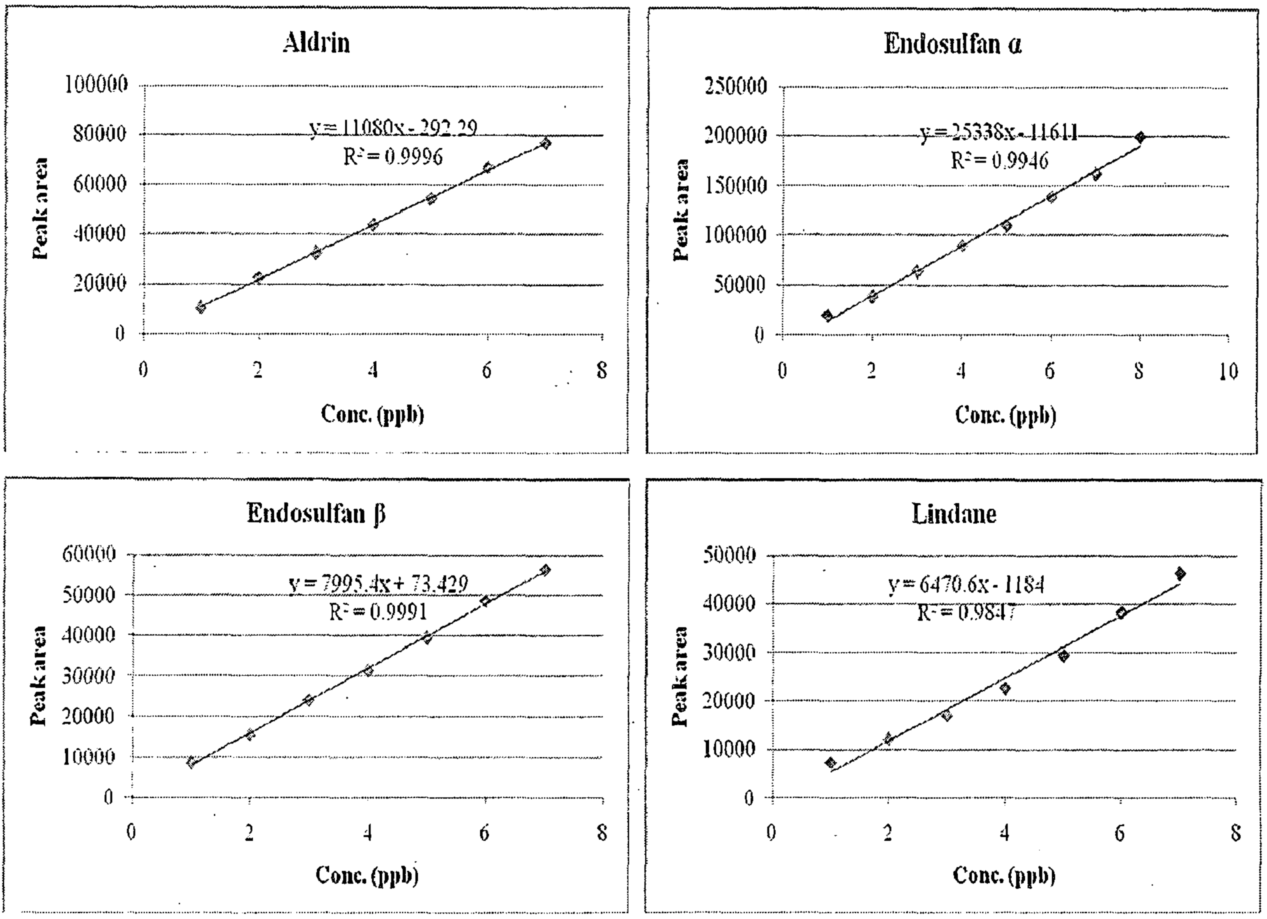


Fig.2.9. Calibration curve of Aldrin, Endosulfan α, Endosulfan β and Lindane Conc. Vs peak area

Table.2.8. Analytical parameters for organochlorine pesticides in compost sample (RSD-relative standard deviation).

Pesticides	**Calibration Curve Equation**	**r^2**	**Retention time, min (RSD, %)**
Aldrin	y =11080x-29229	0.9996	15.39±0.02
Endosulfan α	y =25338x-11611	0.9946	19.16±0.07
Endosulfan β	y =7995x+73429	0.9991	20.30±0.09
Lindane	y =64706x-1184	0.9847	17.64±0.04

- ***Preparation of spiked waste material for house hold batch-scale rotary drum and conventional windrows composting***

(a) Preparation of spiked waste material were prepared for case RD2 and W2 composting

Waste material was prepared by adding different component (vegetable waste, cow dung and tree leaves) and check the each pesticides concentration in waste material and each components by proper mixing in triplicate. The actual concentration of Aldrin, Endosulfan α, Endosulfan β and Lindane was 0.881, 2.721, 1.064 and 2.386 mg/kg respectively. For the enhancement of each pesticides concentration three times we were adding 1L solution of 270, 820, 320 and 720 mg/L pesticides concentration into 150 kg waste material respectively. This spike level corresponds to 1.80, 5.46, 2.13 and 4.80 mg/kg of waste. Mix the waste for 30 minutes by mechanically shaking. After bulk of the solvent was evaporated at room temperature, the waste material stored at room temperature for 24 hours. Next day after proper mixing we feed 50% of waste into the rotary drum (RD2) and make a windrow (W2) of remaining 50% of waste material.

(b) Preparation of spiked waste material were prepared for case RD3 and W3 composting

Waste material prepared by adding different component (vegetable waste, cow dung and tree leaves) and check the each pesticides concentration in waste material and each components by proper mixing in triplicate. The actual concentration of Aldrin, Endosulfan α, Endosulfan β and Lindane was 2.027, 2.018, 0.919 and 2.26 mg/kg respectively. For the enhancement of each pesticides concentration three times we were adding 1L solution of 1520, 1520, 690 and 1700 mg/L pesticides concentration into 150 kg waste material respectively. This spike level corresponds to 10.13, 10.13, 4.60 and 11.30mg/kg of waste.

Mix the waste for 30 minutes by mechanically shaking. After bulk of the solvent was evaporated at room temperature, the waste material stored at room temperature for 24 hours. Next day after proper mixing we feed 50% of waste into the rotary drum (RD2) and make a windrow (W2) of remaining 50% of waste material.

3.6.3 BIOLOGICAL ANALYSIS

Each homogenized sample (wet sample) was analyzed three times for the following parameters.

- ***Bacterial and fungal identification***

Total heterotrophic bacteria: Total number of culturable bacteria was determined by pour plating technique using Nutrient Agar Medium (NAM) for the prepared serial dilutions of sample. Finally, prepared plates were incubated in an inverted position for 24–48 h at 37 °C. The isolated bacterial colonies were considered as pure after a series of four different sub-cultures on NAM plates. The bacterial isolates were stained and identified under microscope as Gram positive or Gram negative, along with their biochemical properties (Hassen, *et al,* 2001).

Total fungus: The number of viable fungus was determined by plating appropriated diluted suspensions onto Potato Dextrose Agar (PDA) plates and counting colonies after 72 h incubation at 25 °C (Hassen, *et al,* 2001).

CO_2 emission rate

Microbial respiration of compost samples, based on CO_2 evolution was measured using static measurement method (Knoepp and Vose, 2002). Approximately, 10 g of sample was sealed in a 0.5 L vessel along with a beaker containing a known weight of oven dried (105°C) soda lime (1.5–2.0 mesh). The samples were incubated at room temperature (24±2°C). Blank necessary for trap CO_2 calculation described as above without putting a sample in a vessel. Soda lime trap were removed after 24 hour, oven dried and reweighed to determine CO_2 absorbed. Finally, the CO_2 test values were used to determine the Solvita maturity index on a scale of 1–8 which then represent the maturity level of the compost samples.

2.7 INSTRUMENTS AND EQUIPMENTS USED

Instruments required for physico-chemical and biological analysis of solid wastes and composts are detailed in table 2.9-2.11.

Table.2.9. Instruments used for physico-chemical analysis

Parameter	Instrument/Equipment	Model/Manufacturer/Specification
Moisture content	Hot air oven	TempStar
pH	Digital pH meter	Toshniwal Instrument Manufacturing Pvt. Ltd. India.
EC	Conductivity benchtop	Orion 4 star, Thermo Electron Corporation
TOC	TOC-V_{CSN}	Shimadzu, Solid Sample Module, SSM-5000A.
Ash content	Muffle furnace	NSW India.
TN	CHNS analyzer	Verio EL III elementar Catalytic tube combustion, TCD detector
NH_4^+-N	Spectrophotometer	DR/4000, HACH, USA
NO_3^--N	Spectrophotometer	DR/4000, HACH, USA
TP	Spectrophotometer	DR/4000, HACH, USA
Pesticides	Varian GC-MS	Mass detector, FactoFour capillary column (VF-5ms, 30m×0.25mm ID, DF=0.25)
FTIR	Thermo Nicolet FT-IR	Nexus system operated with OMNIC software
Thermal analysis	Perkin Elmer Pyris Diamond	Mettler TA-STAR 821

Table.2.10. Instruments used for biological analysis

Parameter	Instrument/Equipment	Model/Manufacturer/Specification
Bacteria	Test tubes and Petri plates	Borosil, India.
Fungi	Test tubes and Petri plates	Borosil, India.
CO_2 evolution	Incubator	TempStar

Table.2.11.Other instruments and accessories used for analysis

Instrument/Equipment	Purpose	Model/Manufacturer/Specification
Shaker	Shaking/Blending	Sara Instruments, Roorkee (India)
Oven	Drying	TempStar
Fume Hood	Digestion chamber	ST 1200 ABP, G LAB
Heater	Digestion	Q-5247, Navyug, India
Grinder	Grinding	Sumeet, India
Sieves	Sieving	Unique Drawing & Survey Emporium, Roorkee (India)
Hand gloves and Apron	Hand precaution	Safety purpose

Chapter 3

Part A: Performance of full-scale continuous rotary rrum composter during composing of herbal pharmaceutical industry solid waste

This chapter (Part A) deals with the performance of full-scale continuous rotary drum composting of herbal pharmaceutical industry waste. In addition, performance of turning frequency, inocula addition and vegetable waste in of herbal pharmaceutical industry solid waste were shown.

Study was spread out in four trials.

1. Trial. 1: Performance under one rotation per day with mixing of herbal industry waste with cattle (buffalo) manure with ratio 3:1 on wet weight basis.
2. Trial. 2: Performance under two rotations per day with the mixing of herbal industry waste with cattle (buffalo) manure with ratio 3:1 on wet weight basis.
3. Trial. 3: Performance under adding of inocula in raw waste to enhance the degradation.
4. Trial. 4: Performance under composting of mixture of vegetable market waste and herbal waste with ratio 1:1 was conducted at one rotation per day.

3.1. INTRODUCTION

Indian herbal pharmaceutical industries are probably the oldest medical care system in the world. Presently, herbal industry is growing almost 30% annually and doing business more than million of dollar every year. About 4,500 plant species (10% of total flora) of both higher and lower plant groups have medicinal values. Therefore, herbal industry solid wastes generated in large quantity after extraction process, often disposed illegally to the environment which cause differet kinds of environmental pollutions such as water, soil and air. Composting could be a viable option for the reduction of these pollutions and permits the return of nutrients back to croplands. It can be designed to handle continuous flow of waste and can be applied for composting diverse organic wastes such as cattle manure, swine manure, municipal biosolids, brewery sludge, chicken litter, animal mortalities and food residuals (Vuorinen and Saharinen, 1997; Mohee and Mudhoo, 2005; Tolvanen *et al.*, 2005; Smith *et al.*, 2006; Aboulam *et al.*, 2006; Kalamdhad *et al.*, 2009).

Application of spectroscopic analyses in composting have significant importance due to the characteristic changes in the functional groups present in organic matters. FT-IR peaks have shown changes for example, at 3400 cm^{-1} (due to alcoholic OH, phenol, COOH, N-H of amides; at 2930 & 2850 cm^{-1} due to CH_3 CH_2 asymmetric stretch; at 1630-1660 cm^{-1} due to aromatic C=C, COO^- & C=O groups; at 1560 cm^{-1} due to amide II ; at 1420–1430 cm^{-1} due to phenolic OH, COO^-, aromatic rings stretching and carbonates; at 1510, 1462, 1454 &1420 cm^{-1} due to aromatic rings of lignin; at 1030 cm^{-1} assigned to C-O stretch of polysaccharide, Si-O asymmetric stretch: at 1429 cm^{-1} due to the O-H of carboxylic acids, COO^- stretch; at 600-500 cm^{-1} due to the phosphate group and aliphatic CH_2 group of alkanes in the composts (Smith, 2002). Therefore, our aim of this study was to look the performance of full-scale rotary drum in terms of physico-chemical and FT-IR analysis during full-scale continuous rotary drum composting of herbal pharmaceutical industrial solid wastes alone and with cattle manure and vegetable wastes.

3.2 RESULTS AND DISCUSSIONS

3.2.1. Physico-chemical parameters

Initial physico-chemical characteristics and composition of herbal wastes with cattle manure and vegetable waste are detailed in Table 2.1 (Chapter 2, Materials and methods).

- ***Temperature***

The change in temperature during herbal waste composting by the heat evolution in the full-scale continuous rotary drum composter is presented (Fig. 3.1). The temperature during trial 1 increased up to 65-70°C in inlet zone of rotary drum composter. It is found that the temperature between 52-60°C are suitable to maintain the highest thermophilic activity in composting. Middle and outlet zones of rotary drum composter, temperature varied from 50-60 °C and 24-32°C respectively when ambient temperature varied from 20-28°C. Here, outlet zone temperature indicates the end of active thermophilic phase. In trial 2, a similar temperature profile as in trial 1 was observed with inlet zone varied from 60-70°C after 8 days. Middle zone temperature reached near to temperature of inlet zone indicating long thermophilic phase. Outlet zone temperature was lower (19-29°C) compared to trial 1 due to excess aeration of the drum leads to loss of heat. During trial 3, the temperature at inlet and middle zones varied between 55-68°C and 51-66°C respectively which indicate long thermophilic phase. The temperature at outlet zone varied from 32-44°C while ambient temperature is 20-32°C. In trial 4, inlet and middle zones temperature were observed 63-73°C and 57-70°C respectively. Meanwhile, high temperature (32-44°C) was observed at outlet zone compared to trial 1, 2 and 3 indicated that a longer composting period will required for further degradation. The observed temperature profiles at inlet and middle zones were similar during all the four trials indicating (1) no loss of temperature due to excess aeration, (2) no extra temperature evolution by addition of inocula and (3) high outlet temperature by mixing of vegetable waste.

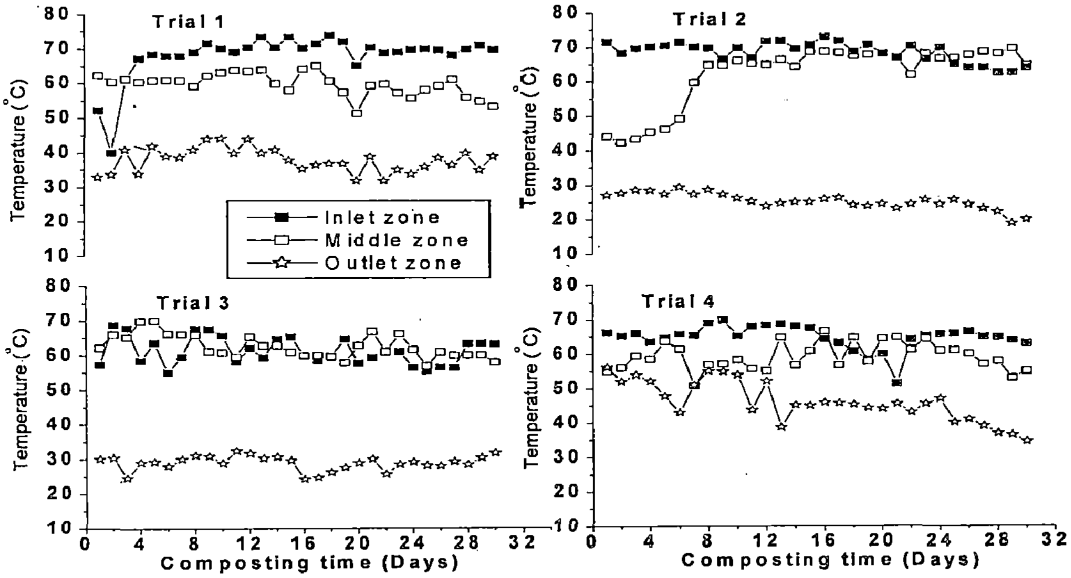


Fig.3.1. Temperature profile during full-scale continuous rotary drum composting over composting period

- ***Moisture content***

Moisture loss can be defined as an index of decomposition rate during the composting process, since heat generation accompanies decomposition and vaporization or moisture loss (Liao *et al.*, 1996). However, the composting material should have bare minimum moisture content for the survival of microorganisms. The optimum initial moisture content should vary between 50-60% (CPHEEO, 2000). In trial 1, the moisture content was reduced to 49-58% from 53-63% indicating only 8% reduction through the drum composting (Fig. 3.2). Because of lower reduction in moisture content from inet to outet zone might be due to inadequate ventilation provided to remove the produced water vapor. The moisture content dropped in trial 2 from 53-66% to 38-45%; a lower final moisture content was observed indicating the lower microbial activities at the end (Gomez *et al.*, 2006) which may be caused by high amount of removal of water vapor during two times turning. In the middle zone, moisture was same as the inlet zone suggesting much of the biological activity was taking place in the first half of the drum. In trial 3, the increase of the moisture in the middle zone was due the amount of ventilation was not enough to remove the water vapor, resulting an increase in moisture content of the compost. In inlet zone, high moisture content (60-76%) was observed during trial 4 compared to trials 1, 2 and 3 due to the presence of vegetable waste in feedstocks. Correspondingly, higher moisture content (47-58%) was monitored at outlet zone compost upto 15 days. It reduced to (41-44%) due to optimization of composting process in later phase of composting period.

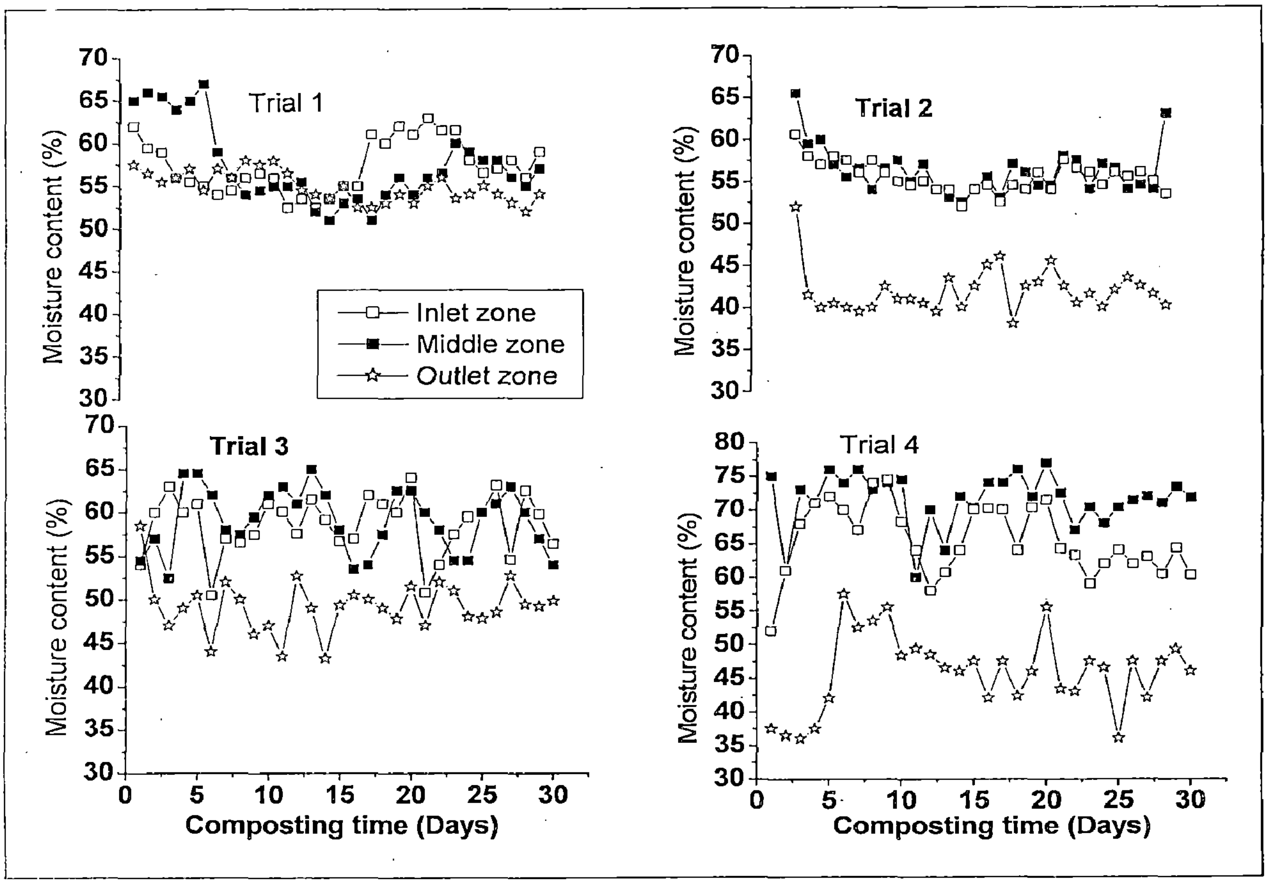


Fig.3.2. Moisture content during full-scale continuous rotary drum composting over composting period

- ***pH and electrical conductivity (EC)***

Table 3.1 shows the pH profile of the inlet zone in trial 1 and 2 ranged from 6.43±0.2-7.57±0.1. A similar pH trends was observed in outlet zone ranged from 7.71±0.1-8.5±0.2 with a gradual increase along the length of the drum. An increase of pH can be attributed to the increase of biological activity along the length of the drum. Also, increase in the pH during composting resulted in increase in volume of ammonia released due to protein degradation (Liao et al., 1996). In the 3rd and 4th trials, the initial pH was low (5.15±0.2-6.9±0.1) compared to trial 1 and 2, might be due to production of acids with the addition of inocula and vegetable waste. Acid derived from the deaminization of amino acids as well as those resulting from the hydrolysis of fatty materials and from carbohydrate fermentation (Liao et al., 1996). The trend of pH at middle zone and outlet zone of the drum was similar as in inlet zone.

A gradual decrease in EC was also observed in all the trials with increase in drum composting time (table 3.1). In trial 1 and 2, EC decreased from 1.64±0.1-2.41±0.2 mS/cm at inlet zone to 1.05±0.01-1.63±0.05 mS/cm at outlet zone, due to the release of ammonium ions throughout the composting process and precipitation of mineral salts as composting progress (Huang et al. 2004). It indicated that two turn per day has no effect on EC of the drum composting. In trial 3, EC profile follow the same trend as in inlet and middle zones, but at outlet, value was much lower indicated higher release of ammonium ions throughout the composting process in the first half of drum due to the volatilization of ammonia and the precipitation of mineral salts at latter stage. High value of EC was observed at inlet zone (4.62±0.08-6.32±0.06 mS/cm) during trial 4 may be due to mixing of vegetable waste, consequently higher EC at outlet zone (2.67±0.05-3.47±0.12 mS/cm) compared to trial 1 and 2.

- ***Ash content***

The ash content increased with composting time, owing to the loss of organic matter through microbial degradation. In trial 1 (table 3.1), inlet zone average value ranged about

5.42% and the outlet zone was 11.55%. Thus, overall increase was 17.5% in ash content indicating intensive decomposition. In trial 2, inlet zone the average ash content ranged 13.33% and in outlet zone range 13.02%. A total of 18% increase was observed in the ash content values. Therefore, we concluded that turning frequency has no effect on ash increase. In trial 3, the average inlet zone ash content was 7.89% and the corresponding outlet zone range 12.66%. In summary, no effect of inocula was observed. The ash content of the system in trial 4, increased from initial value of 10.11% to 14.87% at the outlet zone, with overall increase of 8-15%. The higher increase was observed in this trial, indicating compost of better quality relative to the other trials.

Table.3.1.The given values are reported for the pH, EC, NH_4-N, NO_3-N and Ash Content of the composting material of all trials.

Parameters	**Trial1**			**Trial 2**			**Trial 3**			**Trial 4**		
pH	**Inlet Zone**	**Middle Zone**	**Outlet Zone**	**Inlet Zone**	**Middle Zone**	**Outlet Zone**	**Inlet Zone**	**Middle Zone**	**Outlet Zone**	**Inlet Zone**	**Middle Zone**	**Outlet Zone**
Minimum	6.45	6.89	7.76	6.43	6.89	7.69	5.15	5.88	7.51	5.3	7.3	5.9
Maximum	7.34	7.67	8.35	7.57	7.7	8.46	7.32	8.24	8.1	7.4	8.3	7.9
Average	6.87	7.28	8.07	6.88	7.31	8.1	5.9	6.78	7.79	6.21	7.74	6.54
EC(mS/cm)												
Minimum	1.079	1.244	1.38	1.05	1.244	1.43	0.64	1.07	1.147	4.532	3.154	2.134
Maximum	1.694	2.21	2.53	1.488	2.05	2.56	7.48	6.5	2.26	7.234	5.32	4.343
Average	1.34	1.77	2.07	1.26	1.55	2	4	3.27	1.5	5.55	4.28	3.27
NH_4-N (%)												
Minimum	0.48	1.34	1.24	2.24	2.03	1.34	1.54	1.45	0.89	1.9	2.95	2.3
Maximum	2.47	2.69	2.12	2.62	3.34	1.98	2.33	2.65	1.9	3.4	3.1	2.6
Average	2.58	2.24	1.57	2.13	2.74	1.67	2.41	2.17	1.35	7.68	4.81	2.63
NO_3-N (%)												
Minimum	0.50	0.70	1.03	0.63	0.73	0.8	1.00	1.23	1.40	0.92	1.50	2.13
Maximum	1.12	1.14	2.12	1.43	1.52	1.23	1.20	1.32	1.54	1.32	1.57	2.24
Average	1.10	1.20	1.80	1.32	1.42	1.21	1.16	1.21	1.50	1.24	1.54	2.22
Ash Content (%)												
Minimum	13.51	7.08	16.63	8.11	16.66	14.45	6.83	17.366	14.45	15.2	13.66	12.5
Maximum	17.46	15.5	24.8	16.85	25.96	16.66	16.833	25.5	23	25	20.3	16.66
Average	15.425	11.07	21.55	13.33	21.16	15.02	12.89	21.27	22.66	20.11	18.57	14.875

- ***Solvita Maturity Index***

Compost maturity is one of the parameters for determining the grade of compost as it determines the product performance. Based on CO_2 evolution, Solvita® maturity index was calculated (Brinton, 2001) on a scale of 1-8 depicting least to highest maturity, with 5 as minimum limit of maturity. The Solvita maturity index based on CO_2 evolution in trial 1 to 4 was increased from 5.3-6.6 (avg. 6.1), 5.3-6.4 (avg. 5.9), 5.8-6.8 (avg. 6.2) and 6.3-7.3 (avg. 6.7), respectively (Fig. 3.3). Overall trends in stability observed with the respirometry procedure agreed inversely with those based on the Solvita® maturity index. Solvita® results proved the composts from all trends comes under the well mature condition throughout the study period. The results of index (>5) obtained from the present study proved that the efficacy of the drum under all four arrangement. However trial 4 produced most stable and matured product being compatibility of herbal and vegetable waste.

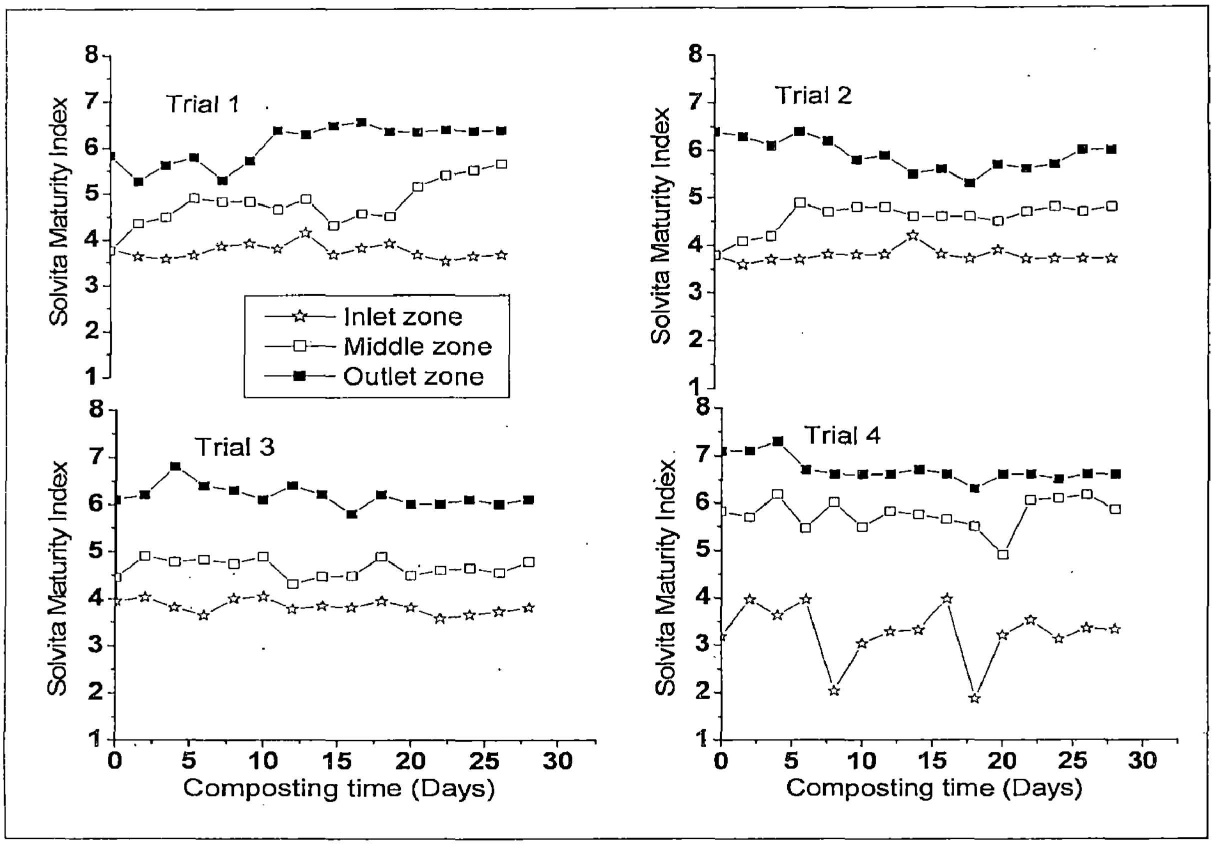


Fig.3.3. Solvita maturity index during full-scale continuous rotary drum composting over composting ding period

- ***Total Organic Carbon Decomposition(TOC)***

Organic matters become fully mineralized after composting, mostly due to the degradation of easily degradable compounds such as proteins, cellulose and hemi-cellulose which are utilized by microorganisms as C and N sources. While degrading organic compounds, microbes utilize 60-70% of the carbon as CO_2 and incorporate (immobilize) only 30-40% of the carbon into their body as cellular components. In aerobic condition, there is a great diversity of decomposers, consisting of fungi, actinomycetes and a wide range of bacteria, which degrade the readily available organic components or transform them into stable components (Garcia *et al.*, 1992).

In trial 1, the initial TOC ranged from 44-46% and the final (outlet zone) ranged 33-37% with the overall percent decrease 15-28% shown in Fig.3.4.

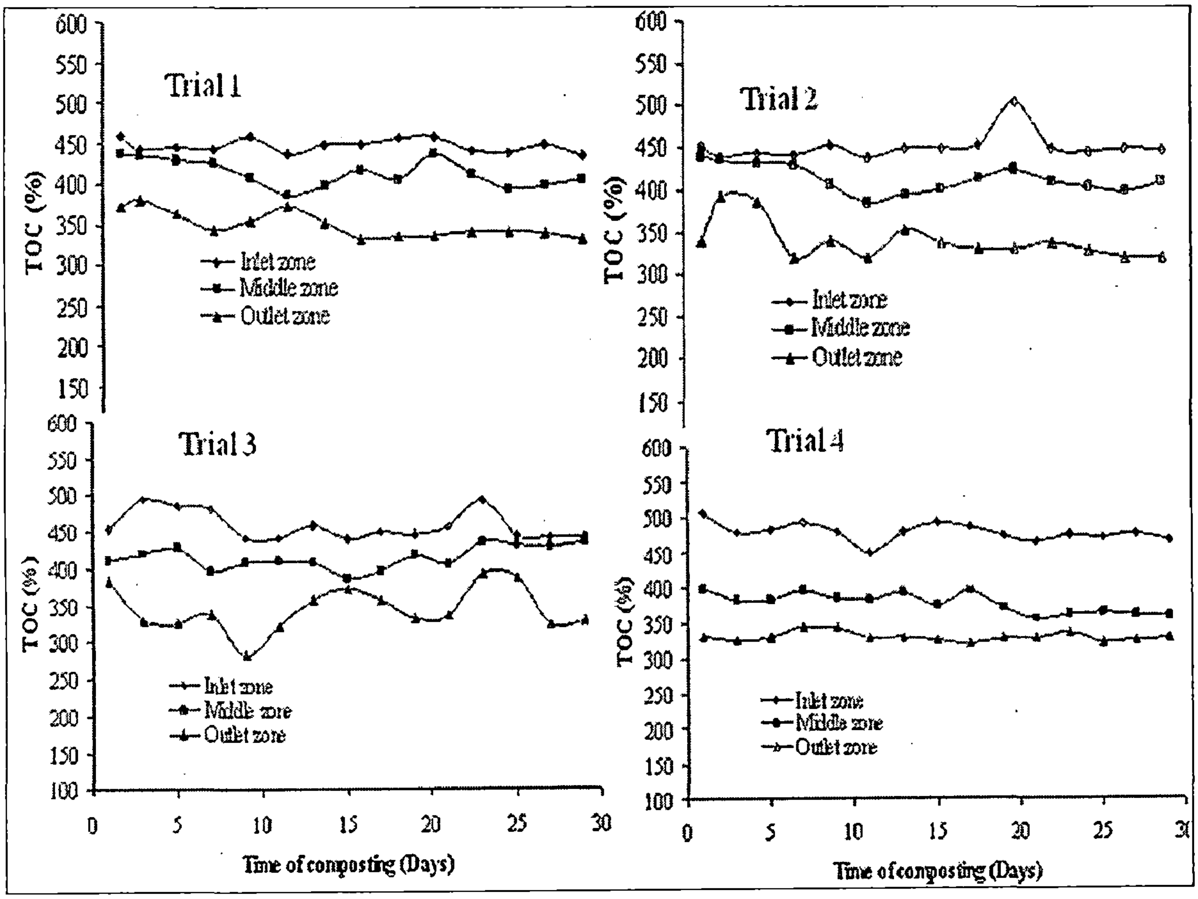


Fig.3.4 Total Organic Carbon of all trials of the composting material over composting period

In trial 2, the TOC in inlet zone was found about 45% and the outlet 32-38%, decreases from inlet to outlet upto 15%. Hence, twice rotation per day has no effect on organic matter removal of the system compared to one rotation per day.

In trial 3, TOC of the inlet zone varies from 44-49% and the outlet zone from 33-38%. The overall percentage reduction from inlet to outlet was observed around 16%. The slight increase in percentage of TOC reduction might be due to the slightly increased rate of multiplication of microbes due to the added inocula.

In trial 4, the TOC in inlet zone ranged between 45-50% and further reduces upto 30-33% at outlet zone, with an overall percent reduction of around 22%. The higher organic matter degradation is due to a dense colonization of microbes as herbal waste and act as a bulking agent for the vegetable wastes.

- ***Total nitrogen (TN) and total phosphorus (TP)***

Total nitrogen contents increased in drum composting due to the net loss of dry mass in terms of CO_2 as well as the water loss by evaporation due to heat evolution during oxidization of organic matter (Haung *et al.*, 2006). Table 3.2 shows the TN at inlet zone was 2.36-2.85% in trial 1, which increased upto 3.03-3.42%. In trial 2, TN varied from 2.67-3.12% at inlet zone to 3.12-3.69% at outlet zone which indicated assenting effect of additional rotation. Similarly, an overall increase of 10-31% in trial 3 and 4 showed no significant effects of inocula addition and vegetable waste addition upon the total nitrogen enrichment. Lower TN concentration profile was observed at inlet and outlet zone during trial 3 may be due to more consumption of nitrogen owing to inocula addition. The notable increase (40-75%) at the outlet zone was observed in phosphorus concentration during trial 1 (table 3.3). Due to more decrease in volume to mass ratio. Compost with 0.1-0.2% phosphorus concentration is primary stabilized after drum composting in trial 1. Similarly, higher phosphorus concentration was observed during trial 2 (0.12-0.14%) compared to trial 3 (0.15-0.24%) and trial 4 (0.45-0.46%) indicated the effects of inocula and vegetable waste addition in herbal waste composting.

Table. 3.2. Variation in Total Nitrogen (TN%) during drum composting

Days	Trial 1						Trial 2						Trial 3						Trial 4					
	Inlet	*SD*	*Middle*	*SD*	*Outlet*	*SD*	*Inlet*	*SD*	*Middle*	*SD*	*Outlet*	*SD*	*Inlet*	*SD*	*Middle*	*SD*	*Outlet*	*SD*	*Inlet*	*SD*	*Middle*	*SD*	*Outlet*	*SD*
1	2.68	0.20	2.81	0.21	3.03	0.23	3.09	0.23	2.78	0.21	3.23	0.44	2.31	0.32	2.25	0.31	2.78	0.38	2.5	0.34	2.76	0.38	3.5	0.27
2	2.72	0.08	2.79	0.28	3.22	0.07	2.84	0.06	2.78	0.06	3.5	0.07	2.27	0.05	2.48	0.05	2.87	0.06	2.69	0.05	2.83	0.18	3.16	0.2
4	2.62	0.17	2.76	0.37	3.21	0.43	3.12	0.42	2.86	0.38	3.69	0.5	2.22	0.3	2.6	0.35	3.1	0.42	2.79	0.38	3	0.4	3.08	0.41
6	2.46	0.15	2.86	0.23	3.42	0.07	2.98	0.06	2.67	0.05	3.61	0.23	2.33	0.15	2.33	0.15	2.61	0.16	2.44	0.15	2.65	0.05	3.04	0.05
8	2.36	0.12	2.63	0.25	3.35	0.32	3.02	0.29	2.68	0.26	3.69	0.36	2.27	0.22	2.42	0.23	2.59	0.25	2.39	0.23	2.51	0.24	2.93	0.28
10	2.49	0.07	2.84	0.28	3.4	0.33	3.1	0.3	3.22	0.32	3.56	0.1	2.03	0.06	2.3	0.06	2.94	0.08	2.42	0.07	2.65	0.29	2.91	0.48
12	2.58	0.20	2.94	0.21	3.12	0.26	2.81	0.23	3.08	0.26	3.45	0.28	2.25	0.18	2.45	0.2	2.75	0.22	2.4	0.2	2.52	0.2	3.02	0.24
14	2.65	0.22	3.01	0.29	3.1	0.23	3.05	0.22	2.67	0.19	3.27	0.24	2.16	0.16	2.62	0.19	2.79	0.2	2.49	0.18	2.65	0.18	3.38	0.26
16	2.65	0.18	2.73	0.18	3.12	0.22	2.82	0.19	2.89	0.2	3.29	0.22	2.32	0.16	2.53	0.17	2.94	0.2	2.81	0.19	2.69	0.18	3.52	0.2
18	2.45	0.15	2.96	0.16	3.09	0.08	2.98	0.08	3	0.08	3.58	0.1	2.21	0.06	2.7	0.07	3.1	0.08	2.48	0.07	2.67	0.18	3.49	0.25
20	2.56	0.20	2.95	0.24	3.21	0.26	2.78	0.22	3.12	0.25	3.45	0.21	2.22	0.13	2.53	0.15	2.82	0.17	2.65	0.16	2.7	0.24	3.5	0.33
22	2.85	0.25	2.98	0.36	3.21	0.34	2.85	0.3	3.13	0.33	3.12	0.54	2.25	0.39	2.52	0.44	3.09	0.54	2.87	0.5	2.85	0.29	3.47	0.35
24	2.67	0.05	3.04	0.64	3.19	0.84	2.69	0.71	3.09	0.81	3.34	0.88	2.16	0.57	2.34	0.62	2.76	0.73	2.68	0.71	2.67	0.7	3.76	0.82
26	2.71	0.07	3.03	0.24	3.2	0.09	2.67	0.07	2.89	0.08	3.16	0.05	2.23	0.04	2.67	0.05	2.98	0.05	2.54	0.04	2.74	0.22	3.69	0.29
28	2.68	0.24	3.08	0.31	3.22	0.32	2.72	0.27	2.94	0.29	3.24	0.33	2.26	0.23	2.68	0.27	3.02	0.31	2.61	0.27	2.69	0.25	3.71	0.23
30	2.67	0.19	3.07	0.21	3.21	0.26	2.69	0.22	2.96	0.24	3.29	0.34	2.21	0.23	2.64	0.27	3.08	0.31	2.59	0.26	2.74	0.22	3.58	0.37

SD= Standard deviation

Table. 3.3. Variation in Total phosphorus (TP%) during drum composting

Days	Trial 1						Trial 2						Trial 3						Trial 4					
	Inlet	***SD***	***Middle***	***SD***	***Outlet***	***SD***	***Inlet***	***SD***	***Middle***	***SD***	***Outlet***	***SD***	***Inlet***	***SD***	***Middle***	***SD***	***Outlet***	***SD***	***Inlet***	***SD***	***Middle***		***Outlet***	***SD***
1	0.054	0.01	0.0900	0.02	0.0720	0.02	0.0560	0.01	0.0900	0.02	0.2300	0.06	0.1042	0.03	0.1166	0.03	0.0910	0.02	0.1640	0.04	0.1000	0.03	0.2600	0.07
2	0.069	0.01	0.0890	0.01	0.1080	0.02	0.0690	0.01	0.0870	0.01	0.2600	0.04	0.1224	0.02	0.1224	0.02	0.1376	0.02	0.2080	0.03	0.1390	0.02	0.2400	0.03
4	0.072	0.03	0.1200	0.06	0.1780	0.08	0.0760	0.04	0.0670	0.03	0.2800	0.13	0.0720	0.01	0.1200	0.02	0.1780	0.03	0.1670	0.03	0.1200	0.02	0.2030	0.03
6	0.109	0.02	0.1340	0.02	0.1800	0.03	0.1090	0.02	0.0760	0.01	0.2300	0.04	0.1090	0.02	0.1340	0.02	0.1800	0.03	0.1450	0.03	0.1340	0.02	0.2400	0.04
8	0.067	0.01	0.1500	0.02	0.1590	0.02	0.0990	0.01	0.1400	0.02	0.2500	0.04	0.1670	0.02	0.1500	0.02	0.1590	0.02	0.0670	0.01	0.1500	0.02	0.1900	0.03
10	0.076	0.04	0.1000	0.05	0.1690	0.09	0.0760	0.04	0.1000	0.05	0.2800	0.15	0.0862	0.04	0.1640	0.09	0.1800	0.09	0.0760	0.04	0.1600	0.08	0.1690	0.09
12	0.080	0.01	0.1190	0.01	0.2010	0.02	0.0890	0.01	0.1500	0.01	0.2600	0.02	0.1600	0.01	0.2080	0.02	0.2300	0.02	0.0800	0.01	0.1190	0.01	0.2010	0.02
14	0.140	0.03	0.1440	0.03	0.2300	0.04	0.1400	0.03	0.1440	0.03	0.2400	0.04	0.1300	0.02	0.1670	0.03	0.2400	0.04	0.1400	0.03	0.1650	0.03	0.2300	0.04
16	0.128	0.01	0.1580	0.01	0.2310	0.02	0.1600	0.01	0.1580	0.01	0.2030	0.01	0.1110	0.01	0.1450	0.01	0.1900	0.01	0.1280	0.01	0.1580	0.01	0.2090	0.01
18	0.098	0.03	0.1000	0.03	0.2600	0.07	0.1300	0.02	0.1670	0.03	0.2400	0.04	0.1600	0.03	0.1780	0.03	0.2090	0.03	0.0980	0.02	0.2300	0.04	0.2450	0.04
20	0.111	0.01	0.1420	0.01	0.2600	0.02	0.1110	0.01	0.1450	0.01	0.1900	0.02	0.0910	0.01	0.1160	0.01	0.2450	0.02	0.1110	0.01	0.1420	0.01	0.2560	0.02
22	0.091	0.01	0.1160	0.01	0.2450	0.02	0.1600	0.01	0.1780	0.02	0.2090	0.02	0.1200	0.01	0.1560	0.01	0.2560	0.02	0.0910	0.01	0.1160	0.01	0.2450	0.02
24	0.120	0.05	0.1560	0.06	0.2560	0.11	0.1500	0.03	0.1560	0.03	0.2100	0.04	0.1382	0.03	0.1900	0.04	0.2010	0.04	0.1200	0.03	0.1560	0.03	0.2560	0.05
26	0.135	0.03	0.1420	0.03	0.2640	0.05	0.1350	0.01	0.1670	0.01	0.2600	0.02	0.1530	0.01	0.1800	0.02	0.2540	0.02	0.1350	0.01	0.1420	0.01	0.3440	0.03
28	0.142	0.01	0.1430	0.01	0.2660	0.02	0.1400	0.01	0.1780	0.02	0.2500	0.02	0.1480	0.04	0.1480	0.04	0.2200	0.06	0.1430	0.04	0.1560	0.04	0.3760	0.10
30	0.153	0.01	0.1430	0.01	0.2680	0.02	0.1700	0.01	0.1790	0.01	0.2700	0.02	0.1480	0.01	0.1490	0.01	0.2400	0.02	0.1550	0.01	0.1650	0.01	0.4500	0.03

SD= Standard deviation

- ***C/N ratio***

C/N ratios lower than 12 indicate a good degree of compost maturity. In trial 1, the initial C/N ratio was 20-21 while at the outlet zone C/N ratio was 10-13 as shown in Fig. 3.5. In trial 2, the inlet zone values 20-21 and the outlet zone 10-13 remained the same. Thus, it was observed that the two turning per day has no effect on the performance of the drum during the composting of herbal waste. In trial 3, the initial outlet C/N ratio slightly increased 20-22 and 10-13.5 respectively with total percentage decrease of 40-50%. This may be explained like once we maintain favorable environment, there is no need to supplement the degradation process with the commercial microbial inocula. In trial 4, reduction in the values of C/N ratio was observed with inlet zone ranging from 20-23 to outlet zone value of about 9-13, an overall percentage reduction in the system was found to be 43-55%.

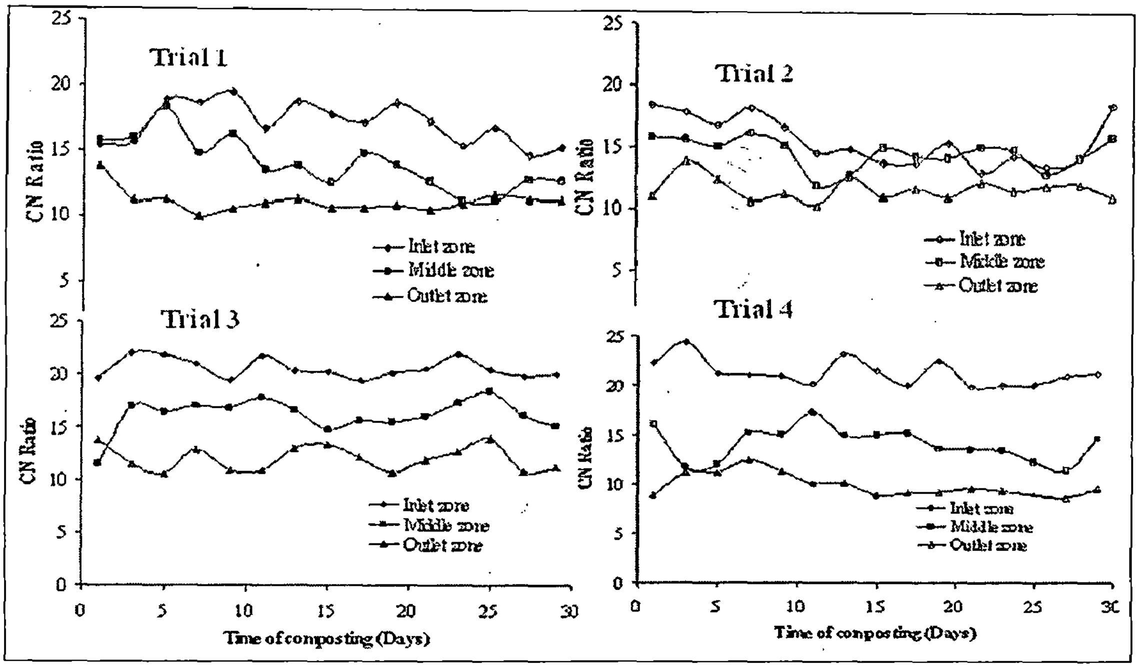


Fig.3.5 C/N ratio in all trials of the composting material over composting period

3.2.2. Spectroscopic parameters

- ***FT-IR Study***

FT-IR spectra of waste material and compost have shown the changes in functional groups, peaks intensity and positions in four different trials and three different stages of composting as inlet, middle and outlet zones as shown in Fig.3.6. and table 3.4 & 3.5. During trial 1, aliphatic CH_3 and CH_2 stretching peaks at 2925 and 2845 cm^{-1} was appeared same in inlet, middle and outlet zones. However, there was a large difference in peak intensity in outlet zone at 1646, 1434, 1322 and 1042 cm^{-1} compared to inlet and middle zone due to aromatic C=C, C=O, amides, carboxylates and Si–O asymmetric stretch. In addition, peaks at 779, 709 and 534 cm^{-1} were also found in outlet zone due to aromatic C=C, halo-compounds and metal-halogen bonds similar to middle and inlet zones at 789 and 586 cm^{-1}. Composting in trial 2, aliphatic CH_3 and CH_2 stretching peaks at 2926 and 2859 cm^{-1} were appeared with large difference in outlet zone compared to inlet and middle zones due to less degradation of aliphatic compounds. However, there is large difference in peak intensity in outlet zone at 1644, 1432, 1319, and 1069 cm^{-1} due to aromatic C=C, C=O, amides, carboxylates and Si–O asymmetric stretch. In addition, peaks at 780 and 583 cm^{-1} were found in outlet zone due to aromatic C=C, halo-compounds and metal-halogen bonds similar to middle and inlet zones at 780 and 583 cm^{-1}. In trial 3, peaks at 3852 and 3803 cm^{-1} appeared in middle and outlet zones due to NH-CO group of proteins and added inocula. Aliphatic CH_3 and CH_2 stretching peaks at 2920 and 2851 cm^{-1} appeared almost same in inlet, middle and outlet zones. However, there is a great difference in peak intensity in middle and outlet zones 1643, 1423, 1318, and 1069 cm^{-1} compared to inlet zone due to aromatic C=C, C=O, amides, carboxylates and Si–O asymmetric stretching. In addition, peaks at 767, and 579 cm^{-1} were found in outlet zone due to aromatic C=C, halo-compounds and metal-halogen bonds, similar to middle and inlet zones at 767 and 579 cm^{-1}. In trial-4, aliphatic CH_3 and CH_2 stretching peaks at 2926 and 2853 cm^{-1} were appeared almost same in inlet, middle and outlet zones. However, there is large difference in peak intensity in outlet zone at 1642, 1420, 1326, and 1045 cm^{-1} compared to inlet and middle zones due to aromatic C=C, C=O, amides, carboxylates, Si–

O asymmetric stretching. In addition, peaks at 786 and 578 cm^{-1} were also found in outlet zone due to aromatic C=C, halo-compounds and metal-halogen bonds, similar to middle and inlet zones at 786 and 578 cm^{-1}. It is concluded that in trial-1 and trial-4 gave quality compost in terms of stability and maturity indicated by the presence of more intense peaks at the aromatic region and less intense peaks were found in aliphatic region compare to trial 2 and trial 3.

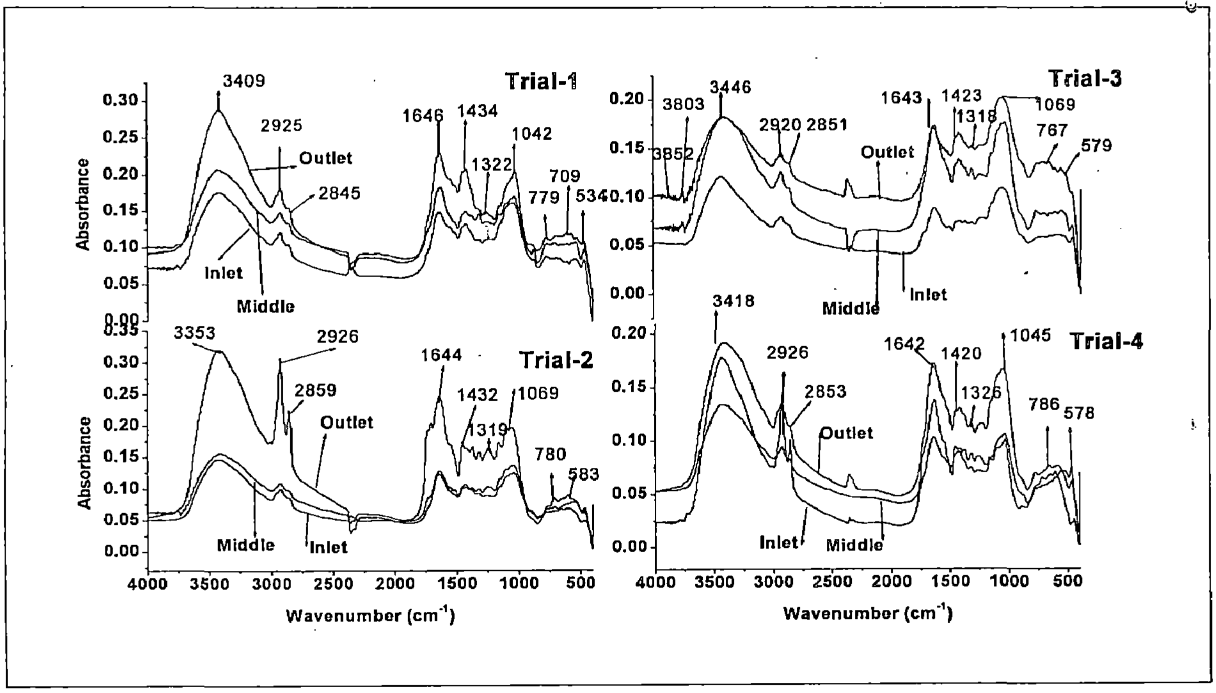


Fig 3.6. FT-IR spectra of four different trials and three different zones of rotary drum composter

Table 3.4. Observed peaks (cm-1) during rotary drum composting in trial 1,2,3 and 4

TRIALS	**ZONES**	**Observed Peaks (cm^{-1})**			
		Aliphatic peaks CH_3 and CH_2 groups	**Aromatic peaks C=C, C=O, amides, carboxylates, and Si–O**	**Aromatic C=C, halo-compounds and metal-halogen bonds**	**Proteins NH-CO groups**
1	Inlet Zone	2925 and 2845		789 and 586	
	Middle Zone	2925 and 2845		789 and 586	
	Outlet Zone	2925 and 2845	1646, 1434, 1322, and 1042	779, 709, 534	
2	Inlet Zone	2926 and 2859		780 and 583	
	Middle Zone	2926 and 2859		780 and 583	
	Outlet Zone	2926 and 2859	1644, 1432, 1319, and 1069	780 and 583	
3	Inlet Zone	2920 and 2851		767 and 579	
	Middle Zone	2920 and 2851		767 and 579	3852, 3803
	Outlet Zone	2920 and 2851	1643, 1423, 1318, and 1069	767, and 579	3852, 3803
4	Inlet Zone	2926 and 2853		786 and 578	
	Middle Zone	2926 and 2853		786 and 578	
	Outlet Zone	2926 and 2853	1642, 1420, 1326, and 1045	786, and 578	

Table.3.5. Wavenumber (cm^{-1}) changes from inlet to outlet zone during composting in Trial 1, 2, 3, and 4

Trial 1 Wavenumber (cm^{-1})			**Trial 2 Wavenumber (cm^{-1})**			**Trial 3 Wavenumber (cm^{-1})**			**Trial 4 Wavenumber (cm^{-1})**		
Inlet zone	Middle zone	Outlet zone	Inlet zone	Middle zone	Outlet zone	Inlet zone	Middle zone	Outlet zone	Inlet zone	Middle zone	Outlet zone
-	-	-	-	-	-	-	-	3852	-	-	-
-	-	-	-	-	-	-	-	3746	3754	-	-
-	-	-	-	-	-	-	-	3680		-	-
3422	3420	3409	3428	3426	3395	3410	3415	3446	3432	3430	3418
2926	2925	2925	2924	2924	2926	2922	2294	2920	2924	2925	2926
2847	2851	2847	2843	2851	2859	2852	2856	2851	2847	2853	2853
1630	1631	1646	1635	1633	1644	1633	1634	1643	1635	1640	1642
-	-	-	-	-	-	1572	1543	1551	-	-	-
-	-	-	-	-	-	1540	-	1523	1515	1512	1507
1424	1426	1434	1422	1419	1432	1466	1454	1453	-	1459	1463
-	-	-	-	-	-	1418	-	1420	1425	1422	1420
-	-	-	-	-	-	1376	1370	1388	1384	1379	1379
1320	1319	1233	1315	1323	1319	1315	1322	1318	1331	1326	1326
1266	1249	1257	1262	1262	1262	1249	1237	1237	1258	1247	1237
1036	1040	1042	1034	1038	1069	1078	1094	1069	1069	1044	1045
780	779	779	780	776	780	718	779	767	775	781	786
690	660	709	641	690	743	-	717	-	-	-	-
615	-	-	612	608	683	661	652	668	665	671	659
571	563	-	554	543	554	576	-	-	-	603	-
534	513	-	530	-	-	-	525	550	-	-	578
469	-	-	-	472	-	-	-	-	471	476	468

3.2.3. Conclusions

Composting of herbal waste with cattle manure in 3:1 (w/w) ratio can be successfully conducted in a rotary drum in 7-8 days detention period. Favorable composting condition was obtained at once a day rotation, during which the inlet zone temperature increased to 70°C leading to higher degradation. However, increase in rotation to twice a day couldn't improve the quality. Conversely, it was resulted in lowering of thermophilic temperature from 70°C to 60°C, slow degradation and unstable compost compared to tial 1. Further, addition of microbial inocula gave no improvement in the quality of the compost. Co-composting of herbal and vegetable wastes gave better quality compost in terms of temperature, moisture, nitrogen, Solvita maturity index in aerobic environment due to high moisture content of vegetable waste and bulking agent of herbal waste because the two materials complement each other, as vegetable waste have higher moisture and herbal waste functions as a bulking agent resulting aerobic environment by increase in molecular oxygen concentration. In addition, FT-IR also characterized that trial-1 (one rotation) and trial 4 (Co-composting herbal & vegetable waste) gave quality compost in terms of stability and maturity compost indicated by the presence of more intensity peaks at aromatic region and less intense peaks in aliphatic region.

Part B: Fate of aggregate organic matter transformation during full-scale rotary drum composting of vegetable waste using Fourier transform-infrared (FT-IR) and thermal studies in three different seasons

This chapter (Part B) deals with the study of the chemical transformation (by the functional groups characterization/variation in the FT-IR) and thermal stability (by thermal methods TG, DTG & DTA) of the compost in inlet, middle and outlet zone products in full scale continuous rotary drum composter during composting of vegetable market waste, amended with cattle manure and saw dust in different seasons like winter, spring and summer seasons.

3.3 INTRODUCTION

The transformation and humification process might differ depending upon raw materials used in composting (Huang *et al*; 2006). The changes in compost stability may be predicted with C/N ratio in the solid phase, soluble organic carbon content in water extract (Inbar *et al;* 1993), plant growth bioassay, NMR and IR spectroscopy (Chen and Inbar 1993). Several studies have investigated organic matter transformation during composting of municipal solid waste, municipal sewage sludge and separated cattle manure using chemical, spectroscopic, thermogravimetry and microbiological methods (Chefetz *et al*; 1996; Chen and Inbar 1993; Iannotti *et al*; 1994; Hsu and Lo 1999; Adani *et al*; 2001; Gea *et al;* 2004; Jouraiphy *et al*; 2005; Huang *et al*; 2006). The understanding of organic matter transformation throughout the composting process and their evaluation as stable and mature are essential for successful utilization of compost. There are many methods for evaluating the maturity of compost that include: (i) physical parameters-temperature, odor emission, color change, particle size reduction, water and air retention capacity (Garcia *et al*; 1992); (ii) chemical parameters- C/N ratio reduction in solid and water phases, cation-exchange capacity variation, change in elemental concentrations, change in organic matter level, water-soluble organic matter and humification indexes (Hsu and Lo 1999; Jimenez and Garcia 1992); (iii) spectroscopic analysis: NMR, FT-IR and fluorescence (Chefetz *et al;* 1996; Chen and Inbar 1993); (iv) biochemical parameters- total and specific enzyme activity (Diaz-Burgos *et al*; 1994; Garcia *et al;* 1993); (v) microbiological parameters-oxygen and CO_2 respirometry (Iannotti *et al*; 1994) and (vi) bio-assay responsesgermination index and plant growth bio-assays conducted in saturated extracts of compost or in compost filled pots (Chefetz *et al*; 1996; Inbar *et al;* 1993). In recent years, spectroscopic techniques such as FT-IR, fluorescence spectroscopy, ESR and NMR have been used as characterization tools for study in the transformation of organic matter and the maturity evaluation of the compost (Chen 2003; Inbar *et al;* 1993; Hsu and Lo 1999). The above mentioned investigations generally dealt with the conventional windrows and static piles types of composting for various kinds of waste. However, the organic matter transformation in high rate in-vessel composting such as rotary drum composter for the mixed organic vegetable waste and municipal solid waste composting is rather limited. No literature found like seasonal variation in rotary drum composting, some spectroscopic and thermal study was carried out on conventional composting like windrow composting. It is reasonable to expect that the transformation process might differ depending on the raw material(s) used for composting. Therefore, our aim of this study is to know the chemical transformation (functional groups) and thermal stability of initial, middle and final region products during full-scale rotary drum composting of vegetable market waste, amended with cattle manure and saw dust in different seasons like winter, spring and summer by FT-IR and thermal methods (TG, DTG & DTA).

3.3.1 EXPERIMENTAL RESULTS AND DISCUSSION

3.3.1.1. Physico-chemical parameters

- ***Temperature***

The change in temperature during composting in the rotary drum composter is presented (Fig. 3.7). Microbial growth started within hour of rotary drum operation, due to temperature rise. In winter season, the observation was recorded since the beginning of the November month where temperature in inlet zone increased initial 20 days followed by decrease from 70 ^{0}C to 58 ^{0}C after 50 days along with decrease in ambient temperature. Further, the temperature increased upto 70°C in summer season since April after 100 days. The maximum temperature in the inlet zone of rotary drum varied between 60-70°C in all three seasons depending upon the ambient temperature (10-40°C). Temperature from 52^{0}C to 60°C is useful to maintain the greatest thermophilic activity in composting systems. In continuously thermophilic composting systems, CO_2 evolution has been found to be submaximal at 64°C and above. The temperature in the middle zone of the drum varied between 50-60°C in all three seasons except initial 20 days in winter season (30-50°C), indicated the lower microbial activities compared to inlet zone. The temperature at the outlet zone was equal to ambient or slightly more (4-10°C) of the drum during all three seasons indicated end of active thermophilic phase.

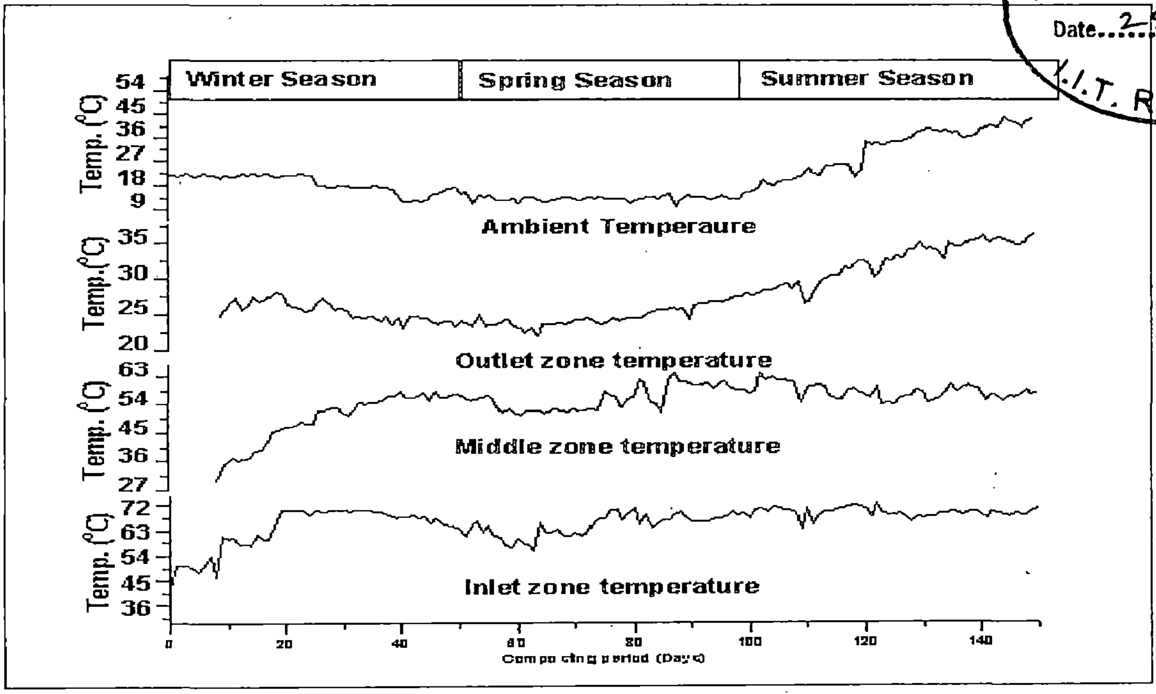


Fig.3.7.Temperature profile during winter, spring and summer season composting

- ***Water content in winter, spring and summer composting***

Moisture loss during active composting can be defined as an index of decomposition rate, since the heat generation accompanies the decomposition and vaporization of moisture. However, the composting material should have certain amount of moisture content in it for the organism to survive. Moisture content in the outlet zone was about 22.01, 29.36 and 19.15 kg respectively in winter, spring and summer seasons as that of the inlet zone (avg. 64.57, 62.37 and 63.48 kg) respectively as shown in Fig. 3.8. This indicated that during the controlled composting process in the drum the air supply was low in spring compared to other seasons. The aeration time period of air blower was increased up to 24 hour during the whole study in spring and winter seasons. After through mixing by rotating the drum, the difference in the moisture content leveled out due to rise in temperature, which indicated that the composting process is still proceeding very actively.

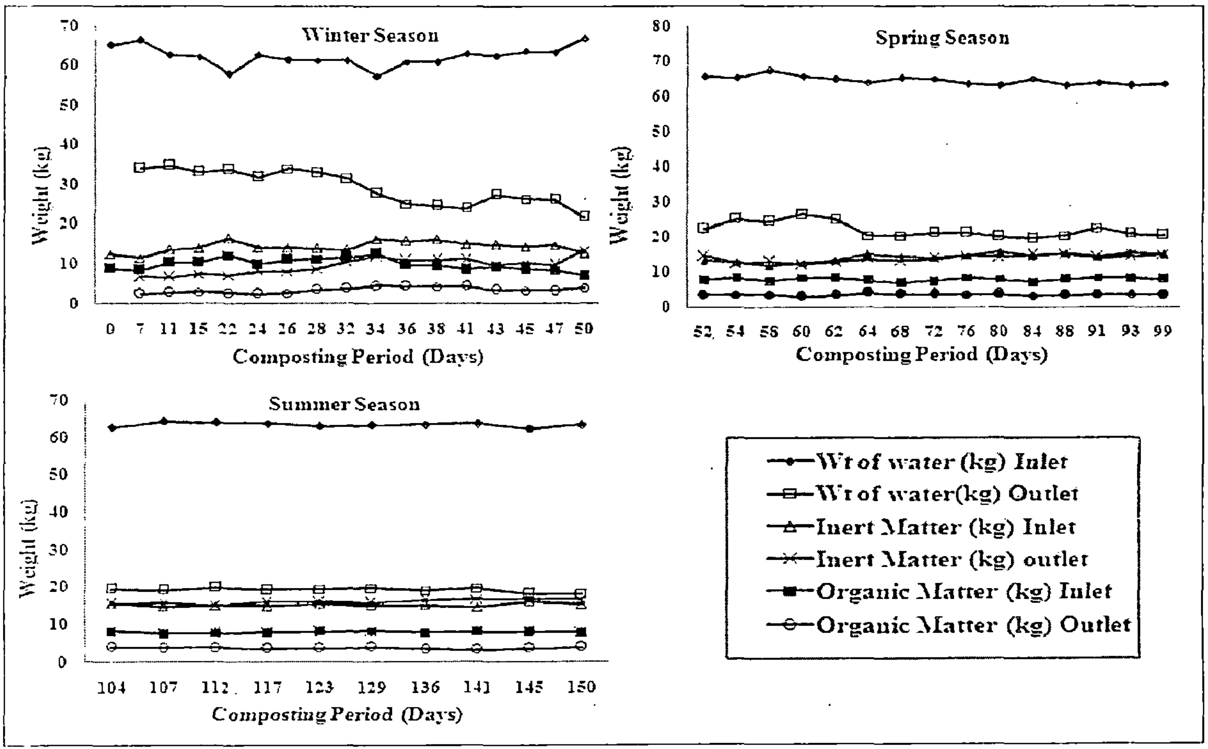


Fig.3.8. Mass balance of water content, organic and inert matters in winter, spring and summer season composting

- ***Organic matter profile in winter, spring and summer composting***

Total organic matter is useful for estimating the age and physical properties of the compost. During the composting process, CO_2 is emitted from the composting mass as a metabolic end product and organic matter content decreased. Changes in the total organic matters (TOMs) content during the drum composting are detailed in Fig. 3.8. Initially, the average amount of organic matter at inlet zone was 7.89, 9.87 and 7.93 kg in winter, spring and summer seasons, which was reduced to 3.56, 3.40 and 3.71 kg respectively. Waste material was retained at inlet after turning serve as an inoculum for the incoming material. It can be observed that the organic carbon content decreased with the drum composting, which reflects a notable mineralization of organic matters.

- ***Inert matter profile in winter, spring and summer composting***

Organic compounds are either decomposed or volatilized at high temperature. The remaining residue is the inert matter. This residue consists of phosphates, chlorides, sulfates, and other halides and cations of sodium, potassium, calcium, magnesium, iron and manganese. During rotary drum composting, the average yield inert matter in inlet zone was 14.17, 14.31 and 15.22 kg (Fig. 3.8). Due to variable vegetable waste in raw material and the outlet ash content 13.87, 9.45 and 15.00 kg respectively in winter, spring and summer seasons. In spring and winter seasons, the inert matter (9.45 & 13.87 kg) reduced more due to some leachate generation and the fraction of inert matter was drained in leachate.

3.3.1.2. Infrared spectroscopy analysis

- ***Infrared spectroscopy study of composting in winter, spring and summer season***

FT-IR spectra of the compost were recorded in three different seasons (winter, spring and summer) and three different stages during composting (inlet, middle and outlet zones). Literature reveals some characteristic changes in the functional groups present in organic and inorganic matters in compost for example, peaks at 3400 cm^{-1} (may be due to alcoholic OH, phenol, carboxylic (COOH) or N-H (amides) groups); peaks at 2930 & 2850 cm^{-1} (due to C-H asymmetric, C-H stretch of -CH aliphatic); peak at 2365 cm^{-1} (due to CO_2); peak at 1630- 1660 cm^{-1} (due to aromatic structure, COO^- & C=O (e.g., amides, ketones and quinines) groups; peak at 1560 cm^{-1} (due to amide II bonds); peaks at 1420–1430 cm^{-1} (due to absorbance of several aliphatic structures, phenolic OH groups, COO^- groups, stretching vibrations of aromatic rings and carbonates); peaks at 1510, 1462, 1454 &1420 cm^{-1} (due to aromatic rings of lignin); peak at 1380 cm^{-1} (due to ammonium carbonate formed by reaction of ammonia and CO_2) and a broad peak at 1030 cm^{-1} assigned to C-O stretch of polysaccharide, Si-O asymmetric stretch of silicate impurities. A band was found at around 1429 cm^{-1} due to the O-H in-plane bend of carboxylic acids, the CO_2 stretch of carboxylates and the aliphatic CH_2 group of alkanes (Smith 1999; Smidt *et al*; 2002; Zaccheo *et al*; 2002; Chen and Inbar, 1993; Hsu and Lo, 1999; Jouraiphy *et al*; 2005; Huang *et al*; 2006; Grube, M., *et al*; 2006). In addition, the absorption peaks at 600-500 cm^{-1} due to the phosphate in the form of orthophosphoric acid is present in compost (Smith *et.al;* 2002) and peaks at 778, 722, 560 and 536 cm^{-1} are due to aromatic ring and halogens (chloro-compounds) and some metal halogen bonds. In our study, we have shown the functional groups variation in FT-IR peaks (position/intensity) in different drum regions and variations in different seasons during three different composting stages.

Winter season composting

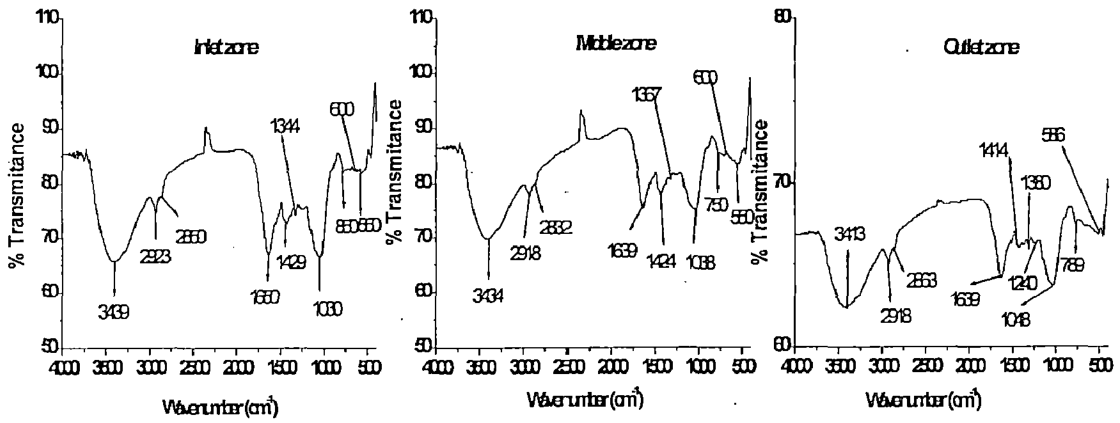


Fig.3.9. FT-IR spectra of Inlet, Middle and Outlet zones of rotary drum compost in winter seasons

During composting in winter season, aliphatic CH_3 stretching and CH_2 (methylene) bands at 2923 and 2850 cm^{-1} were appeared in inlet zone and when the material reaches to middle zone (4th day) their band intensity decreased (8.62 & 2.69%) respectively at same wave number (Fig.3.9). The degraded material reached to outlet zone (8th day), peak intensity further reduced (8.48 & 5.23%) respectively. However, inlet zone peaks at 1650, 1639cm^{-1} due to aromatic C=C and C=O group was observed in middle and outlet zone with high peak intensity (4.27 & 11.03%) respectively due to amides or carboxylates. The decreased and increased in peak intensity reflected decomposition of waste material and new products formation. An inlet band was found at 1429 cm^{-1} due to in-plane bend of carboxylic acids, CO_2 stretch of carboxylates and the aliphatic CH_2 group of alkanes. The C=O stretch vibration of carbonates also contributed to this band which was also found in middle and outlet zones at 1424 and 1440 cm^{-1} respectively with same peak intensity. Because of the organic compounds decrease and inorganic components increase relatively during decomposition, nitrate band at 1380 cm^{-1} was visible in outlet zone. An inlet peak at 1344 cm^{-1} was disappeared and no peak at this wave number was appeared in middle zone. A broad peak at 1030 cm^{-1} was found in inlet due to C–O stretching of polysaccharides or polysaccharide-like substances, Si–O asymmetric stretch of silicate impurities which was disappeared in middle zone and a new peak appeared at 1038 cm^{-1} with higher peak intensity due to some biochemical changes in polysaccharides degradation. This was further disappeared in outlet zone and a new peak at 1048 cm^{-1} was found with less intensity than the middle and inlet zones. In addition, peaks at 850, 600 and 550 cm^{-1} were found in inlet due to aromatic ring and halo-compounds and some metal-halogen bonds, which were found at same wave number in middle zone and further shifted to 789 and 586 cm^{-1} in outlet zone.

- ***Spring season composting***

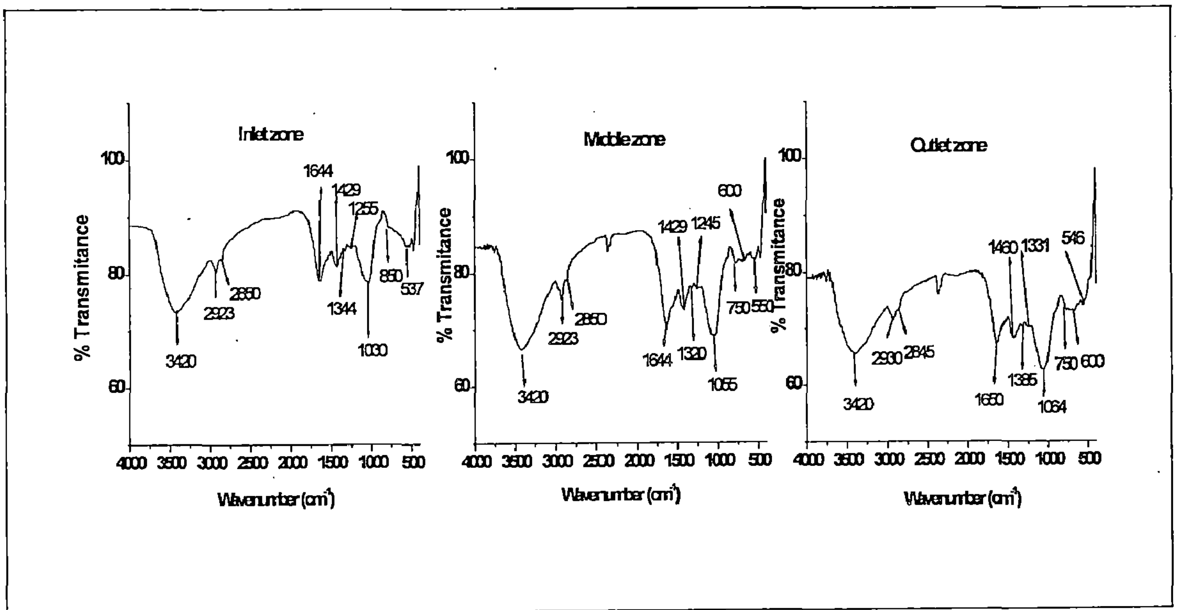
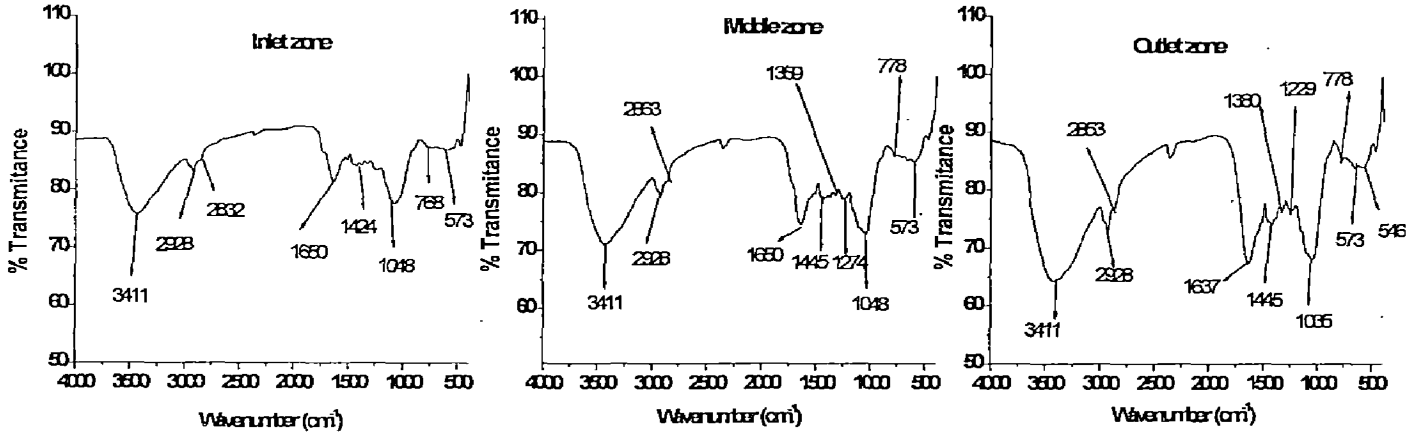


Fig.3.10. FT-IR spectra of Inlet, Middle and Outlet zones of rotary drum compost in spring seasons

During composting in spring season, aliphatic CH_3 stretching and CH_2 (methylene) bands were appeared at 2923 and 2850 cm^{-1} in inlet zone and when the material reaches to middle zone (4th day) their band intensity decreased (6.19 & 4.73%) respectively at same wave number (Fig.3.10). The degraded material reached to outlet zone (8th day), peaks intensity further reduced (11.12 & 10.6%) respectively. However, inlet peak at 1644 cm^{-1} due to aromatic C=C bond and C=O group was observed. Peaks at 1644-1650 cm^{-1} in middle and outlet zones with high peak intensity was observed due to amides or carboxylates (14.76 & 10.09%) respectively. The increased and decreased in peaks intensity reflects decomposition of waste material and new products formation. An inlet peak was found at 1429 cm^{-1} due to in-plane bend of carboxylic

cids, CO_2 stretch of carboxylates and the aliphatic CH_2 group of alkanes. The C=
retch vibration of carbonates also contributed to this band which was also found
iddle and outlet zones at same wave number and peak intensity. A new peak w
ppeared at 1460 cm^{-1} due to lignin content when the material goes to outlet zo
ecause of the organic compounds decrease and inorganic components increa
latively during decomposition, nitrate bands at 1385 and 1331 cm^{-1} was visible
utlet zone. An inlet peak at 1344 cm^{-1} was disappeared and new peak at 1320 cn
ppeared in middle zone due to primary and secondary aromatic amines. A broad pe
t 1030 cm^{-1} was found in inlet due to C–O stretching of polysaccharides
olysaccharide-like substances and Si–O asymmetric stretch of silicate impuriti
hich was disappeared in middle zone and a new peak appeared at 1053 cm^{-1} w
igher peak intensity due to some biochemical changes in polysaccharides degradati
his was further disappeared in outlet zone and a new peak at 1064 cm^{-1} was fou
ith less intensity than the middle and inlet zone. In addition, peaks at 850 and 537 c
were found in inlet due to aromatic ring and halo-compounds and some met
alogen bonds, which were shifted to 750, 600 and 550 cm^{-1} and 750, 600 and 516 cr
spectively in middle and outlet zones.

ummer season composting



ig.3.11. FT-IR spectra of Inlet, Middle and Outlet zones of rotary drum compost in summer seasons

During composting in summer season, aliphatic CH_3 stretching and CH_2 (methylene) bands were appeared at 2928 and 2832 cm^{-1} in inlet zone and when the material reaches to middle zone (4th day) their band intensity decreased (4.37 & 3.12%) respectively (Fig.3.11). Degraded material reached to outlet zone (8th day) peaks intensity further reduced (8.00 & 10.08%) respectively. However, inlet peak at 1650 cm^{-1} due to aromatic C=C bond and C=O group was observed. Peaks at 1650-1637 cm^{-1} in middle and outlet zone with high peak intensity (8.60 & 13.92%) was observed due to amides or carboxylates. The increase in peak intensity from inlet to middle and outlet zone reflects new products formation. An inlet peak was found at 1424 cm^{-1} due to in-plane bend of carboxylic acids, CO_2 stretch of carboxylates and the aliphatic CH_2 group of alkanes. The C=O stretch vibration of carbonates also contributed to this band which was also found in middle and outlet zones at same wave number and peak intensity. Because of the organic compounds decrease and inorganic components increase relatively during decomposition, nitrate band at 1380 cm^{-1} was visible in outlet zone. An inlet peak at 1320 cm^{-1} was disappeared and new peak at 1359 cm^{-1} appeared in middle zone due to primary and secondary aromatic amines. A broad peak at 1030 cm^{-1} was found in inlet due to C–O stretching of polysaccharides or polysaccharide-like substances and Si–O asymmetric stretch of silicate impurities which was disappeared in middle zone. A new peak appeared at 1048 cm^{-1} with higher peak intensity due to some biochemical changes in polysaccharides degradation. This was further disappeared in outlet zone and a new band at 1035 cm^{-1} was found with high intensity than the middle and inlet zone. In addition, peaks at 768, and 573 cm^{-1} were found in inlet due to aromatic ring, halo-compounds and some metal-halogen bonds, which were shifted to 778, 573 cm^{-1} and 778, 573 and 546 cm^{-1} respectively in middle and outlet zones.

Thus, in rotary drum composting FT-IR spectra showed that the spring and summer seasons gave better and stable compost than winter season because of the fast rate of decomposition indicated at 1650 cm^{-1} increase (humic acid formation) and at 2930 and 2850 cm^{-1} decrease (carbohydrates and proteins depletion).

3.3.1.3. Thermal Analysis

- ***Thermal Analysis study of composting in winter, spring and summer season***

The compost maturity was also characterized on thermal techniques such as differential thermal analysis (DTA) (Otero *et al;* 2002), differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) (Dell'Abate *et al*, 2000; Melis and Castaldi, 2004; Gomez-Rico *et al.*, 2005; Smidt and Lechner, 2005). In the presence of atmospheric oxygen two exothermic phenomena may occur in compost characterization such as volatilization of aliphatic compounds (Dell'Abate *et al*, 2000) or carbohydrates (Orteo *et al.*, 2002) and the oxidation of high molecular weight compounds. Thermo gravimetric (TG), differential thermal analysis (DTA) and differential thermal gravimetric (DTG) analysis were performed under an oxidant air (combustion condition). In an oxidant atmosphere, TG, DTA, and DTG data were reported (Fig. 3.12, 3.13, 3.14. and Table.3.6, 3.7, 3.8) from inlet, middle, and outlet zone in winter, spring and summer seasons respectively for rotary drum composting. Endothermic peaks were observed between 50-200^{o}C due to dehydration (water loss) and 600-750^{o}C attributed due to the carbonates thermal degradation. Similarly, two exothermic peaks were obtained in the range of 200-600^{o}C which corresponds to the degradation of organic matter. The first peak at 250-350^{o}C corresponds to the combustion of carbohydrates such as cellulose and lignocelluloses and the second peak at 350-500^{o}C corresponds to the degradation of complex aromatic structures

- ***Winter season composting***

During composting in winter season, the percentage mass loss, rate of mass loss and enthalpy change are given in table.3.6, 3.7, 3.8 and Fig. 3.12. Mass loss at 200-400^{o}C was 57.79, 55.0 and 53.6% and at 400-600^{o}C 16.13, 19.53, and 21.53% in inlet, middle, and outlet zones respectively. The overall mass loss from Inlet to outlet zone was 4.19%. However, the increment in mass from inlet to outlet zone was 5.4% due to less amount of aromatic fraction in compost. DTA curve shows two exothermic peaks, first peak shows decrease 9^{o}C from inlet to outlet zone due to less availability of carbohydrates such as cellulose and lignocelluloses and second peak shows 5^{o}C increment from inlet to outlet zone due to present of less availability of highly complex aromatic compounds which take more energy for decomposition. Similarly, in DTG profile decreases the rate of combustion of carbohydrate 65µg/min from inlet to outlet zone due to less availability of easily degradable material (carbohydrates and protein) and decrease the rate of combustion of aromatic complex compounds 428µg/min from inlet to outlet zone during rotary drum composting.

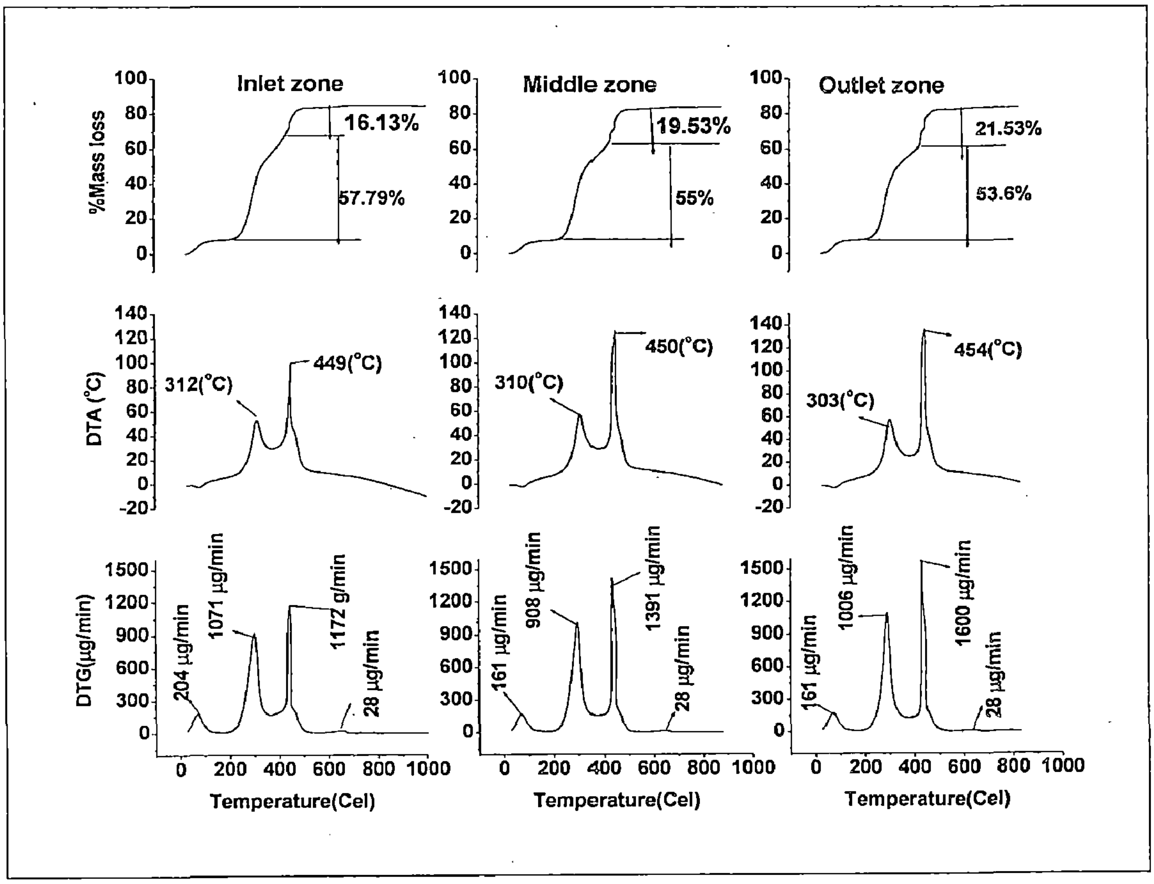


Fig.3.12. Mass loss (%), DTA, and DTG curve of inlet, middle, and outlet zone compost of rotary drum in winter season

- ***Spring season composting***

During composting in spring season, the percentage mass loss, rate of mass loss and enthalpy change were given in Table.3.6, 3.7, 3.8 and Fig. 3.13. Mass loss at 200-400°C was 50.59, 48.99 and 29.76% and at 400-600°C, 18.08, 21.01, and 25.67% in inlet, middle, and outlet zones respectively. The overall mass loss from inlet to outlet zone was 20.83%. However; the increase in mass loss from inlet to outlet zone was 7.59% due to sufficient amount of aromatic fraction in compost. DTA curve shows two exothermic peaks, first peak shows decreased in temperature 6°C from inlet to outlet zone due to less availability of carbohydrates such as cellulose and lignocelluloses in outlet zone and second peak shows 16°C increments in temperature from inlet to outlet zone due to highly complex aromatic compounds which take more energy for decomposition. Similarly, in DTG profile decrease the rate of carbohydrate combustion (65µg/min) from inlet to outlet zone and increases the rate of aromatic complex compounds combustion (428µg/min) from inlet to outlet zone during rotary drum composting.

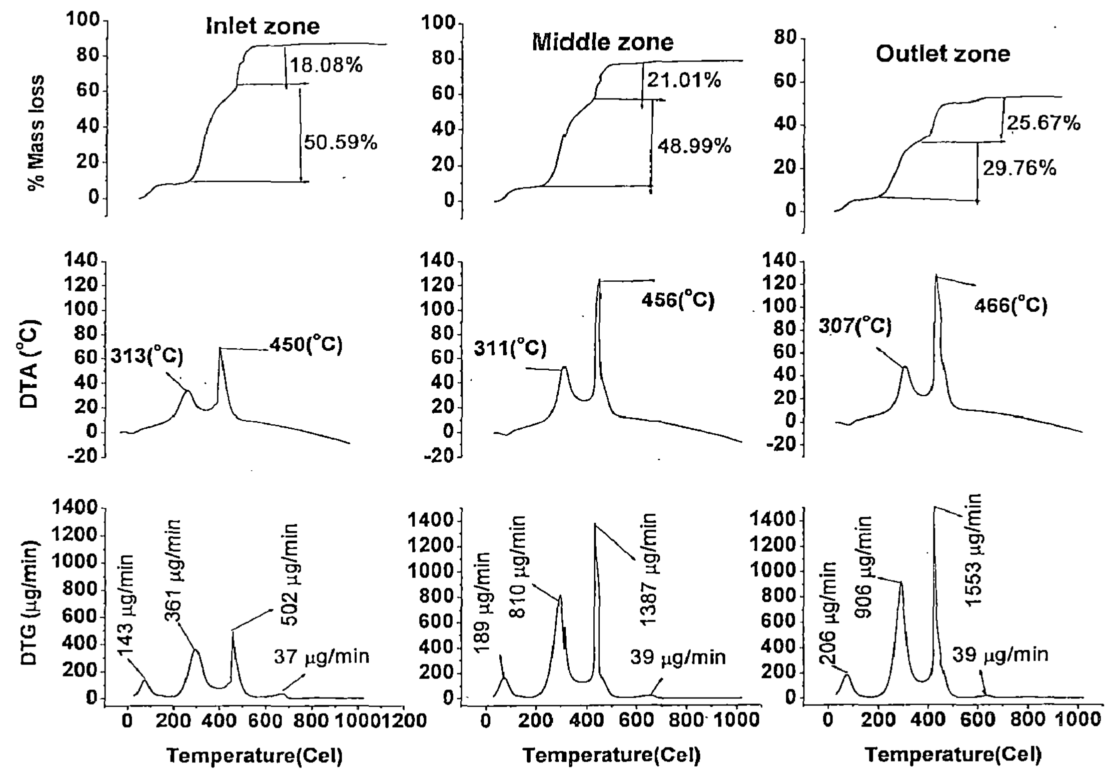


Fig.3.13. Mass loss (%), DTA, and DTG curve of inlet, middle, and outlet zone compost of rotary drum in spring season

- ***Summer season composting***

During composting in summer season percentage mass loss, rate of mass loss and enthalpy change were given in Table.3.6, 3.7, 3.8 and Fig. 3.14. Mass loss at 200-400°C was 38.06, 29.1 and 28.15% and at 400-600°C 14.27, 14.27, and 22.71% in inlet, middle and outlet zones respectively. The overall mass loss from Inlet to outlet zone was 9.91%. However, the increment in mass from inlet to outlet zone was 8.44% due to present of high aromatic fraction in outlet zone. DTA curve shows two exothermic peaks, first peak shows decrease 6°C from inlet to outlet zone due to less availability of carbohydrates such as cellulose and lignocelluloses and second peak shows 24°C increment from inlet to outlet zone due to present of highly complex aromatic compounds which take more energy for decomposition. Similarly, in DTG profile decrease the rate of combustion of carbohydrate 215µg/min from inlet to outlet zone and increases the rate of combustion of aromatic complex compounds

859μg/min from inlet to outlet zone during rotary drum composting. In contrast to the other season i.e. winter, summer and spring season have optimum conditions for the full-scale continuous rotary drum composting.

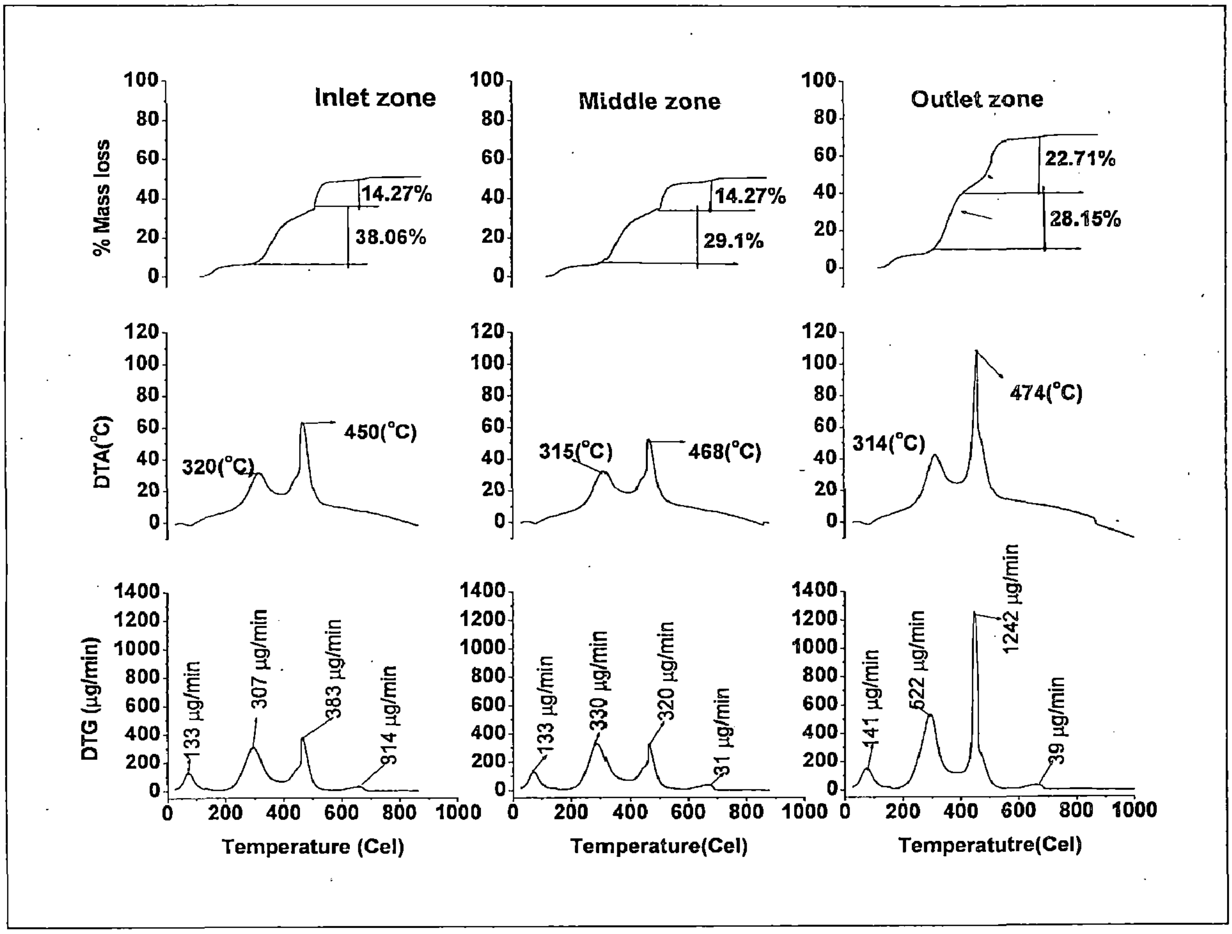


Fig.3.14. Mass loss (%), DTA, and DTG curve of inlet, middle, and outlet zone compost of rotary drum in summer season

Table.3.6: %Mass loss at 200-400°C and at 400-600°C of TG curve in inlet, middle, and outlet zone

% Mass Loss	**Spring Season**			**Winter Season**			**Summer Season**		
	Inlet zone	*Middle zone*	*Outlet zone*	*Inlet zone*	*Middle zone*	*Outlet zone*	*Inlet zone*	*Middle zone*	*Outlet zone*
At 200-400°C	50.59	48.99	29.76	57.79	55.0	53.6	38.15	29.1	28.71
At 400-600°C	18	21.01	25.67	16.08	19.53	21.53	14.27	14.27	22.71

Table.3.7: Change in enthalpy and relative intensity (RI) in spring, winter and summer season composting

Seasons/zones	**1st exothermic peak**	**2nd exothermic peak**	**ΔH (J/mg)**	**ΔH (J/mg)**	**Relative Intensity(RI)**
			1st peak	**2nd peak**	
		Spring Season			
Inlet zone	312	449	6.58	1.04	1.49
Middle zone	311	452	9.29	1.18	1.46
Outlet zone	303	454	8.68	1.65	1.47
		Winter Season			
Inlet zone	313	466	8.36	8.93	1.44
Middle zone	311	452	8.13	1.23	1.46
Outlet zone	307	450	8.34	1.36	1.50
		Summer Season			
Inlet zone	314	459	7.07	1.28	1.46
Middle zone	315	468	5.97	8.87	1.49
Outlet zone	320	474	6.3	1.21	1.48

Table.3.8: Derivative thermogravimetry analysis in spring, winter and summer season composting

Exothermic Peaks DTG Curve(μg/min)	**Winter Season**			**Spring Season**			**Summer Season**		
	Inlet zone	*Middle zone*	*Outlet zone*	*Inlet zone*	*Middle zone*	*Outlet zone*	*Inlet zone*	*Middle zone*	*Outlet zone*
At 50-200°C (Moisture)	204	161	161	143	189	206	133	133	141
At 200-400°C	1071	908	1006	361	810	906	307	330	522
At 400-600°C	1172	1331	1600	502	1387	1553	383	320	1242
At 600-750°C (Carbonate)	28	28	28	37	39	39	31.43	31	39

- ***Temperature and CO_2 emission rate correlation models for the stability of compost.***

The analysis of the temperature and CO_2 correlation was also performed. The observed relation was modeled using two different models, the Andrews and Kambhu/Haug model and the Ratkowsky model. The two models that were used are shown below:

- **Andrews and Kambhu/ Haug model:**

$$Rco_2 = K\,[\theta_1^{(T-T_1)} - \theta_2^{(T-T_2)}]$$

Rco_2 = co_2 evolution rate (g CO_2/kg Vs-day)
K = First order rate constant at reference temperature T_1 (day^{-1})
T_1, T_2 = reference temperature parameters (°C)
θ_1, θ_2 = empirically estimated coefficients

Table.3.9. Andrews and Kambhu/ Haug constants taken and recommended values

Parameter	Value taken	Recommended
K	4.0656	0.9*max obs rate
θ_1	□.03	1.01-1.10
θ_2	1.09	1.05-1.50
T_1	20	20°C
T_2	60	40-70°C

- **Ratkowsky model:**

$$Rco_2 = b\,(T-T_{min})\,\{1-e^{[c(T-T_{max})]}\}$$

Rco_2 = CO_2 evolution rate (g CO_2/kg Vs-day)
T_{max} = maximum temperature for biodegradation
T_{min} = min temperature for biodegradation (at T_{max} and T_{min} biodegradation rate is zero)

b = an empirically estimated coefficient which determines the maximum rate for biodegradation

C= an empirically estimated coefficient which determines the behavior of the model near the optimum temperature

Table.3.10. Ratkowsky constants taken recommended values

Parameter	**Value taken**	**Recommended**
b	0.3	0.0001-1.0
c	0.295	0.01-1.0
T_{max}	75	65 - 90°C
T_{min}	34	0 - 25°C

This method directly allowed us to use these values to make the best fit curves for the temperature-CO_2 correlation using the above models. The final values of the error functions were then compared to evaluate the relative applicability of these models to the full-scale continuous rotary drum composter.

The Andrews – Kambhu – Haug model was found to be better model compared to the Ratkowsky model (table. 3.11 and Fig. 3.15). Because, a rapid microbial growth temperature (max. 65°C) was obtained in the former model (optimum temperature 62.1°C) while, the later model gave 66.4°C as optimum temperature which is unfavorable for microbial growth.

Table.3.11, Observations of CO_2 & temperature and calculated RCO_2 values for Haug and Ratkowsky model.

	Observations at Inlet of Drum		**Calculated R_{CO2} values**	
Days	**CO_2 Evolution**	**Temperature**	**Haug**	**Ratkowsky**
7	9.03	54	8.68265	5.9877624
11	9.15	60.3	9.208188	7.7867812
15	9.21	61.4	9.235547	8.0712413
22	9.18	70.5	8.040043	8.0467249
24	8.96	68.8	8.522927	8.7636068
26	9.24	70.1	8.167913	8.2781462
28	9.06	70.2	8.136808	8.2244647
32	8.92	70.6	8.00662	7.9816101
34	8.86	70.3	8.105131	8.1680598
36	8.73	70	8.198455	8.3291897
38	8.82	68.8	8.522927	8.7636068
41	8.77	68.1	8.678739	8.8938069
43	8.45	67.8	8.738524	8.927738
45	8.76	65.5	9.072509	8.8767798
47	8.46	65.7	9.051487	8.8980815
50	8.35	63.4	9.214535	8.5320528
52	8.22	64.2	9.176464	8.6854878
54	8.49	62.1	9.239309	8.2424488
58	8.36	57.8	9.063695	7.0953226
60	8.15	60.1	9.200612	7.7334349
62	8.01	57.8	9.063695	7.0953226
64	7.78	66	9.017272	8.9251311
68	7.83	61.3	9.234109	8.0460927
72	8.11	61.6	9.237761	8.1210486
76	8.06	70.7	7.972602	7.9134024
80	7.79	71	7.866923	7.689206

---Continued from previous page

84	7.25	65.4	9.082495	8.8652096
88	7.43	69.8	8.257865	8.4236907
91	7.16	66.4	8.96648	8.9511154
93	6.89	66.2	8.992628	8.9396416
99	7.32	69.1	8.448837	8.6826941
104	6.98	71.5	7.678332	7.2437
107	6.75	70.2	8.136808	8.2244647
112	6.15	68.6	8.569841	8.8087352
117	5.98	71.7	7.598386	7.0375506
123	5.91	69.5	8.342887	8.5476413
129	5.82	68	8.699121	8.9064534
136	5.93	69.3	8.396903	8.6192579
141	5.74	67.8	8.738524	8.927738
145	5.81	68.3	8.636593	8.8642863

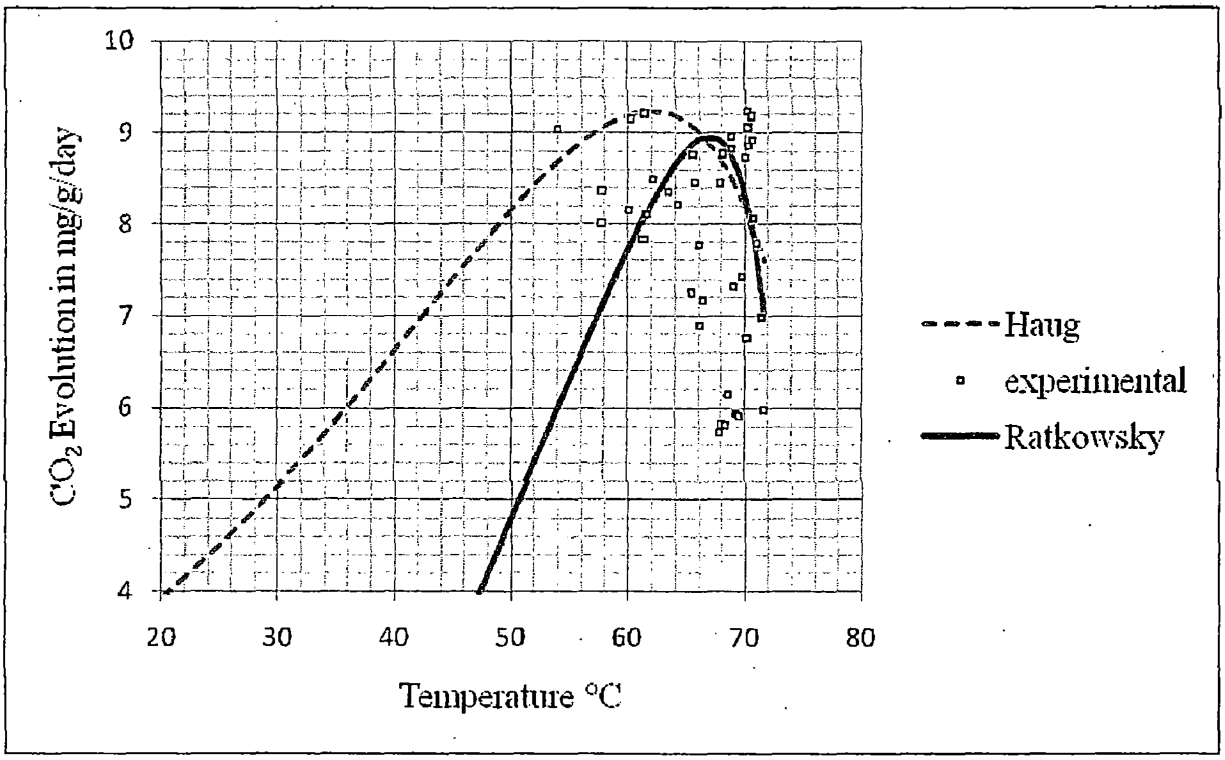


Fig.3.15. Temperature and CO_2 evolution rate curve between Haug Ratkowsk and experimental values.

3.3.2. Conclusions

In rotary drum composting process, various physico-chemical and spectroscopic analyses were reported for the compost characterization and to monitor the evolution and aggregate transformation of organic matters (OMs) in different composting periods and seasons. FT-IR, TG, DTG and DTA were used for quality and maturity evaluation of composted materials for better demand and acceptability. Our results showed that the composting time and seasonal variations determines an increase of the molecular complexity of compost by decreasing the aliphatic and polysaccharide components while increasing the oxygenated group content and the aromatic complex compounds. FT-IR spectroscopy was found a promising technique for functional groups identification in composting. Some new peaks and their intensity were also found in FT-IR bands for example, presence of bands at 778 722, and 560 cm^{-1} due to aromatic ring, halogen-compounds and some metal-halogen bonds. Higher degree of maturity was achieved in spring and summer seasons composting in terms of mass loss (TG), rate of mass loss (DTG), enthalpy change (DTA) in fina compost compared to winter season.

In addition the correlation between temperatures - CO_2 emission rate was shown using Andrews – Kambhu – Haug and Ratkowsky models. In our study, the Andrews – Kambhu – Haug model was found to be better compared to the Ratkowsky model. Because, a rapid microbial growth temperature (max.65°C) was obtained in the former model (optimum temperature 62.1°C) while the later model gave 66.4°C as optimum temperature which is unfavorable for microbial growth.

Chapter 4

Part A: Fate and degradation kinetics of Aldrin, Endosulfans and Lindane Pesticides in household batch-scale rotary drum and conventional windrows composting

In this chapter (Part A) deals with the fate and degradation kinetics of Aldrin, Endosulfans and Lindane pesticides in household batch-scale rotary drum and conventional windrows composting. During the study three cases was conducted for pesticides degradation in the both composting systems i.e. Case 1: actual pesticides degradation found in vegetable waste (RD1 and W1), Case 2: degradation of pesticides after three time enhancement of actual concentration (RD2 and W2) and Case 3: degradation of pesticides after six time enhancement of actual concentration (RD3 and W3).

4.1. INTRODUCTION

Organochlorines are widely used in the agriculture for pest and disease control in plants. These pesticides have resistance to degrade even in longer time and so resulted in universal contaminants in water, soil and food. A widespread pesticide contamination has been found in food commodities basically due to their non-judicious use. It has been observed that their long-term, low-dose exposure to human are increasingly linked to health problems such as immune-suppression, hormone disruption, diminished intelligence, reproductive abnormalities and cancer (Gupta; 2004). It is found that 51% of Indian food commodities are contaminated with pesticide residues of which 20% have above the upper residue level of pesticides on a worldwide basis (Gupta; 2004). They are also a major group of environmental contaminants due to the persistence of these pesticides in food waste, sediments, waste water sludge and soil (Serpil Yenisoy-Karakas; 2006, Barriada-Pereira *et al*; 2005, Nakada, *et al*; 2008 and Reungsang *et al*; 2006). Pesticides may take longer time to degrade because of their limited bioavailability to strong sorption, or ''ageing'' (Troxler; 1998).

However, some organochlorine pesticides such as Lindane and organo-phosphorus pesticides such as chlorpyrifos-methyl and Malathion almost fully degraded during composting process (>99%) (Kim, *et al*; 2008). However, Endosulfan was 50% degraded and its concentration was always found greater than Lindane in compost and waste material. Characterization and removal of pesticides by adsorption using hypercrosslinked polymer and Hexagonal Mesoporous Silicate and bioremediation in soil were also reported but these process limited to laboratory scale (Memon, *et al*; 2005, C.F., Chang, *et al*; 2007 & 2008, Punyapalakul, *et al*; 2006, Mathava, K. S, *et al*; 2006, Pranab, *et al;* 2006, Kumar, *et al*; 2009). But some organochlorine pesticides such as aldrin, dieldrin and endrin could not degraded and long recognized for their environmental persistence and risk involved for non-target organisms (Strom; 1985). Therefore, many countries like United States in 1974, Poland and Belgium in 1975, Netherlands in 1981 have banned their usages (Lichtenstein, *et al;* 1960). These pesticides are also been listed among 12 persistent organic pollutants (POPs) in the UNEP Stockholm Convention on POPs signed in 2001. Nevertheless, according to the Food and Agricultural Organization of the United Nations (FAO, http://www.fao.org/ag/AGP/AGPP/Pesticid/Disposal/index_en.htm; 2002), there are still considerable amounts of these compounds stockpiled worldwide. Aldrin, dieldrin and endrin belong to the most persistent pesticides in the environment (Zablotowicz, *et al;* 1998).

Mostly reported microbial transformations have little effect on their chemical structures. A widespread reaction in the environment is aldrin epoxidation to the more persistent dieldrin (Lichtenstein, *et al*; 1960, Serpil Yenisoy-Karakas; 2006). The often reported metabolites of these two pesticides are: trans-aldrindiol and photodieldrin (Patil, *et al*; 1970 and 1972), the latter being more toxic than the parent compound aldrin (Georgacakis, *et al*; 1971). A full microbial conversion of any of these cyclodiene pesticides has not been confirmed so far. There is only one indication of such a possibility (Jagnow, *et al;* 1972), who have reported a $^{14}CO_2$ formation from labeled dieldrin. However, this process occurred almost at trace level, <1% was converted in several weeks.

Dechlorinating processes are of particular interest as they often produce less toxic and/or less recalcitrant metabolites. Eekert and Schraa, (2001) suggested that methanogenic granular sludge grown in Upflow Anaerobic Sludge Bed (UASB) reactor is the best biocatalyst for the dechlorination of higher chlorinated pesticides. It is supposed that some heat-stable transition metal co-factors present in anaerobic bacteria may play important role in the dechlorinating ability of granular sludge (Hendriksen, *et al*; 1992, Duff, *et al;* 1995, Eekert, *et al;* 1998a, 1998b, 1999a and 1999b). But Lindane, Hexachlorobenzene (HCB), pentachlorobenzene (PeCB), 1,2,3,5-tetrachlorobenzene (TeCB) and 1,3,5-trichlorobenzene (TCB) are resistant to aerobic transformation. Also, no oxidation of chlorobenzene has been shown under nitrate, sulphate, or iron-reducing conditions due to strong hydrophobicity, highly chlorinated benzene accumulation in organic-rich anoxic environments like sludge and sediment. The only known transformation of highly chlorinated benzene is the reductive dechlorination leading to the formation of less chlorinated benzene. A combined anaerobic/aerobic treatment of contaminated waters has been proposed to achieve mineralisation of all chlorobenzene congeners in a single process (Fathepure, *et al*; 1991and Selent, *et al*; 1999). Abiotic reductive dechlorination of chlorobenzenes by vitamin B_{12} or transition metals have also been reported. However, in these studies high concentration of the catalyst was employed leading to only low conversion rates (Wiegel, *et al*; 1999).

However, experimental study of compost made from shredded paper and food scraps have found that only few bacterial species remained active at temperatures above 60°C; those that survived were predominantly *Bacillus sp.* Fungi were found only in the narrow temperature interval from 55-61°C, but the data were limited to the recovery of one *Aspergillus* species. Non-spore forming bacteria were broadly categorized in two groups (*Pseudomonas* and *Arthrobacter* types), which were found at temperature intervals as high as 50 - 57°C (Strom, *et al;* 1985a and 1985b). Patil, *et al*; (1970) have reported the insecticide degradation comparative study that bacterial species such as *pseudomonas sp., bacillus species and micrococcus* species were responsible for the aldrin degradation. Moreover, evidences showed that *Bacillus circulans* I and II degraded majority of endosulfan in aerobic system (Kumar, *et al*; 2006) and the degradation of Lindane achieved after 3 days of aerobic incubation by a native bacterial consortium (*B. thiooxidans* and *S. Paucimobilis)* isolated from contaminated soil (Pesce, *et al*; 2004). The properties of targeted pesticides are given (table.4.1 Appendix).

The degradative pathways and kinetics of these target pesticides have not been completely characterized. To understand whether the pesticide residue from waste material has been effectively eliminated or not by conversion of one toxic form to another, this study was focused on fate and degradation kinetics of organochlorine pesticides in vegetable waste by two common composting techniques i.e. High rate Rotary drum and conventional Windrows composting.

4.1.1 Results and Discussions

4.1.1.1 Physico-chemical parameters

- ***Temperature, Moisture content and pH profile***

Temperature is one of the key indicator of pesticides disappearance during composting which determines the rate of the biological processes, takes place and plays a selective role on evolution and succession on the microbiological communities (Kearney, *et al*; 2005 and Kiigemagi, *et al*; 1958). With increase in temperature, pesticides start desorbing from organic matter, subsequently dissolved in aqueous phase of the composting material and make accessible for degradation by microbes which were activated throughout due to the swelling of temperature. The optimal pH values for composting range from pH 5.5 -8.0. Bacteria favor a near acidic and basic to neutral pH, whereas fungi favor more acidic pH. The pH drops initially as a result of acid forming bacteria. Then increases to become alkaline and finally drops back to near neutral. Similarly, the optimal moisture content in composting has been determined between 50 - 60% for bacterial growth. Bacterial metabolic activity and the colonizing property failed when the moisture content drops below 40%. During the study, temperature increases from ambient to 60°C within 2 days during all the cases in rotary drum (RD1, RD2, RD3) and rotary drum preventing escape of excessive heat generation during the thermophilic phase till 12th day of composting, attributed to the higher microbial activity which degrade the pesticides at greater rate or shorter half life compared to windrow (W1, W2, W3), in which temperature suddenly decreases from 55°C to 40°C within 4 to 6 days (Fig.4.1) and then decreases to 30°C till composting ends. However, after 12th day microbial activity decreases owing to the lesser availability of organic matters & nutrients result in lowering of temperature to 45°C.

Similarly, composting with 70% moisture content (till 12th day) was reduced significantly in all the cases. During RD2 and RD3 moisture was reduced gradually and remains in optimum range (50%) and slowly reduced to 40% till end of composting. During windrow (W1, W2, W3, Fig.4.2) composting moisture content was reduced comparatively faster due to evaporation and leaching out water.

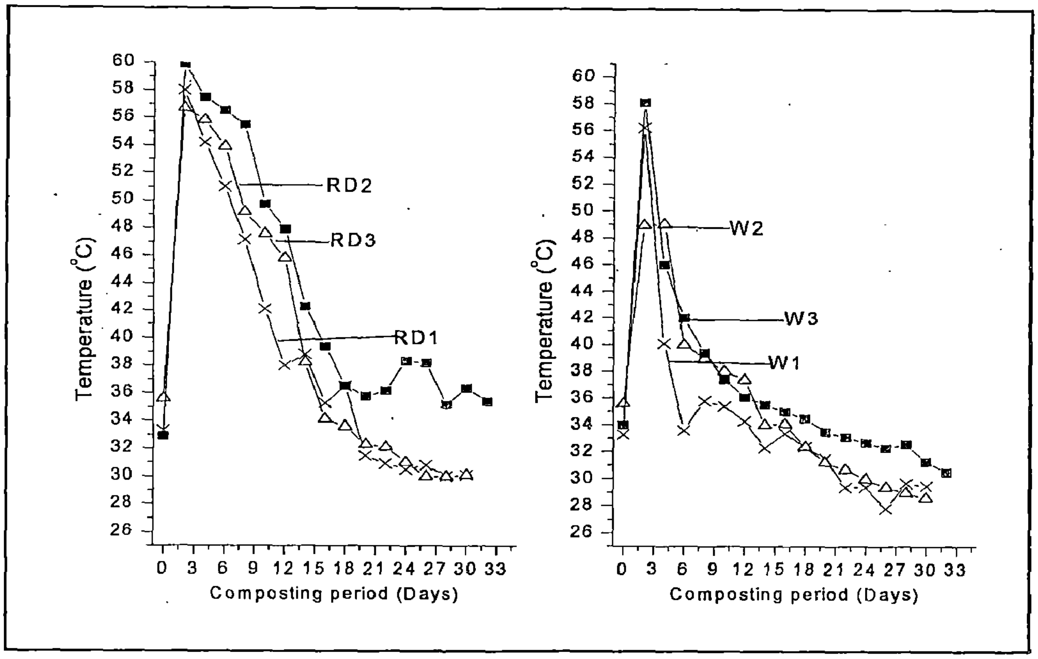


Fig.4.1.Temperature profile of the composting materials during RD1, RD2, RD3 and W1, W2, W3 over composting period

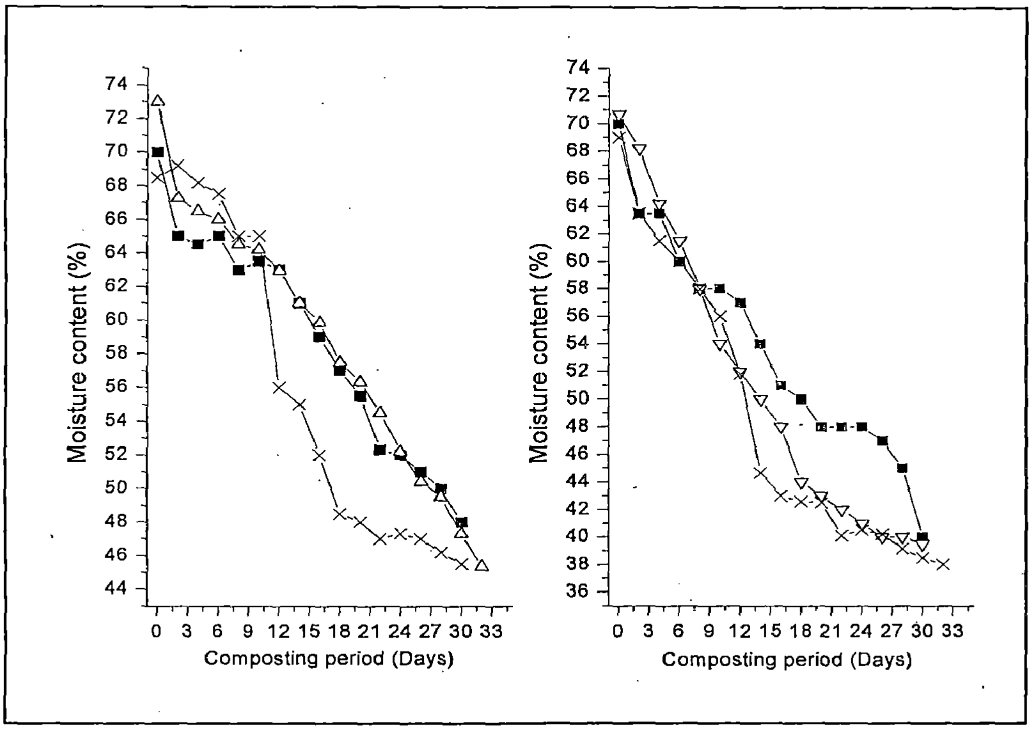


Fig.4.2. Moisture content profile of the composting materials during RD1, RD2, RD3 and W1, W2, W3 over composting period

However, pH was in more alkaline (8.5±0.2 to10.6±0.1) in RD1, RD2 and RD3 till 6th day of composting which results more degradation of pesticides and become neutral when the composting was at end. Similarly, windrow composting (Fig.4.3) was in almost similar pH (8.5±0.2 to 9.72±0.2) but less alkaline in beginning than the rotary drum composting.

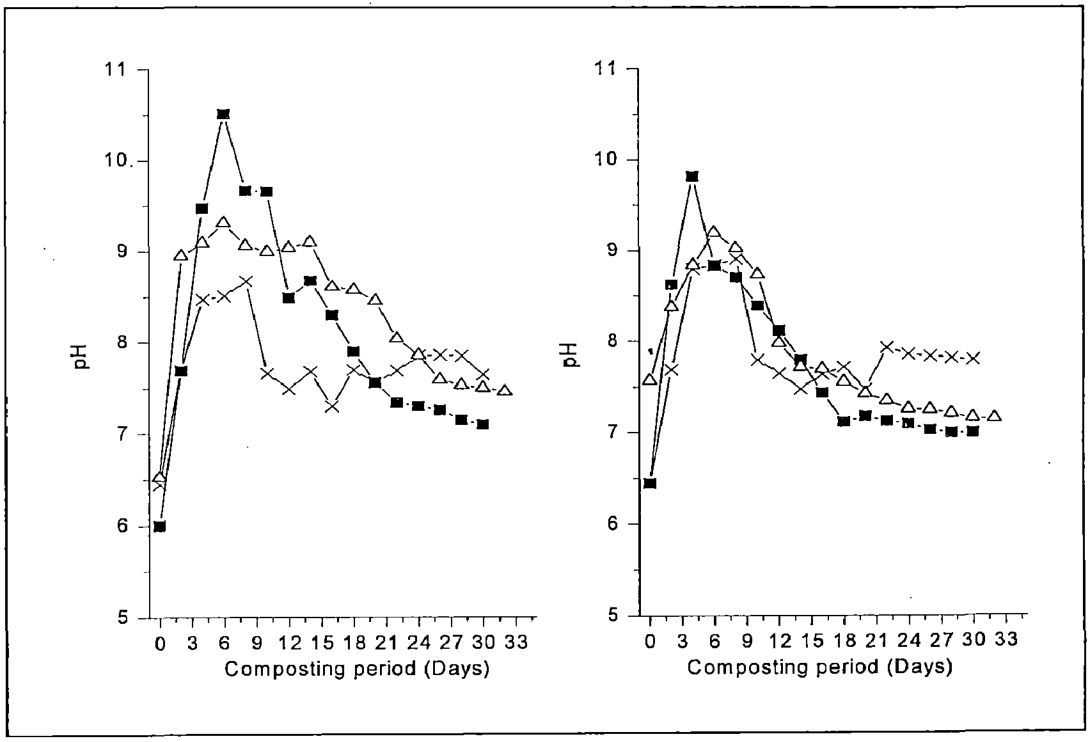


Fig.4.3. pH profile of the composting materials during RD1, RD2, RD3 and W1, W2, W3 over composting period

- ***Total organic carbon (TOC)***

Initially, the amount of total organic carbon (Fig.4.4.) was found to be 42, 38 and 35 % RD1, RD2 and RD3 composting respectively. While, in W1, W2 and W3 composting the initial total organic carbon was 36, 31 and 30 %, which reduced to 61% and 53 % respectively in household rotary drum and conventional windrow composting. After 2 days, sudden decrease in the content of organic carbon was observed that can be attributed to release of leachate produced. At the later stages, organic matter becomes fully mineralized in composting due to the degradation of easily degradable compounds such as proteins, cellulose and hemi-cellulose and utilized by microorganisms as C & N sources.

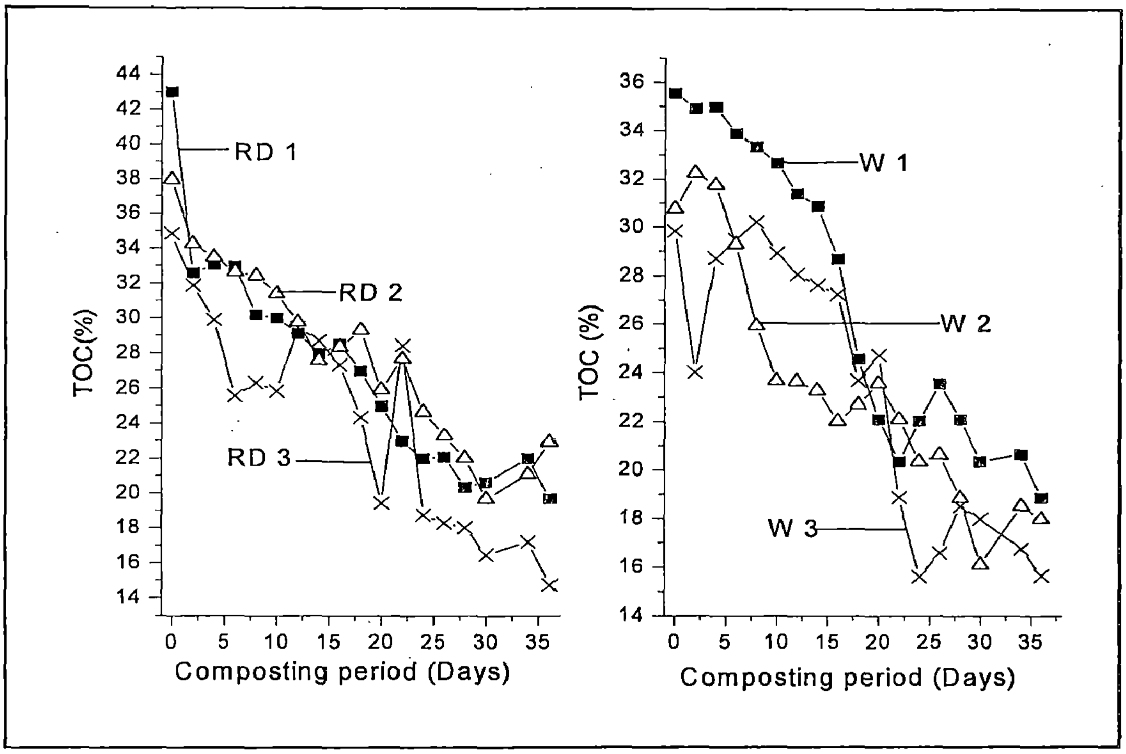


Fig.4.4. Total organic carbon of composting material during RD1, RD2, RD3 and W1, W2, W3 over composting period

- ***Total nitrogen profile***

Fig.4.5. shows the time course of the total nitrogen (TN) during drum and windrow composting consisting of inorganic forms of nitrogen (ammonium (NH_4-N), nitrate (NO_3-N)) and organic nitrogen (N_{org}). Total nitrogen contents during house hold batch-scale rotary drum and conventional windrows composting increased within 30 days of composting period due to the net loss of dry mass in terms of CO_2, as well as the water loss by evaporation due to heat evolution during oxidation of organic matter (Fang, *et al*; 1999, Huang, *et al*; 2006). Nitrogen fixing bacteria might have also contributed to increase in TN in the later stage of composting (Bishop and Godfrey, 1983). However, during drum composting in 2-3 days total nitrogen slightly decrease due to librating some leachate. After 5th day nitrogen concentration increases from 1.40-1.82% to-2.32% in 36 days in RD1, RD2 and RD3. While in conventional windrows composting the total nitrogen increases from 1.5-1.9% to 1.80-2.12% during 36 days in W1, W2 and W3. This suggested that the drum composting rate of degradation of organic matter was more due to higher loss of dry mass i.e. librating CO_2 compared to the windrow composting.

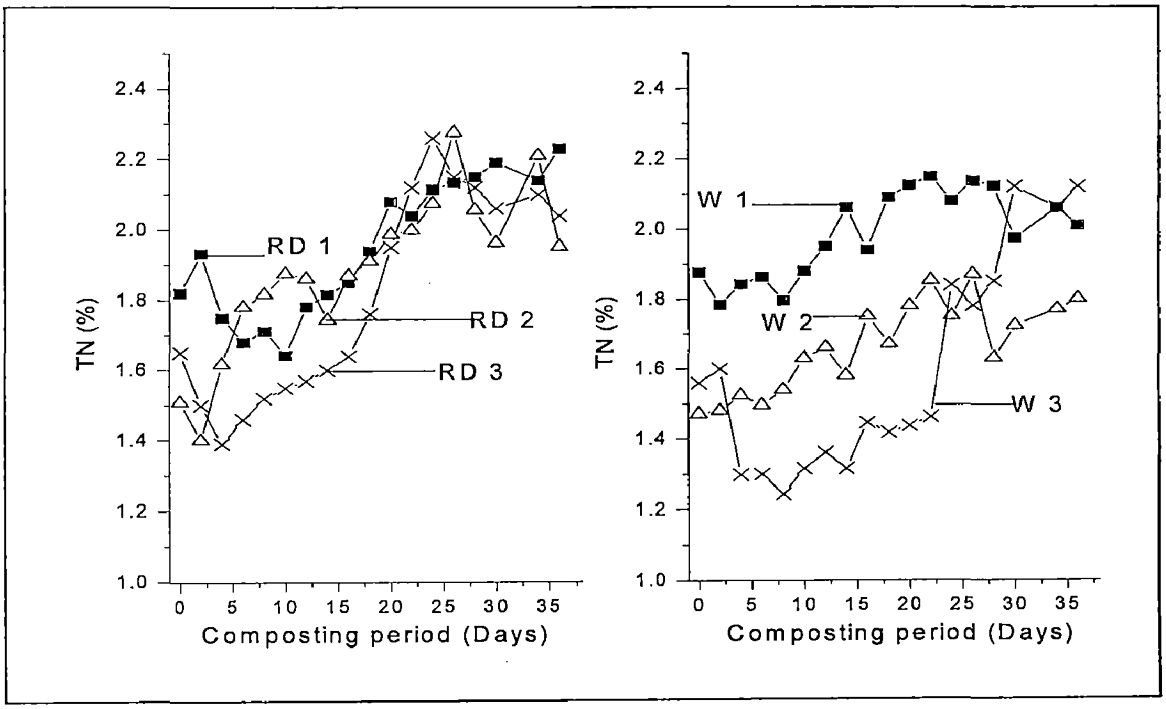


Fig.4.5. Total nitrogen of composting material during RD1, RD2, RD3 and W1, W2, W3 over composting period

- ***Carbon dioxide emission rate***

CO_2 evolution rate initially increased from 12 mg/g/VS/day to 9.12-10.98 mg/g/VS/day during drum composting in RD1, RD2 and RD3 due to increase in temperature and degradation rate while in case of windrows the rate is comparatively (8.50-10.62 mg/g/VS/day) in W1, W2 and W3. At the later stages of composting as degradation rate decreased, the maturity/stability increases in the final product and rate of CO_2 evolution was lowered upto 3.80-3.72 mg/g/VS/day in drum and 4.2-7.2 mg/g/VS/day in windrows composting (Fig. 4.6).

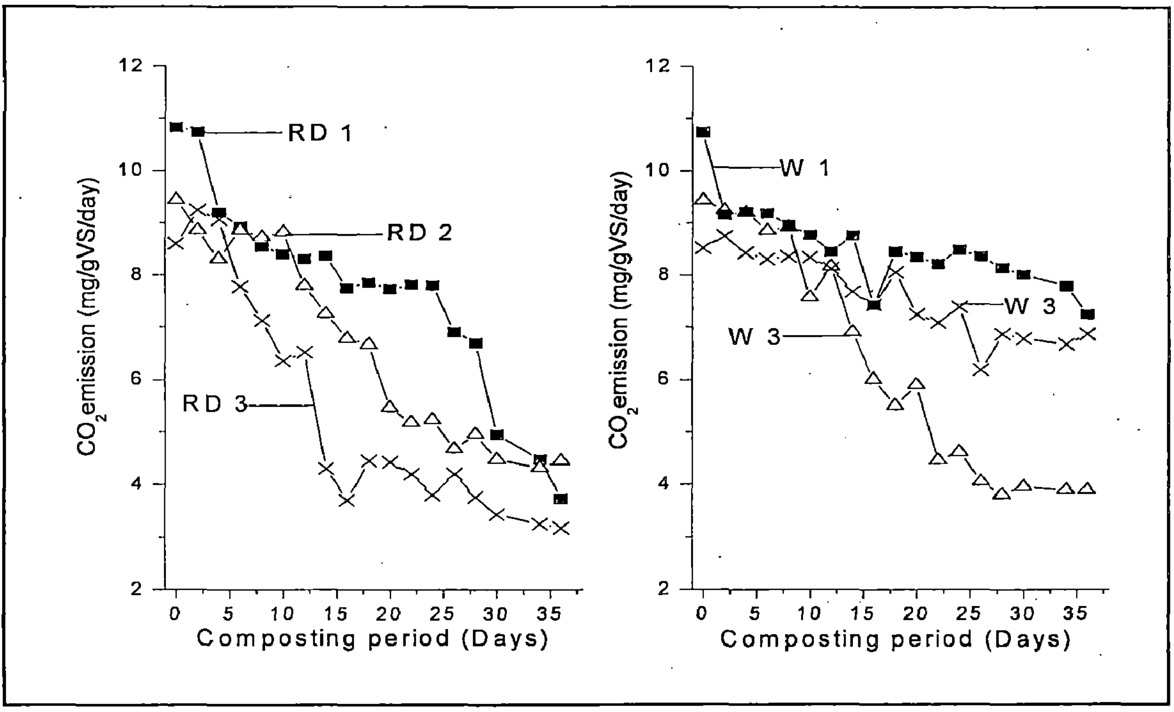


Fig.4.6. CO_2 emission of composting material during RD1, RD2, RD3 and W1, W2, W3 over composting period

4.1.1.2. Degradation or removal of pesticides

- ***Removal of Aldrin, Endosulfan (α and β) and Lindane during RD1 and W1***

The initial concentration of aldrin, Endosulfan α and β and Lindane (Fig.4.7 and table 4.2) in compost waste material during RD1 and W1 composting was found 697.81, 960.29, 447.54, 169.27 μg/kg (Cumulative 2273 μg/kg) respectively. During RD1 composting, the concentration of all pesticides except Lindane rapidly decreases upto 50% in 10-12 days. Endosulfan α degraded more fast than the Endosulfan β (Fig.4.7) because of Endosulfan α changed to Endosulfan β and further change to another moieties. After 12th day, removal was slow and degradation takes place till 28th day, thereafter concentration was found to be relatively constant. Lindane decreases initial 15 days with a constant rate (0.0428/day). After that it was also reduced rapidly with almost same rate from 2-15 days and no degradation takes place after 25th day due to less concentration and contact of Lindane with microbial community. In case of W1 composting of aldrin and Endosulfan α degraded same as RD1 but with slow rate. They reduce more than 50% till 20 days. Lindane degraded very slow rate initial 15 days afterword it reduces slowly due to less contact to microbes in later phase of composting during W1. The overall removal efficiency of

RD1for Aldrin, Endosulfan α, Endosulfan β and Lindane pesticides was found 84.98, 83.20, 81.36 and 85.18 % respectively, 77.65, 67.20, 67.25, and 54.50% respectively during W1 composting attributed to higher temperature for 2-20 days. pH (more alkaline) and moisture also sustained more than the windrow composting during the process. Higher the temperature, alkaline pH and optimum moisture content more will be the desorption of aldrin, Endosulfan α, Endosulfan β and Lindane in water phase present in the material and making it readily available for microbial degradation.

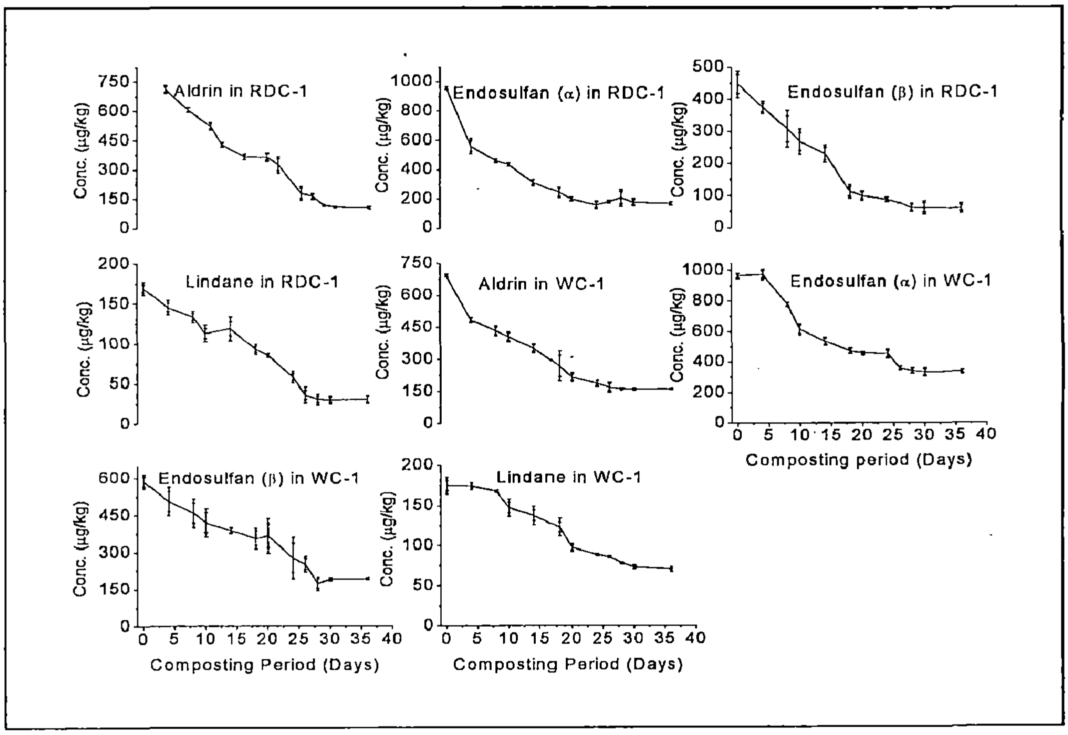


Fig.4.7. Removal of Aldrin, Endosulfan (α and β) and Lindane with error bars during RD1 and W1

- ***Removal of Aldrin, Endosulfan (α and β) and Lindane during RD 2 and W 2***

Initial concentration of aldrin, Endosulfan α and β and Lindane (Fig.4.8 and table 4.3) after three times enhancement , the actual concentration in feedstock material during RD2 and W2 composting was found 2.644, 8.165, 3.192 and 7.159 mg/kg respectively (cumulative 21.17mg/kg) and 2.576, 7.311, 3.161 and 7.160 mg/kg respectively (cumulative 20.207 mg/kg). During RD2 composting the concentration of aldrin degraded as in RD1 composting but endosulfan α suddenly decreases around 60% within 12 days and increase the concentration of endosulfan β same time which confirmed the initially Endosulfan α conversion to Endosulfan β. Subsequently, endosulfan β decreases gradually after 7th day of converting other moieties till end of composting. In case of Lindane 50%

reduction takes place within 5th day and around 30% Lindane degraded in later phase of composting due to the more Lindane was in contact with microbial community and excellent moisture condition compare to RD1 composting. In case of W2 composting, aldrin, Endosulfan β and Lindane decrease in concentration same as degraded in RD2 but with slow rate. They reduce only 50% till 20 days. Endosulfan α decreases very slow rate (0.0309/day) and degraded only 50% in whole composting process. Lindane removed very fast from the system for 15 days might be due to leachate generation, afterword it reduced due to microbial degradation like fungi because in later phase the fungi was the dominant in both the composting systems. The overall removal efficiency of Aldrin, Endosulfan α, Endosulfan β and Lindane pesticides was found 68.28, 59.93, 68.81 and 85.31% respectively during RD2, 66.60, 55.57, 67.59, and 70.93 % respectively during W2 composting. In RD2, the removal of Aldrin, Endosulfan α, Endosulfan β except Lindane are less than the RD1 may be due to moisture lost in the form of leachate and pesticides (might be removed in dissolved form).

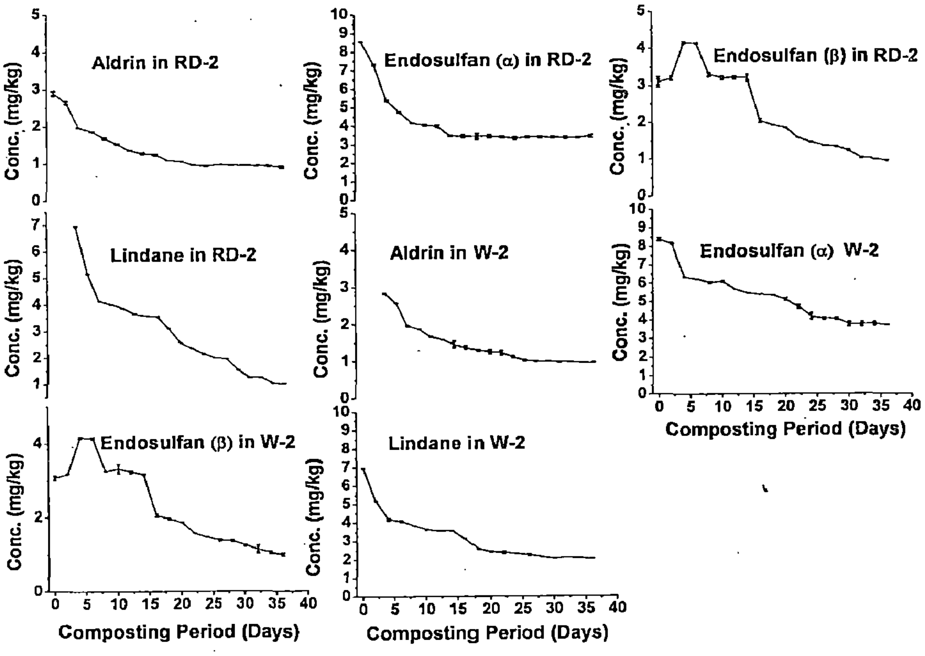


Fig.4.8. Removal of Aldrin, Endosulfan (α and β) and Lindane with error bars during RD2 and W2

- ***Removal of Aldrin, Endosulfan (α and β) and Lindane during RD3 and W3***

In this case, degradation of pesticides, Aldrin, Endosulfan α, Endosulfan β and Lindane during Rotary drum, RD3 W3 composting listed in Fig.4.9 and table 4.4. The initial concentration of aldrin, Endosulfan α and β and Lindane, after six times enhancement of pesticides than the actual concentration in feedstock material during RD3 and W3 composting was found 12.1643, 12.1096, 5.5163, 13.5876 mg/kg respectively (cumulative 43.3778 mg/kg). During RD3 the concentration of all the pesticides except Endosulfan β rapidly decreases upto 50% in 15 -16 days. Endosulfan β increases upto 8 mg/kg till 16th day and then decreases to 1.5 mg/kg when the composting ended.

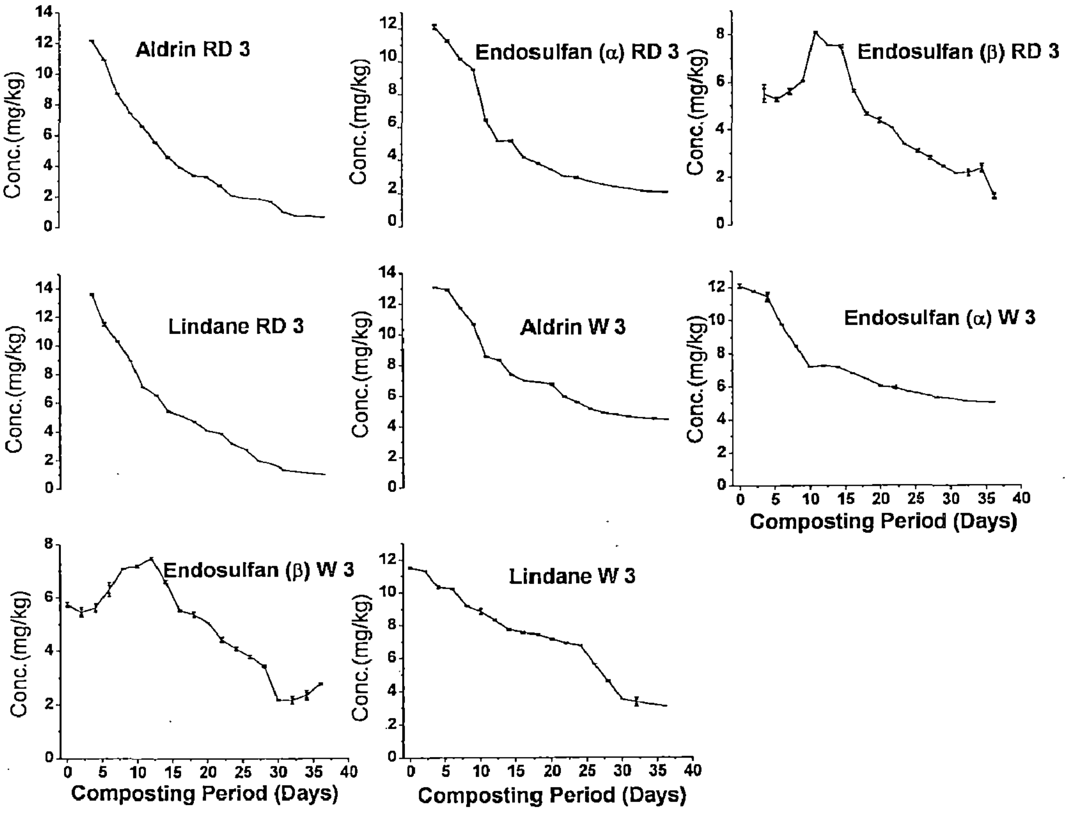


Fig.4.9. Removal of Aldrin, Endosulfan (α & β) and Lindane with error bars during RD3 and W3.

After 16th day degradation/removal was with slower rate (0.0092/day) till the end of composting during rotary drum due to fungal degradation in later phase of composting. In case of W3, Aldrin, Endosulfan α and Lindane degraded same like RD1 but with slow rate 0.03, 0.0095 and 0.02/day respectively. They reduce 50% till 20 days might be less growth of microbial communities due to negative effects of high concentration of pesticides. Lindane degraded at a very slow rate in initial 26 days, afterword it reduced fast for 2-4 days might be due to contact of microbes like fungi which stopped degradation. The overall removal efficiency of Aldrin, Endosulfan α, Endosulfan β and Lindane pesticides was found 86.75, 83.30, 78.35 and 89.29 % respectively during RD3, 53.69, 58.53, 51.98 and 76.85 % respectively during W3 composting was attributed to higher temperature range sustained from 2nd to 20th days, pH (more alkaline) and moisture also sustained more than the windrow composting. Higher the temperature, alkaline pH and optimum moisture content, more will be desorption of aldrin, Endosulfan α, Endosulfan β and Lindane present in the material and making it readily available for microbial degradation. It also attributed that in windrow composting might be some high concentration of pesticides (more than 12 mg/kg) inhibited microbial growth due to pesticides toxicity, this negative effect in case of rotary drum composting was not observed so the rotary drum composting is an excellent composting technique for the removal of pesticides residue from waste material especially from vegetable waste.

Table.4.2. Pesticides concentration with standard deviation for Aldrin, Lindane, and Endosulfan-α and Endosulfan-β during RD1and W1 composting

RD1								
Days	**Aldrin (µg/kg)**	***SD***	**Endosulfan α(µg/kg)**	***SD***	**Endosulfan β(µg/kg)**	***SD***	**Lindane (µg/kg)**	***SD***
0	712.4600	20.72	960.2950	10.63	447.5431	19.10	169.2667	8.21
4	605.2300	14.28	561.3650	52.38	374.3675	13.34	145.1900	9.00
8	523.0600	21.50	460.8450	14.18	307.9475	20.55	133.4967	7.15
10	427.8350	14.15	434.4450	14.15	268.6781	27.52	112.7167	10.58
14	365.9700	16.31	312.4500	21.26	230.8205	19.49	118.7600	15.15
18	365.2500	21.92	243.8100	17.00	112.8152	15.00	93.3767	6.56
20	325.5450	12.48	199.8350	14.19	99.5013	10.00	85.4500	2.63
24	178.7700	15.36	160.7200	27.93	87.8549	4.96	58.4633	7.33
26	162.7500	15.56	182.0850	10.61	77.5915	1.50	36.0067	9.95
28	120.3450	7.01	206.9400	56.64	63.0214	10.00	30.4400	6.73
30	109.8500	7.00	177.5700	24.75	62.5243	15.00	29.8000	4.88
36	105.6700	8.54	168.6573	10.37	60.5420	10.00	30.5320	5.38
W1								
Days	**Aldrin (µg/kg)**	***SD***	**Endosulfan α(µg/kg)**	***SD***	**Endosulfan β(µg/kg)**	***SD***	**Lindane (µg/kg)**	***SD***
0	692.3350	7.74	966.1300	18.88	585.8563	20.04	174.9000	10.66
4	485.5200	12.80	973.9600	33.80	505.6116	10.15	174.1533	4.77
8	434.3300	23.33	778.4950	14.15	458.6921	10.25	167.7000	1.93
10	406.8700	22.77	614.7600	15.38	419.5413	20.04	147.4067	11.06
14	353.0150	21.84	537.1600	27.61	388.5014	10.00	137.6333	11.58
18	269.5350	10.75	473.5550	21.23	356.7699	10.20	123.1133	10.86
20	216.7100	20.86	457.0600	13.44	366.5156	19.25	97.5967	5.19
24	188.2700	14.84	454.3750	30.41	276.5480	19.75	89.0667	1.51
26	170.1700	23.19	359.4800	15.91	251.2392	23.02	86.4433	1.55
28	163.2800	7.14	342.0350	20.56	173.2428	20.01	78.3767	1.11
30	160.8000	6.86	332.4700	28.31	190.9638	5.71	73.3733	3.00
36	161.5476	5.79	335.6320	15.79	192.7632	2.59	70.5268	3.59

SD = Standard deviation

Table.4.3. Pesticides concentration with standard deviation for Aldrin, Lindane, Endosulfan-α and Endosulfan-β during RD2 and W2 composting

RD2									
Days	**Aldrin (mg/kg)**	***SD***	**Endosulfan α(mg/kg)**	***SD***	**Endosulfan β(mg/kg)**	***SD***	**Lindane (mg/kg)**	***SD***
0	2.6443	0.05	7.3115	0.05	3.1929	0.06	5.1594	0.01
4	1.9764	0.02	5.3663	0.06	4.1550	0.04	4.1387	0.01
8	1.8739	0.02	4.7641	0.06	4.1394	0.03	4.0254	0.02
10	1.6904	0.03	4.1766	0.03	3.2944	0.05	3.8747	0.02
14	1.5490	0.03	4.0588	0.07	3.2048	0.05	3.6614	0.02
18	1.3687	0.01	3.9842	0.09	3.2184	0.05	3.5914	0.00
20	1.2942	0.04	3.4616	0.04	3.2159	0.10	3.5667	0.02
24	1.2543	0.03	3.4323	0.09	2.0508	0.05	3.1150	0.01
26	1.0995	0.01	3.4393	0.16	1.9337	0.02	2.5760	0.01
28	1.0728	0.02	3.4359	0.10	1.8668	0.01	2.3725	0.02
30	0.9732	0.02	3.3784	0.05	1.5786	0.01	2.1554	0.03
36	0.9478	0.02	3.3313	0.07	1.4730	0.02	2.0070	0.01
W2								
Days	**Aldrin (mg/kg)**	***SD***	**Endosulfan α(mg/kg)**	***SD***	**Endosulfan β(mg/kg)**	***SD***	**Lindane (mg/kg)**	***SD***
0	2.5762	0.01	8.1653	0.06	3.1619	0.01	5.1604	0.02
4	1.9607	0.01	6.3186	0.01	4.1627	0.03	4.1821	0.06
8	1.8712	0.02	6.2131	0.01	4.1461	0.03	4.0725	0.06
10	1.6638	0.02	6.0382	0.05	3.2625	0.02	3.8529	0.02
14	1.5875	0.01	6.0870	0.06	3.3271	0.14	3.6427	0.04
18	1.4579	0.10	5.6930	0.02	3.2396	0.05	3.5641	0.02
20	1.3775	0.06	5.4837	0.01	3.1609	0.01	3.5752	0.02
24	1.2928	0.03	5.4174	0.03	2.0623	0.05	3.1248	0.02
26	1.2554	0.06	5.3501	0.10	1.9674	0.03	2.5686	0.03
28	1.2291	0.06	5.1210	0.10	1.8767	0.02	2.4265	0.03
30	1.1174	0.04	4.7166	0.12	1.5805	0.01	2.3866	0.06
36	1.0156	0.03	4.2097	0.20	1.4707	0.01	2.3142	0.02

SD = Standard deviation

Table.4.4. Pesticides concentration with standard deviation for Aldrin, Lindane, Endosulfan-α and Endosulfan-β during RD3 and W3 composting

<table>
<tr><th colspan="9">RD3</th></tr>
<tr><th>Days</th><th>Aldrin (mg/kg)</th><th><i>SD</i></th><th>Endosulfan α(mg/kg)</th><th><i>SD</i></th><th>Endosulfan β(mg/kg)</th><th><i>SD</i></th><th>Lindane (mg/kg)</th><th><i>SD</i></th></tr>
<tr><td>0</td><td>10.9421</td><td>0.03</td><td>11.2507</td><td>0.10</td><td>5.2661</td><td>0.10</td><td>11.4710</td><td>0.13</td></tr>
<tr><td>4</td><td>8.7250</td><td>0.05</td><td>10.1724</td><td>0.07</td><td>5.6136</td><td>0.15</td><td>10.3141</td><td>0.06</td></tr>
<tr><td>8</td><td>7.4704</td><td>0.03</td><td>9.5164</td><td>0.05</td><td>6.0450</td><td>0.01</td><td>8.9831</td><td>0.01</td></tr>
<tr><td>10</td><td>6.6287</td><td>0.07</td><td>6.4557</td><td>0.08</td><td>8.0986</td><td>0.03</td><td>7.1659</td><td>0.03</td></tr>
<tr><td>14</td><td>5.5766</td><td>0.05</td><td>5.1825</td><td>0.01</td><td>7.5343</td><td>0.01</td><td>6.5973</td><td>0.05</td></tr>
<tr><td>18</td><td>4.5720</td><td>0.08</td><td>5.1950</td><td>0.07</td><td>7.5006</td><td>0.07</td><td>5.4445</td><td>0.05</td></tr>
<tr><td>20</td><td>3.9091</td><td>0.02</td><td>4.1697</td><td>0.06</td><td>5.6198</td><td>0.07</td><td>5.1363</td><td>0.01</td></tr>
<tr><td>24</td><td>3.3855</td><td>0.06</td><td>3.8106</td><td>0.04</td><td>4.6587</td><td>0.08</td><td>4.7303</td><td>0.06</td></tr>
<tr><td>26</td><td>3.2983</td><td>0.07</td><td>3.4478</td><td>0.01</td><td>4.3804</td><td>0.12</td><td>4.0923</td><td>0.01</td></tr>
<tr><td>28</td><td>2.7091</td><td>0.06</td><td>3.0295</td><td>0.02</td><td>4.0729</td><td>0.01</td><td>3.8852</td><td>0.01</td></tr>
<tr><td>30</td><td>2.0728</td><td>0.02</td><td>2.9428</td><td>0.09</td><td>3.3690</td><td>0.01</td><td>3.1640</td><td>0.01</td></tr>
<tr><td>36</td><td>1.9107</td><td>0.01</td><td>2.6998</td><td>0.01</td><td>3.0812</td><td>0.08</td><td>2.7697</td><td>0.01</td></tr>
<tr><th colspan="9">W3</th></tr>
<tr><th>Days</th><th>Aldrin (mg/kg)</th><th><i>SD</i></th><th>Endosulfan α(mg/kg)</th><th><i>SD</i></th><th>Endosulfan β(mg/kg)</th><th><i>SD</i></th><th>Lindane (mg/kg)</th><th><i>SD</i></th></tr>
<tr><td>0</td><td>12.8911</td><td>0.08</td><td>11.7841</td><td>0.05</td><td>5.4718</td><td>0.19</td><td>11.3147</td><td>0.01</td></tr>
<tr><td>4</td><td>11.7353</td><td>0.05</td><td>11.4451</td><td>0.29</td><td>5.6264</td><td>0.16</td><td>10.3395</td><td>0.11</td></tr>
<tr><td>8</td><td>10.6371</td><td>0.06</td><td>9.7498</td><td>0.05</td><td>6.3169</td><td>0.26</td><td>10.2437</td><td>0.06</td></tr>
<tr><td>10</td><td>8.5287</td><td>0.04</td><td>8.4557</td><td>0.08</td><td>7.0986</td><td>0.03</td><td>9.1874</td><td>0.01</td></tr>
<tr><td>14</td><td>8.3299</td><td>0.07</td><td>7.1825</td><td>0.01</td><td>7.2010</td><td>0.06</td><td>8.8640</td><td>0.20</td></tr>
<tr><td>18</td><td>7.3393</td><td>0.03</td><td>7.2617</td><td>0.06</td><td>7.5006</td><td>0.07</td><td>8.3239</td><td>0.06</td></tr>
<tr><td>20</td><td>6.9493</td><td>0.03</td><td>7.1697</td><td>0.06</td><td>6.6198</td><td>0.07</td><td>7.7314</td><td>0.08</td></tr>
<tr><td>24</td><td>6.8522</td><td>0.02</td><td>6.8106</td><td>0.04</td><td>5.5339</td><td>0.05</td><td>7.5558</td><td>0.08</td></tr>
<tr><td>26</td><td>6.7287</td><td>0.07</td><td>6.4478</td><td>0.01</td><td>5.3804</td><td>0.12</td><td>7.4283</td><td>0.06</td></tr>
<tr><td>28</td><td>5.9178</td><td>0.05</td><td>6.0295</td><td>0.02</td><td>5.0729</td><td>0.01</td><td>7.1639</td><td>0.07</td></tr>
<tr><td>30</td><td>5.5495</td><td>0.05</td><td>5.9428</td><td>0.09</td><td>4.4374</td><td>0.11</td><td>6.9021</td><td>0.06</td></tr>
<tr><td>36</td><td>5.1115</td><td>0.04</td><td>5.6998</td><td>0.01</td><td>4.0812</td><td>0.08</td><td>6.7749</td><td>0.04</td></tr>
</table>

SD = Standard deviation

- ***Removal of Aldrin, Endosulfan (α & β) and Lindane in leachate generation during W1, W2 and W3 composting.***

The removal of pesticides through leachate generation in windrow composting (W1, W2 and W3) shown in Fig.4.10 & 4.11. This is the drawback of windrow composting in which organic fraction, nutrients and pollutant like pesticides and heavy metals leachate out into the soil and further accumulate into the soil, crops and pollute the ground water. During the windrows composting, the removal of Aldrin, Endosulfan α, Endosulfan β and Lindane through leachate generation was 0.3878, 0.4903, 0.2775 and 0.9927 mg/kg (cumulative 2.1483mg/kg) in W1, 1.7844, 4.865, 2.092 and 4.2359 mg/kg(cumulative 12.9773 mg/kg) in W2 and 4.9864, 4.931, 2.5163, 6.5793 mg/kg (cumulative 19.013mg/kg) respectively in W3. It is found that around 40 -45% of pesticides were removed without degradation through leachate generation during windrows composting.

Fig.4.10. Leachate generation during windrows composting

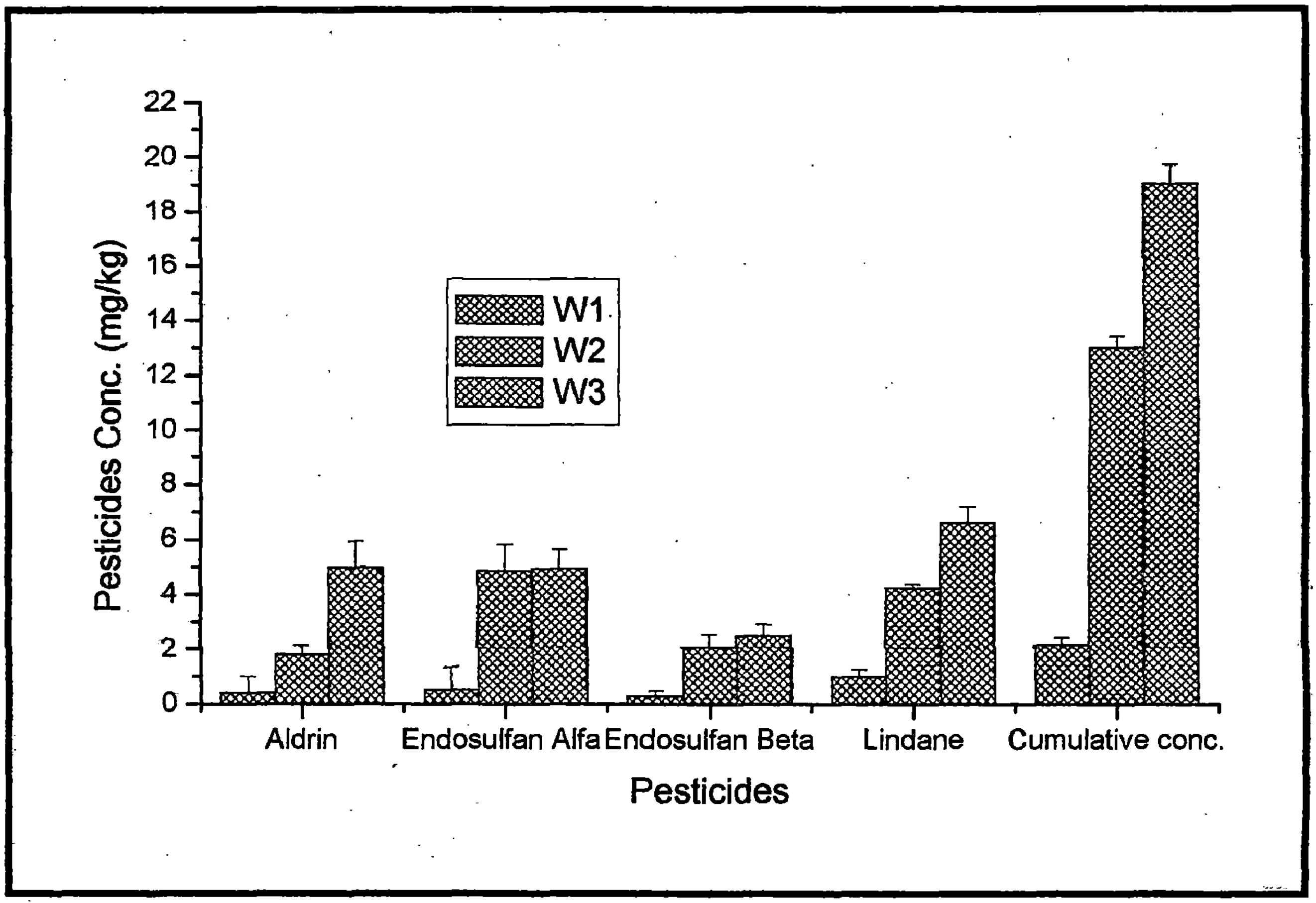


Fig.4.11. Removal of Aldrin, Endosulfan (α & β) and Lindane with error bars in leachate generation during W1, W2 and W3 composting.

4.1.1.3. First Order kinetics

For the degradation of organochlorine pesticides, rate constant of degradation and half-life period of the three pesticides in three different cases during rotary drum and windrow composting are thus calculated using, Eqs.1 and 2 respectively.

$$\ln c = -kt + A \quad \ldots\ldots 1$$

Generally, the rate of abiotic hydrolysis for organic compounds in water is directly proportional

to the concentration of the organic compound (Lyman, *et al*; 1990). Assuming this relation, abiotic hydrolysis can be described using a first order degradation curve:

$$C_t = C_0 e^{-kt} \quad \ldots\ldots 2$$

Where C_t is the concentration of the organic species at time t, C_0 is the initial concentration of the organic species, and k is the rate constant (Wang, *et al;* 1991).

- ***Half-life calculation***

A plot of ln (C_t/C_0) versus time yields a straight line with slope equal to k. The rate constant can then be used to derive the half life $t_{1/2}$:

$$t_{1/2} = \ln 2/k \quad \ldots\ldots 3$$

Or

$$t_{1/2} = 0.693/k \quad \ldots\ldots 4$$

Where k is a constant and $t_{1/2}$ is half-life period of the pesticide. The obtained values are listed in table. 4.5.

To compare the degradation of pesticides Aldrin, Endosulfan α, Endosulfan β and Lindane in the composting through rotary drum and windrows with different concentration levels, the corresponding rate constants and half life periods and degradation kinetics were listed in table 4.5 and Fig. 4.12, 4.13, 4.14, 4.15, 4.16 and 4.17. The degradation of Aldrin, Endosulfan α, Endosulfan β and Lindane in all three cases during RD1, RD2, and RD3 composting increased due to higher temperature range, optimum moisture range and more alkaline pH throughout the composting process, lead to a larger rate constant of degradation 0.0410, 0.0761, 0.0606 and 0.0428/day for Aldrin, Endosulfan α, Endosulfan β and Lindane respectively or a shorter half-live period 17.03, 9.71, 11.85 and 17.49 days respectively of these pesticides in case 1 compared to case 1 of windrow composting (table 4.5). Similarly, in case 2 the rate constant for Aldrin, Endosulfan α, Endosulfan β and Lindane, 0.0537, 0.0566, 0.0096, and 0.0664/day is higher and half life period is lower for Aldrin, Endosulfan α, Endosulfan β and Lindane, 13.6305, 13.8828, 30.4645 and 11.5886 days respectively during drum composting compare to windrow composting (rate constant 0.0488, 0.0309, 0.0088 0.0206/day) and (half life period 15.3965, 25.0770, 37.7564, and 13.4252 days). In case 3, at higher pesticide concentration (cumulative 42.21-43.38 mg/kg) in both the rotary drum and windrow composting, the rate constant was more (0.0778, 0.0610, 0.0092 and 0.0719/day) and half life period less (9.02, 11.95, 21.97 and 9.69 days) than the conventional windrows composting given in table 4.5. It is due to more and easily available pesticides compared to pesticides found in real vegetable waste.

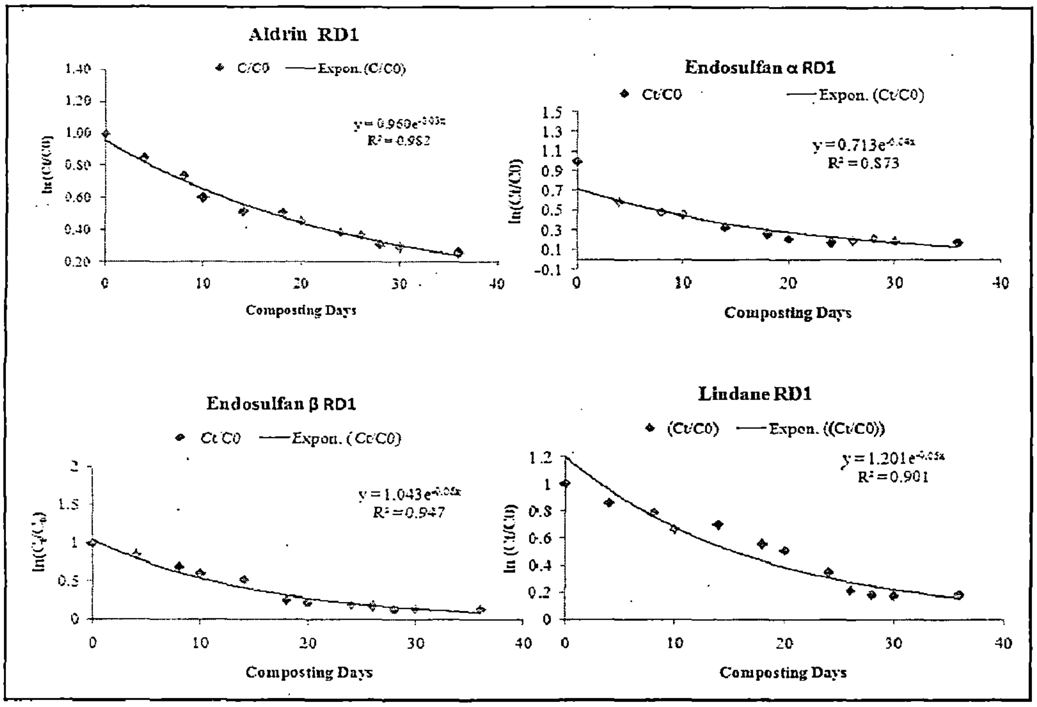


Fig.4.12. Degradation kinetics of Aldrin, Endosulfan (α & β) and Lindane during RD 1 composting.

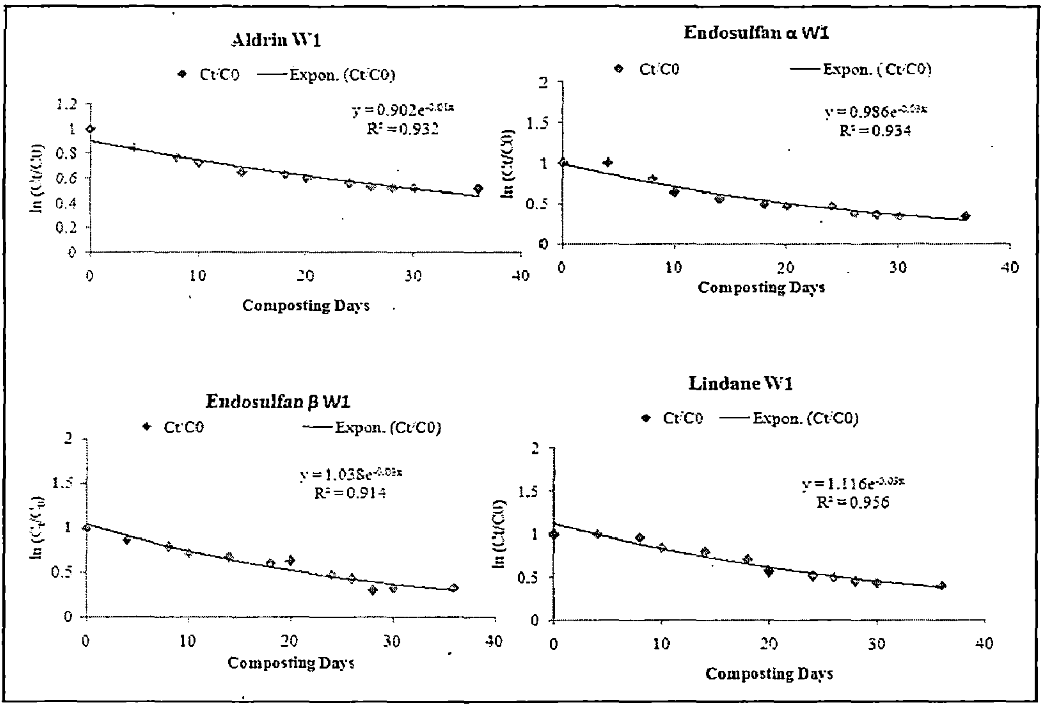


Fig.4.13. Degradation kinetics of Aldrin, Endosulfan (α & β) and Lindane during W 1 composting.

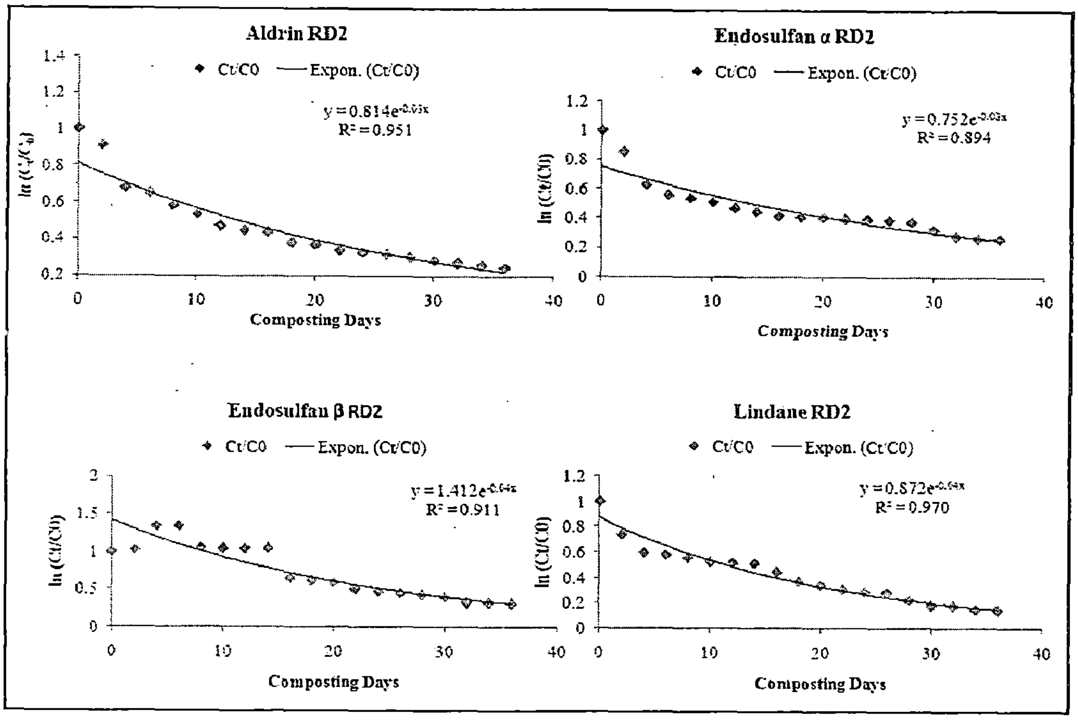


Fig.4.14. Degradation kinetics of Aldrin, Endosulfan (α & β) and Lindane during RD 2 composting.

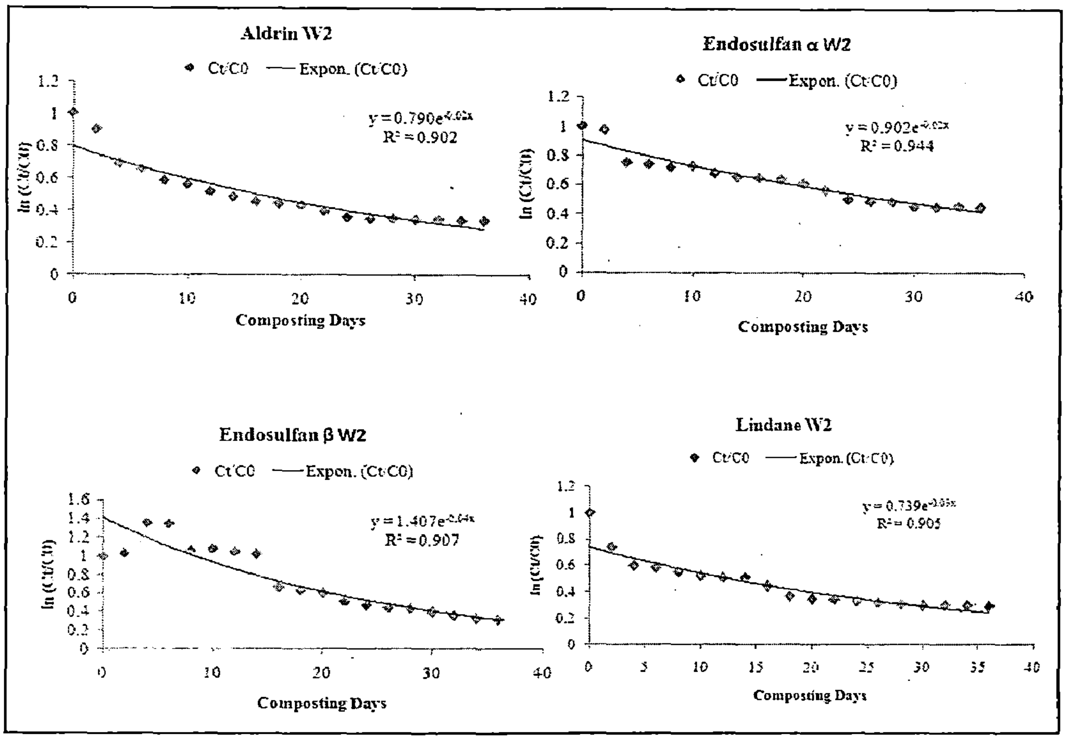


Fig.4.15. Degradation kinetics of Aldrin, Endosulfan (α & β) and Lindane during W 2 composting.

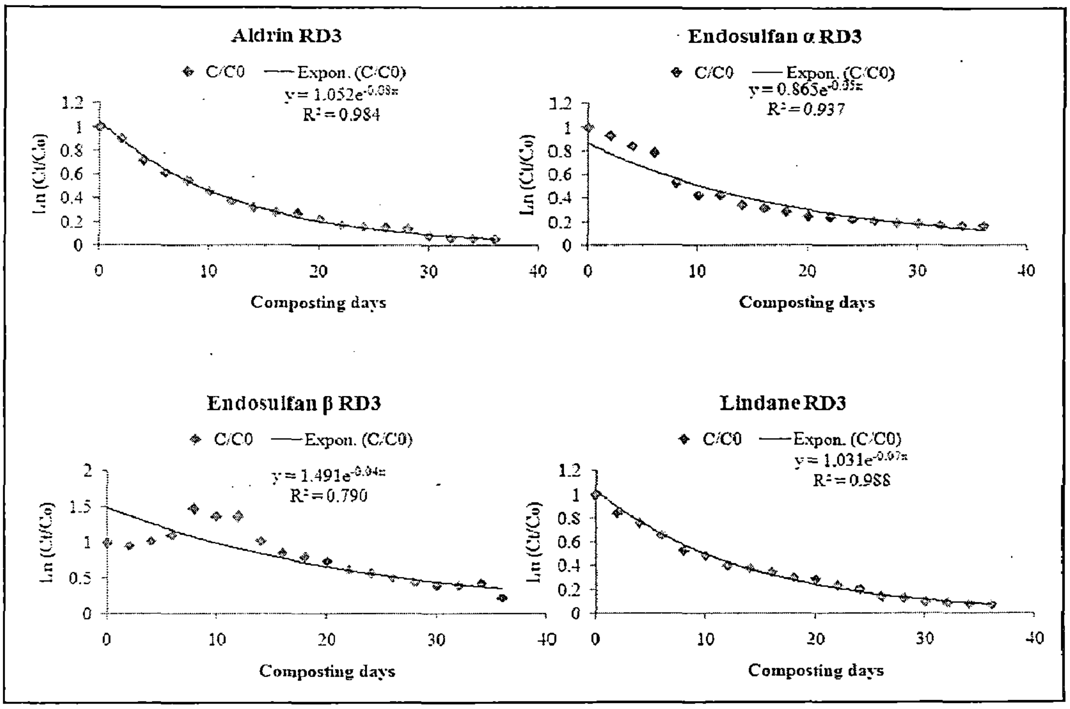


Fig.4.16. Degradation kinetics of Aldrin, Endosulfan (α & β) and Lindane during RD 3 composting.

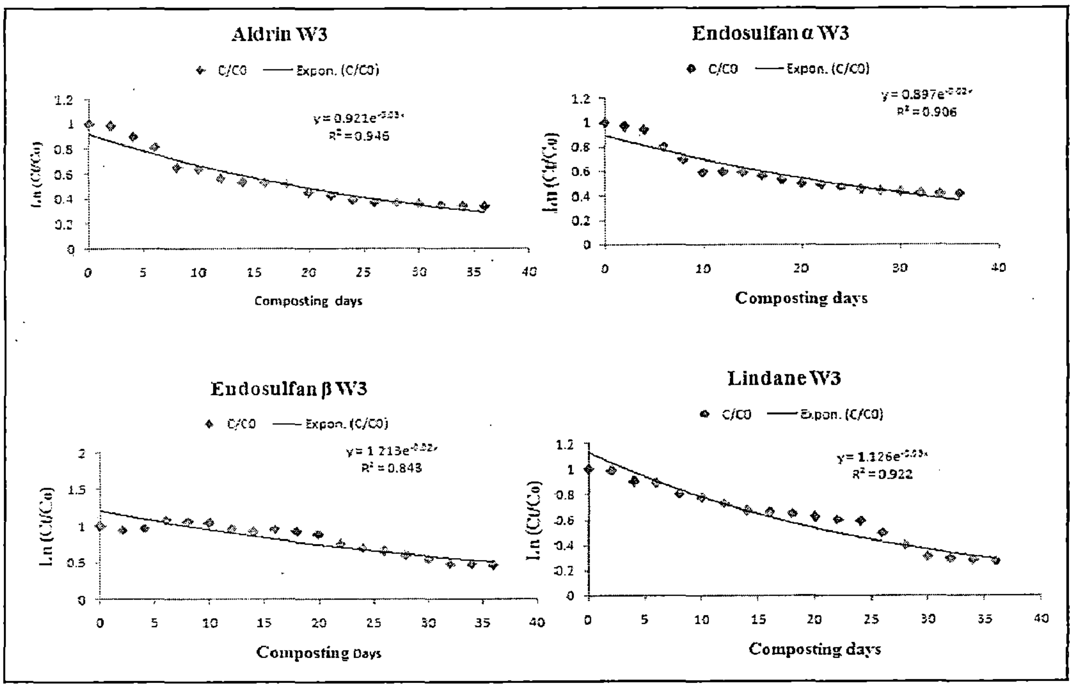


Fig.4.17. Degradation kinetics of Aldrin, Endosulfan (α & β) and Lindane during W 3 composting.

Table.4.5. Kinetic parameters for degradation of four pesticides in the RD1, RD2, RD3 and W1, W2, W3 composting.

Kinetic parameters						
(Case-1)	**RD1**			**W1**		
Pesticides	***k value* (day^{-1})**	R^2	$t_{1/2 (Days)}$	***k value***	R^2	$t_{1/2 (Days)}$
Aldrin	0.0410	0.9820	17.0366	0.0270	0.9320	26.8097
Endosulfan α	0.0761	0.8730	9.7805	0.0327	0.9340	13.4539
Endosulfan β	0.0606	0.9470	11.8579	0.0324	0.9140	21.9251
Lindane	0.0428	0.9010	17.4942	0.0206	0.9560	95.1898
(Case-2)	**RD2**			**W2**		
Pesticides	***k value* (day^{-1})**	R^2	$t_{1/2 (Days)}$	***k value***	R^2	$t_{1/2 (Days)}$
Aldrin	0.0537	0.9510	13.6305	0.0488	0.9020	15.3965
Endosulfan α	0.0566	0.8940	13.8828	0.0309	0.9440	25.0770
Endosulfan β	0.0096	0.9110	30.4642	0.0088	0.9070	27.7564
Lindane	0.0664	0.9700	11.5886	0.0607	0.9050	13.4252
(Case-3)	**RD3**			**W3**		
Pesticides	***k value* (day^{-1})**	R^2	$t_{1/2 (Days)}$	***k value***	R^2	$t_{1/2 (Days)}$
Aldrin	0.0778	0.9840	9.0188	0.0365	0.9460	23.3892
Endosulfan α	0.0610	0.9370	11.9557	0.0319	0.9060	24.3501
Endosulfanβ	0.0092	0.7900	21.9707	0.0095	0.8430	59.7707
Lindane	0.0719	0.9880	9.6988	0.0274	0.9220	28.7912

k- Rate constant of degradation, R-coefficient of regression, $t_{1/2}$- half life period.

4.1.1.4. Mechanism of Pesticides Biotransformation

- ***Mechanism of Aldrin Biotransformation***

Aldrin converts to dieldrin by epoxidation by taking oxygen from the system. Dieldrin then converted to the Aldrin diol by the hydroxylation reaction (Fig.4.18). After that aldrin diol liberate ethylene molecule to give product (A) and rearrangement give 1-hydroxychlordene and its isomer. 1-Hydroxychlordene further oxidized by the two hydroxyl group and further oxidized to acidic (B) and aldehydic (C) product. Then, it converted to aldehydic (D) product by the liberation of CO_2 gas. Aldehydic moiety of aldrin finally converted to 4,7-methanoisobenzofuran, 4,5,6,7,8,8-hexachloro-1,3,3a,4,7,7a-hexahydro-, by the elimination of H_2O.

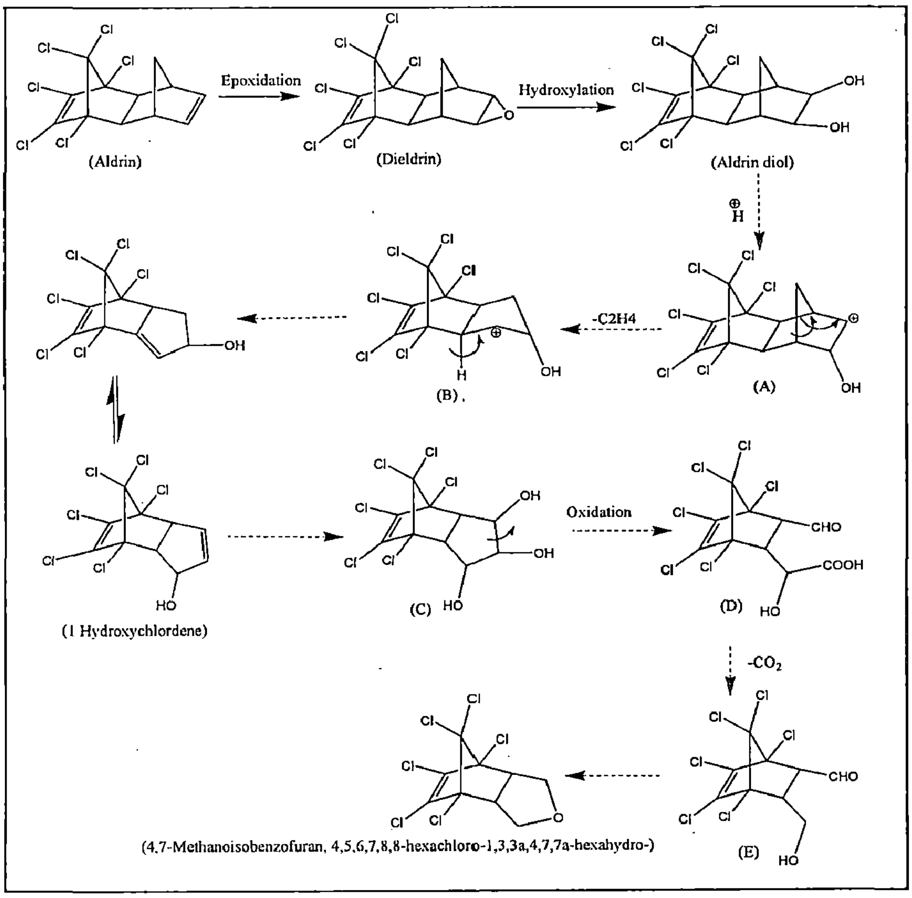


Fig.4.18. Degradation pathway of Aldrin under aerobic condition, (Bold arrow for reported compounds and dotted arrow for new compounds), A, B, C, D, E, is the possible intermediates, formed in composting.

- ***Mass spectra of Aldrin and its intermediate compounds and their conformation***

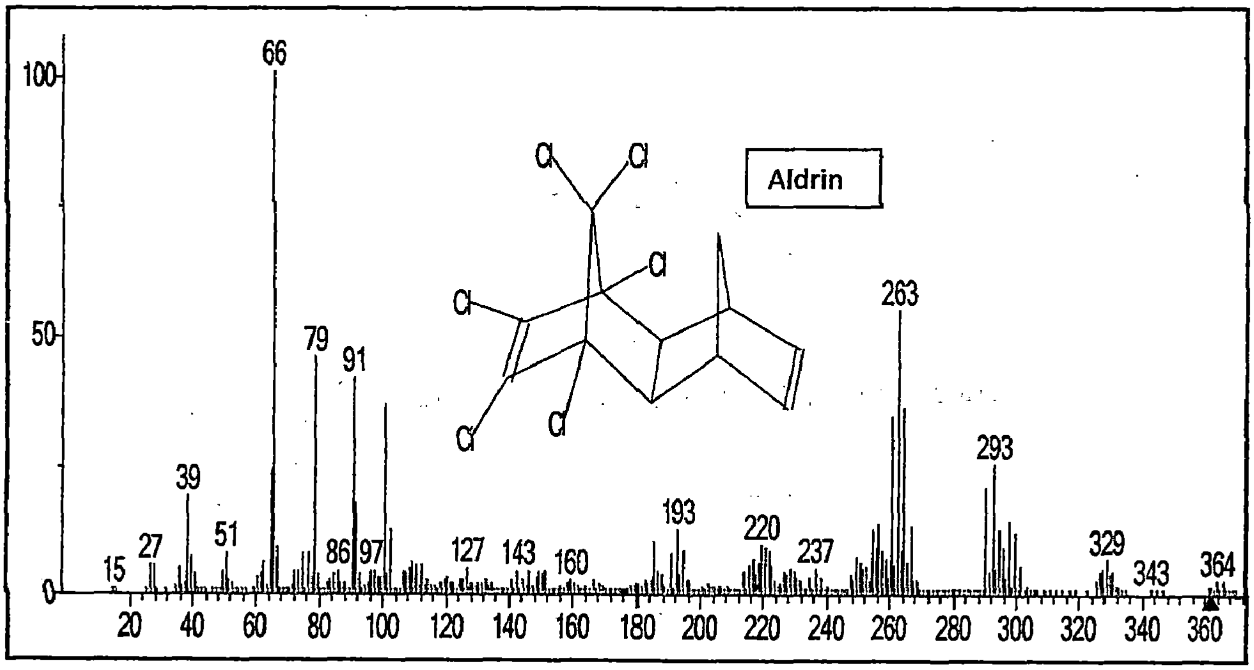
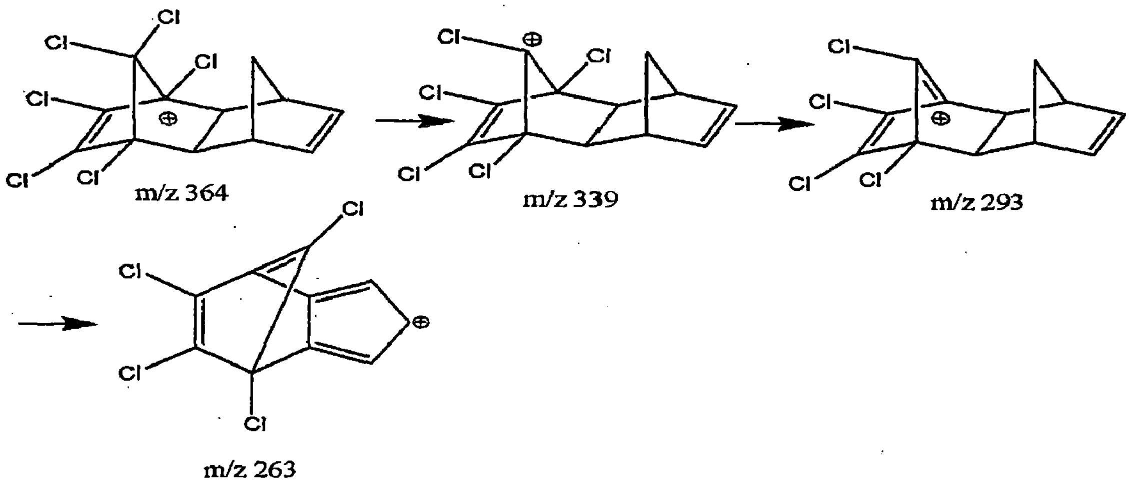
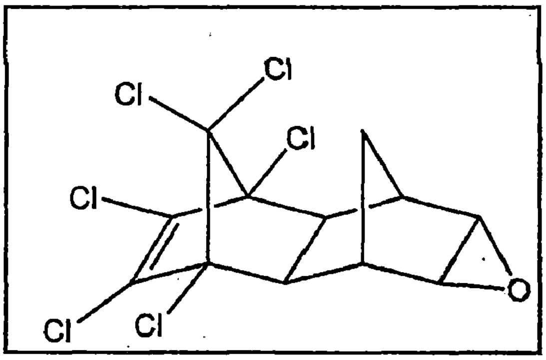


Fig.4.19. Mass fragments of Aldrin



Relative intensities of chlorine isotopic peaks at m/z 364, 293, 263 and 193 are 60:80:40:1. It confirmed the compounds have six chlorine atoms in its formula.



Dieldrin

(2,7,3,6-Dimethanonaphth[2,3-b] oxiren-8-ol,3,4,5,6,9,10-chloro-)

(M.W. 378)

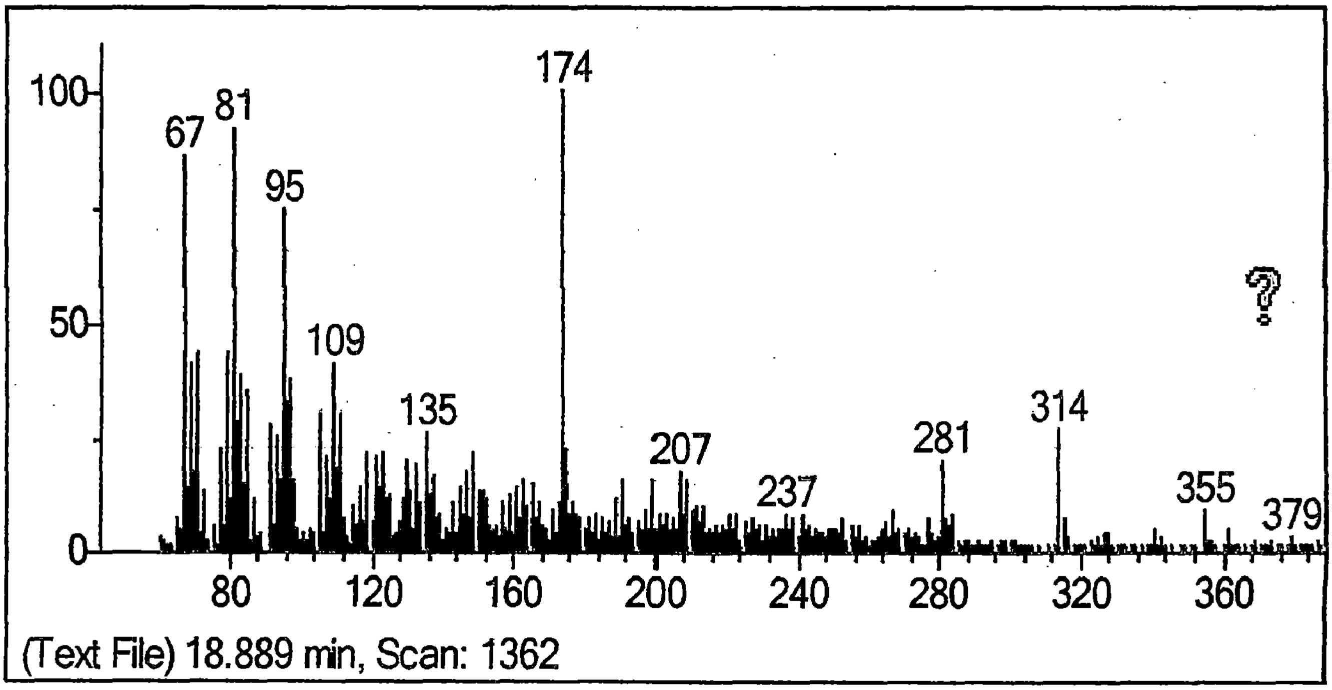
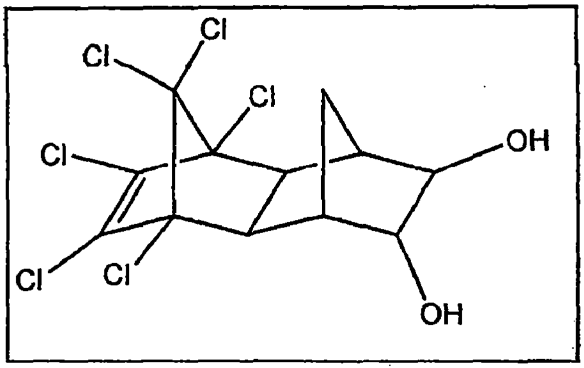


Fig.4.20. Mass fragments of Dieldrin

Relative intensities of chlorine isotopes peaks at m/z 378, 281 and 109 are 60:80:40:1. It confirmed the compounds have six chlorine atoms in its formula and m/z at 174 isotopic ratio 3:1 confirmed mono-chlorinated compound in its decomposition.



Dihydroxydieldrin

(2, 7, 3, 6-Dimethanonapth [2, 3-b] oxiran-8-ol, 3,4,5,6,9,10 chloro-) M.W. 398.9

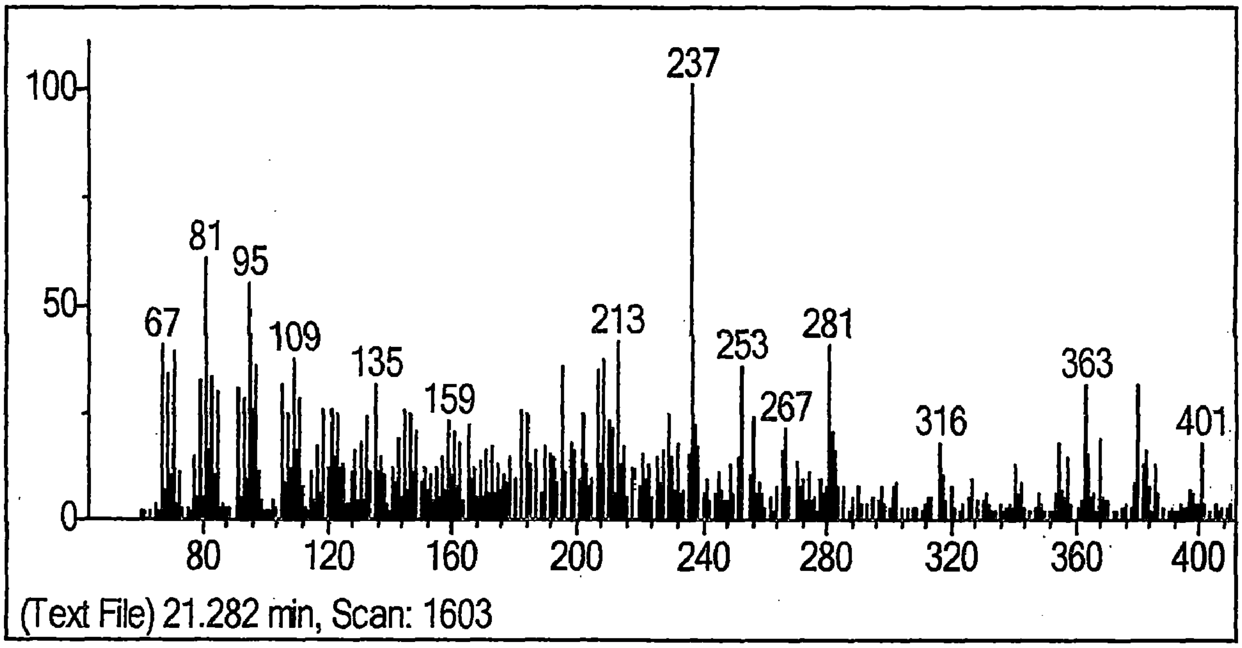
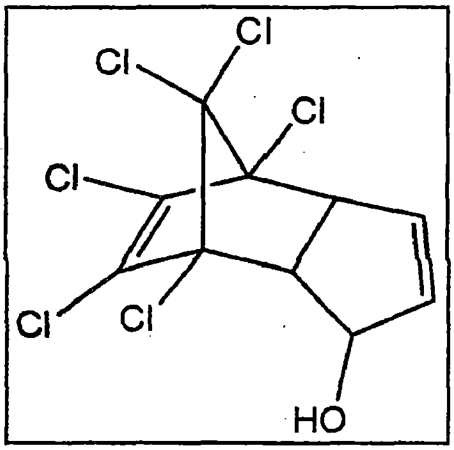


Fig.4.21. Mass fragments of Dihydroxydieldrin

Relative intensities of chlorine isotopes peaks at m/z 293, 263 and 168 are 60:80:40:1. It confirmed the compounds have six chlorine atoms in its formula and m/z at 237 isotopic ratio 3:1 confirmed mono-chlorinated compound in its decomposition.



1- Hydroxychordin

(M.W. 357.8)

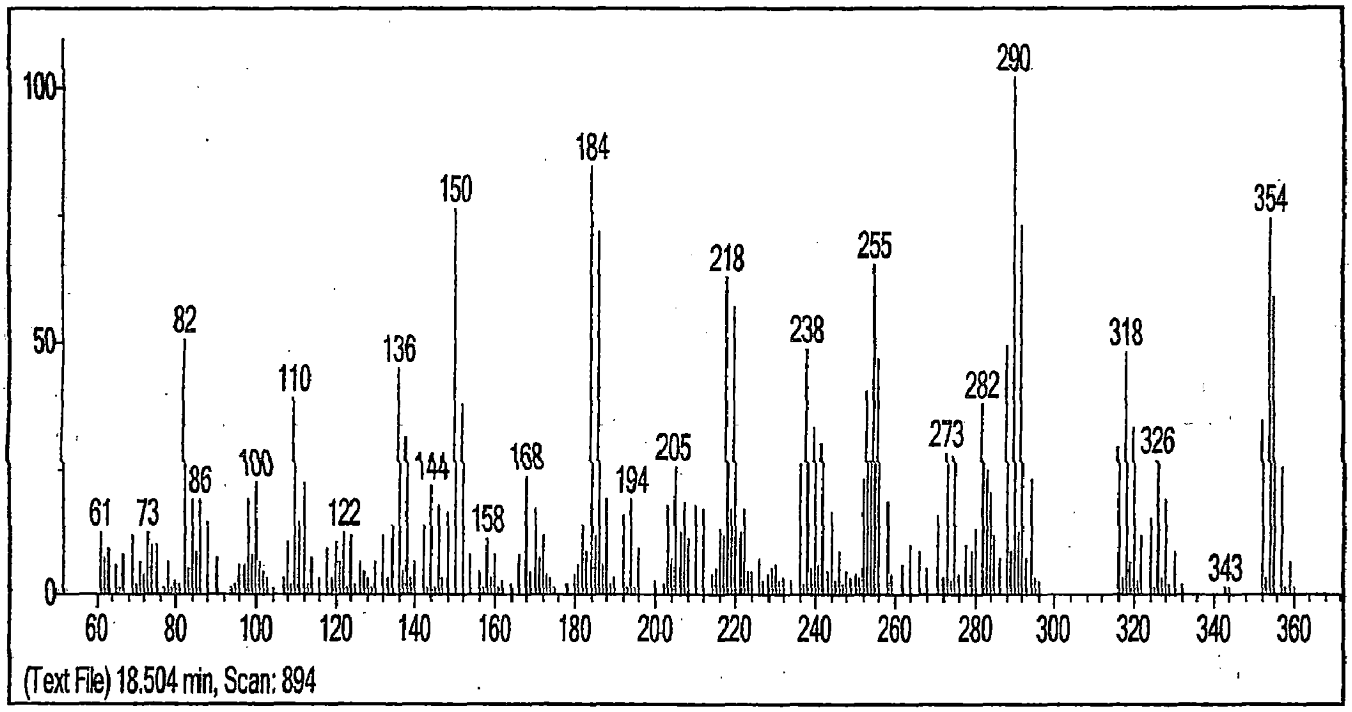


Fig.4.22. Mass fragments of 1-Hydroxychordin

Relative intensities of chlorine isotopes peaks at m/z 354, 318 and 290 are 60:80:40:1. It confirmed the compounds have six chlorine atoms in its formula and m/z at 184 and 150 isotopic ratio 9: 6:1 confirmed di-chlorinated compounds in its decomposition.

Mechanism of Endosulfan Biotransformation

There are several considerable factors for microorganisms to live in composting material, like moisture content as one of the most influential factor in endosulfan degradation. pH, concentration of endosulfan and composting period to be the principal factor in endosulfan degradation. Photolysis may be another factor. Endosulfan in this study converted several moieties with the complex microbial communities of composting material in rotary drum and windrows. Initially, endosulfan isomerised to the endosulfan β and by taking one oxygen molecule converted to endosulfan sulfate (Fig.4.23). Endosulfan sulfate is very toxic and persistent in environment but in the rotary drum composting it was easily converted to endosulfan ether by the liberation of SO_3 gas. Endosulfan ether suddenly converted to chlorendic acid by taking water molecule and then changed to chlorendic anhydride by dehydration. Finally, chlorendic anhydride converted by the microbial species to the 4, 5, 6, 7-tetrachloro-3-hydroxy-3H-isobenzofuran-1-one, taking out of two chloride ions. 4, 5, 6, 7-Tetrachloro-3-hydroxy-3H-isobenzofuran-1-one, was not degraded further and persist in the composting environment but less toxic.

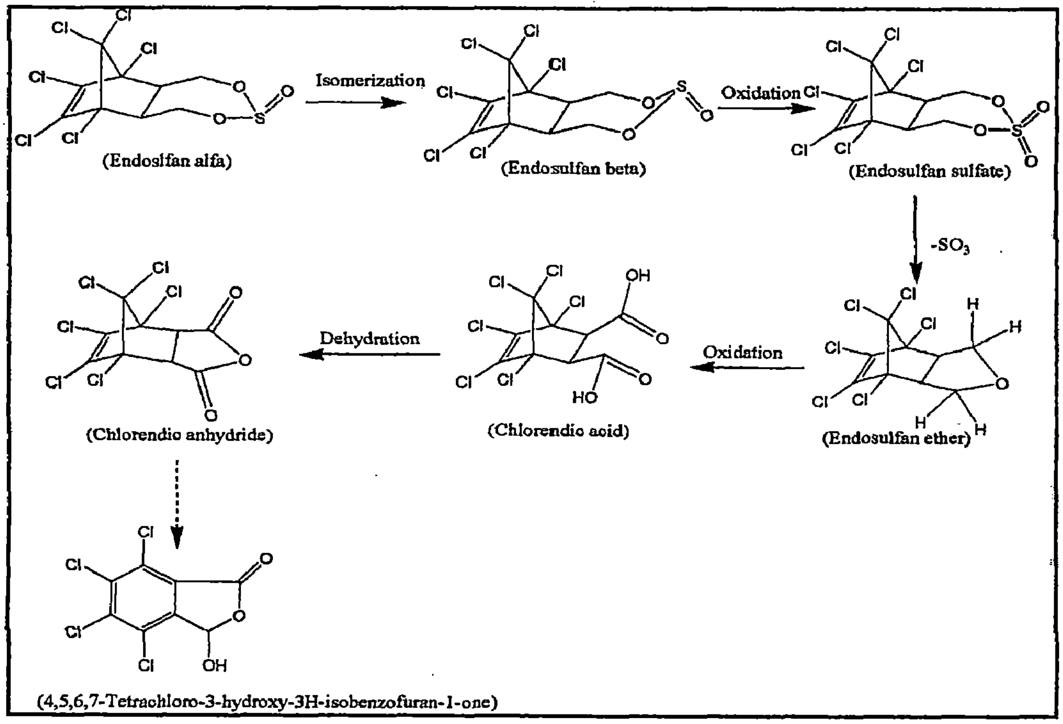


Fig.4.23. Degradation pathway of Endosulfan under aerobic condition, (Bold arrow for reported compounds and dotted arrow for new compounds.

- ***Mass spectra of Endosulfan and its intermediate compounds and their conformation***

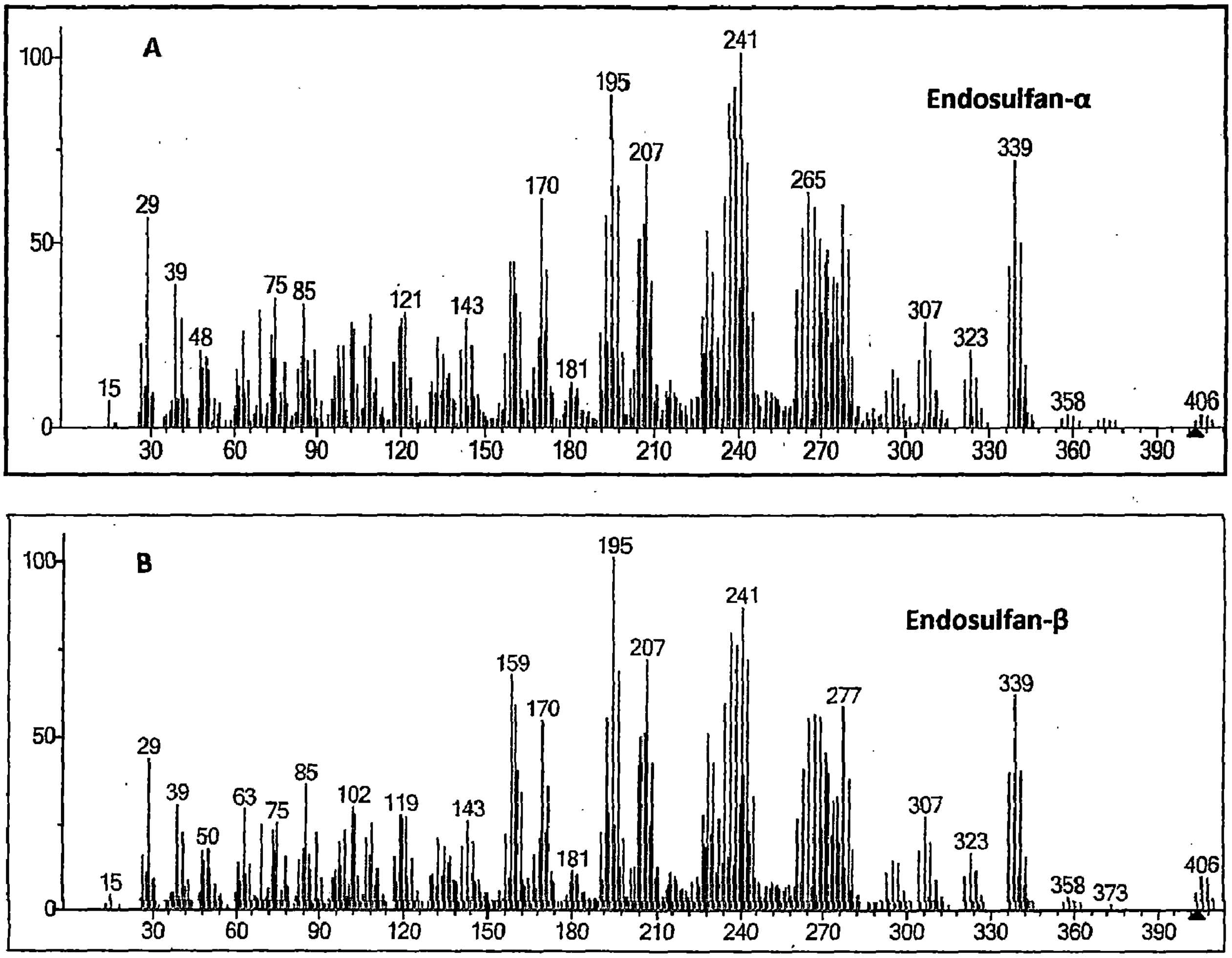
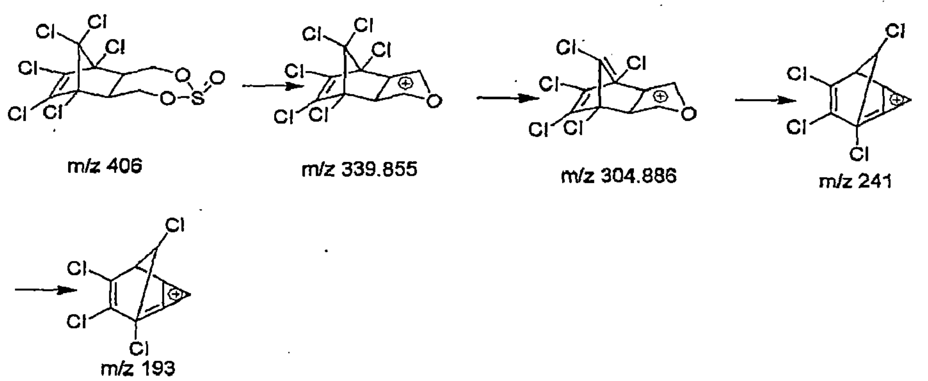
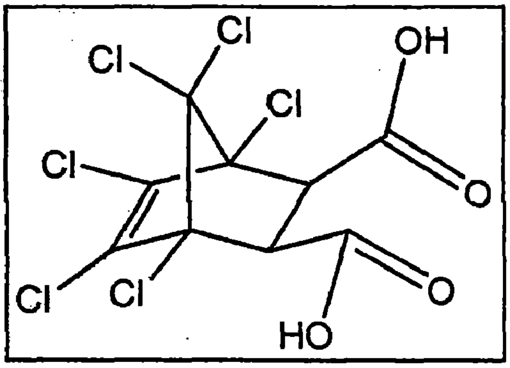


Fig.4.24 Mass fragments (A) Endosulfan-α; (B) Endosulfan-β



Relative intensities of chlorine isotopes peaks at m/z 406, 339, 241 and 195 are 60:80:40:1. It confirmed the compounds have six chlorine atoms in its formula.



Chlorendic acid
(M.W. 388.84)

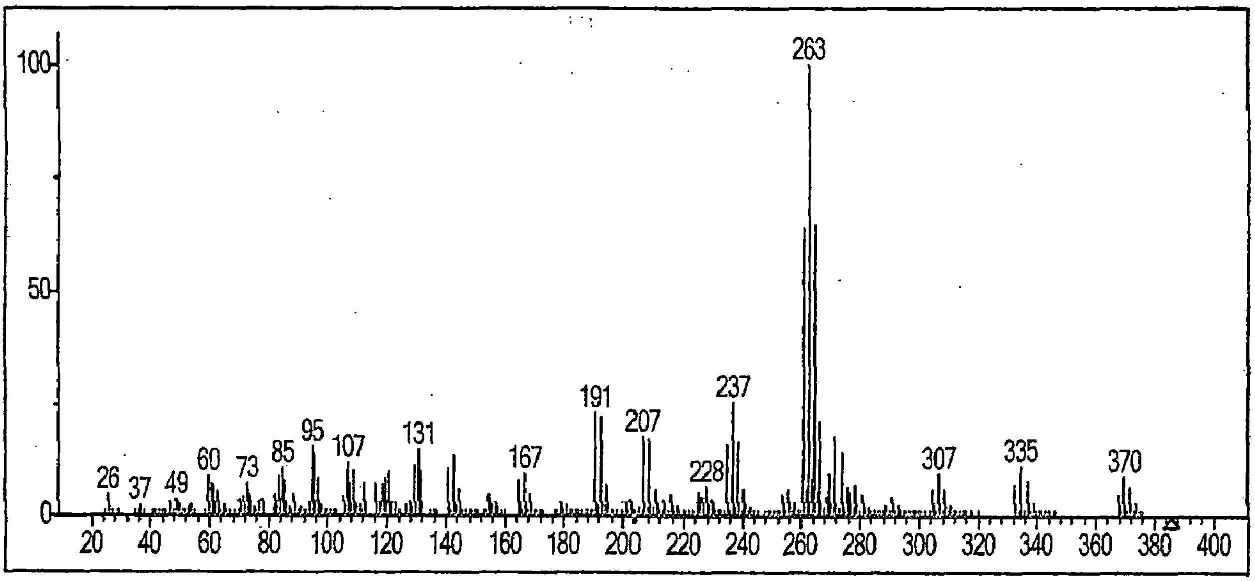
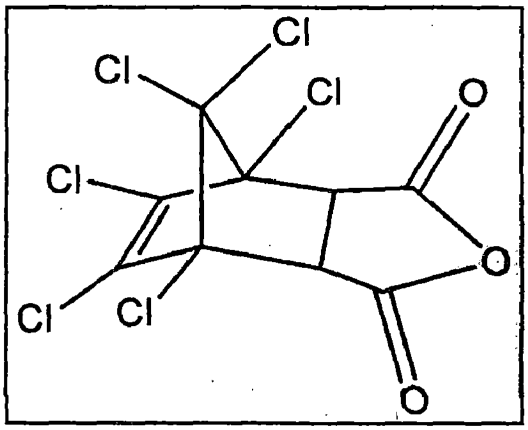


Fig.4.25. Mass fragments of Chlorendic acid

Relative intensities of chlorine isotopes peaks at m/z 237, 263, 307 and 270 are 60:80:40:1. It confirmed the compounds have six chlorine atoms in its formula.



Chlorendic anhydrid
(M.W. 370)

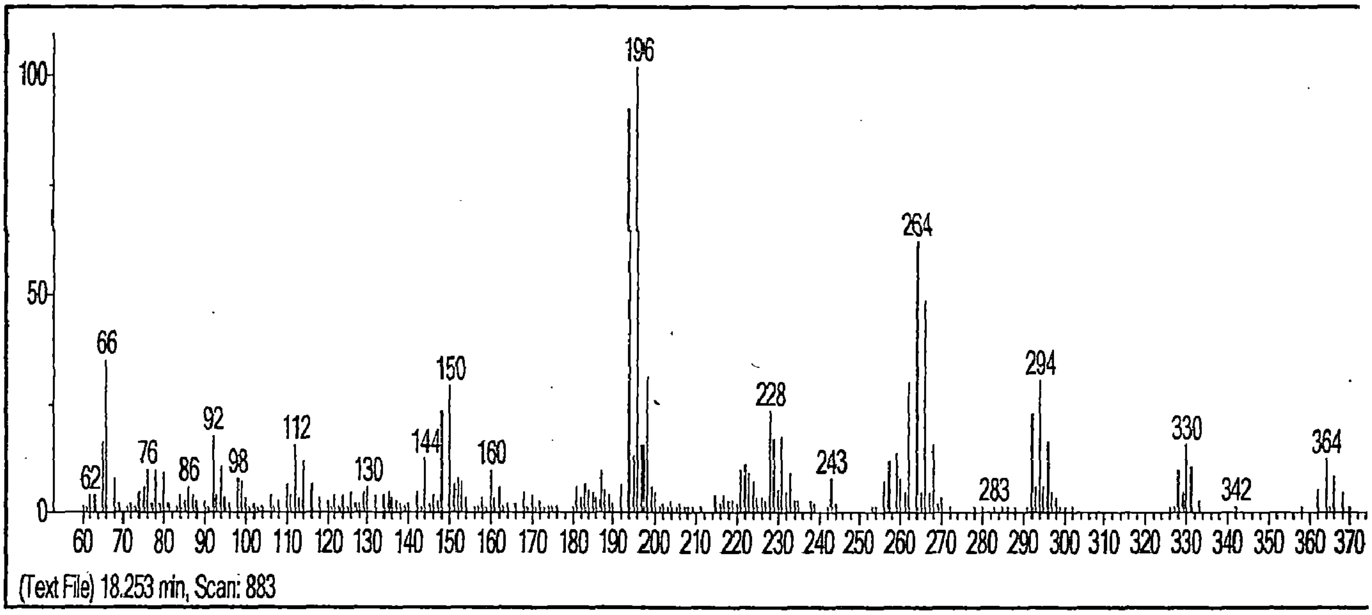
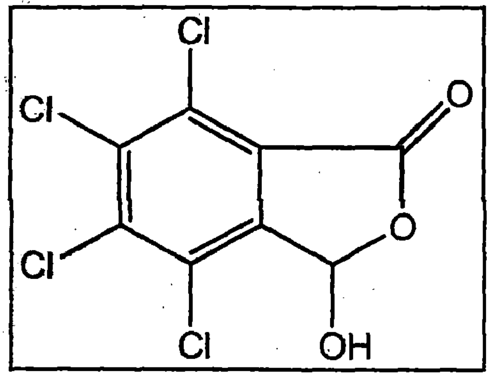


Fig.4.26. Mass fragments of Chlorendic anhydrid

Relative intensities of chlorine isotopes peaks at m/z 364, 330 264 and 196 are 60:80:40:1. It confirmed the compounds have six chlorine atoms in its formula.



4,5,6,7-Tetrachloro-3-hydroxy-3H-isobenzofuran-1-one

(M.W. 285.88)

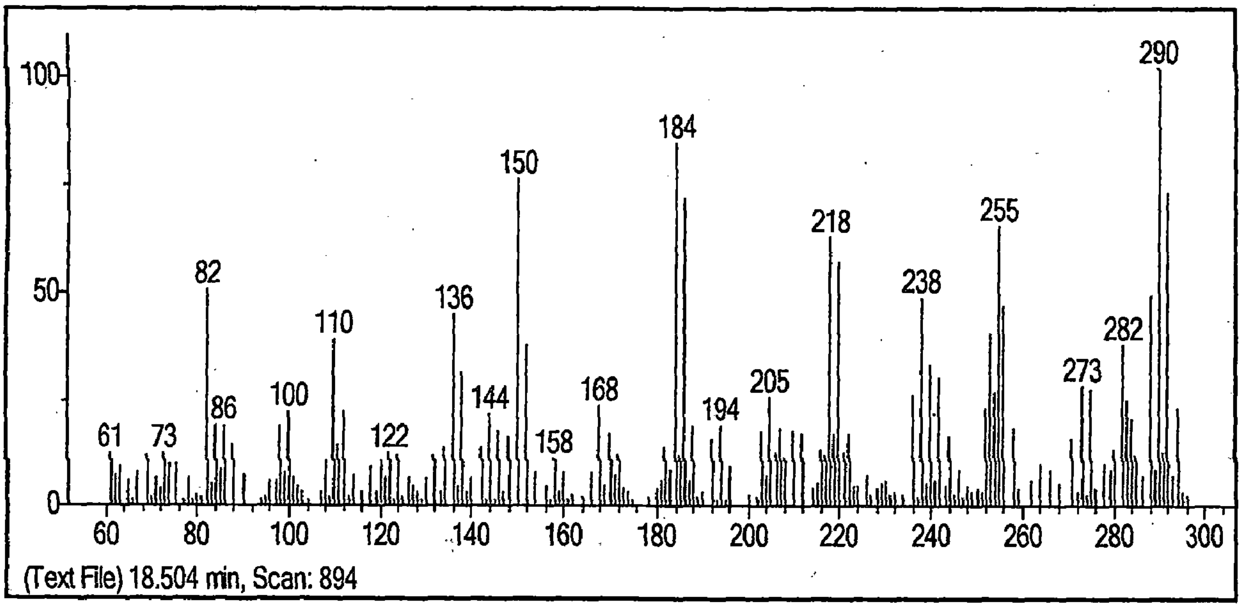


Fig.4.27. Mass fragments of 4,5,6,7-Tetrachloro-3-hydroxy-3H-isobenzofuran-1-one

Relative intensities of chlorine isotopes peaks at m/z 390, 255 and 238 are 60:80:40:1. It confirmed the compounds have four chlorine atoms in its formula and m/z at 184 and 218 was 9: 6:1 showed four chlorine atom compunds eleminating two Cl atoms.

- ***Mechanism of Lindane Biotransformation:***

Under aerobic condition, γ-Lindane isomer converted to β-Lindane, which is most persistent in the environment (Fig.4.28 and 4.29). However, in drum composting β-isomer undergoes dehydrohelogenation and dehalogenation to afford pentachlorocychlohexene (PeCCh) and tetrachlorocychlohexene (TeCCh) compounds respectively. Then, PeCCh converted to pentachlorocychlohexanone under aerobic condition followed by 1,2,3,5-tetrachlorocychlohexanone after dehalohydrogenation and finally converted to 1,2,3 trichlorocychlohexenone after dehydrogenation. TeCCh gave 1,3,5-trichloro-1,4-dihydroxybenzen intermediate by oxidation followed by 1,2,3 trichlorocychlohexenone and 1,3,5-trichloro-1,4-dihydroxybenzen, less toxicity than the Lindane and its β-isome.

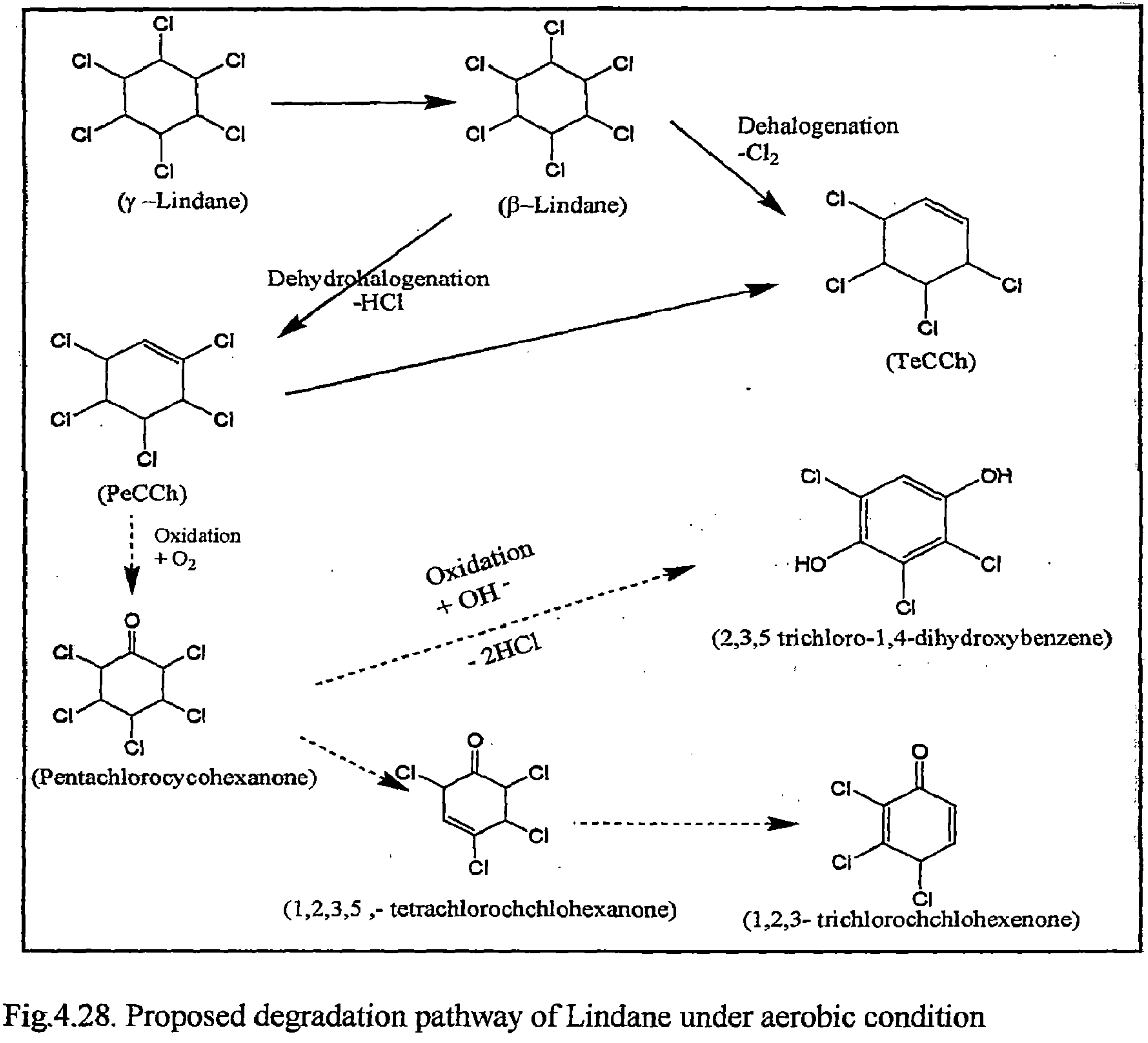


Fig.4.28. Proposed degradation pathway of Lindane under aerobic condition
(Bold arrow for reported compounds and dotted arrow for new compounds, PeCCh-Pentachlorocychlohexene, TeCCh-Tetrachlorocychlohexene)

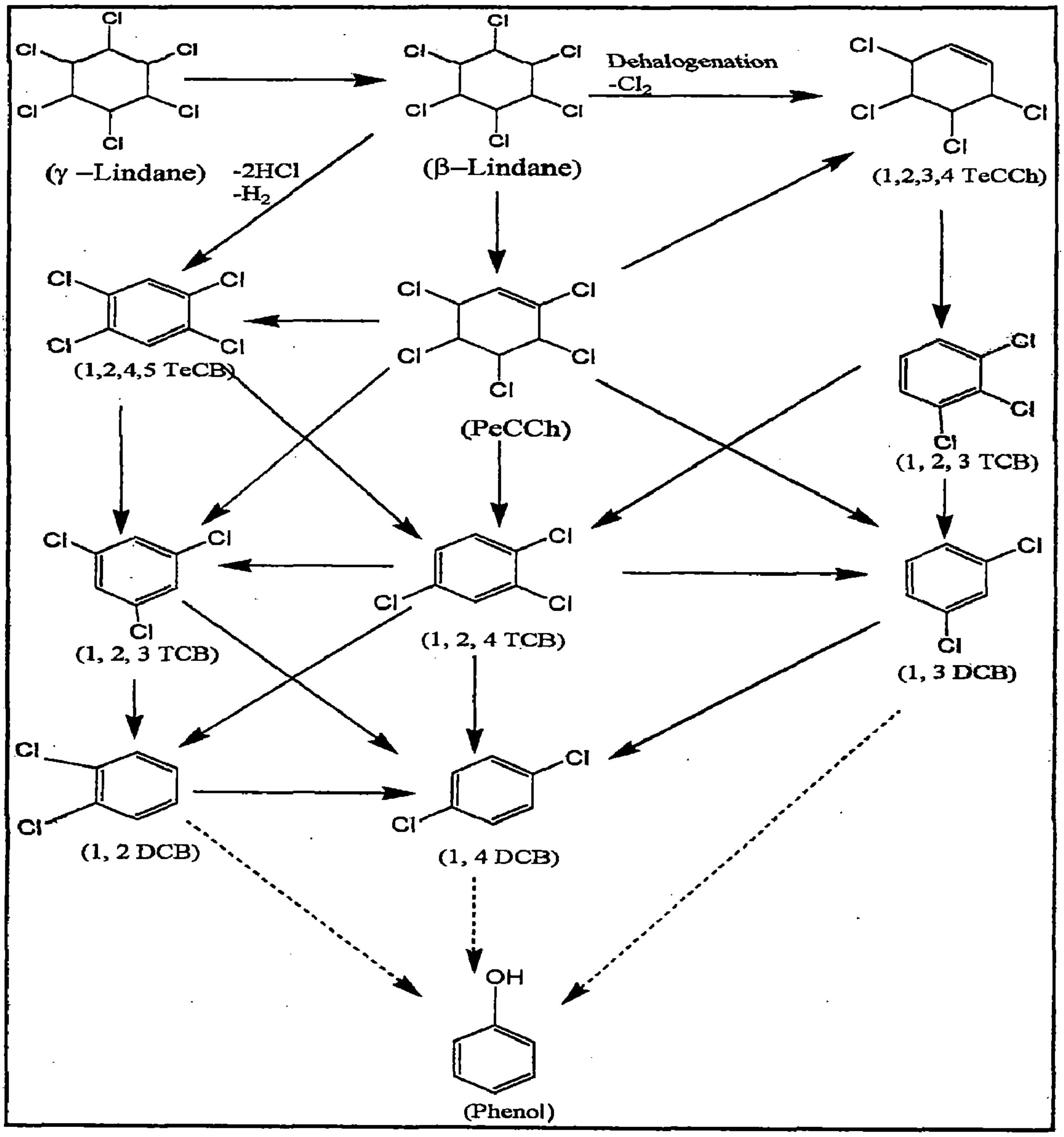


Fig.4.29. Degradation pathway of Lindane

(Bold arrow for reported compounds and dotted arrow for new compounds), PeCCh-Pentachlorocyclohexene, TeCCh-Tetrachlorocyclohexene, TCB-Trichlorobenzene, DCB-Dichlorobenzene

- ***Mass spectra of Lindane and its intermediate compounds and their conformation***

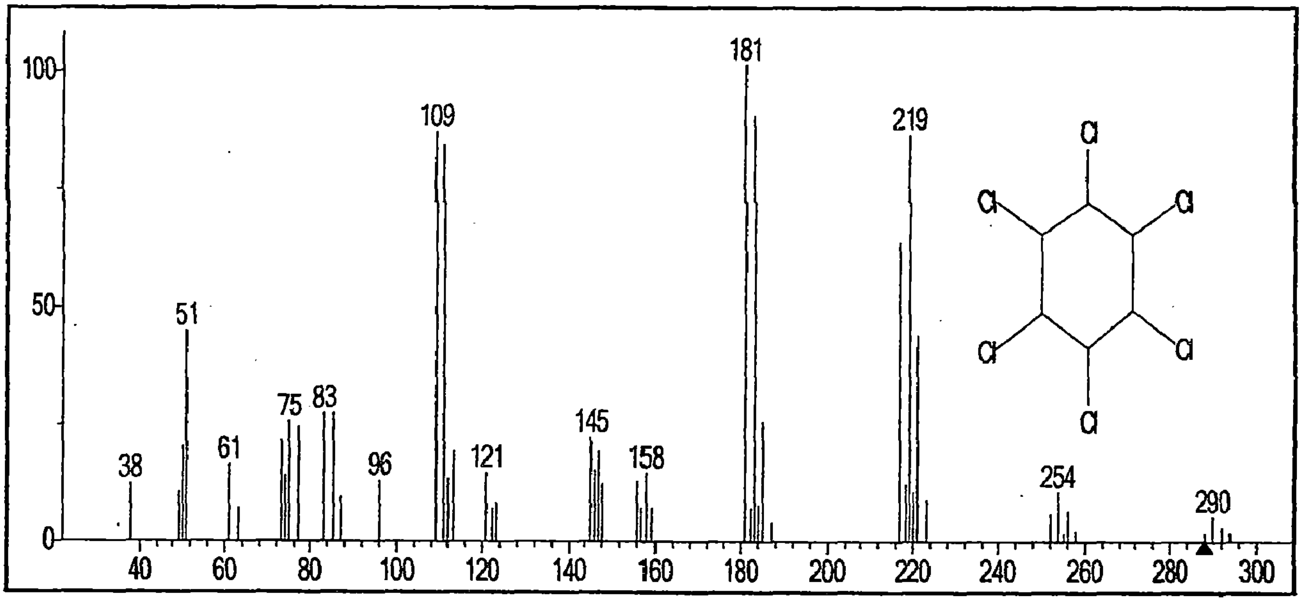
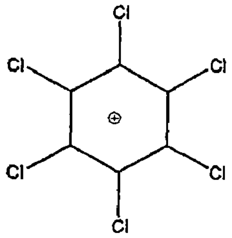
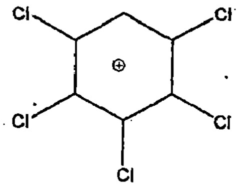


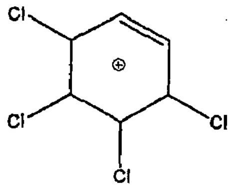
Fig.4.30. Mass fragments of Lindane



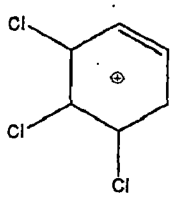
m/z 290



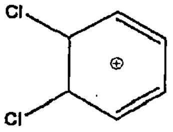
m/z 254
chlorine isotopic ratio 60:80:40:10



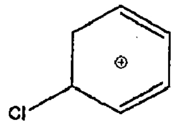
m/z 219
chlorine isotopic ratio 60:80:40:10



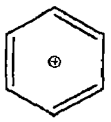
m/z 183
chlorine isotopic ratio 27:27:9:1



m/z 147
chlorine isotopic ratio 9:6:4

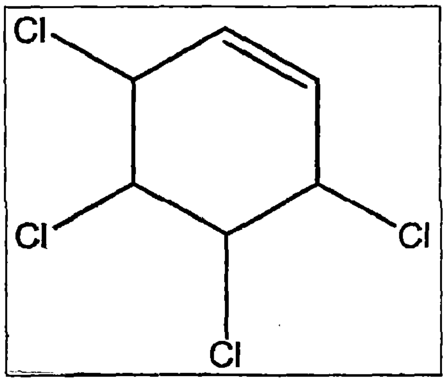


m/z 114
chlorine isotopic ratio 3:1



m/z 78

Relative intensities of chlorine isotopes peaks at m/z 254 and 219 are 60:80:40:1. It confirmed the compounds have six chlorine atoms in its formula and m/z at 183 is 27:27:9:1; m/z at 147 and 145 are 9: 6:1 and 9:1 respectively confirmed two and one chlorine having compounds after elemination of two Cl atoms.



Tetrachlorocyclohexzene

(M.W.219)

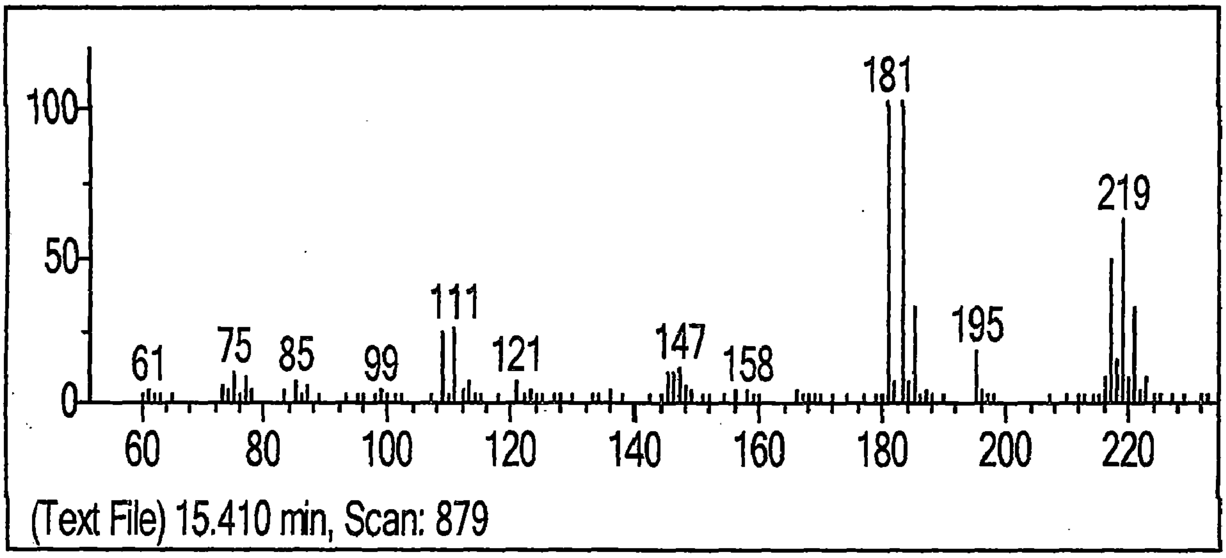
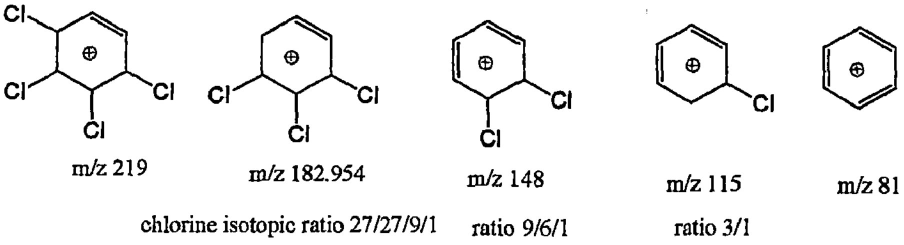
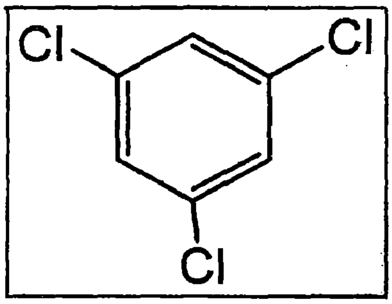


Fig.4.31. Mass fragments of tetrachlorocyclohexene



Relative intensities of chlorine isotopes peaks at m/z 219 and 182 are 27:27:9:1. It confirmed the compounds have four chlorine atoms in its formula and m/z at 148 and 115 is 9: 6:1 and 9:1 respectively showed two and one chlorine having compounds after elemination of two Cl atoms.



1,2,3 trichlorobenzene
(M.W. 181.4)

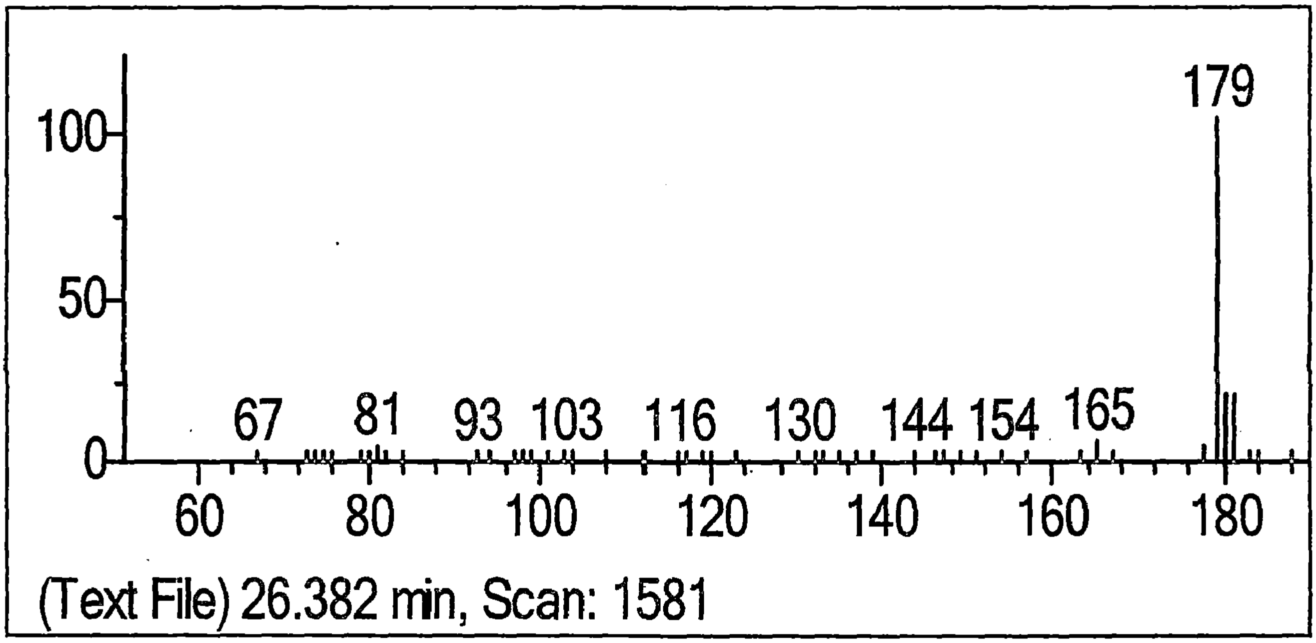
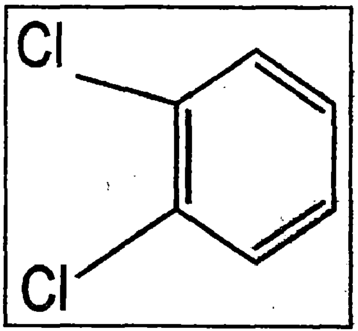


Fig.4.32 Mass fragments of 1, 2, 3 trichlorobenzene

Relative intensity of chlorine isotopes peaks at m/z 179 is 27: 27:9:1. It confirmed the compounds have three chlorine atoms in its formula.



Benzene-1,2 Dichloro

(M.W. 162)

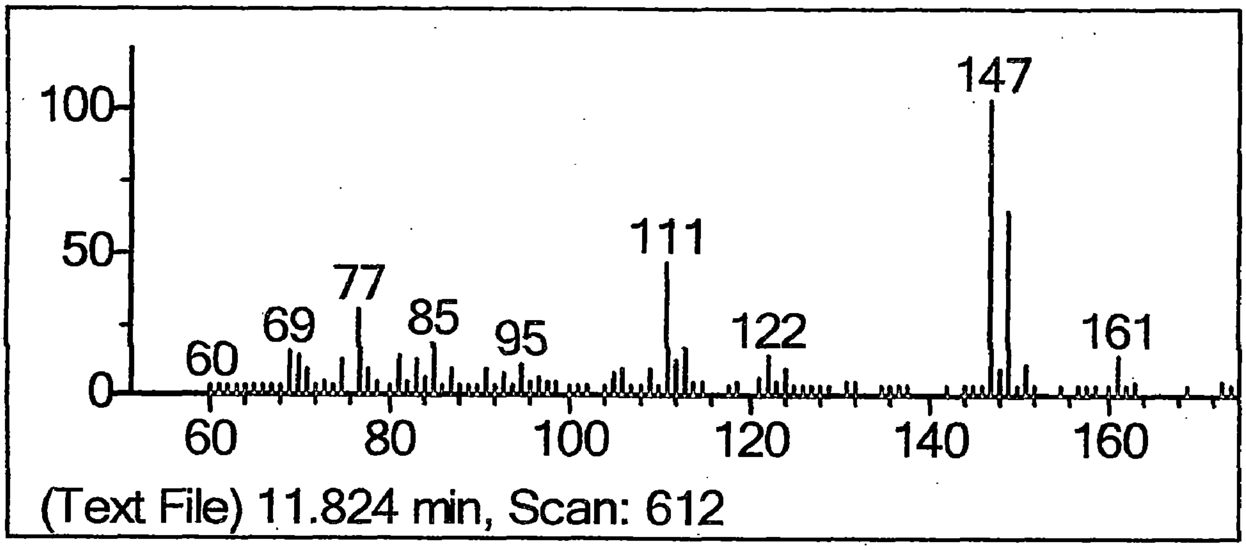
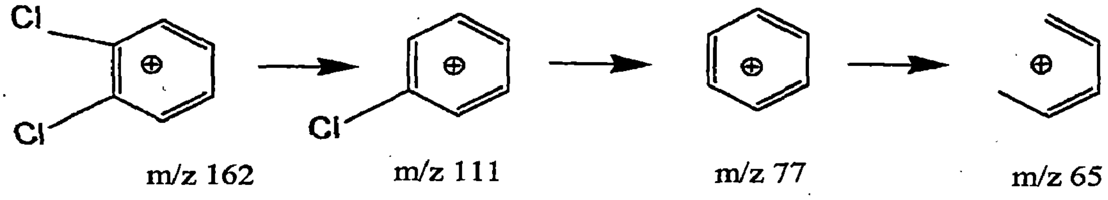
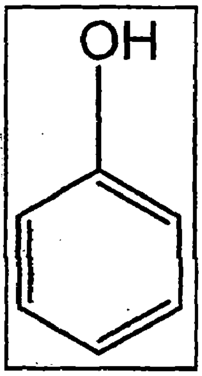


Fig.4.33. Mass fragments of benzene-1,2 Dichloro



Relative intensity of chlorine isotopes peaks at m/z 147 is 9: 6:1. It confirmed the compound has two chlorine atoms in its formula.



Phenol

(M.W. 94)

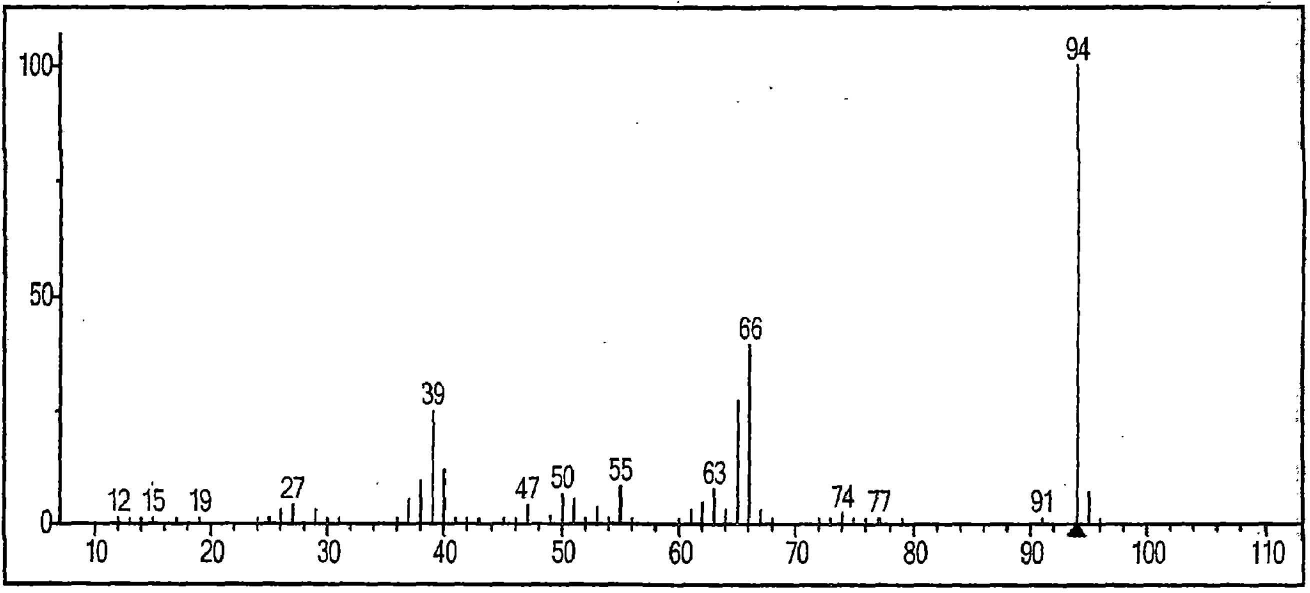
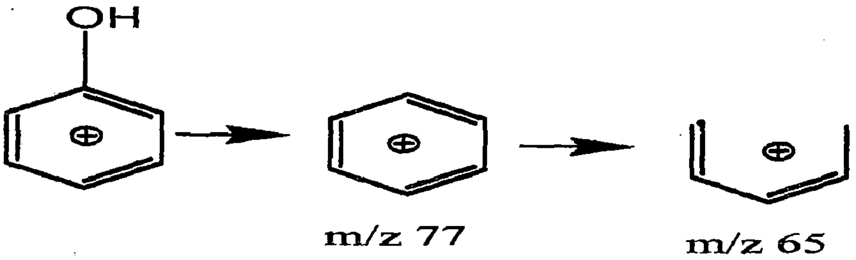
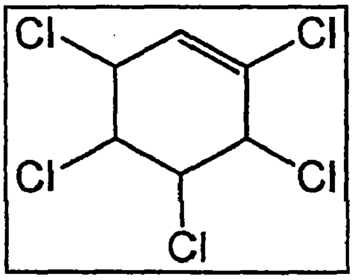


Fig.4.34. Mass fragments of phenol





Pentachlorocychlohaxene (PeCCh)

(M.W. 254)

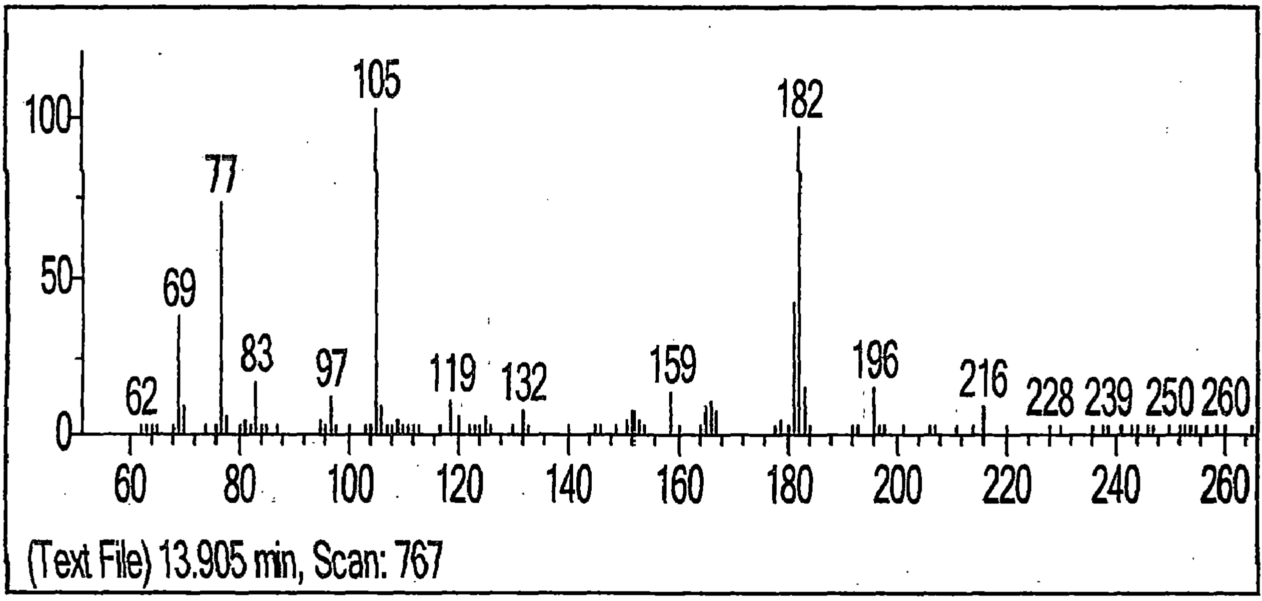
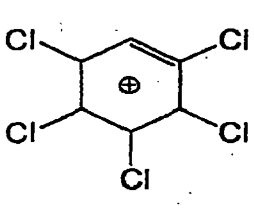
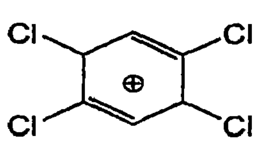


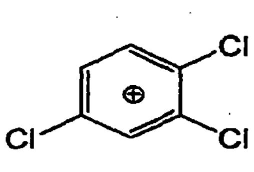
Fig.4.35. Mass fragments of pentachlorocychlohaxene (PeCCh)



m/z 254

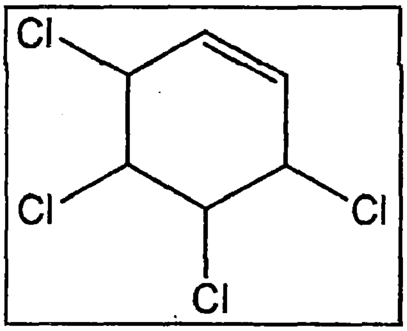


m/z 217



m/z 181

Relative intensity of chlorine isotopes peaks at m/z 182 is 60:80:40:1. It confirmed the compound has five chlorine atoms in its formula.



Tetrachlorocychlohexene (TeCCh)

(M.W. 219.9)

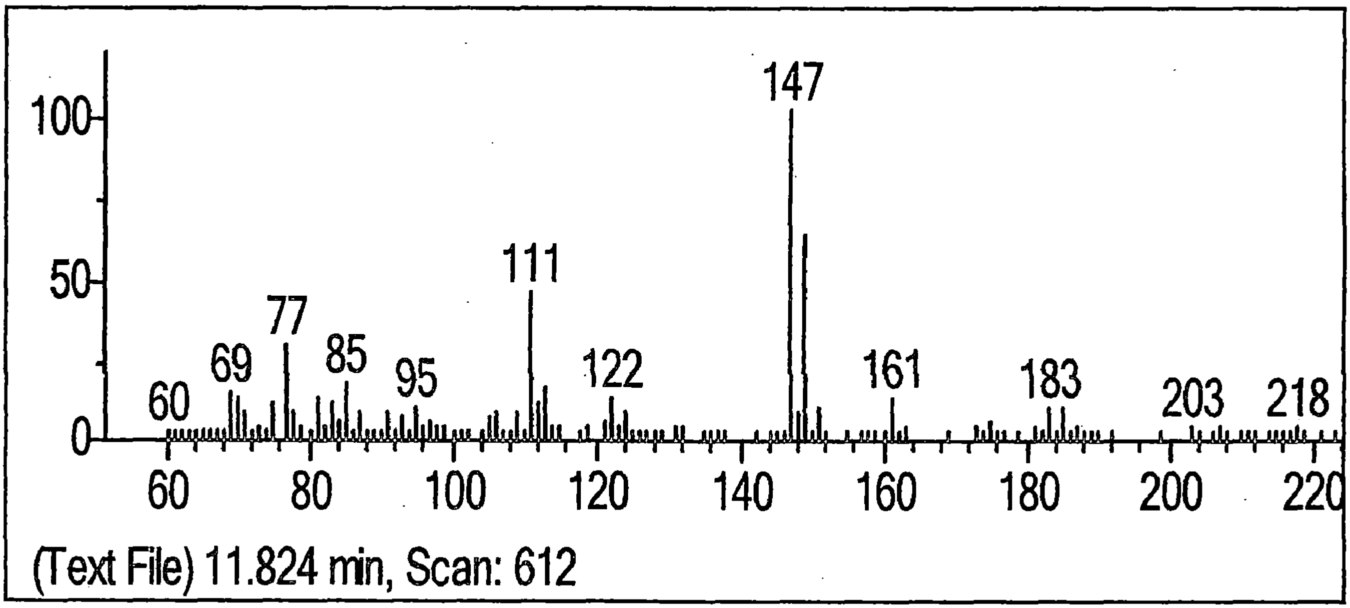
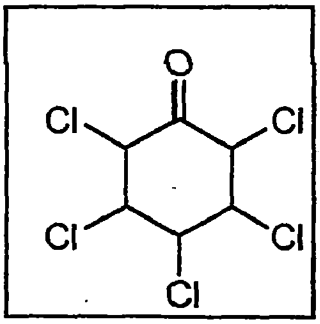


Fig.4.36. Mass fragments of tetrachlorocychlohexene (TeCCh)

Relative intensity of chlorine isotopes peaks at m/z 218 is 60:80:40:1. It confirmed the compound has four chlorine atoms in its formula and m/z at 147 is 9: 6:1 confirmed di-chlorinated compound.



Pentachlorocychlohexanone

(M.W. 268)

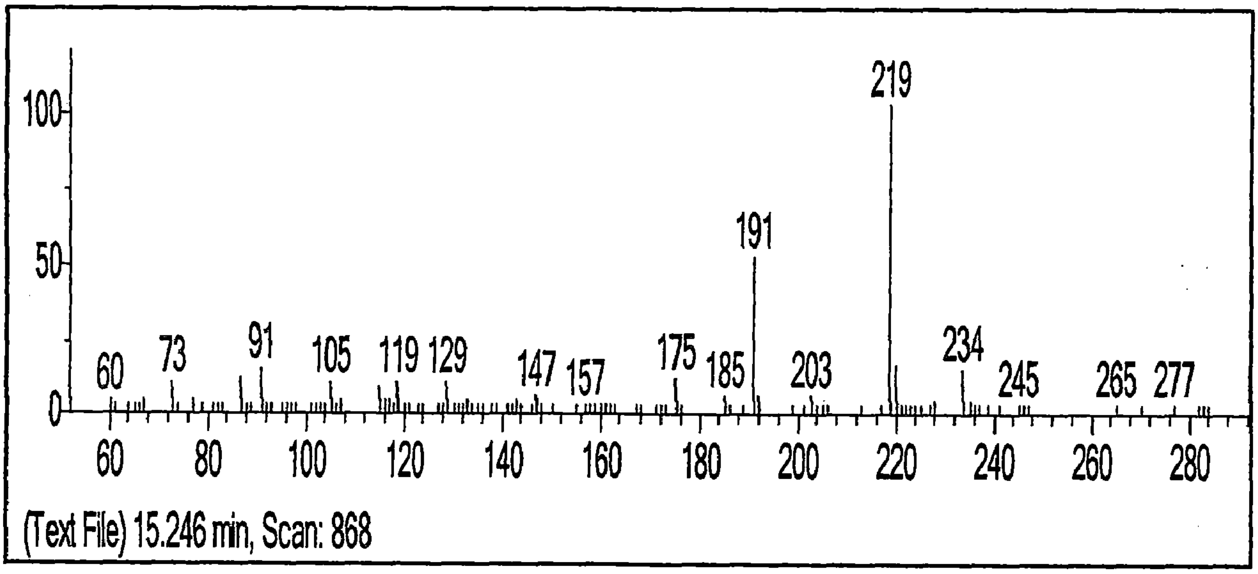
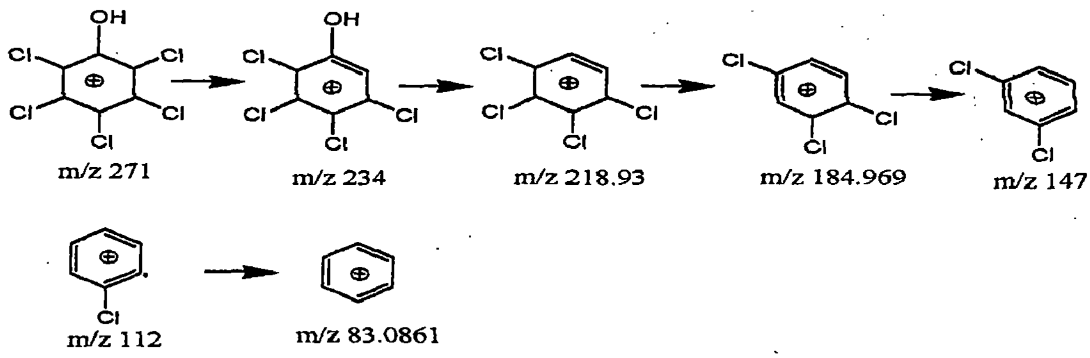
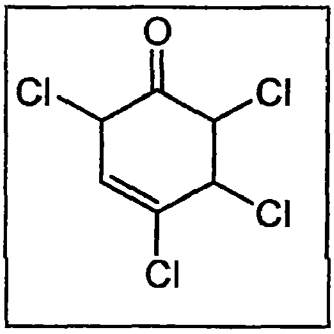


Fig.4.37. Mass fragments of pentachlorocychlohexanone



Relative intensities of chlorine isotopes peaks at m/z 234 are 27:27:9:1. It confirmed the compounds have four chlorine atoms in its formula and m/z at 219 is 9: 6:1 confirmed di-chlorinated compound after elimination of two Cl atoms.



1, 2, 3, 5-Tatrachlorocychlohexenol
(M.W. 234)

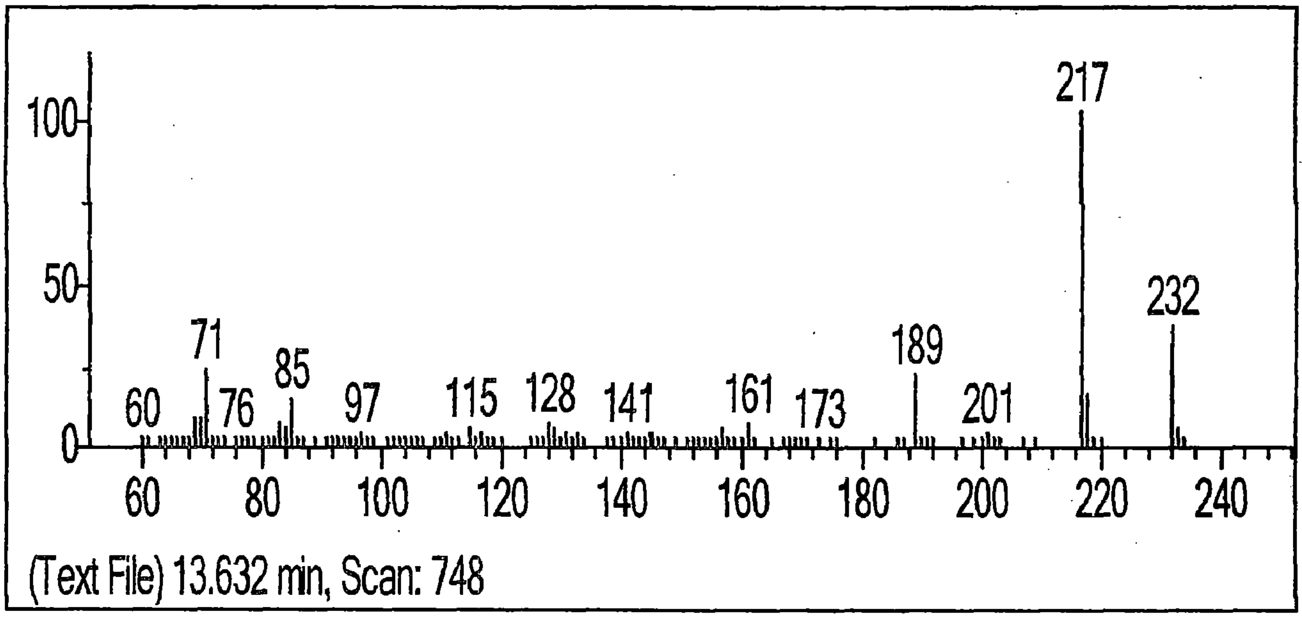
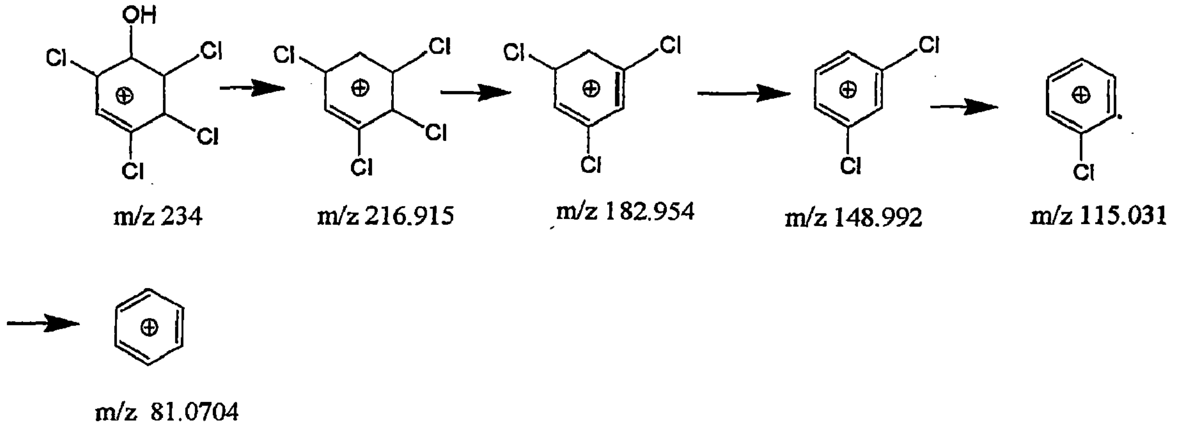
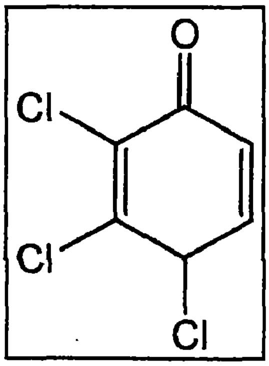


Fig.4.38. Mass fragments of 1, 2, 3, 5-tatrachlorocychlohexenol



Relative intensities of chlorine isotopes peaks at m/z 217 and 232 are 27:27:9:1. It confirmed the compounds have four chlorine atoms in its formula.



1, 2, 3-trichlorocychlohexanone-1, 4-diene

(M.W. 197)

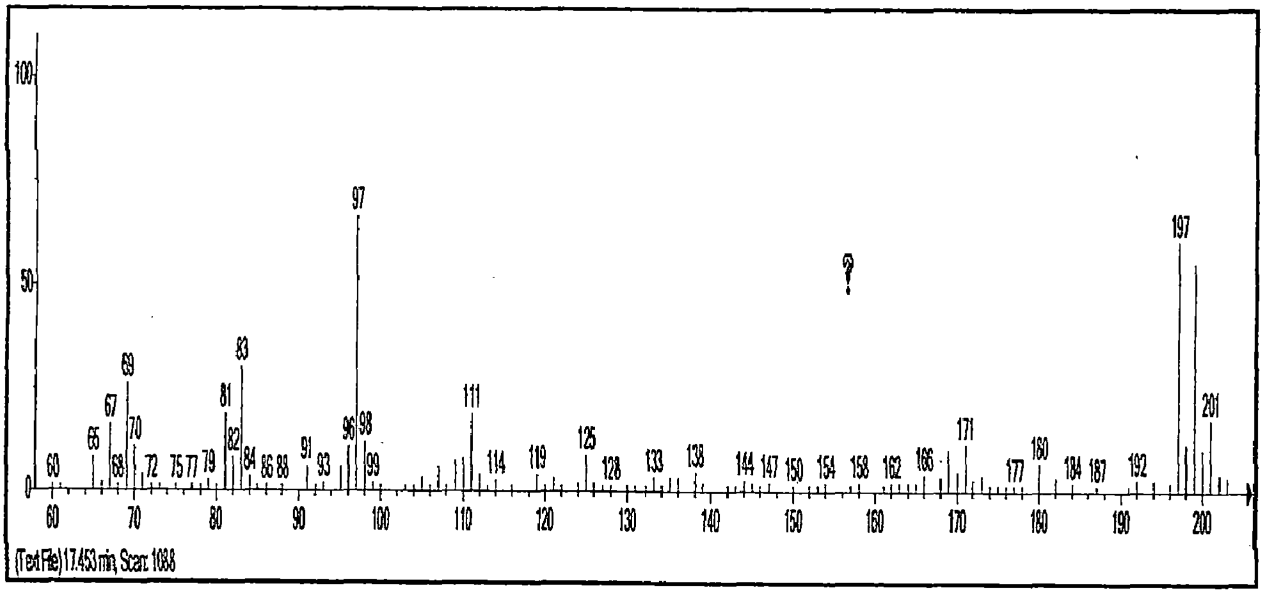
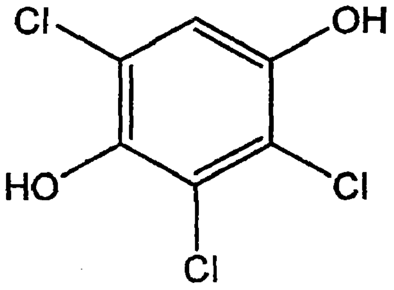


Fig.4.39. Mass fragments of 1, 2, 3-trichlorocychlohexanone-1, 4-diene

Relative intensity of chlorine isotopes peaks at m/z 197 is 27:27:9:1. It confirmed the compound has three chlorine atoms in its formula.



2, 3, 5 trichloro-1, 4-dihydroxybenzene

(M.W. 211)

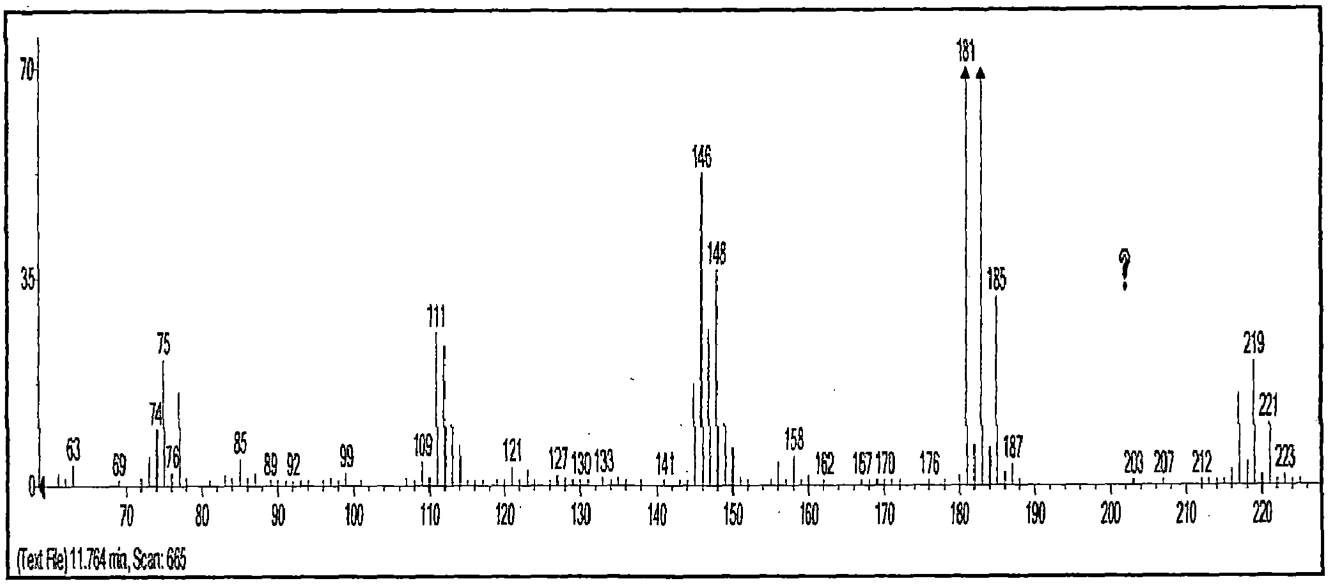


Fig.4.40. Mass fragments of 2, 3, 5 trichloro-1, 4-dihydroxybenzene

Relative intensity of chlorine isotopes peaks at m/z 161 is 27:27:9:1. It confirmed the compound has three chlorine atoms in its formula.

4.1.1.5. Microbiological analysis

The population of total heterotrophic bacteria in the feedstock was 9.3×10^5 CFU/g. The average bacterial number increased within initial 6 days due to the availability of large amount of organic matters/energy sources. Finally, the number reduced to 1.8×10^2 CFU/g and 1.5×10^3 CFU/g in rotary drum and windrow composting respectively (Fig.4.41 & 4.42) and total fungal load initially increased from 2.3×10^2 CFU/g to 4.3×10^4 CFU/g within initial 4 days and subsequently reduced to 1.4×10^2 CFU/g in the rotary drum and 2.3×10^3 CFU/g in windrow composting. Furthermore, microbial identification during rotary drum and windrows composting revealed that the major bacterial groups in the beginning of the composting process are mesophilic in nature (*Lactobacillus* sp., *Clostridium* sp., and *Pseudomonas* sp. responsible for aldrin degradation), which produce organic acids. Later, thermophilic bacteria such as *Bacillus* sp. and *Actinobacteria* sp. became dominant which survived above the 60°C temperature and help in degradation of other chlorinated pesticides. Bacterial communities revealed three groups: Gram positive rods, Gram negative cocci and Gram negative rods. Gram positive rods started the cycle of composting and their number increased with the advancement of the cycle. As soon as decomposition of organic matters proceeds, gram negative bacilli shaped bacteria increased in their number and became dominant in the later stages. *Aspergillus* species and *Rhizopus* species were identified as the major mycofloral. They can survive at higher temperature (55 - 61°C) during the composting process. In proposed study, the most efficient composting process is achieved by mixed communities of bacteria and fungi which are responsible for organochlorine pesticides degradation. These microbial communities were dominant during rotary drum compared to windrows composting.

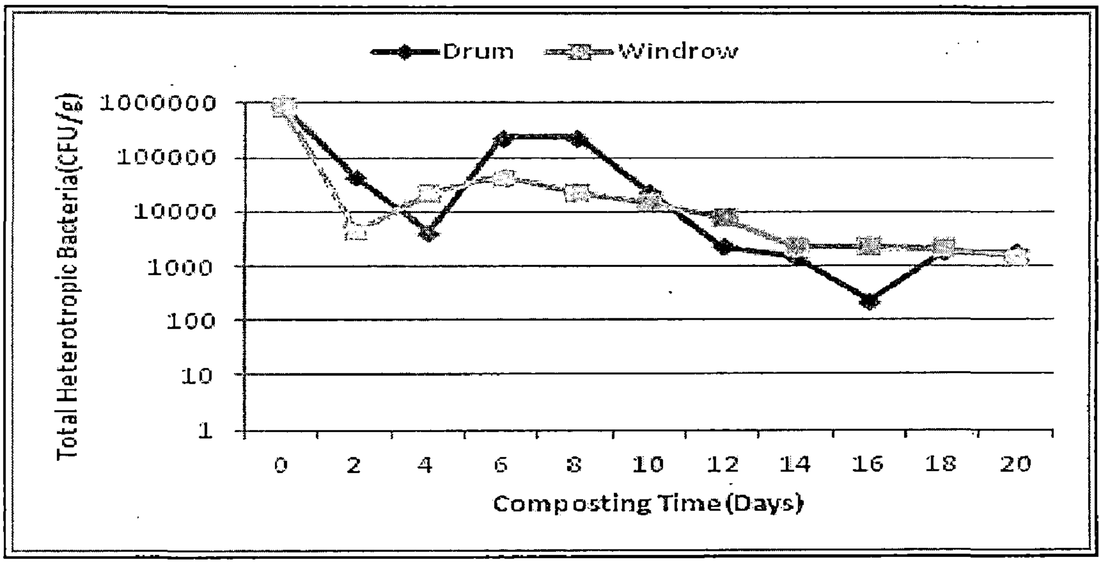


Fig.4.41. Total bacterial population during rotary drum and windrow composting

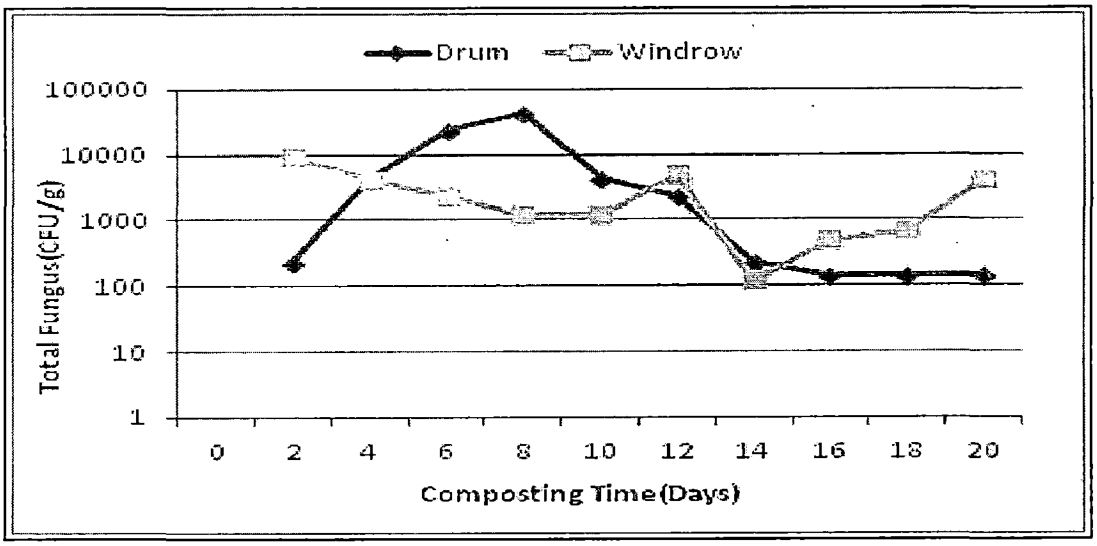


Fig.4.42. Total fungal population during rotary drum and windrow composting

4.1.1.6. Conclusion

In brief, > 70% organochlorine pesticides can be removal in 20 days with high rate rotary drum composting techniques due to better mixing, optimal temperature, pH and moisture contents. While, in conventional windrows technique, it is only 50-60 % in 36 days in which 40-45% through leachate generation. First order degradation kinetics has been observed in pesticides degradation and the half life reduced to 12-20 days from 1095 days, 9-17 days from 60 days, 11-30 days from 270 days and 9-11 days from 160 days for Aldrin, Endosulfan α, Endosulfan β, and Lindane respectively in high rate rotary drum composting compared to natural decay. In addition, intermediate compounds were also characterized using GC-MS. Furthermore, microbial analysis revealed that the mesophilic bacteria such as *Lactobacillus* sp., *Clostridium* sp. and *Pesudomonas* sp. have developed as a major group in the beginning of composting. Later, thermophilic bacteria such as *Bacillus* sp., *Actinobacteria* sp. (gram-positive) and *Aspergillus* and *Rhizopus* species (major mycofloral) were dominant in rotary drum compared to windrows composting. It is also confirmed that identified bacterial and fungal genera are responsible for pesticides degradation Therefore; rotary drum composting is more suitable for the development of bacteria and fungi communities, efficient eradication of harmful pesticide residues in vegetable waste.

Part B: Fate and degradation kinetics of Aldrin, Endosulfans and Lindane Pesticides during full-scale continuous rotary drum

In this chapter (Part B) deals with the fate and degradation kinetics of Aldrin, Endosulfans and Lindane pesticides in full-scale continuous rotary drum composting. Study was carried out for 100 days to evaluate the degradation of pesticides under full-scale mode using vegetable waste. In addition, a 24 hours study of pesticides degradation was also done during full-scale continuous rotary drum composting.

4.2.1. INTRODUCTION

Considerable remediation of the hazardous wastes or contaminated food, plants, soils, and sediments can be accomplished by composting. High microbial diversity and activity during composting due to many substrates in waste material, which promotes degradation of xenobiotic organic compounds such as pesticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Allen, *et al;* 2002). The composting of waste material such as vegetable, food, MSW, yard waste in in-vessels or on-site addition of organic matter to soils (sheet composting) accelerates degradation of organic pollutants and binds metallic pollutants. Recalcitrant materials such as organochlorines, may not undergo degradation in composts and the effects of forming organic complexes with metallic pollutants may be nonpermanent or short lived (Allen, *et al;* 2002).

Modern pesticides (insecticides, fungicides, herbicides) are mostly organic compounds that are subject to biological decomposition. However, composting can degrade various organic compounds that might be present in feedstock. If, the process is carried out with proper aeration, moisture, CN ratios, and composting time (Sikora, *et al;* 1998). Strom (1998) noted that pesticide levels in composts were low, partly because of low initial contamination of feedstock and because of degradation of pesticides during composting. Chaney, *et al;* (1996) and Vogtmann and Fricke, (1992) noted that either mature or immature composts are generally low in xenobiotic organic compounds, suggesting that degradation of pesticides occurs early in the process. Composting typically proceeds in three phases: a rapid decomposition phase of about 30 days duration, followed by a stabilization phase of about 50 days duration and a maturation phase following the stabilization phase (Hsu, *et al*; 1999). Rapid degradation of xenobiotics commonly occurs during the first 30 days. Some xenobiotics that resemble aromatic substances in mature compost might be recalcitrant to decay. Buyuksonmez, *et al;* (1999 and 2000) noted that the majority of the pesticides detected in waste material or composts were organochlorine insecticides, which were resistant to biodegradation and included some banned in the U.S. Strom (1998) noted detectable levels of chlordane (a polychlorinated hydrocarbon, methanoindine derivative) in yard trimmings but no detectable level of 26 other pesticides. Mineralization of organic pesticides was only a small fraction of pesticide degradation with other prominent fates of the pesticides being partial degradation to secondary compounds, adsorption to compost and volatilization. (Buyuksonmez, 1999).

Studies of pesticides degradation during composting of various kinds of waste are limited to the laboratory scale in-vessel or windrows composting. Less study is reported to characterize degradative pathways and kinetics of organochlorine pesticides during full-scale in-vessel composting. After a successful study of fate and degradation kinetics of organochlorine pesticides namely Aldrin, Endosulfan α, Endosulfan β and Lindane in part A of this chapter. Our study focused on the degradation kinetics of these pesticides in full-scale high rate rotary drum composting of vegetable market waste with same CN ratio of 22 used in previous reports. The results of this study would be useful in defining removal of organic pollutants like pesticides and their fate from waste material of industrial-scale rotary drum composter (RDC) dealing with different kind of organic wastes.

4.2.2. Results and discussions

4.2.2.1. Physico-chemical parameters

- ***Temperature profile***

Temperature is one of the key indicator for pesticides degradation during composting. It determines the rate at which many of the biological processes take place and plays a selective role on evolution and succession on the microbiological communities (Hassen, *et al.*, 2001). However, when temperature increased by the microbial degradation of organic matter pesticides and other organic pollutants getting dissolved into the aqueous phase present in the composting material. Fig. 4.43 shows the temperature profile during high rate full-scale composting which revealed the maximum temperature in the rotary drum inlet zone varied between 50-60°C depending upon the ambient temperature. During the composting in 12, 47 and 98 days, the temperature of inlet zone was around 40-45°C due to not loading of waste materials into the rotary drum. This was also effects the temperature of middle zone temperature. The temperature in the middle zone of the drum varied between 50-54°C indicated the lower microbial activities compared to inlet. The temperature at the outlet zone of the drum was equal to ambient or slightly more (30-28°C) indicated the end of active thermophilic phase. The variation in the temperature range in the three zones could be attributed to the microbial activity and availability of degradable material and pesticides.

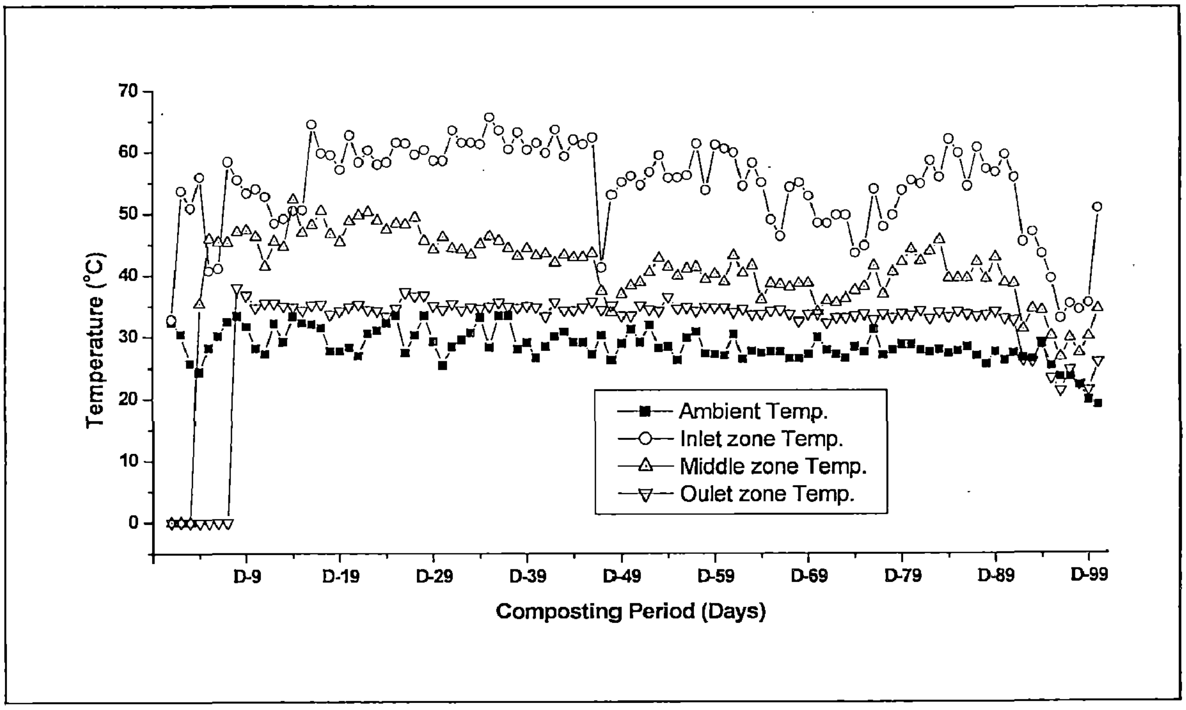


Fig. 4.43.Temperature profile during full-scale high rate composting over composting period

- ***Moisture content profile***

Optimum moisture content of the compost mixture is important for the microbial decomposition of the organic wastes. Moisture loss during the active composting can be defined as an index of decomposition rate of organic pollutants like pesticides, since the heat generation accompanies decomposition drives as vaporization or moisture loss (Liao, *et al.*, 1996). Moisture content was 75% in inlet zone (waste material), which dropped to 62 % in the middle zone and measured as 72% in outlet zone (Fig.4.44). The increased moisture content in outlet zone might be due to excess humidity (99%) in the surrounding which goes to the drum. Similarly, reduction of moisture content in inlet, middle and outlet zones was due to not loading of waste material during 44th day of composting might be due to unavailability and higher temperature lead to evaporation. A massive variation of moisture content in inlet, middle and outlet zones might be due to the variation of waste composition and rain.

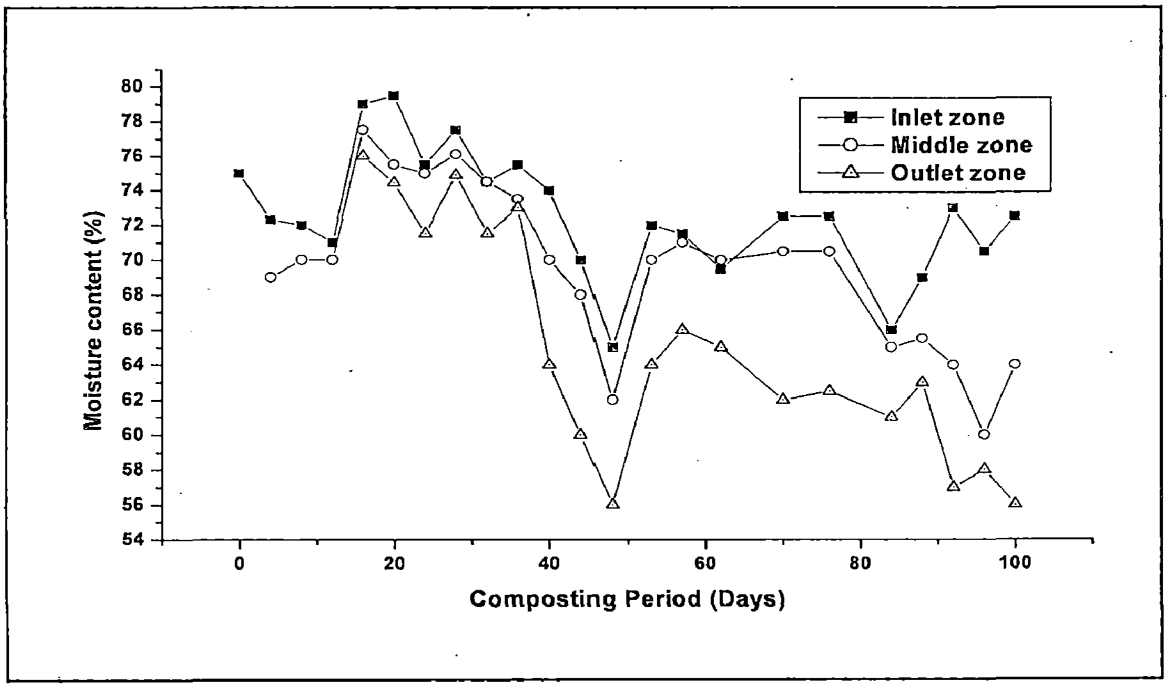


Fig.4.44. Moisture content profile during high rate rotary drum over composting period

- *pH profile*

Composting proceeds most efficiently at the thermophilic temperature when the pH is approximately 8 (Liao, *et al;* 1996). The pH of the inlet was ranged from 6.6-7.8 except the lower values observed during 70–87 days of loading. This was probably due to higher amount of variable vegetable wastes used as initial waste material. Compost pH generally increased during the composting process (Smith, *et al;* 2006). Increase in the pH level during composting resulted in increase in volume of ammonia released due to protein degradation. Increased rate of aeration in the drum by daily turning tend to decrease CO_2 levels in the compost, which in turn tend to increase pH (Haug, 1993). The trend of pH at middle zone and outlet zone of the drum was different as inlet zone pH. Ammonium formation was very low after primary stabilization due to low rate of organic matter degradation. During the nitrification process, the nitrifying bacteria reduced the pH of the medium due to the liberation of hydrogen ions. Once nitrification had begun after the thermophilic stage, pH decreased. Therefore, pH value of the compost was directly related to nitrification (Sanchez-Monedero, *et al.,* 2001). Fig.4.45 displays the results of the monitored pH of the composting materials, pH values of inlet, middle and outlet zones varied from acidic pH to slightly basic nature i.e., 6.4, 8.38 and 8.68 respectively.

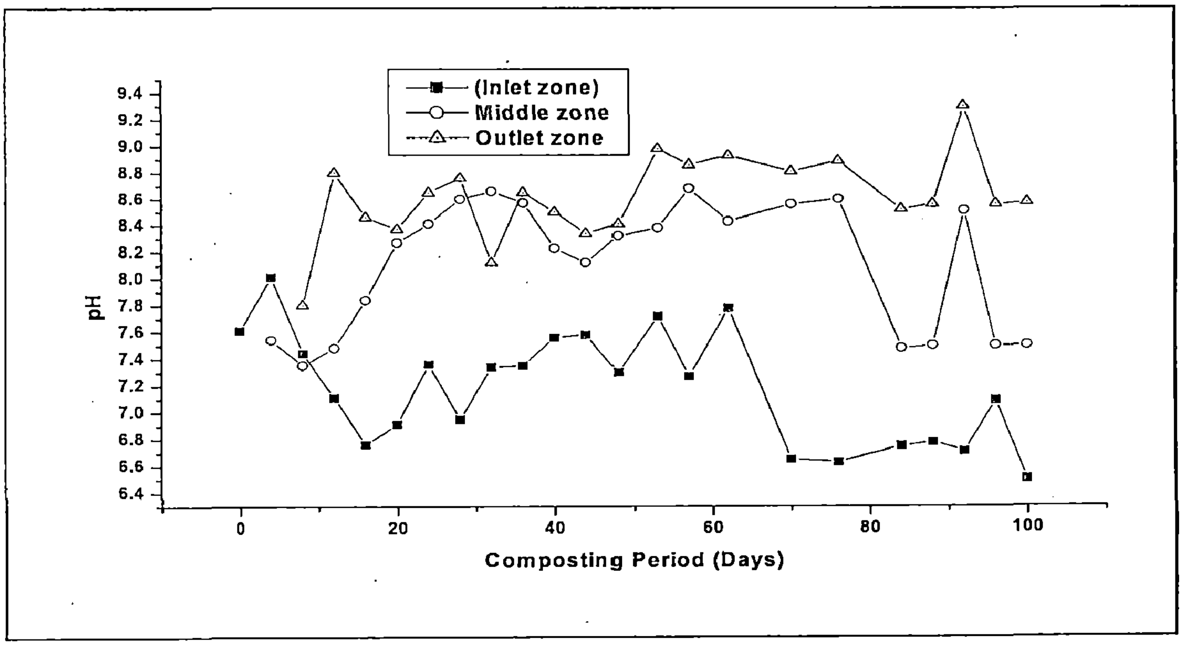


Fig.4.45. pH profile during high rate rotary drum over composting period

- ***Electrical Conductivity***

EC of mixture shown in Fig.4.46 gave decrement upto 8-12 days and then increased, followed by a steady decrease till the end of the composting. In the beginning, EC peaks could be due to release of mineral salts and ammonium ions through the decomposition of organic matter (Huang, *et al;* 2004). The volatilization of ammonia and the precipitation of mineral salts could be the possible reasons for the decrease in EC at the later phase of composting (Wong, *et al*; 1995).

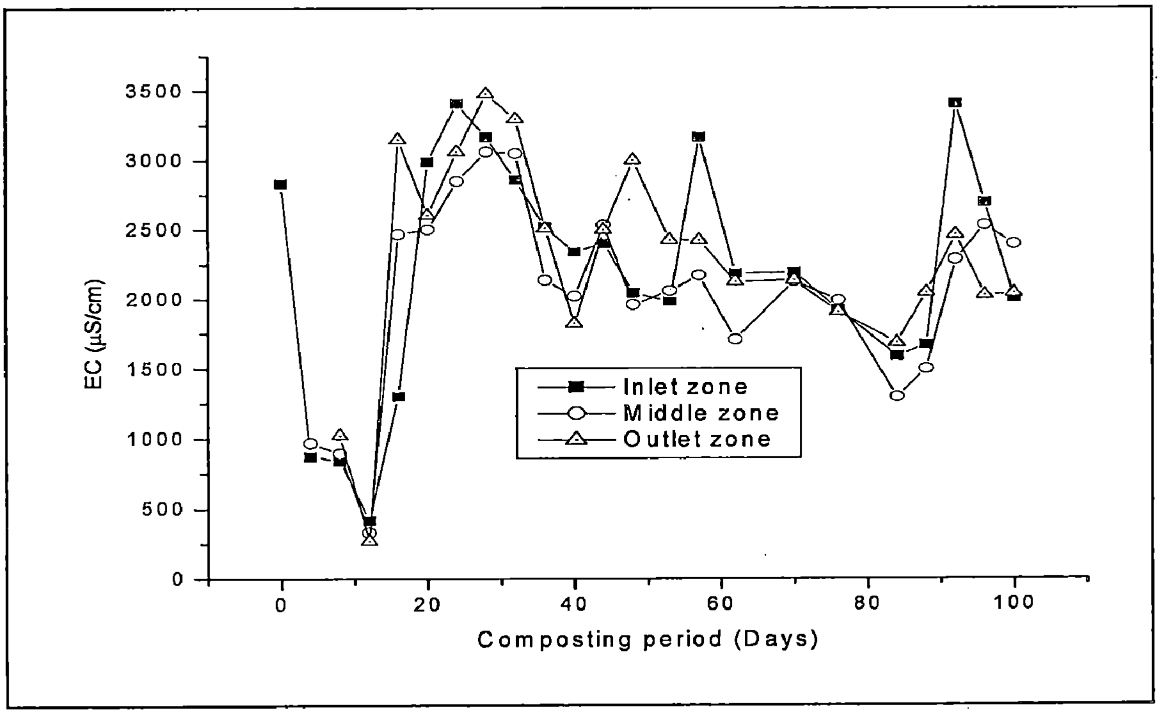


Fig.4.46. Electrical conductivity (EC) of the composting materials over composting period

- ***Carbon dioxide emission rate***

CO_2 evolution is the most direct technique of compost stability because it measures carbon derived directly from the compost being tested. Thus, CO_2 evolution directly correlates to aerobic respiration, the truest measure of respiration and hence aerobic biological activity. Fig.4.47 shows the CO_2 emission during 100 days composting through full scale rotary drum, the initial inlet zone CO_2 around 14 mg/g VS/day till 8 days. The inlet zone CO_2 emission was varied 9-10 mg/g VS/day due to variation in waste composition and acclimatization of composting for long time. When waste material reaches to middle zone after 4 days, the CO_2 emission reduced around 40% in inlet zone. After reaching material to outlet zone in next 4 days CO_2 emission reduced to around 70% from inlet zone (2-4mg/g/VS/day).

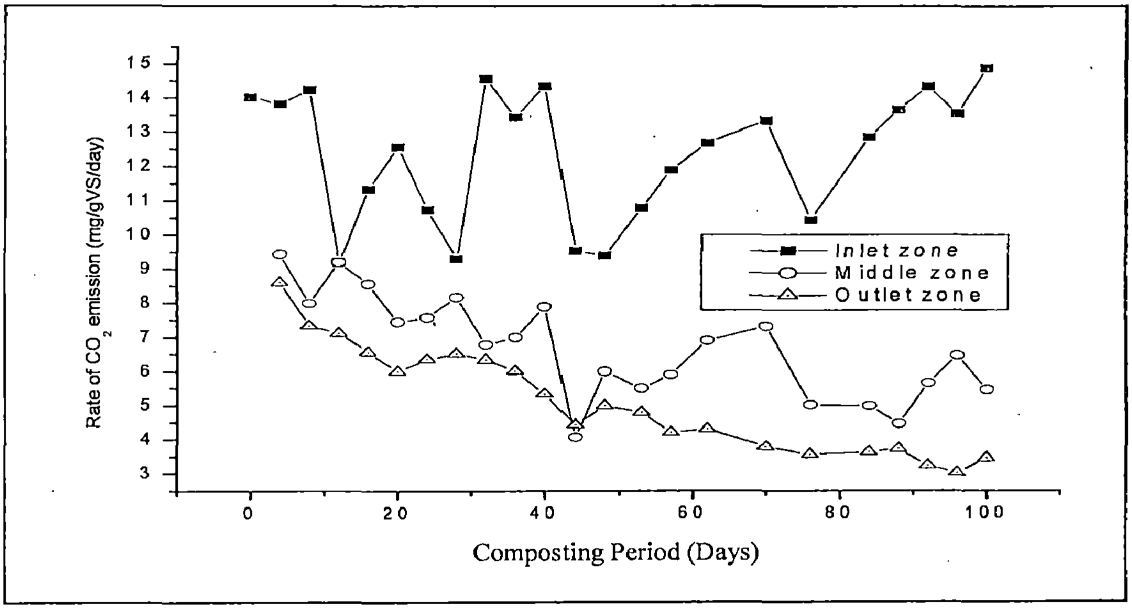


Fig.4.47. Rate of carbon dioxide emission from composting materials over composting period

- ***Total Organic Carbon profile (TOC)***

Mineralization of organic matters such as proteins, cellulose and hemi-cellulose might be possible cause for carbon reduction by the emission of CO_2 gas. Fig.4.48 shows that the initial amount of total organic carbon was found 33% reduced to 28% and 22% in middle zone and outlet zones respectively.

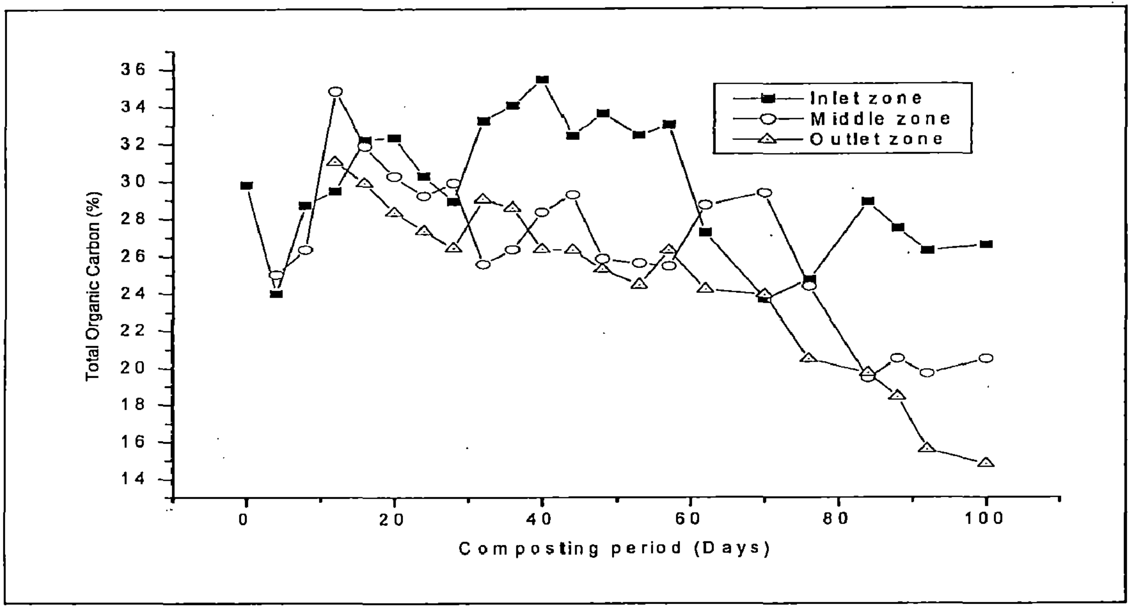


Fig.4.48. Total carbon of the composting materials over composting period

- ***Total Nitrogen profile***

The increase in value of total nitrogen could be attributed to water loss by evaporation due to heat evolution in oxidation of organic matter (Fang, *et al*; 1999, Huang, *et al;* 2004). The total nitrogen concentration in waste material was found 0.90-1.40% due to huge variation of vegetable waste. Nitrogen concentration from inlet to middle zone increased from 1.20% to 1.56% till 20 days and 20-40 days nitrogen concentration was found to be decreased from 1.52% to 1.22%. After 50 days to 100 days huge variations taking place. Total nitrogen value increased from 1.09% to 1.46% from inlet to middle zone while for outlet zone value increased to 1.652 % (Fig. 4.49) during whole composting period..

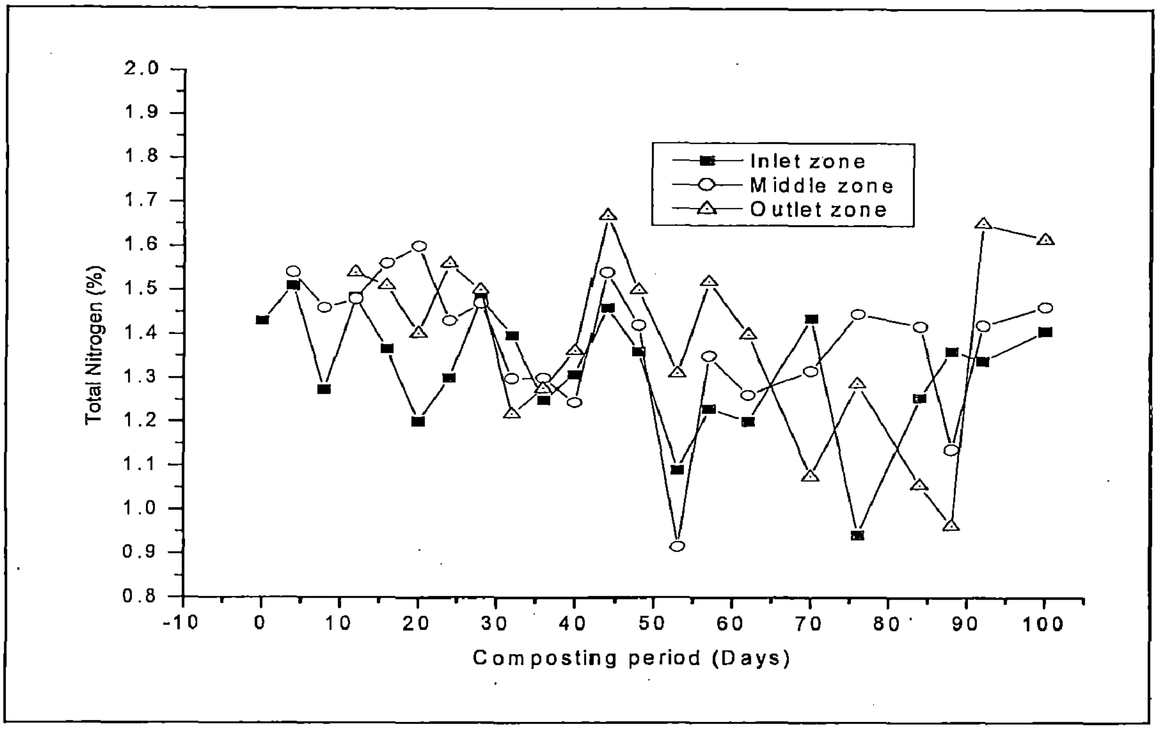


Fig.4.49. Total nitrogen of the composting materials over time

4.2.2.2. Pesticides Degradation

- ***Degradation of Aldrin***

Pesticides degraded by microbial species during composting for energy and building blocks of microbial cell by a complex processes. Initially, pesticides dissolved in aqueous phase of composting material and then consumed by microbes. Pesticides degradation in composting faster than the ambient environment due the temperature increase in composting by heat libration of breakdown of chemical bonds present in organic matter and dissolution of pesticides increases in aqueous phase of composting by the increasing the temperature and these pesticides made available to the microbial species for their degradation.

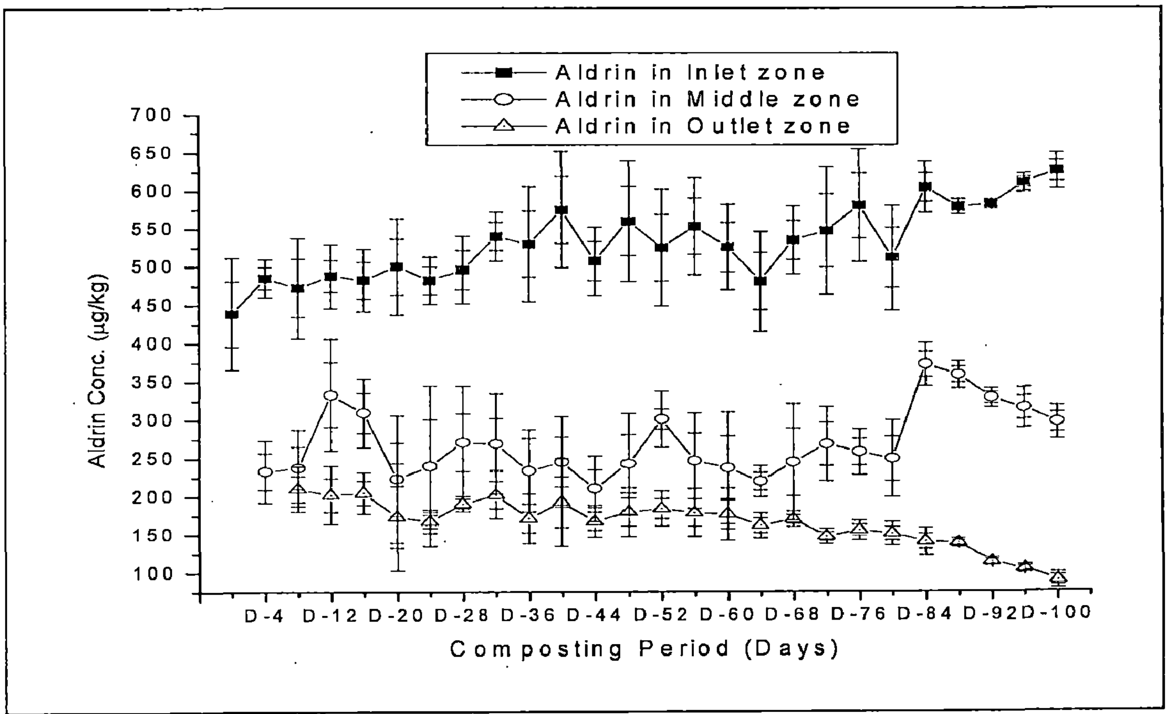


Fig.4.50. Aldrin degradation during high rate rotary drum over composting period

Degradation or removal of Aldrin is given in Fig.4.50. Aldrin concentration was found in raw wastes from 450 to 650µg/kg due to variation in waste collection time from market. However, when waste material feeded into the drum, around 20% aldrin degraded within 24 hours in inlet zone of the drum due high temperature range (60-65°C), then feeding continues next day, waste material goes to forward direction with degradation, after 4 days material reaches to middle zone and aldrin concentration was found 250-350µg/kg during whole composting process. Approximately, 46.15% Aldrin removed in 4 days. After that material was reached to outlet zone in next 4 days, aldrin concentration was analyzed ranges 100-200 µg/kg. Removal efficiency (42.8%) was achieved in this zone as compared to middle or outlet zone and overall removal efficiency of aldrin in 8 days composting was 70% due to the high temperature range, optimum moisture, aeration, proper mixing of waste material and high microbial community growth into the drum.

- ***Degradation of Endosulfan α and β***

Endosulfan was subjected to degrade by oxidation and hydrolysis processes. Conclusively, endosulfan sulfate formation was found to be favored as oxidative product and a novel hydrolysis product tentatively identified as endosulfan monoaldehyde. pH and contact of endosulfan to enzymes of microorganisms enhanced degradation. Oxygen is other factor because the biological oxidation reaction needs the oxygen.

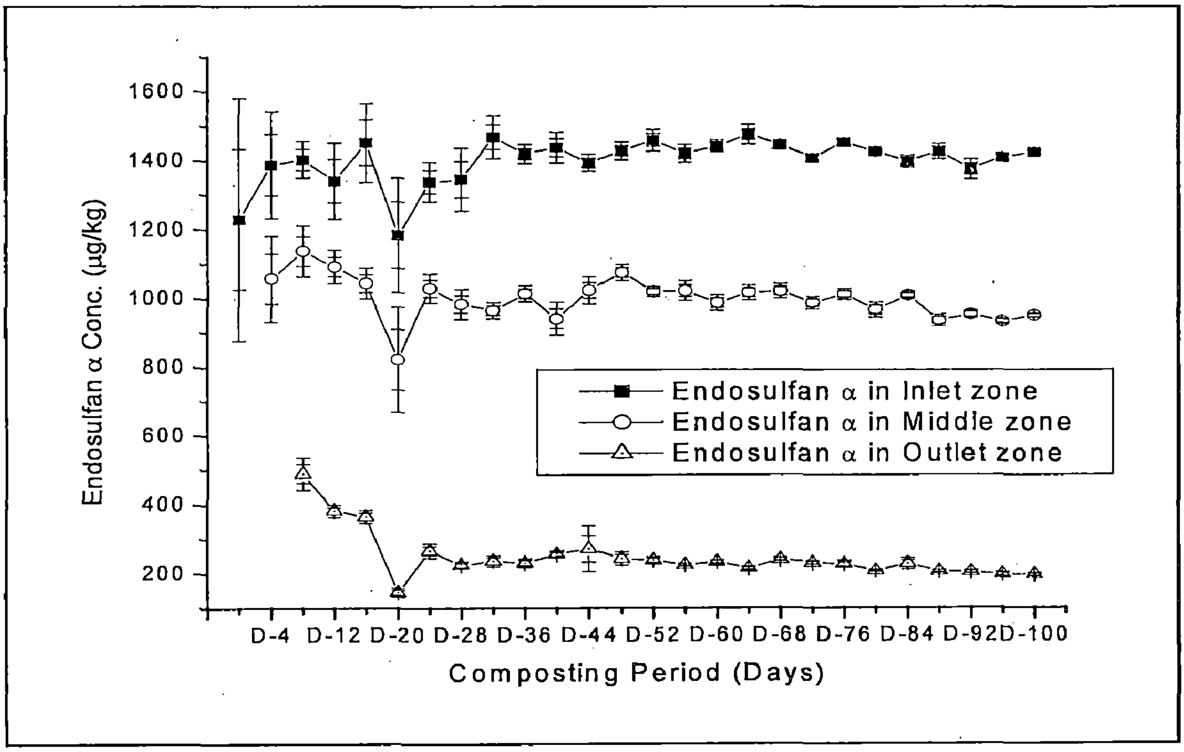


Fig.4.51. Endosulfan α degradation during high rate rotary drum over composting period

Degradation/removal of Endosulfan α and β during rotary drum composting is given in Fig 4.51 & 4.52. The Endosulfan α and β concentration was found in raw wastes from 1200-1400 and 650-700µg/kg respectively due to variation in waste collection time from market. When waste material feeded into the drum, degradation started and around 15-20%. Endosulfan α and β degraded in 24 hours in inlet zone due high temperature (60-65°C), then feeding continues next day, waste material goes to forward direction with degradation, after 4 days material reached in middle zone, Endosulfan α and β concentration was found 950-1050 and 200-250µg/kg respectively. This was assumed that 25% and 64% of Endosulfan α and β removed in 4 days. After that material was reached to outlet zone in next 4 days, Endosulfan α and β concentration was analyzed ranges 200-300 and 100-150 µg/kg respectively. Removal efficiency was achieved from middle to outlet zone 71.42%

and 40% respectively and overall removal efficiency of Endosulfan α and β in 8 days composting was 78% and 78.56% due to the high temperature range, optimum moisture, aeration, proper mixing of waste material and high microbial community growth into the drum.

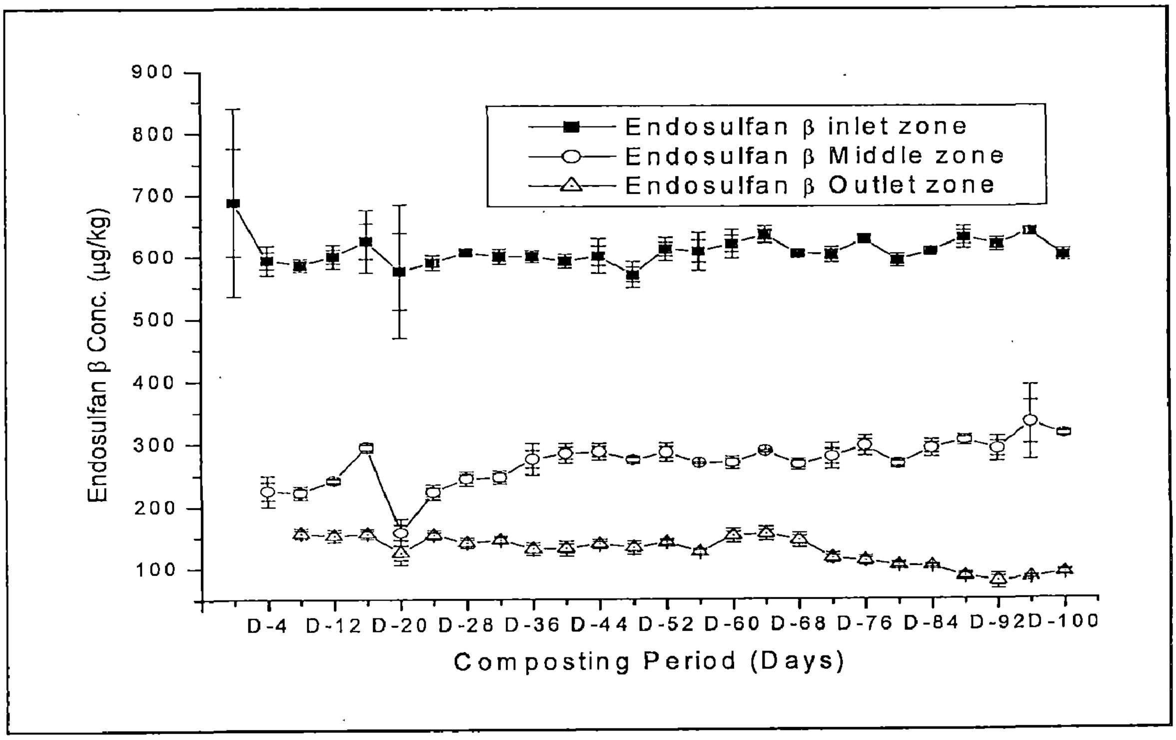


Fig.4.52. Endosulfan β degradation during high rate rotary drum over composting period

- **Degradation of Lindane**

Lindane (γ-hexachlorocyclohexane) has been widely used as an insecticide for crop protection for over two decade. γ-HCH was found to be extremely persistent in the environment under aerobic conditions. During the degradation of the pesticide lindane, by-products like α, β and δ-HCH isomers were also formed (Peter, J. M., *et al*; 1996).

Degradation/removal of Lindane during rotary drum composting is given in Fig.4.53. The Lindane concentration was found in raw wastes from 350-500μg/kg due to variation in components in waste material. When waste material feeded into the drum, degradation started and around 15-20% Lindane degraded in 24 hours in inlet zone due high temperature (60-65°C). Feeding continues next day, waste material goes to forward direction with their degradation, after 4 days material reached in middle zone, Lindane concentration was found 250-300μg/kg. This was assumed that 40% Lindane removed in 4 days. After that material reached to outlet zone in next 4 days, Lindane concentration was analyzed ranges 100-150 µg/kg. Removal efficiency was achieved 50% from middle to outlet zone and overall removal efficiency of Lindane in 8 days composting was 70% due to the high temperature, optimum moisture, aeration, proper mixing of waste material and high microbial community growth in the drum.

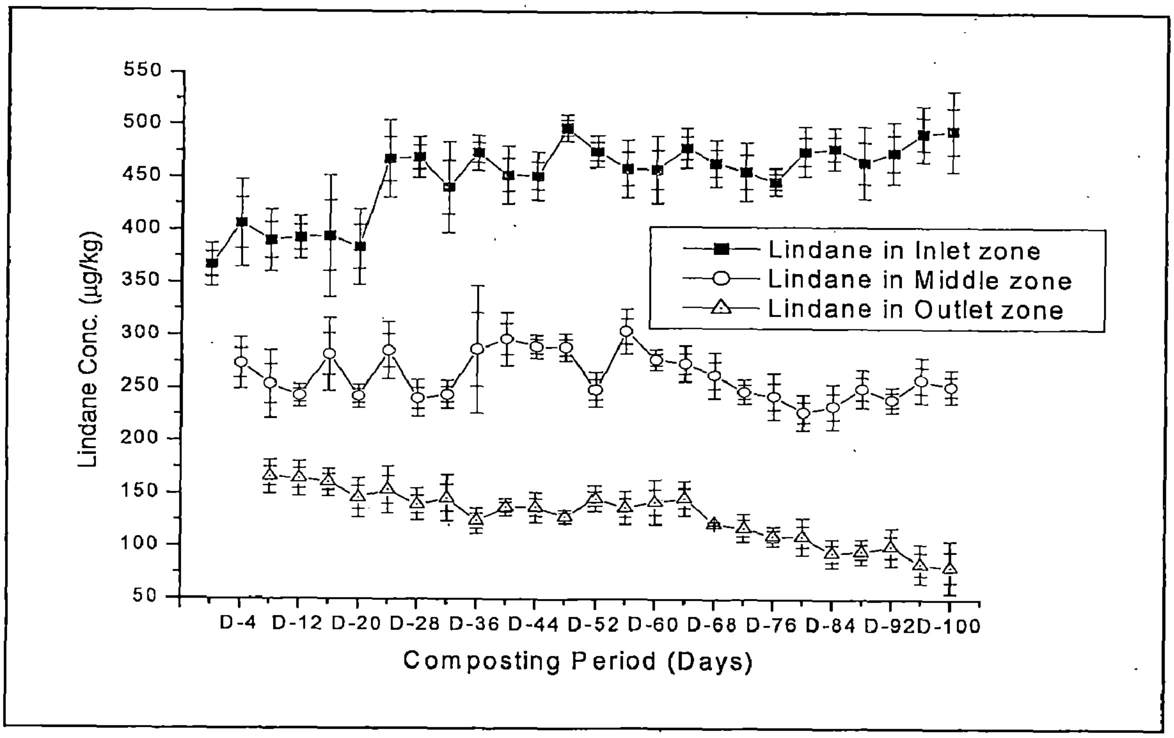


Fig.4.53. Lindane degradation during high rate rotary drum over composting period

Table.4.6. Standard deviation for targeted pesticides Aldrin and Endosulfan-α in different zones of rotary drum composter through composting

	Aldrin						**Endosulfan α**					
Days	*Inlet zone*		*Middle zone*		*Outlet zone*		*Inlet zone*		*Middle zone*		*Outlet zone*	
	μg/kg	*SD*	*μg/kg*	*SD*	*μg/kg*	*SD*	*μg/kg*	*SD*	*μg/kg*	*SD*	*μg/kg*	
0	438.0000	12.16	0.0000	--	0.0000	--	1229.4667	23.1	0.0000	0.0000	0.0000	--
4	484.5100	14.32	232.1567	23.76	0.0000	--	1387.3300	19.43	1057.1933	72.44	0.0000	--
8	471.7800	38.05	236.9233	27.66	209.4433	17.17	1402.5200	10.56	1137.4467	42.5	489.5100	27.4
12	487.5167	20.83	332.6733	12.07	201.4800	21.99	1340.6000	13.58	1091.9600	27.76	381.6633	10.38
16	482.1533	24.01	308.9700	26.07	204.3733	15.61	1451.1867	15.87	1043.8433	25.67	364.5867	11.12
20	500.1200	16.44	222.2667	17.92	172.8833	40.51	1184.2767	15.77	822.0900	88.73	145.7367	7.51
24	481.6033	17.83	239.5167	10.63	166.8333	8.85	1337.5200	13.19	1029.1067	24.27	266.2500	12.15
28	495.4400	25.63	270.4333	13.6	190.1233	5.82	1345.2867	12.39	983.6967	25.34	225.0233	5.32
32	539.7667	18.65	268.4141	15.6	201.5367	17.79	1468.5233	15.96	965.6000	13.66	236.2200	9.21
36	529.5667	13.54	233.0957	13.68	170.7700	18.77	1419.3300	15.83	1014.3933	13.39	231.2500	7
40	574.7400	44.16	244.6767	19.21	192.0733	33.24	1437.7367	25.76	941.4400	28	256.1833	5.73
44	507.0300	25.8	209.7467	24.58	166.8300	12.07	1393.2033	14.38	1023.6267	22.42	271.9967	18.26
48	559.4967	15.85	242.0767	18.15	178.9667	18.37	1428.1133	14.89	1075.1500	13.83	243.4400	10.85
52	524.6033	14.18	300.5667	13.29	183.6533	13.29	1458.7033	18.32	1020.1200	8.28	238.7000	5.71
56	552.6133	17.07	246.0433	35.96	178.1200	18.07	1419.9867	15.05	1022.4480	16.48	225.2833	2.52
60	525.2333	12.66	236.6100	12.15	176.2800	19.77	1441.7967	9.8	987.3300	12.91	233.8567	3.08
64	480.3967	17.68	219.0067	11.71	161.1533	9.59	1475.5233	16.56	1016.8833	12.04	215.4333	3.39
68	534.6533	25.98	244.2167	44	169.4267	5.86	1445.7800	5.88	1021.3367	12.14	240.7800	3.01
72	546.9167	18.54	267.8800	18.08	147.0133	5.55	1407.3967	7.08	987.2633	10.77	230.8667	3.11
76	580.2900	12.9	257.4533	17.37	154.9900	7.43	1453.0400	6.33	1012.8000	8.92	227.1733	5.75
80	511.0767	19.76	248.6633	29	150.5467	8.7	1425.5200	2.74	967.3733	12.77	207.4833	1.77
84	604.1100	19.24	371.6700	16.43	140.1533	10.23	1397.4100	10.11	1009.8900	6.18	228.1867	9.53
88	578.4867	5.87	358.1167	10.28	138.5900	3.34	1426.6333	12.7	936.1133	9.77	205.4833	2.77
92	581.9667	3.94	328.0800	7.08	114.0300	3.09	1375.6633	16.71	954.5200	6.38	204.1500	2.68
96	610.3000	7.02	315.2967	15.02	104.7767	3.24	1409.9600	6.99	934.4400	4.57	197.0700	3.82
100	625.3000	13.65	295.9533	12.72	89.2567	6.07	1424.2000	4.39	950.6333	3.18	195.4333	3.11

Table.4.7. Standard deviation for targeted pesticides Endosulfan-β and Lindane in different zones of rotary drum composter through composting

	Endosulfan β						**Lindane**					
Days	*Inlet zone*		*Middle zone*		*Outlet zone*		*Inlet zone*		*Middle zone*		*Outlet zone*	
	µg/kg	*SD*	*µg/kg*	*SD*	*µg/kg*	*SD*	*µg/kg*	*SD*	*µg/kg*	*SD*	*µg/kg*	*SD*
0	687.6833	17.43	0.0000	--	0.0000	--	366.9000	11.84	0.0000	--	0.0000	--
4	593.3167	13.6	224.4767	14.44	0.0000	--	405.9533	24.08	273.0433	13.98	0.0000	--
8	585.7867	5.89	221.5833	5.84	156.0933	4.83	389.8733	17.05	253.6200	18.6	165.8133	9.2
12	599.4000	10.9	241.0667	2.61	152.4667	5.9	392.5567	11.72	242.6333	6.33	163.9233	9.59
16	624.3333	28.76	294.3767	4.15	155.7000	4.65	394.1900	33.45	282.0400	19.97	160.4633	7.48
20	575.4800	12.16	157.8167	12.36	125.3167	11.55	383.6733	20.8	242.1000	6.47	145.6867	10.78
24	589.7333	6.83	222.5333	6.95	153.4667	4.6	467.6567	21.17	285.5933	15.69	153.3833	12.97
28	606.2800	3.04	244.2333	6.47	140.9000	4.83	469.3133	11.25	240.2667	10.14	139.3800	8.73
32	599.4833	7.22	246.4667	6.12	145.3333	3.84	440.6933	25.18	244.1833	7.62	145.6367	12.64
36	599.4233	5.69	275.3733	14.44	131.0333	5.65	473.9433	9.57	286.9033	34.97	123.9333	6.94
40	591.9167	6.4	284.8000	9.16	132.0333	6.79	452.8153	15.85	296.7900	14.63	137.0333	4.7
44	600.3933	15.99	287.2267	7.75	138.5000	4.44	451.7433	13.18	289.7133	6.42	136.8100	8.4
48	570.0500	12.22	273.9333	3.29	132.9667	6.15	497.7267	7.33	288.9700	7.52	127.8233	3.63
52	610.9467	10.77	286.1000	8.56	140.9000	3.3	475.3233	8.78	248.9533	9.54	145.0267	7
56	607.5000	17.76	268.8000	1.01	125.6333	2.84	458.8800	15.87	304.4433	12.11	136.5500	9.05
60	619.5500	13.16	269.6667	5.85	152.3333	6.47	458.2567	18.41	277.6200	5.63	141.9567	12.13
64	634.6000	7.96	288.0333	1.44	155.3333	6.4	478.8233	10.85	273.9300	9.83	145.3433	9.45
68	603.8000	2.4	266.5000	5.27	145.0000	6.9	464.5067	12.83	262.9233	12.63	121.5833	0.94
72	602.3667	7.5	279.2667	11.9	116.2667	4.8	456.3333	16.19	247.4100	6.71	117.5100	7.69
76	627.3000	4.37	296.5833	9.15	111.6667	4.54	447.1433	7.61	243.1000	12.65	109.7800	5.34
80	592.6233	6.06	267.4000	3.97	103.9667	3.3	475.5467	13.48	227.7433	9.66	109.2200	10.06
84	607.8500	1.5	292.2000	7.71	102.3667	1.63	478.4867	11.33	233.4867	12.42	93.3300	7.72
88	629.9667	10.56	304.5000	4.97	85.9000	3.69	465.3733	19.78	250.4833	10.53	95.0767	6.73
92	618.6333	5.93	290.8333	11.63	78.1667	7.08	474.6267	16.87	239.9300	7.09	99.8167	10.25
96	638.6000	4.23	332.3333	34.38	83.0333	1.59	492.9600	15.53	258.7367	12.44	83.4033	10.8
100	600.8333	5.63	314.4667	3.01	91.0000	3.14	495.6333	22.09	252.5200	9.14	80.3967	14.43

4.2.2.3. First Order Kinetics

For the degradation of organochlorine pesticides, rate constant of degradation and half-life period of the three pesticides and one isomer during rotary drum and windrow composting are thus calculated using, Ēqs. (1) & (2) respectively

$$\ln c = -kt + A \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Generally, the rate of biotic hydrolysis for organic compounds in water is directly proportional to the concentration of the organic compound (Lyman and others, 1990). Assuming this relation, biotic hydrolysis can be described using a first order degradation curve:

$$C_t = C_0 e^{-kt} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where C_t is the concentration of the pesticides at time t, C_0 is the initial concentration of the pesticides, and k is the rate constant (Wang and Hoffman, 1991).

- **Half-life calculation**

A plot of ln (C_t/C_0) versus time yields a straight line with slope equal to k. The rate constant can then be used to derive the half life $t_{1/2}$:

$$t_{\frac{1}{2}} = \frac{\ln 2}{\mathrm{k}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

Or

$$t_{\frac{1}{2}} = \frac{0.693}{\mathrm{k}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where k is a constant and $t_{1/2}$ is half-life period of the pesticide. The obtained values are listed in table. 4.8.

For the degradation of pesticides Aldrin, Endosulfan α, Endosulfan β and Lindane in the composting through full-scale high rate rotary drum composting and half life period listed in table 4.8 and Fig.4.54. The degradation of Aldrin, Endosulfan α, Endosulfan β and Lindane in drum composting increased due to higher temperature, optimum moisture and more alkaline pH throughout the composting process, lead to a larger rate constant of degradation 0.03, 0.04, 0.04 and 0.03/ day for Aldrin, Endosulfan α, Endosulfan β and Lindane respectively or a shorter half-live period (average) 25.54, 18.43, 18.43 and 27.43 days respectively of these pesticides in case of drum composting (table 4.7) due to more and easily available pesticides compared to pesticides found in real vegetable waste.

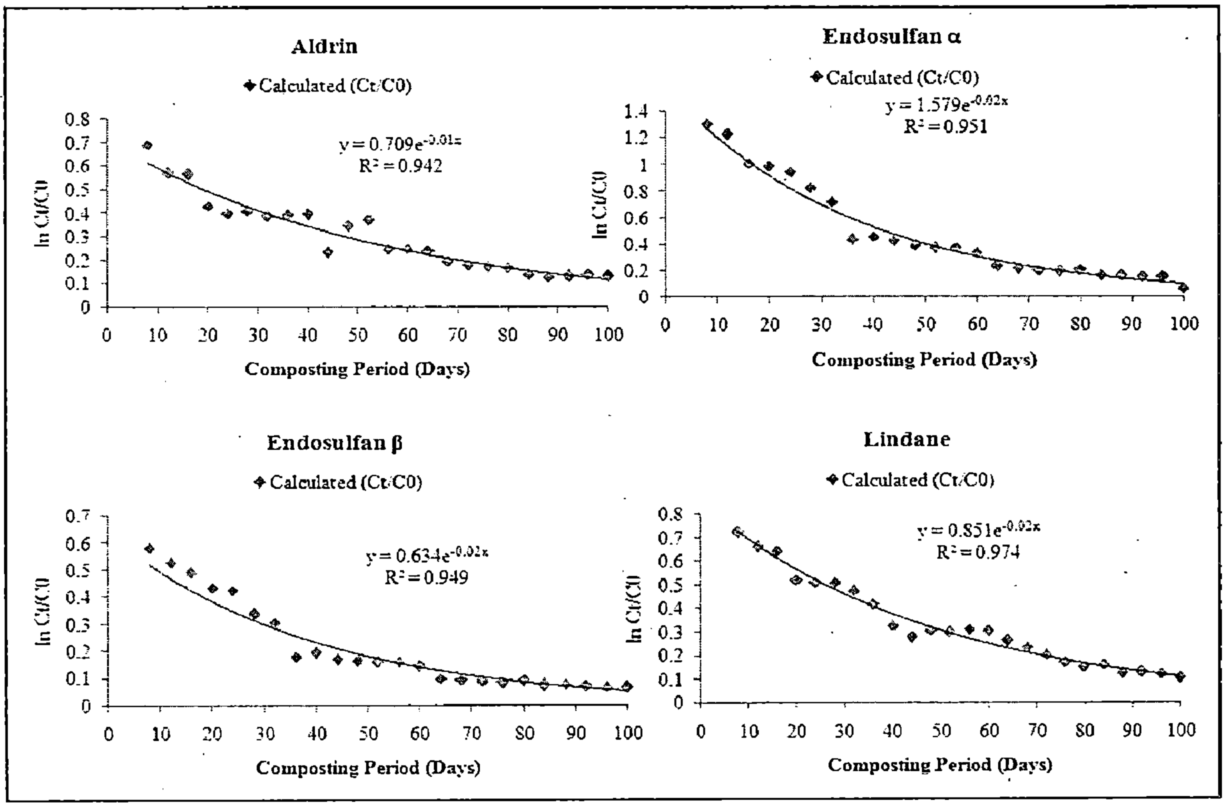


Fig.4.54. Kinetics of degradation of pesticides during full-scale continuous rotary drum over composting period

Table.4.8. Kinetic parameters, k value, half life ($T_{1/2}$ in day) for Aldrin, Endosulfan and Lindane with their average value through rotary drum composting

Kinetic parameters								
	Aldrin		**Endosulfan α**		**Endosulfan β**		**Lindane**	
Days	**K value**	**$T_{1/2/day}$**	**K value**	**$T_{1/2/day}$**	**K value**	**$T_{1/2/day}$**	**K value**	**$T_{1/2/day}$**
4	0.06	11.07	0.14	4.82	0.14	4.82	0.07	10.04
8	0.05	14.93	0.07	10.28	0.07	10.28	0.04	17.11
12	0.05	14.78	0.05	13.03	0.05	13.03	0.03	20.07
16	0.04	19.44	0.04	15.56	0.04	15.56	0.03	24.87
20	0.04	16.41	0.04	16.66	0.04	16.66	0.03	21.22
24	0.04	18.02	0.04	19.44	0.04	19.44	0.03	24.70
28	0.03	21.71	0.04	17.88	0.04	17.88	0.02	28.98
32	0.03	23.26	0.04	18.61	0.04	18.61	0.02	29.57
36	0.03	26.64	0.05	14.46	0.05	14.46	0.02	28.73
40	0.02	30.02	0.04	16.97	0.04	16.97	0.03	24.66
44	0.03	20.94	0.04	17.23	0.04	17.23	0.03	23.74
48	0.02	31.27	0.04	18.37	0.04	18.37	0.02	28.02
52	0.02	36.38	0.04	19.57	0.04	19.57	0.02	29.72
56	0.03	27.66	0.03	21.33	0.03	21.33	0.02	33.11
60	0.02	29.54	0.03	21.61	0.03	21.61	0.02	34.87
64	0.02	31.09	0.04	19.04	0.04	19.04	0.02	33.08
68	0.02	28.64	0.03	19.84	0.03	19.84	0.02	32.59
72	0.02	28.90	0.03	20.48	0.03	20.48	0.02	31.29
76	0.02	30.26	0.03	21.10	0.03	21.10	0.02	30.00
80	0.02	31.12	0.03	23.20	0.03	23.20	0.02	29.55
84	0.02	29.21	0.03	22.35	0.03	22.35	0.02	31.90
88	0.02	29.47	0.03	23.63	0.03	23.63	0.02	29.68
92	0.02	31.25	0.03	24.28	0.03	24.28	0.02	31.08
96	0.02	33.19	0.03	24.61	0.03	24.61	0.02	31.60
100	0.03	23.37	0.04	16.41	0.04	16.41	0.03	25.57
Average	0.03	25.54	0.04	18.43	0.04	18.43	0.03	27.43

4.2.2.4. Biochemical transformation of Aldrin, Endosulfan α, Endosulfan β and Lindane

Aldrin, Endosulfan α, Endosulfan β and Lindane transformation was also observe during full-scale continuous high rate composting, results are almost same as given in part A. However, intermediates of each pesticide were different in different zones (inlet, middle and outlet zone). Aldrin converted to dieldrin by epoxidation. Dieldrin converted to the Aldrin diol by hydroxylation (Fig.4.18) in inlet zone. After that material moved to midde zone in next 4 days, aldrin diol liberated ethylene molecule to obtain product (A) and rearrangement products like 1-hydroxychlordene and its isomers.1-Hydroxychlordene oxidized into dihydroxyl group and further oxidized to acidic (B) and aldehydic (C) products. Then, it converted to aldehydic (D) by the liberation of CO_2 gas in middle zone. Aldehydic moiety of aldrin finally converted to 4,7-methanoisobenzofuran and 4,5,6,7,8,8-hexachloro-1,3,3a,4,7,7a-hexahydro-, by the elimination of H_2O when the material reached to outlet zone in next 4 days. Similarly, endosulfan isomerised to the endosulfan β and then endosulfan sulfate (Fig.4.23) in inlet zone. Endosulfan sulfate is very toxic and persistent in environment but in the rotary drum composting easily converted to endosulfan ether by the liberation of SO_3 gas when the material reached to middle zone in 4 days. During the next 4 days material goes to outlet zone, Endosulfan ether suddenly converted to chlorendic acid taking of water and then changed to chlorendic anhydride by dehydration. Finally, chlorendic anhydride converted by microbial communities to the 4, 5, 6, 7-tetrachloro-3-hydroxy-3H-isobenzofuran-1-one taking out of two chloride ions. 4, 5, 6, 7-tetrachloro-3-hydroxy-3H-isobenzofuran-1-one was not degraded further and persist to the composting environment however less toxic in nature. Under aerobic condition, γ-Lindane converted to β-Lindane, which is most persistent in environment (Fig.4.28 and 4.29). However, in drum composting β-isomer undergoes dehydrohelogenation and dehalogenation to afford pentachlorocychlohexene (PeCCh) and tetrachlorocychlohexene (TeCCh) compounds respectively next day in inlet zone. During the 4 days when material reached to middle zone in inlet zone, PeCCh converted to pentachlorocychlohexanone under oxidation in aerobic condition followed 1,2,3,5 -tetrachlorocychlohexanone by the dehalohydrogenation. Finally, it converted to 1,2,3 trichlorocychlohexenone after dehydrogenation. When material goes to outlet zone during next 4 days, TeCCh also gave 1,3,5-trichloro-1,4-dihydroxybenzene intermediate. 1,2,3 trichlorocychlohexenone and

1,3,5-trichloro-1,4-dihydroxybenzene intermediates have less toxicity than the Lindane and its β-isome.

4.2.2.5 Microbiological assays

- ***Total Heterotrophic Bacteria***

Total heterotrophic bacterial count in the feedstock was 2.3 × 10^4 CFU/g. Finally, number reduced to 2.5 × 10^2 CFU/g and 2.3 × 10^2 CFU/g in middle zone and outlet respectively (Fig.4. 55). Certainly, environmental conditions as well as many other factors, could affect the bacteria populations and when temperature increases, the species variety has been found to decrease (Stoffella & Kahn, 2001).

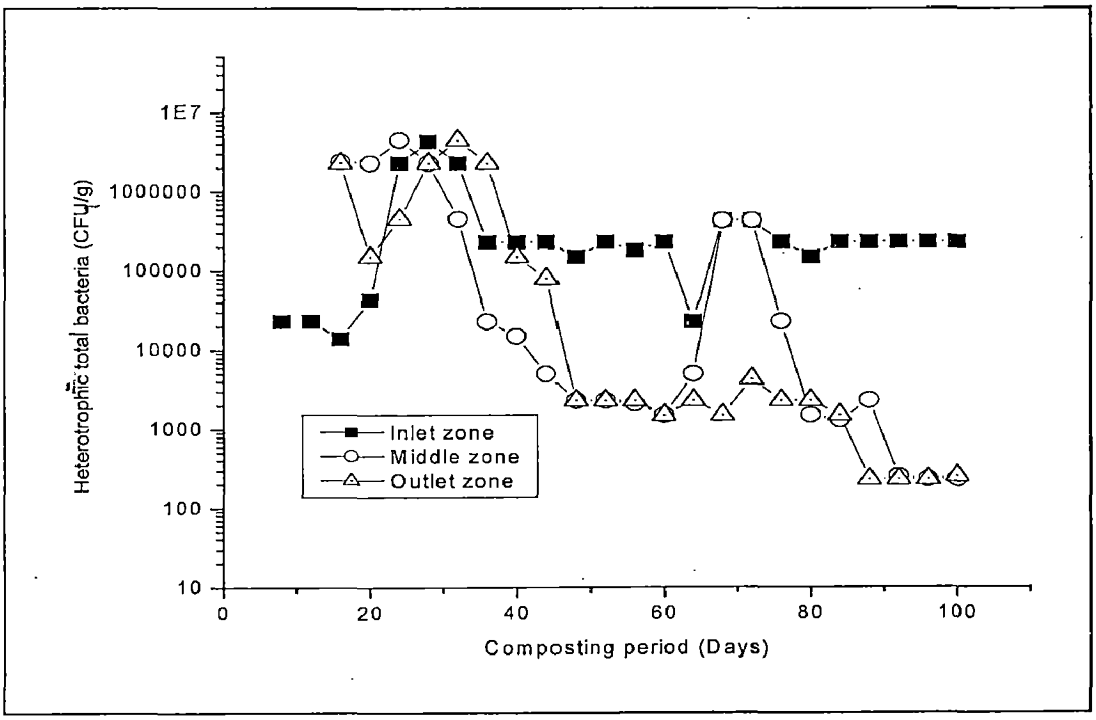


Fig.4.55. Total bacterial count of the composting materials over composting period

- ***Total fungus***

The population of total fungal load initially increased from inlet to outlet zone was 2.3×10^2 CFU/g to 2.5×10^4 CFU/g within initial 50 days and subsequently increased to 4.5×10^5 CFU/g in days 60 and days 72 in full-scale rotary drum composting, due to the optimization of composting process and then population of fungi suddenly decreased to 1.2×10^4 CFU/g in 80th day might be due to high humidity (99%) (Fig.4.56). After 84 days the population of fungus was remain constant (2.3×10^4) till the end of composting process. *Aspergillus* species and *Rhizopus* species were identified as the major mycofloral in fungus population. They can survive at higher temperature (55-61°C) in inlet, middle as well as lower temperature (30-40°C) at outlet zone during the composting process.

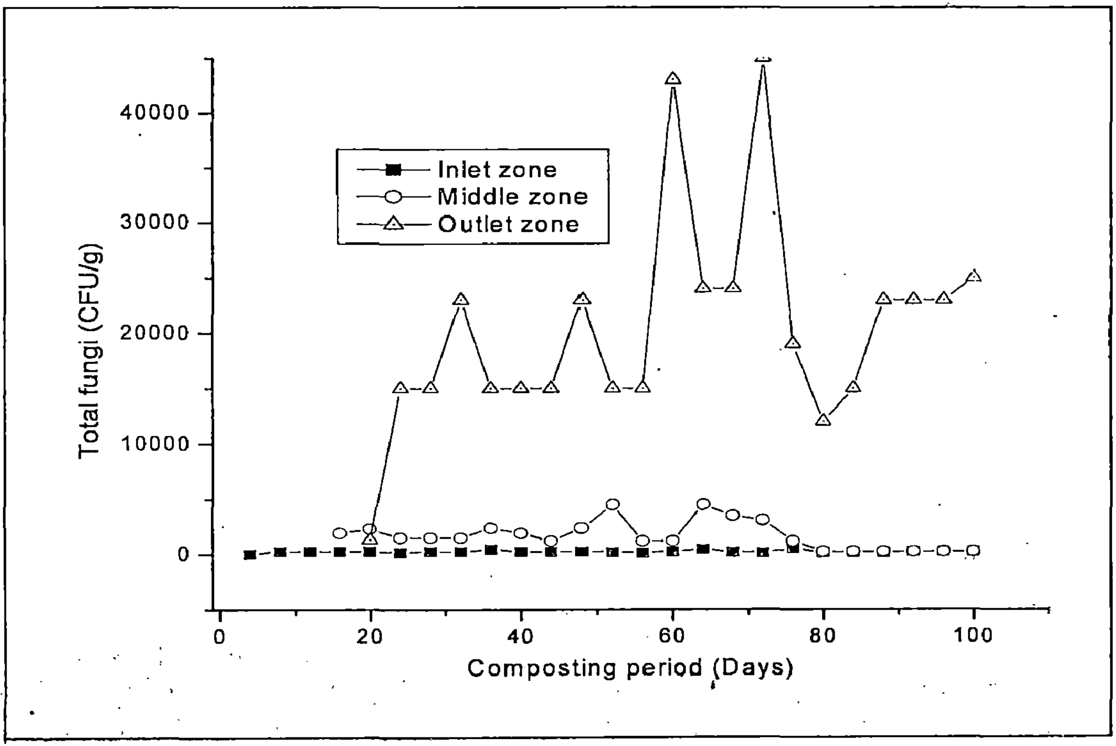


Fig.4.56. Total fungus count of the composting materials over composting period

4.2.2.6. 24-hour Study of Aldrin, Endosulfan α, Endosulfan β and Lindane degradation

4.2.2.6.1 Physico-chemical parameters

- ***Temperature profile***

Temperature plays a key role in pesticides degradation due to variation of microbial communities and increase of dissolution of pesticides in aqueous phase of composting material. 24 h temperature study of Aldrin, Endosulfan α, Endosulfan β and Lindane degradation suggested that the temperature at inlet zone (Active stage of composting), after feeding and turning reduced to 38°C and reached to 60-65°C within 7-8 hours (Fig.4.57) due to entering new waste material, atmospheric air and ventilation of heat from the composting material and change in microbial communities. Thus, inlet zone might be varies in microbial populated region of RDC and effect the degradation of pesticides. Similarly, there were no magnificent changes we were found in middle and outlet zones temperature after rotation of drum.

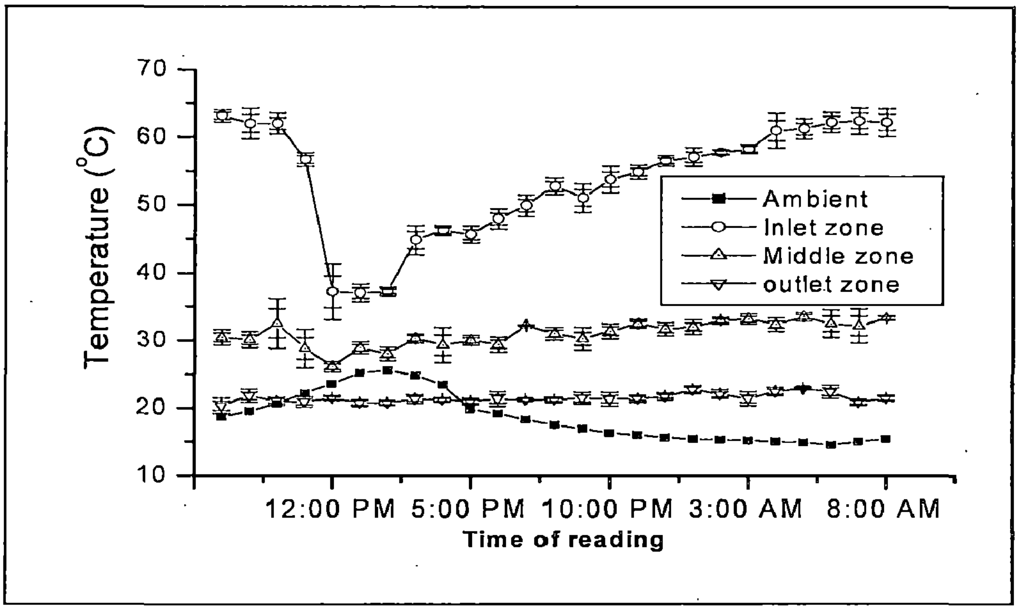
- ***pH profile***

pH during 24 hours in rotary drum composting varies after feeding and rotation of drum due to entering of new food materials, atmospheric CO_2 by aeration and escaping of heat and microbial growth in the system. In inlet zone, after rotation pH suddenly decreased from 7.5±0.3 to 5.3±0.2 in 4th hour (Fig.4.57). After 4 hour, pH increased gradually and reached to initial pH (7.5±0.3) in 10th hour due to gradual increase in temperature might be increased microbial population. pH remains constant after 10 hour to 24 hour in inlet zone of the drum. In middle and outlet zones slight changes in pH from 8.4±0.3 to 7.9±0.2 and 8.2±0.2 to 8.6±0.3 due to basic in nature in middle and outlet zones respectively in 24 hours. The variation in pH during 24 hours in inlet, middle and outlet zones of rotary drum suggested that the variation in temperature might be due to the variations in microbial communities causing pesticides degradation.

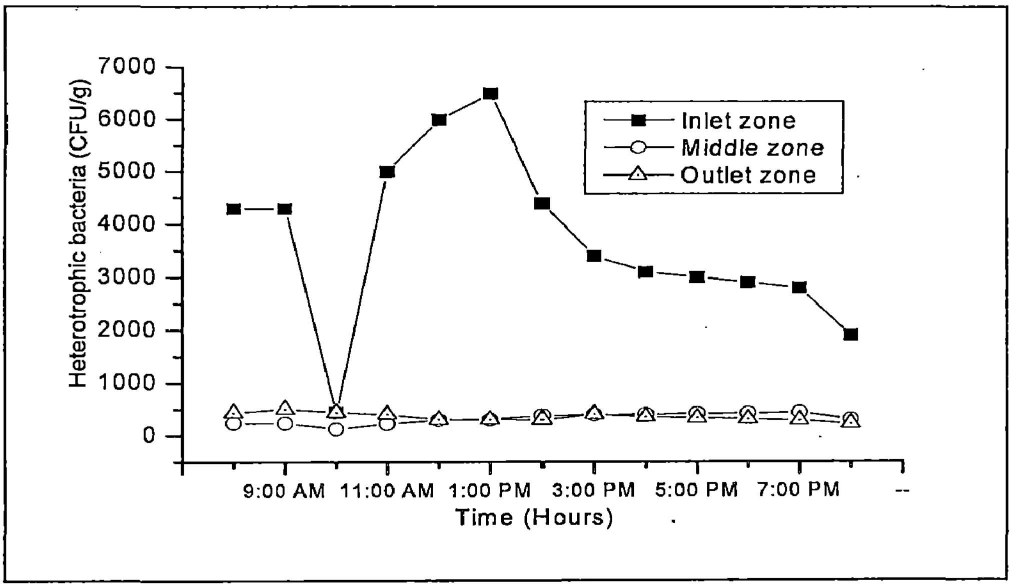
- ***Heterotrophic bacteria***

During the study of heterotrophic bacteria, decreased from 8.00×10^3 to 7.80×10^2 CFU/g (Fig.4.57) after feeding and rotation in inlet zone of rotary drum composter in 2 hours due to decrease in temperature, pH and entering of fresh waste material into the system.

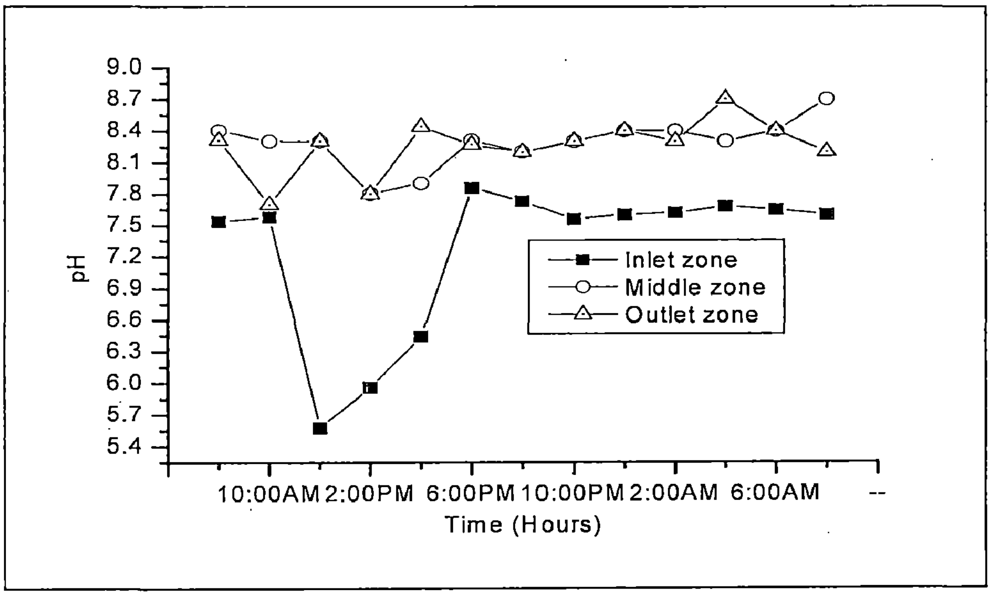
Followed by, heterotrophic bacteria also decreased from 4.00×10^2 to 1.00×10^2CFU/g in middle zone of drum due to decrease in temperature and pH. No significant changes in bacterial communities were observed in outlet zone with feeding and rotation due to less variation in temperature and pH. The major changes in heterotrophic bacteria in inlet and middle zone of rotary drum attributed that these zones have diverse microbial communities which affect the degradation of pesticides and organic matters present in waste material.



(A)



(B)



(C)

Fig.4.57 (A, B, C): Temperature, hetrotrophic bacteria and pH profile in inlet, middle and middle zone after feeding and rotation in 24 hours during full-scale continuous rotary drum composting

4.2.2.6.2 Pesticides degradation

- ***Aldrin degradation***

  Degradation/removal of Aldrin after feeding and rotation in 24 hours during full-scale continuous rotary drum composting is given in Fig.4.58. The Aldrin concentration was found in raw waste 1.23mg/kg when waste material loaded into the inlet zone of the drum due to variation in waste material, collected in different time from vegetable market. The concentration of Aldrin was decreased from 1.23 to 0.92 mg/kg by 20% degradation during 24 hours in inlet zone. Since, no significant effect on pesticides degradation was observed by the feeding and rotation of rotary drum composter. Similarly, around 40% aldrin degradation was also observed in middle zone within 24 hour in and after feeding and rotation of drum. No significant changes in aldrin concentration were found in outlet zone in 24 hour after feeding and rotation.

- ***Endosulfan α degradation***

  Degradation/removal of Endosulfan α after feeding and rotation in 24 hour during full-scale continuous rotary drum composting is given in Fig.4.58. The Endosulfan α concentration was found in raw waste 1.199 mg/kg when waste material loaded into the inlet zone of the drum due to variation in waste material, collected at different time from vegetable market. The concentration of Endosulfan α was decreased from 11.99 to 7.8 mg/kg by 35% degradation during 24 hour in inlet zone. No significant effect on pesticides degradation was observed by the feeding and rotation of rotary drum composter. Similarly, around 30% Endosulfan degradation was also observed in middle zone within 24 hour in and after feeding and rotation of drum. In outlet zone around 20% reduction in concentration of Endosulfan α was observed in 24 hour after feeding and rotation.

- ***Endosulfan β degradation***

  Degradation/removal of Endosulfan β after feeding and rotation in 24 hour during full-scale continuous rotary drum composting is given in Fig.4. 58. The Endosulfan β concentration was found in raw waste 5.42 mg/kg when waste material loaded into the inlet zone of the drum. After 2 hours, the concentration of Endosulfan α increased from 5.42 to 6.38 mg/kg due to conversion of Endosulfan α to Endosulfan β during composting. Followed by, the concentration of Endosulfan β was decreased to 3 mg/kg by 30% degradation during 24 hour in inlet zone. Pesticides degradation was also observed by the feeding and rotation of rotary drum composter in middle and outlet zone by the reduction of 20-24% and 20-32% in Endosulfan β concentration respectively within 24 hours.

- ***Lindane degradation***

  Degradation/removal of Lindane after feeding and rotation in 24 hour during full-scale continuous rotary drum composting is given in Fig.4.58. Lindane concentration was found in raw waste 4.42 mg/kg when waste material loaded into the inlet zone of the drum. After 2 hours, the concentration of Lindane decreased suddenly from 4.40 to 3.18 mg/kg. Followed by, the concentration of Lindane was decreased slowly 3.18 to 2.73 mg/kg by 25-30% degradation during 24 hour in inlet zone. Pesticides degradation was observed by the feeding and rotation of drum composter in middle and outlet zones by the reduction of 20-22% and 20-33% Lindane concentration respectively in 24 hours.

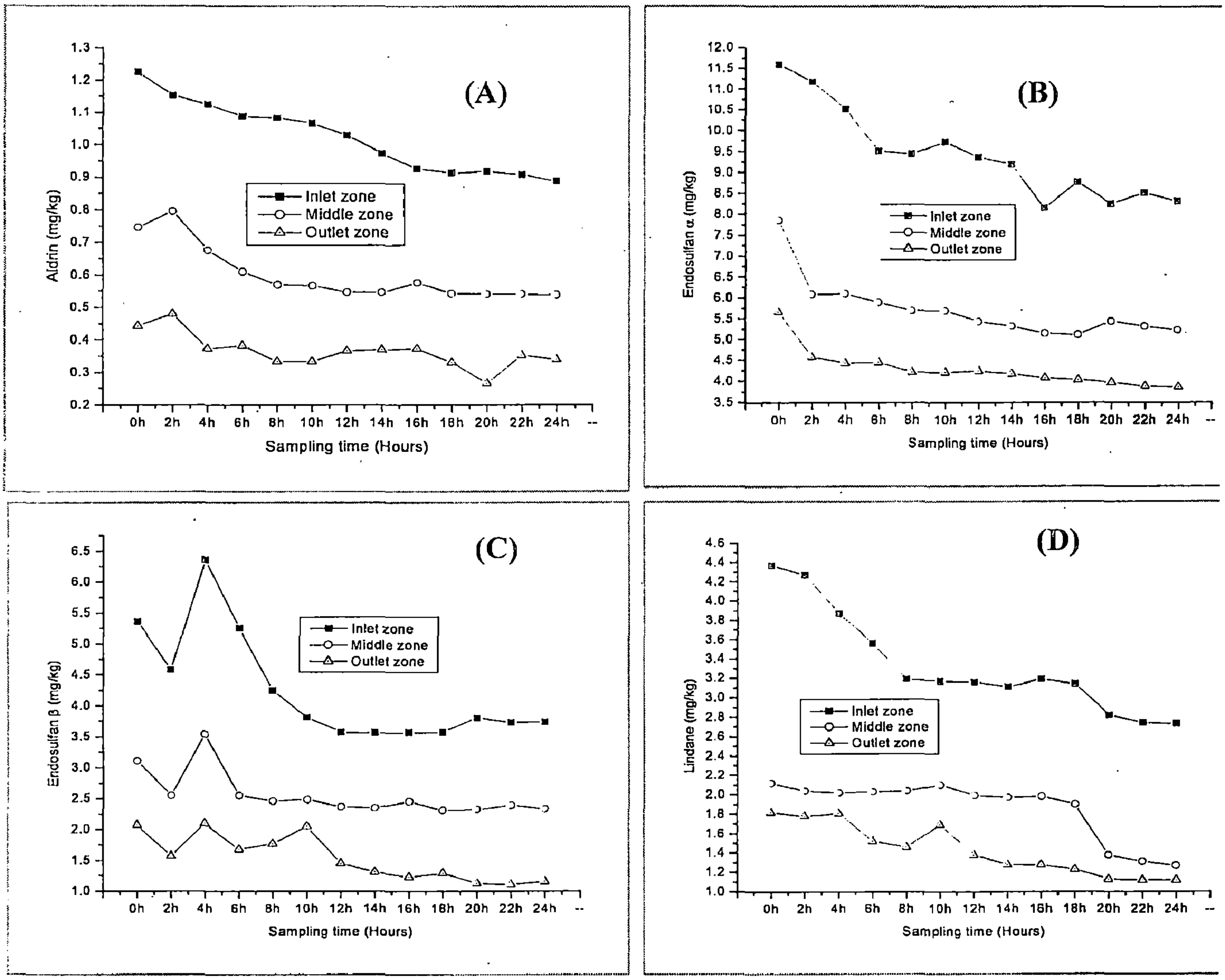


Fig.4.58. (A, B, C and D) Aldrin, Endosulfan α, Endosulfan β and Lindane degradation after feeding and rotation in 24 hours during full-scale continuous rotary drum composting

4.2.2.7 Conclusions

In conclusion, the removal efficiency of respective pesticides namely Aldrin, Endosulfan α, Endosulfan β and Lindane was calculated as 85.67, 84.95, 83.20 & 81.36% respectively in the rotary drum composting (RDC) might be due to the optimum temperature, moisture, pH and enhanced microbial activity. Temperature of inlet or feeding zone drum was around 65°C, highly suitable for microbial population. Similarly, in 24h study of pesticides degradation suggested that temperature at inlet zone after feeding and turning reduced to 38°C and reached to 60-65°C within 7-8 hours might be due to a complex microbial populated region in which heterotrophic bacteria such as *Bacillus species, Pseudomonas sp. and Lactobacillus* species varied with turning, temperature and pH variations. During our study, the targeted pesticides Aldrin, Endosulfan α, Endosulfan β and Lindane degraded around 20-30% in inlet 30-60% in middle and remaining 20% in outlet zone of the rotary drum, might be due to variation of complex microbial communities. However, there was no significant change found in middle and outlet zone temperatures. Meantime, the first order degradation kinetics of pesticides degradation was observed during rotary drum composting and the half life period for respective pesticides, Aldrin, Endosulfan α, Endosulfan β and Lindane as 25.54, 18.43, 18.43, and 27.43 days from 1095 days, 60 days, 270 days and 160 days respectively. Biochemical transformation of these pesticides also gave same intermediates as given in small-scale drum composting. Therefore, observations in contrast of removal and degradation kinetics of organochlorine pesticides residues in vegetable waste though high rate composting proved that full-scale rotary drum composter is the best suited technique and suggested that this technique is useful for removal of organic pollutants like pesticides in full-scale composting plants used for various kinds of waste.

CHAPTER 5

Effects of seasonal variations on fate of pesticides under full-scale continuous rotary drum composting

This chapter deals with the effect of seasonal variations on degradation of Aldrin, Endosulfans and Lindane pesticides in full-scale continuous rotary drum composting.

5.1. INTRODUCTION

The chemical composition of vegetable waste, yard waste, municipal solid waste (MSW) and compost varies widely according to the geographic region, seasonal variations in raw input and pretreatment process (McGrowin, *et al*; 2001 and He, *et al*; 1992). However, some questions concerning the potential health hazard have been raised related to the presence of organic contaminants in composts (He, *et al*; 1995, McGrowin, *et al*; 2001, Lazzari, *et al*; 1999). Among the organic contaminants, there are organochlorine pesticides, which are known as persistent organic pollutants (POPs) and varied seasonally (McGrowin, *et al*; 2001, Grossi, *et al;* 1998 and 1999). Due to their considerable thermal stability, POPs resist the composting process and remain in the finished product, which will be deposited on an uncontaminated site (Lee, *et al*; 2003). Lazzari and co–workers (1999) described that during a composting process, pesticides could be relatively lost by volatilization. In fact, the composting time, about three months, is too short to give rise to a significant loss of pesticides from microbial decomposition. In soil, microbial degradation of polychlorinated biphenyls (PCBs) occurs significantly only after twelve months (Lazzari, *et al*; 1999).

Researchers were surprised to find seasonal variations by class of pesticides, three classes of insecticides and two classes of herbicides. The pesticide content in the raw waste generally peaked in the winter months. The primary rationales for seasonal sampling when the program was designed have had an anticipated peak time in the spring and/or early summer for the most pesticides (Terrance, *et al;* 1992). In mentioned literature the detection of pesticides were carried out in raw waste and compost and their persistence in natural environment. However, studies limited only for windrow composting which has drawbacks like more time, land requirement and pollute environment such as ground water, air and soil. Therefore, studies to remove these pollutants have some environment benefits for the long time seasonal variations, we required. Therefore, an effect of seasonal variations on fate of pesticides under full scale continuous high rate rotary drum composting is considered.

5.2. Results and discussions

5.2.1. Physico-chemical parameters

- ***Temperature profile***

The temperature variation during rotary drum composting is presented in Fig.5.1. In winter season, the temperature in inlet zone increased 65-70°C during initial 20 days, followed by decreased 60-65°C during next 50-60 days along with decrease in ambient temperature. Furthermore, the temperature decreased upto 50-60°C in spring season (60-120 days) due to not feeding and rain depending upon the ambient temperature. During summer season (120-180 days) temperature remained between 65-70°C in inlet zone of the drum. The temperature in the middle zone varied between 40-55°C during winter season, whereas in spring and summer season, temperature was found 40-50°C and 35-40°C respectively due to lower microbial activity in inlet zone. The temperature at the outlet zone of the drum was found equal to ambient or slightly more (25-40°C) during all seasons except winter season, indicated the end of active thermophilic composting.

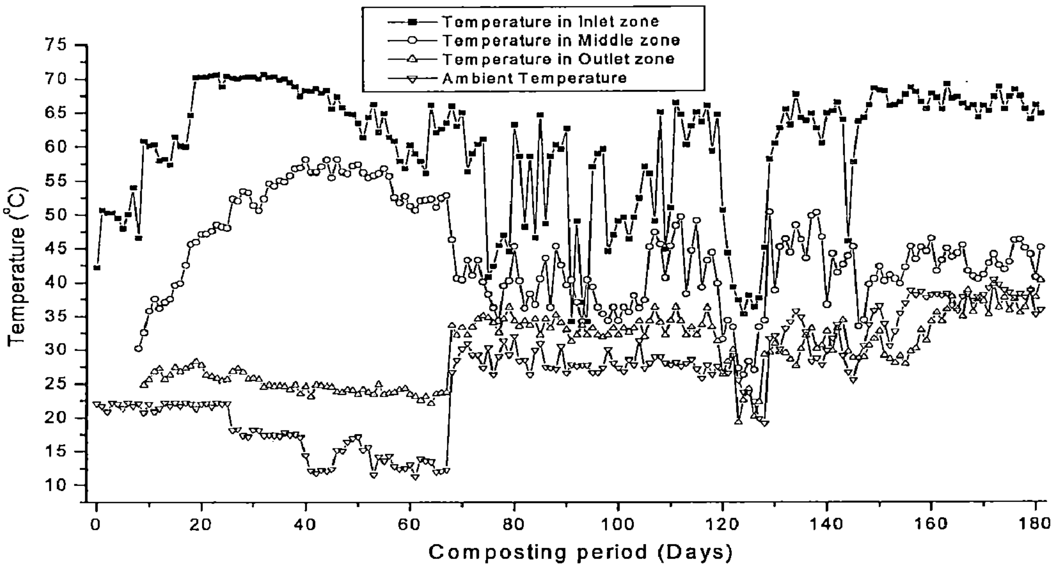


Fig. 5.1.Temperature profile during full-scale continuous rotary drum composting over composting period

- ***Moisture content***

Moisture loss during the full-scale continuous rotary drum composting has shown in Fig. 5.2. Moisture content in the middle zone was about the same as that of the inlet zone during all seasons (except in summer season, after 140 days). In outlet zone, moisture content was found 55-62% after 20 days in winter season and reduced to 58-50% during 40-60 days due to leachate generation (1-2 L/day). Thus, the controlled composting process in the drum was adjusted the air supply in order to remove the extra water from the process. Therefore, the time period of aeration through air blower was increased upto 24 h during the whole study. The possible reason for leachate generation was the condensation of water vapors aroused due to temperature increase inside the drum. One of the possibilities for moisture control could be increasing the number of rotations of the drum 1-2 times/day, but it causes excess aeration and reduction in temperature. Another option for the moisture reduction could be the addition of dry materials such as dry tree leaves, saw dust or wheat/rice straw to the initial waste material but these gradients increased carbon content in the feedstocks. During spring and summer seasons, moisture content was found 46-55% and 45-52% respectively in outlet zone.

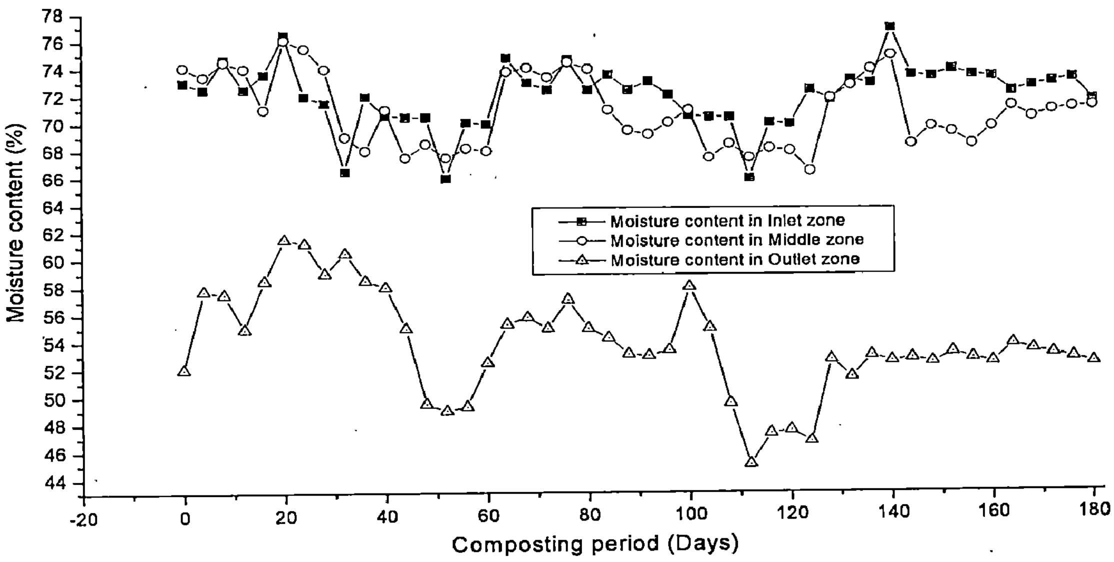


Fig. 5.2.Moisture content during full-scale continuous rotary drum composting over composting period

- ***pH profile***

Fig. 5.3 displays the pH profile of the composting material during full-scale continuous rotary drum composting. Increase in the pH level during composting results in increase of volume of ammonia released due to protein degradation. Increased rate of aeration in the drum by daily turning tend to decrease CO_2 levels in the compost, which in turn tend to increase pH (Haug, 1993). The trend of pH at middle zone and outlet zone of the drum was similar in all seasons except days 40-60 in winter season, days 80-100 in spring season and days 120-140 in summer might be due to not feeding and variation of waste material. In inlet zone pH was found 6.0-6.5 during winter season from 0-40 days. After 40th day pH increased 6.0-7.0 till 60 days might be due to development of high microbial activity. During spring season (60-120 days) pH was found 6.5-7.0 except 100-110 days (5.0-5.5) due to variable waste material and not feeding. In summer season the pH was also found near 6.0-6.5 in inlet zone except 164th day. Hence, with the huge variation in pH from inlet to outlet zone of the drum during seasonal variations changed the microbial population of the drum, resulted in enhanced the degradation of pesticides.

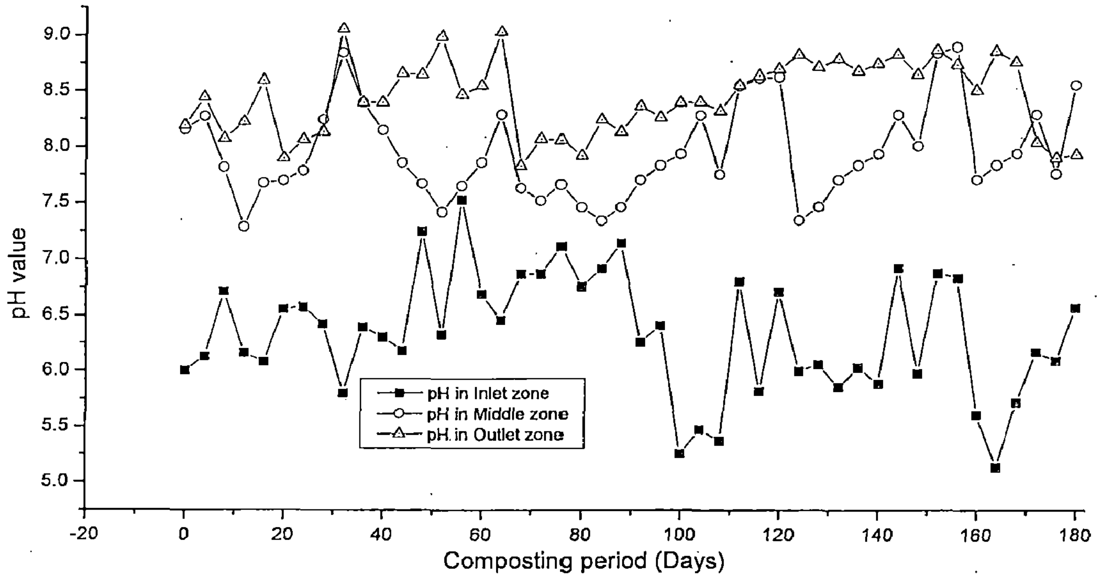


Fig. 5.3.pH profile during full-scale continuous rotary drum composting over composting period

- ***Carbon decomposition (TOC) profile***

Total carbon content is useful substrate for the degradation of pesticides in compost. During the composting process, CO_2 is emitted from the composting mass as a metabolic end product.

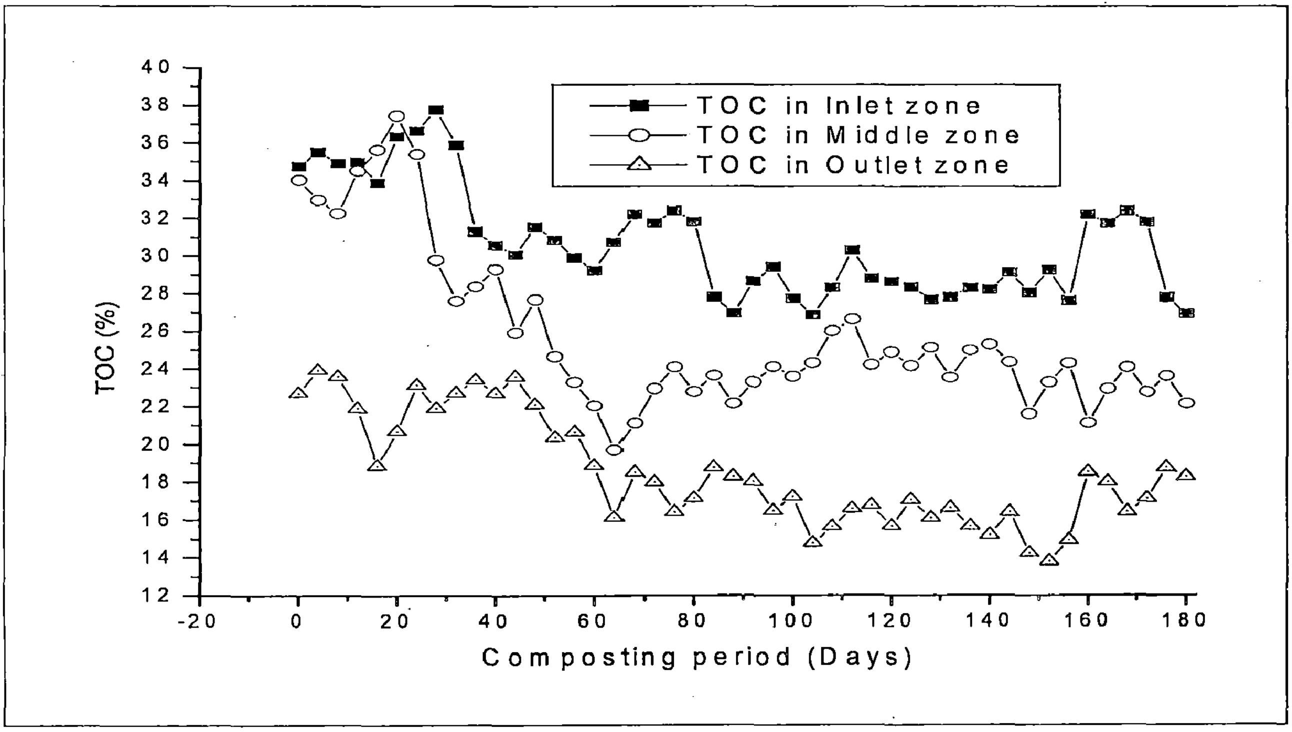


Fig. 5.4.TOC profile during full-scale continuous rotary drum composting over composting period

Thus, the content of organic carbon decrease as the decomposition progressed. Changes in the TOC during the drum composting are given in Fig. 5.4. Initially, the amount of TOC at inlet zone was upto 30–37% in 60 days of loading (winter season), which reduced to 27–30% due to proper conditions for microbial degradation achieved in inlet. Similarly, when the material reached to outlet zone of the drum in 8 days, total organic carbon at outlet zone was reduced from 18–23% in middle zone and 15–18% in outlet zone. It was observed that the organic carbon content decreased with the drum composting, which reflects a notable mineralization of organic matter and pesticides degradation. During spring season (60-120 days) TOC in inlet zone was ranges 28-32%. It reduces 31% when the material reached in middle zone and the TOC concentration 22-24% in this zone. When the material goes to outlet zone, TOC in this zone was found 16-18% by the reduction of 32%. During summer season (120-180 days) TOC concentration in inlet zone was ranges 28-33%. When the material goes to middle zone in four days TOC was found 22-24%, reduced about 27.27%. Furthermore, when the material goes to outlet zone in next four days TOC concentration was found 14-17%, reduced about 41.66%. However, the overall TOC concentration during winter, spring, and summer seasons in full scale rotary drum composting in 8 days composting period was found 65, 63, and 69% respectively. High reduction in summer season (69%) due to more microbial population and optimum temperature conditions resulting in high degradation of pesticides. The TOC reduction in winter season (65%) was more than spring season (63%) due to TOC might be removed by leachate generation (1-2 L/day).

- ***Total Nitrogen profile (TN)***

Fig. 5.5 shows the time course of the TN consisting of inorganic forms of nitrogen (NH_4–N and NO_3–N) and organic nitrogen (Norg). TN increased within full-scale continuous rotary drum composting due to the net loss of dry mass in terms of CO_2 as well as the water loss by evaporation due to heat evolution during oxidization of organic matter (Kalamdhad, *et al*; 2009). Nitrogen fixing bacteria might also be contributed to the increase in TN in later stage of composting (Bishop and Godfrey, 1983). Both TN and Norg behaved in a similar manner during composting as observed by Sanchez- Monedero, *et al.* (2001). An increase in Norg can be attributed as a consequence of strong degradation of organic carbon compounds. The increment in TN from inlet to outlet zone 1.42-1.70% in winter (0-60 days), 1.41-1.80% in spring season (60-120 days) and 1.34-2.20% in summer season (120-180 days). A large increase in TN in summer season from 1.34- 2.20% was observed compared to winter and spring seasons due to high temperature, no leachate generation from composting system, better environmental condition.

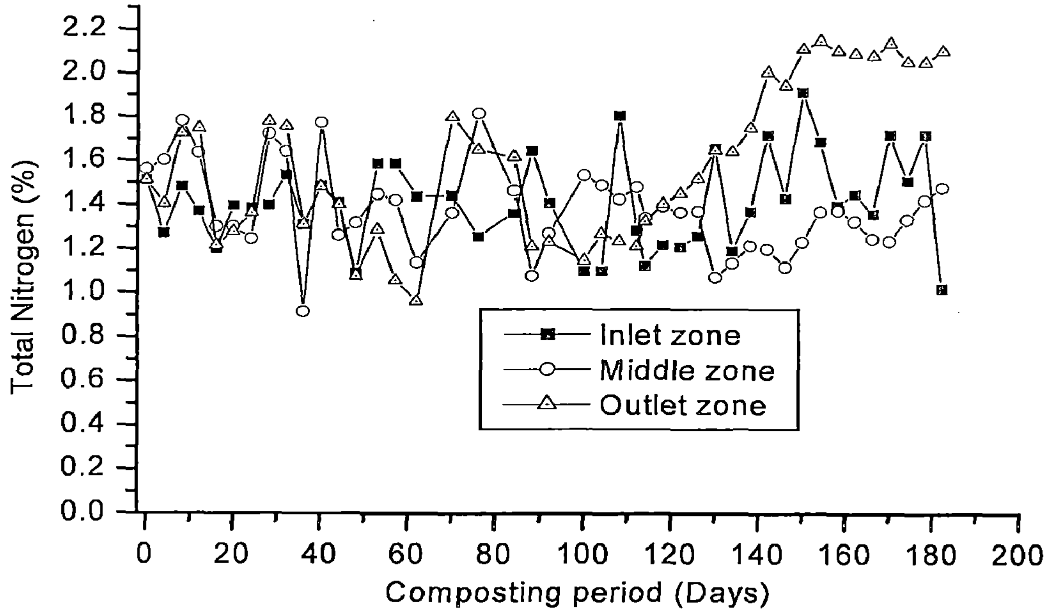


Fig.5.5. Total nitrogen during full-scale continuous rotary drum in different seasons over composting period

- ***Carbon dioxide (CO_2) emission rate profile***

High CO_2 emission rate (8.43-9.45mg/g VS (volatile solids)/ day) was observed at inlet zone during winter season composting. Subsequently the rate of CO_2 emission increased up to 9.52-10.23mg/g VS/day in spring season (80-100 days). Further, CO_2 emission rate increase significantly 13-14.4 mg/g VS/day in summer season (120-180 day) due to high temperature, higher degradation of waste material at inlet zone (Fig. 5.6). When the material reached in middle zone in winter season reduction of CO_2 emission rate was found very low (10%) and emission rate (7-8 mg/g VS/day) in winter season. During spring season the reduction of CO_2 emission rate at middle zone was found 27-30% and the rate of emission 6.4-7.5 mg/g VS/day. Subsequently, in summer season the reduction of CO_2 emission rate at middle zone was found 45-50%. Furthermore, when material reached in outlet zone, the reduction of CO_2 emission was found 25-30%, 24-28% and 40-44% and the rate of emission 5.23-7.43 mg/g VS/day, 4.56-5.67 mg/g VS/day and 3.42-3.56 mg/g VS/day in winter, spring and summer season composting respectively.

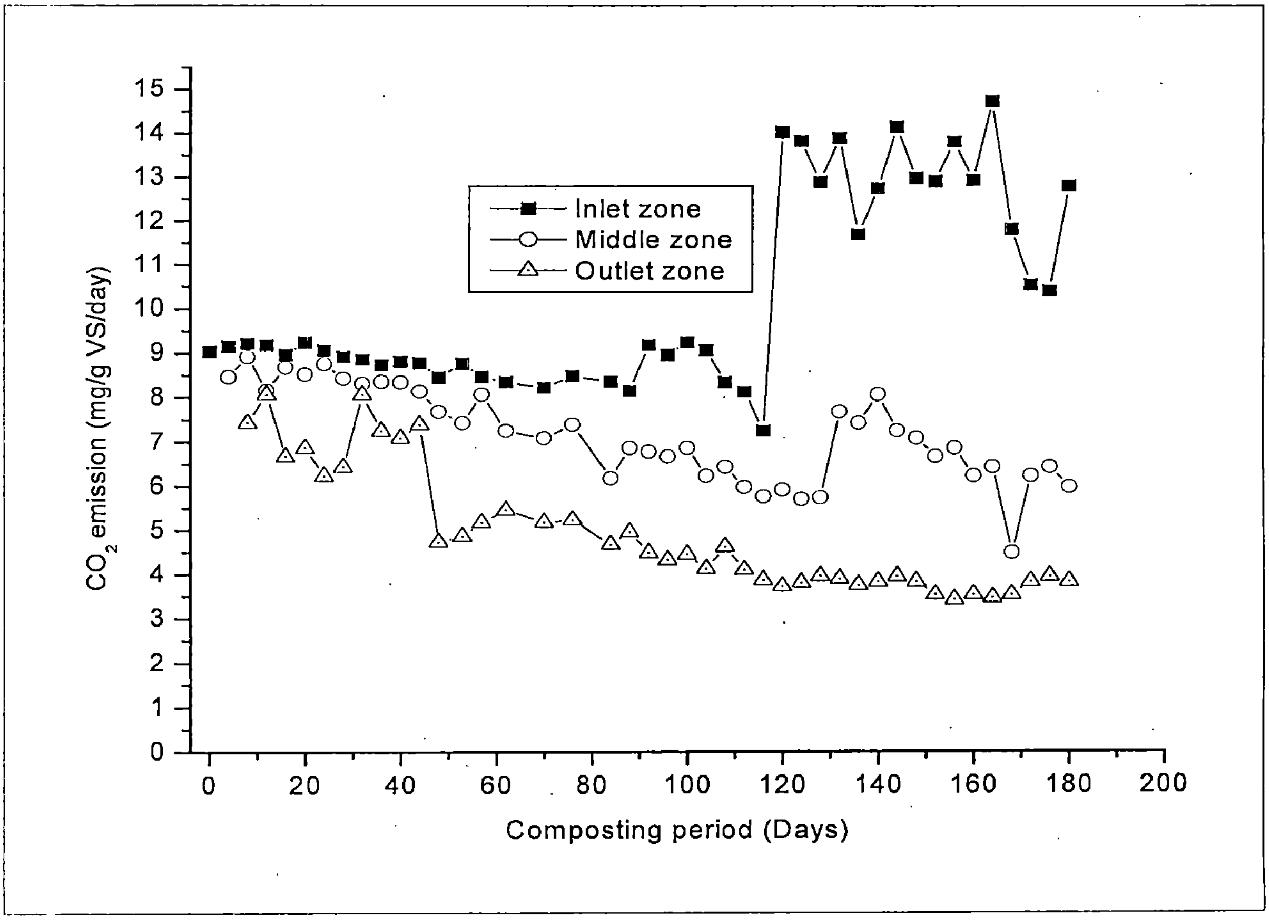


Fig.5.6. CO_2 emission rate during full-scale continuous rotary drum in different seasons over composting period

5.2.2. Pesticides degradation

- ***Degradation of Aldrin, Endosulfan α, Endosulfan β and Lindane during winter season***

Organochlorine pesticides such as aldrin, dieldrin and endrin could not degraded and long recognized for their environmental persistence and risk involved for non-target organisms (Strom; 1985). During winter season the concentration of Aldrin, Endosulfan α, Endosulfan β and Lindane was found 1.00, 9.32, 5.92 and 3.68 mg/kg in waste material respectively. This concentration was more compared to spring and summer seasons due to low ambient temperature and low microbial activity in natural environment which results more accumulation of these pesticides. Degradation/removal of Aldrin Endosulfan α, Endosulfan β and Lindane rotary drum composting started in inlet zone of the drum and about 20-35% removed after 24 hours feeding due high temperature range (60-65°C) and microbial activity. Feeding continues next day, waste material moved to middle zone and Aldrin Endosulfan α, Endosulfan β and Lindane concentration was found 0.56, 5.71,3.54 and 1.99 mg/kg respectively, followed by waste material reached to outlet zone in next four days where concentration of these pesticides was found 0.31,2.91,1.77 and 1.07 mg/kg respectively (Fig. 5.7 and table 5.1, 5.2). The overall removal efficiency of pesticides namely Aldrin, Endosulfan α, Endosulfan β and Lindane was 69.31, 65.03, 69.84 and 71.94% respectively. This was due to the high temperature range, optimum moisture, aeration, proper mixing of waste material and high microbial community growth in the drum. However, pesticides might be removed by leachate generation during winter season because in this season 1-2 L/day leachate generated.

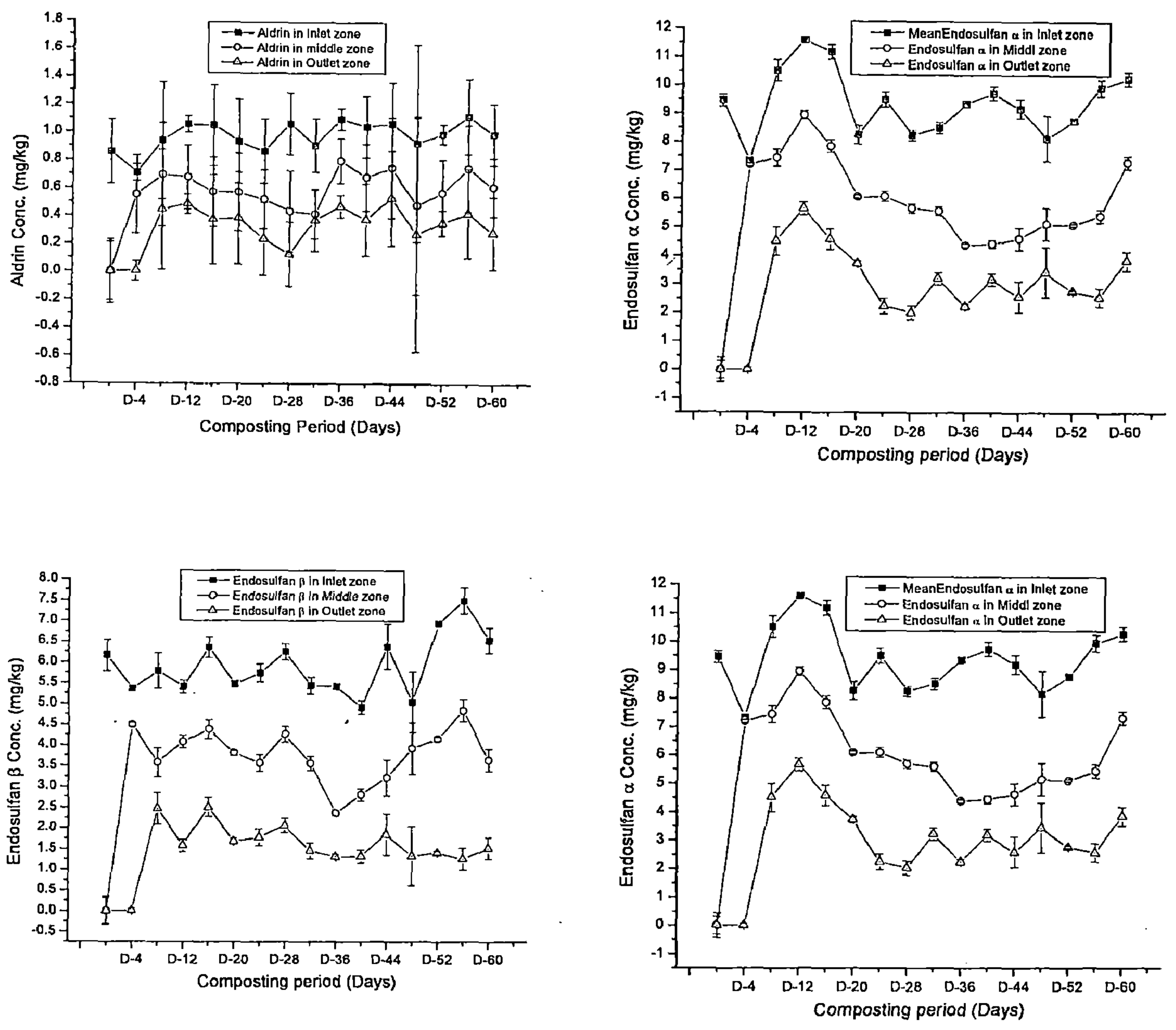


Fig. 5.7.Pesticides degradation during full-scale continuous rotary drum composting over composting period in winter season

Table.5.1 Concentration of Aldrin and Endosulfan α with standard deviation during winter season composting

Days	**Aldrin (mg/kg)**						**Endosulfan α (mg/kg)**					
	Inlet zone	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***	***Inlet zone***	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***
D-0	0.8580	0.23	0	0	0	0	9.4573	0.21	0	0	0	0
D-4	0.7038	0.06	0.5472	0.28	0	0	7.3300	0.06	7.1933	0.05	0	0
D-8	0.9368	0.42	0.6923	0.37	0.4433	0.43	10.5200	0.38	7.4467	0.3	4.5100	0.5
D-12	1.0525	0.06	0.6733	0.23	0.4800	0.07	11.6000	0.05	8.9600	0.15	5.6633	0.23
D-16	1.0472	0.29	0.5700	0.25	0.3733	0.32	11.1867	0.26	7.8682	0.22	4.5867	0.36
D-20	0.9321	0.3	0.5667	0.28	0.3833	0.33	8.2767	0.32	6.0900	0.06	3.7367	0.1
D-24	0.8616	0.23	0.5167	0.21	0.2333	0.26	9.5200	0.26	6.1073	0.18	2.2500	0.28
D-28	1.0604	0.22	0.4333	0.29	0.1233	0.23	8.2683	0.19	5.6967	0.16	2.0233	0.24
D-32	0.9048	0.19	0.4141	0.18	0.3667	0.22	8.5233	0.2	5.6000	0.16	3.2200	0.22
D-36	1.0946	0.08	0.7957	0.16	0.4700	0.08	9.3763	0.08	4.3933	0.06	2.2500	0.1
D-40	1.0394	0.22	0.6767	0.24	0.3733	0.26	9.7367	0.25	4.4400	0.13	3.1833	0.21
D-44	1.0620	0.3	0.7467	0.36	0.5300	0.34	9.2033	0.33	4.6267	0.39	2.5842	0.54
D-48	0.9245	0.71	0.4767	0.64	0.2667	0.84	8.1643	0.81	5.1500	0.57	3.4400	0.88
D-52	0.9896	0.07	0.5667	0.24	0.3533	0.09	8.7842	0.08	5.1200	0.04	2.7764	0.05
D-56	1.1176	0.27	0.7433	0.31	0.4200	0.32	9.9642	0.29	5.4480	0.23	2.5783	0.33
D-60	0.9902	0.22	0.6100	0.21	0.2800	0.26	10.2855	0.24	7.3300	0.23	3.8558	0.34

SD= Standard deviation

Table.5.2 Concentration of Endosulfan β and Lindane with standard deviation during winter season composting

Days	**Endosulfan β (mg/kg)**						**Lindane (mg/kg)**					
	Inlet zone	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***	***Inlet zone***	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***
D-0	6.1600	0.38	0	0	0	0	9.4573	0.21	0	0	0	0
D-4	5.3500	0.06	4.4800	0.05	0	0	7.3300	0.06	7.1933	0.05	0	0
D-8	5.7900	0.42	3.5800	0.35	2.4700	0.38	10.5200	0.38	7.4467	0.3	4.5100	0.5
D-12	5.4000	0.16	4.0700	0.15	1.5700	0.15	11.6000	0.05	8.9600	0.15	5.6633	0.23
D-16	6.3600	0.25	4.3800	0.23	2.5000	0.23	11.1867	0.26	7.8682	0.22	4.5867	0.36
D-20	5.4800	0.08	3.8100	0.06	1.6800	0.07	8.2767	0.32	6.0900	0.06	3.7367	0.1
D-24	5.7400	0.22	3.5700	0.2	1.7700	0.2	9.5200	0.26	6.1073	0.18	2.2500	0.28
D-28	6.2500	0.2	4.2600	0.19	2.0500	0.18	8.2683	0.19	5.6967	0.16	2.0233	0.24
D-32	5.4400	0.2	3.5600	0.17	1.4500	0.19	8.5233	0.2	5.6000	0.16	3.2200	0.22
D-36	5.4200	0.08	2.3700	0.07	1.3100	0.07	9.3763	0.08	4.3933	0.06	2.2500	0.1
D-40	4.9200	0.17	2.8000	0.15	1.3200	0.16	9.7367	0.25	4.4400	0.13	3.1833	0.21
D-44	6.3900	0.54	3.2200	0.44	1.8500	0.5	9.2033	0.33	4.6267	0.39	2.5842	0.54
D-48	5.0500	0.73	3.9300	0.62	1.3300	0.71	8.1643	0.81	5.1500	0.57	3.4400	0.88
D-52	6.9500	0.05	4.1600	0.05	1.4100	0.04	8.7842	0.08	5.1200	0.04	2.7764	0.05
D-56	7.5000	0.31	4.8500	0.27	1.2600	0.27	9.9642	0.29	5.4480	0.23	2.5783	0.33
D-60	6.5500	0.31	3.6500	0.27	1.5200	0.26	10.2855	0.24	7.3300	0.23	3.8558	0.34

SD= Standard deviation

- ***Leach out pesticides concentration during rotary drum composting in winter season***

The removal of pesticides through leachate generation in full scale rotary drum composting has shown in Fig.5.8. The drawbacks of rotary drum composter in winter season in which organic fraction, nutrients and pollutant like pesticides and heavy metals leachate were found. During this season the removal of Aldrin, Endosulfan α, Endosulfan β and Lindane through leachate generation was 0.2878, 0.4503, 0.2375 and 0.8827 mg/kg (cumulative 1.8583 mg/kg). It is found that around 30-35% of pesticides were removed without degradation through leachate generation (1-2 L/day) during high rate rotary drum composting. We have some solution as leachate collection arrangement and treatment of leachate in waste water treatment plants for the degradation of these hazardous organochlorine pesticides along with some other hazards which leachout in leachate generation.

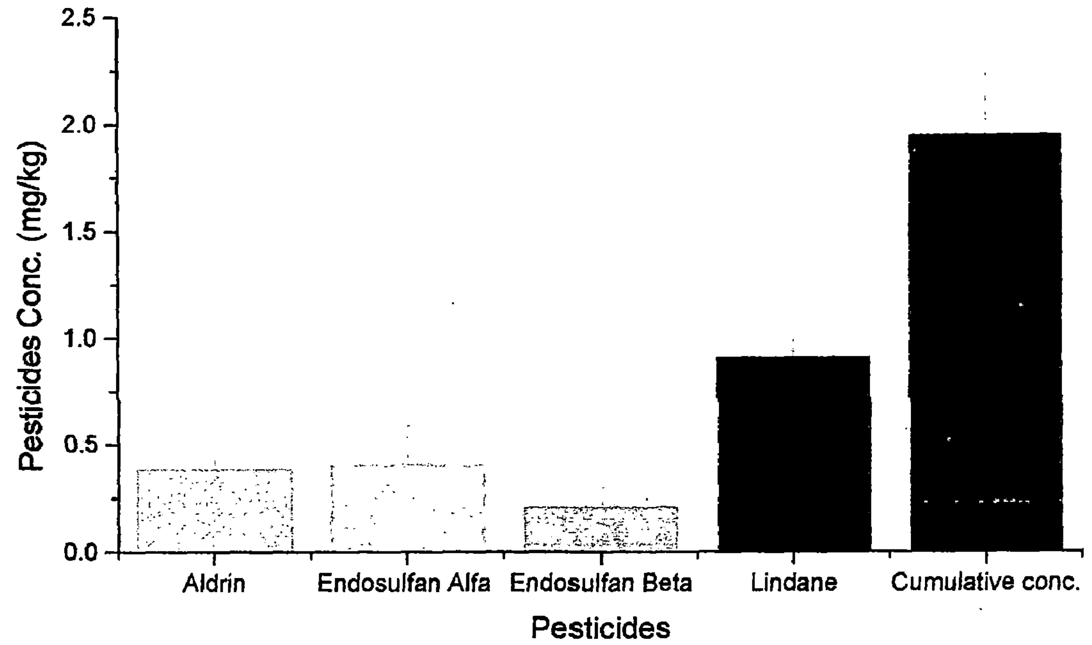


Fig. 5.8. Pesticides concentration in leachate generate during full scale continuous rotary drum composting in winter season

- ***Degradation of Aldrin, Endosulfan α, Endosulfan β and Lindane during spring season***

During spring season the concentration of Aldrin, Endosulfan α, Endosulfan β and Lindane was 1.16, 8.79, 4.12 and 3.88 mg/kg respectively. This concentration was more compared to summer season due to low ambient temperature and low microbial activity in natural environment which results more accumulation of these pesticides. Degradation/removal of Aldrin Endosulfan α, Endosulfan β and Lindane in rotary drum composting started in inlet zone and about 20-30% degraded in 24 hours after feeding due high temperature range (55-60°C) and microbial activity. Feeding continues next day, waste material moved to forward direction with their degradation (Fig.5.9 and table 5.3, 5.4). After four days material reaches to middle zone the pesticides concentration was assumed to 0.69, 5.19, 1.92, and 2.47 mg/kg respectively. Finally, waste material reached to outlet zone of the drum in next four days where concentration of these pesticides was found 0.42, 3.01, 0.73 and 1.25 mg/kg respectively. The overall removal efficiency of pesticides namely Aldrin, Endosulfan α, Endosulfan β and Lindane was found 64.33, 65.61, 63.28 and 68.23% respectively. This was due to the high temperature range, optimum moisture, aeration, proper mixing of waste material and high microbial community growth in the drum. Leachate generation was not found during this season so whole degradation might be due to the microbial activity.

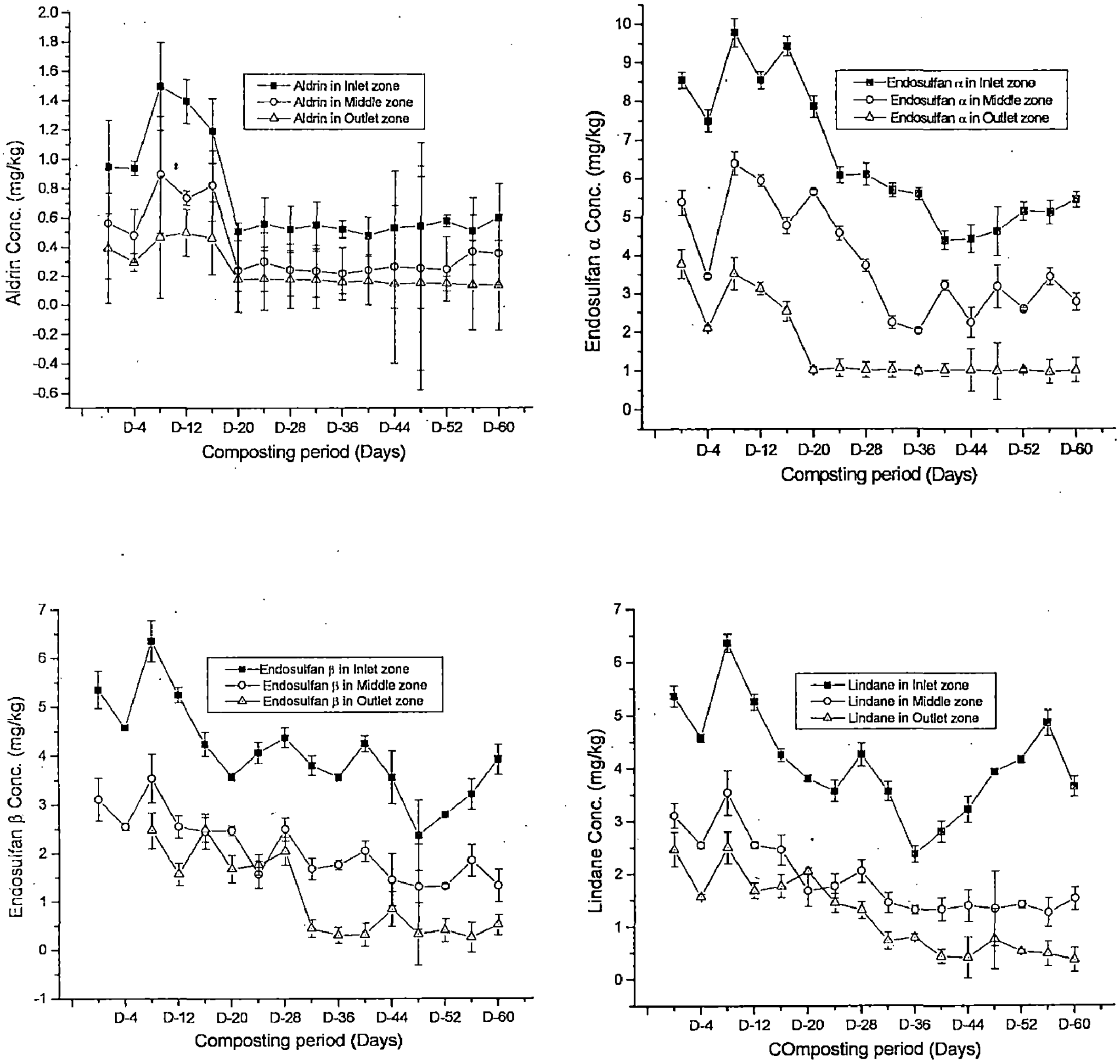


Fig. 5.9.Pesticides degradation during full scale continuous rotary drum composting over composting period in spring season

Table.5.3 Concentration of Aldrin and Endosulfan α with standard deviation during spring season composting

Days	**Aldrin (mg/kg)**						**Endosulfan α (mg/kg)**					
	Inlet zone	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***	***Inlet zone***	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***
D-0	0.9497	0.32	0	0	0	0	8.5482	0.21	0	0	0	0
D-4	0.9382	0.05	0.4782	0.18	0	0	7.4921	0.28	3.4582	0.05	0	0
D-8	1.4976	0.3	0.8940	0.4	0.4672	0.42	9.7832	0.37	6.3923	0.3	3.5281	0.42
D-12	1.3962	0.15	0.7372	0.05	0.4982	0.16	8.5491	0.23	5.9423	0.15	3.1295	0.16
D-16	1.1942	0.22	0.8217	0.24	0.4633	0.25	9.4319	0.25	4.7821	0.22	2.5358	0.25
D-20	0.5070	0.06	0.2421	0.29	0.1790	0.08	7.8682	0.28	5.6633	0.06	1.0236	0.08
D-24	0.5595	0.18	0.3006	0.2	0.1837	0.22	6.0900	0.21	4.5867	0.18	1.0752	0.22
D-28	0.5246	0.16	0.2460	0.18	0.1781	0.2	6.1073	0.29	3.7367	0.16	1.0201	0.2
D-32	0.5526	0.16	0.2366	0.18	0.1763	0.2	5.6967	0.18	2.2500	0.16	1.0225	0.2
D-36	0.5252	0.06	0.2190	0.18	0.1612	0.08	5.6000	0.16	2.0233	0.06	0.9873	0.08
D-40	0.4804	0.13	0.2442	0.24	0.1694	0.17	4.3933	0.24	3.2200	0.13	1.0169	0.17
D-44	0.5347	0.39	0.2679	0.29	0.1470	0.54	4.4400	0.36	2.2500	0.39	1.0213	0.54
D-48	0.5469	0.57	0.2575	0.7	0.1550	0.73	4.6267	0.64	3.1833	0.57	0.9873	0.73
D-52	0.5803	0.04	0.2487	0.22	0.1506	0.05	5.1500	0.24	2.5842	0.04	1.0128	0.05
D-56	0.5111	0.23	0.3717	0.25	0.1402	0.31	5.1200	0.31	3.4400	0.23	0.9674	0.31
D-60	0.6041	0.23	0.3581	0.22	0.1386	0.31	5.4480	0.21	2.7764	0.23	1.0099	0.31

SD= Standard deviation

Table.5.4 Concentration of Endosulfan β and Lindane with standard deviation during spring season composting

Days	**Endosulfan β (mg/kg)**						**Lindane (mg/kg)**					
	Inlet zone	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***	***Inlet zone***	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***
D-0	4.5800	0.06	0	0	0	0	4.5800	4.58	0	0	0	0
D-4	6.3600	0.42	3.5400	0.5	0	0	6.3600	6.36	0.1700	3.54	0	0
D-8	5.2500	0.16	2.5500	0.23	1.5700	0.23	5.2500	5.25	0.1500	2.55	0.0600	1.68
D-12	4.2500	0.25	2.4600	0.36	2.5000	0.25	4.2500	4.25	0.1200	2.46	0.2900	1.77
D-16	3.5800	0.08	2.4700	0.1	1.6800	0.28	3.8100	3.81	0.0700	1.68	0.3000	2.05
D-20	4.0700	0.22	1.5700	0.28	1.7700	0.21	3.5700	3.57	0.2000	1.77	0.2300	1.45
D-24	4.3800	0.2	2.5000	0.24	2.0500	0.29	4.2600	4.26	0.2200	2.05	0.2200	1.31
D-28	3.8100	0.2	1.6800	0.22	0.4500	0.18	3.5600	3.56	0.1800	1.45	0.1900	0.73
D-32	3.5700	0.08	1.7700	0.1	0.3100	0.16	2.3700	2.37	0.1500	1.31	0.0800	0.79
D-36	4.2600	0.17	2.0500	0.21	0.3200	0.24	2.8000	2.8	0.2000	1.32	0.2200	0.43
D-40	3.5600	0.54	1.4500	0.54	0.8500	0.36	3.2200	3.22	0.2500	1.39	0.3000	0.41
D-44	2.3700	0.73	1.3100	0.88	0.3300	0.64	3.9300	3.93	0.0500	1.33	0.7100	0.76
D-48	2.8000	0.05	1.3200	0.05	0.4100	0.24	4.1600	4.16	0.0700	1.41	0.0700	0.52
D-52	3.2200	0.31	1.8500	0.33	0.2600	0.31	4.8500	4.85	0.2400	1.26	0.2700	0.48
D-56	3.9300	0.31	1.3300	0.34	0.5200	0.21	3.6500	3.65	0.1900	1.52	0.2200	0.36
D-60	3.6041	0.23	1.3581	0.22	0.5386	0.31	3.4480	0.21	0.7764	0.23	0.2099	0.31

SD= Standard deviation

- ***Degradation of Aldrin, Endosulfan α, Endosulfan β and Lindane during summer season***

During summer season the concentration of Aldrin, Endosulfan α, Endosulfan β and Lindane was 450-650, 1200-1400, 650-700 and 350-500 µg/kg respectively. The concentration was low compared to winter and spring seasons due to high ambient temperature (37-44°C) and high microbial activity in natural environment which results in less accumulation of these pesticides. Degradation/removal of Aldrin Endosulfan α, Endosulfan β and Lindane in rotary drum composting started in inlet zone and about 30-35% degraded after 24 hours of feeding due high temperature range (60-68°C) and microbial activity. Feeding continues next day, waste material moved to forward direction with their degradation (Fig.5.10 and table 5.5, 5.6). After four days material reached to middle zone and the pesticides concentration was found 200-250, 900-1000, 250-300, and 260-280 µg/kg respectively. Material reached to outlet zone of the drum in next four days and the concentration of these pesticides was found 150-180,200-400,180-200 and 140-160 µg/kg respectively. The overall removal efficiency of pesticides namely Aldrin, Endosulfan α, Endosulfan β and Lindane was found 85.67, 84.95, 83.20 and 81.36% respectively. This was due to the high temperature range, optimum moisture, aeration, proper mixing of waste material and high microbial community growth in the drum. It is enhanced values compared to winter and spring seasons. Leachate generation was also not assumed during this season so whole degradation might be due to the microbial activity.

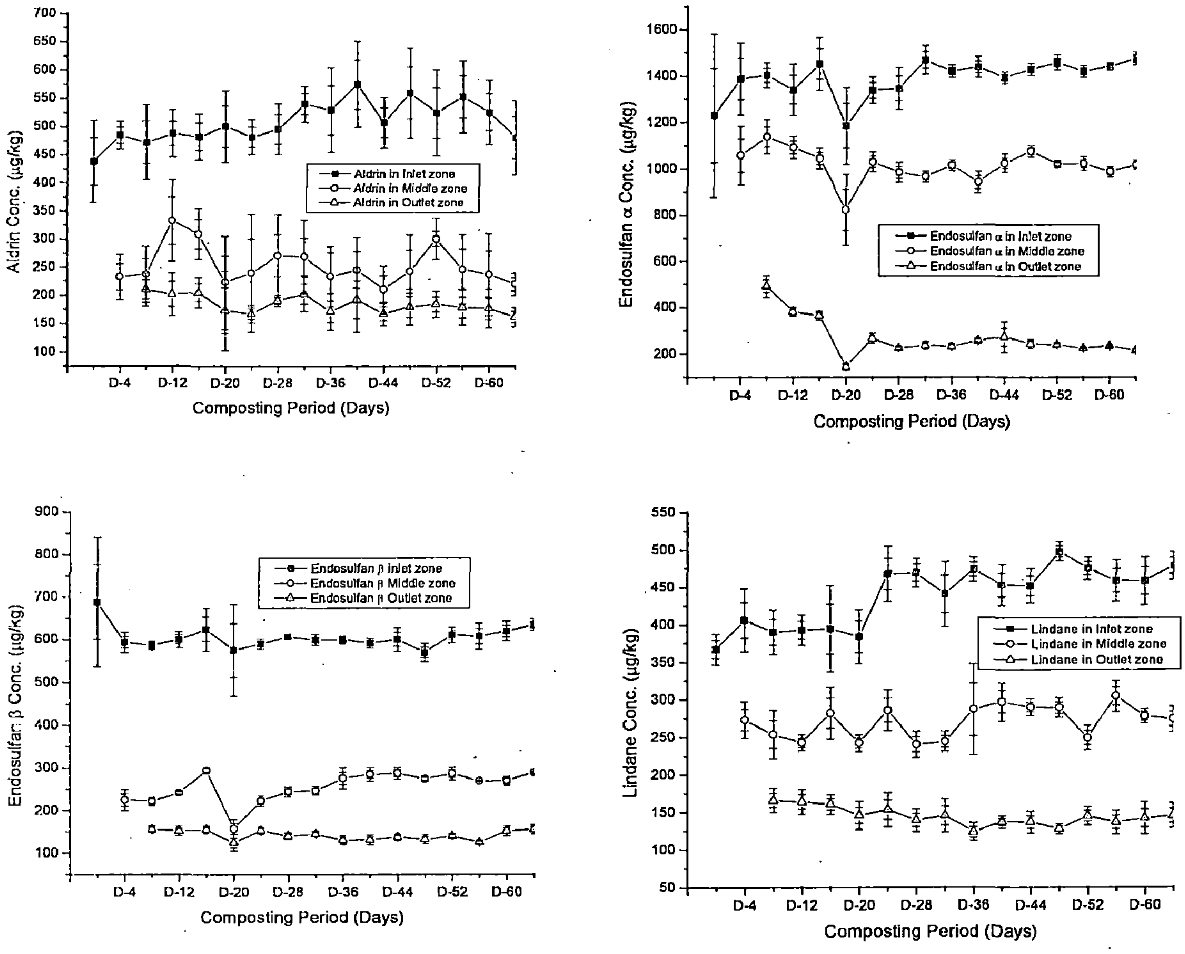


Fig. 5.10.Pesticides degradation during full scale continuous rotary drum composting over composting period in summer season

Table.5.5 Concentration of Aldrin and Endosulfan α with standard deviation during summer season composting

Days	Aldrin (µg/kg)						Endosulfan α (µg/kg)					
	Inlet zone	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***	***Inlet zone***	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***
D-0	438.0000	12.16	0	0	0	9.73	1387.3300	9.43	0	0	0	0
D-4	484.5100	14.32	232.1567	23.76	0	8.08	1402.5200	2.56	1137.4467	2.50	0	0
D-8	471.7800	18.05	236.9233	27.66	209.4433	7.04	1340.6000	3.58	1091.9600	7.76	381.6633	10.38
D-12	487.5167	20.83	332.6733	12.07	201.4800	10.16	1451.1867	5.87	1043.8434	5.67	364.5867	1.12
D-16	482.1533	14.01	308.9700	26.07	204.3733	5.33	1184.2766	5.77	822.0900	8.00	145.7367	7.51
D-20	500.1200	36.44	222.2667	17.92	172.8833	10.08	1337.5200	3.19	1029.1067	4.27	266.2500	2.15
D-24	481.6033	17.83	239.5167	10.63	166.8333	0.81	1345.2866	2.39	983.6967	5.34	225.0233	5.32
D-28	495.4400	25.63	270.4333	13.60	190.1233	2.50	1468.5233	5.96	965.6000	3.66	236.2200	9.21
D-32	539.7667	18.65	268.4133	15.60	201.5367	7.57	1419.3300	5.83	1014.3933	3.39	231.2500	7.00
D-36	529.5667	13.54	233.0967	13.68	170.7700	20.90	1437.7367	5.76	941.4400	8.00	256.1833	5.73
D-40	574.7400	14.16	244.6767	19.21	192.0733	1.82	1393.2034	4.38	1023.6267	2.42	271.9967	8.26
D-44	507.0300	25.80	209.7467	14.58	166.8300	3.02	1428.1133	4.89	1075.1500	3.83	243.4400	10.85
D-48	559.4966	15.85	242.0767	8.15	178.9667	1.30	1458.7034	8.32	1020.1200	8.28	238.7000	5.71
D-52	524.6033	14.18	300.5667	3.29	183.6533	4.24	1419.9867	5.05	1022.4480	6.48	225.2833	2.52
D-56	552.6133	17.07	246.0433	5.96	178.1200	6.60	1441.7966	9.80	987.3300	2.91	233.8567	3.08
D-60	525.2333	12.66	236.6100	2.15	176.2800	2.15	1475.5233	6.56	1016.8834	2.04	215.4333	3.39

SD= Standard deviation

Table.5.6 Concentration of Endosulfan β and Lindane with standard deviation during summer season composting

Days	**Endosulfan β (µg/kg)**						**Lindane (µg/kg)**					
	Inlet zone	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***	***Inlet zone***	***SD***	***Middle zone***	***SD***	***Outlet zone***	***SD***
D-0	593.3167	13.60	0	0	0	0	405.9533	24.08	0	0	0	0
D-4	585.7867	5.89	221.5833	5.84	0	0	389.8733	17.05	273.0433	13.98	0	0
D-8	599.4000	10.90	241.0667	2.61	152.4667	4.65	392.5567	11.72	253.6200	18.60	165.8133	9.20
D-12	624.3333	8.76	294.3767	4.15	155.7000	11.55	394.1900	33.45	242.6333	6.33	163.9233	9.59
D-16	575.4800	2.16	157.8167	12.36	125.3167	4.60	383.6733	20.80	282.0400	19.97	160.4633	7.48
D-20	589.7333	6.83	222.5333	6.95	153.4667	4.83	467.6567	21.17	242.1000	6.47	145.6867	10.78
D-24	606.2800	3.04	244.2333	6.47	140.9000	3.84	469.3133	11.25	285.5933	15.69	153.3833	12.97
D-28	599.4833	7.22	246.4667	6.12	145.3333	5.65	440.6933	25.18	240.2667	10.14	139.3800	8.73
D-32	599.4233	5.69	275.3733	14.44	131.0333	6.79	473.9433	9.57	244.1833	7.62	145.6367	12.64
D-36	591.9167	6.40	284.8000	9.16	132.0333	4.44	452.8153	15.85	286.9033	4.97	123.9333	6.94
D-40	600.3933	5.99	287.2267	7.75	138.5000	6.15	451.7434	13.18	296.7900	14.63	137.0333	4.70
D-44	570.0500	12.22	273.9333	3.29	132.9667	3.30	497.7267	7.33	289.7134	6.42	136.8100	8.40
D-48	610.9467	10.77	286.1000	8.56	140.9000	2.84	475.3233	8.78	288.9700	7.52	127.8233	3.63
D-52	607.5000	7.76	268.8000	1.01	125.6333	6.47	458.8800	15.87	248.9533	9.54	145.0267	7.00
D-56	619.5500	13.16	269.6667	5.85	152.3333	6.40	458.2567	18.41	304.4433	12.11	136.5500	9.05
D-60	634.6000	7.96	288.0333	1.44	155.3333	6.90	478.8233	10.85	277.6200	5.63	141.9567	12.13

SD= Standard deviation

5.3. Conclusion

In conclusion, the removal efficiency of respective pesticides namely Aldrin, Endosulf Endosulfan β and Lindane was found 85.67, 84.95, 83.20 & 81.36% respectively dı summer season which is higher than the winter and spring seasons i.e. 69.31, 65.03, 6 71.94% and 64.33, 65.61, 63.28, 68.23% respectively in the full-scale continuous higl composting. This is due to the optimum temperature, moisture and pH and devel microbial activity causing depletion of dissolved pesticides in summer se Temperature of drum was about 55-70°C during entire active stage (Inlet or feeding z that was most suitable for microbial population. It is also observed that in winter se some of these pesticides removed (30-35%) through leachate generation (1-2 L/day). S solution as leachate collection arrangement from composting plants in winter seasor treatment of leachate in waste water treatment plants for the degradation of these hazaı organochlorine pesticides along with some other hazards which leachout in lea generation. Therefore, full-scale continuous rotary drum composting is the best s technique for the removal of organic pollutants like pesticides during compostir seasonal variations for various kinds of waste.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

This chapter deals with the conclusions from each specific study i.e., performance evaluation of rotary drum composter and fate of aggregate organic matter transformation in full-scale continuous rotary drum composting (chapter 3, part A and B), fate and degradation kinetics of trace hazardous organochlorine pesticides during household batch-scale rotary drum and comparison with conventional windrows composting (chapter 4, part A), fate and degradation kinetics of trace hazardous organochlorine pesticides during full-scale continuous rotary drum composting (chapter 4, part B) and effects of seasonal variation on trace hazardous organochlorine pesticides degradation during full-scale continuous rotary drum composting (chapter 5).

6.1. Performance evaluation of rotary drum composter and fate of aggregate organic matter transformation of waste material by advanced chemical techniques- FT-IR and thermal studies during full-scale continuous composting

Chapter 3, part A

- Composting of herbal waste and cattle manure in 3:1 (w/w) ratio can be successfully conducted in a rotary drum with 7-8 days detention period.
- Favorable composting conditions were obtained at once a day rotation.
- Increase in rotation to twice a day (trial-2) couldn't improve the quality, resulting lowering of thermophilic temperature from 70 to 60°C, which gave slow degradation and unstable compost as compared to one rotation (trial-1).
- Addition of microbial inocula gave no improvement in the quality of the compost.
- Co-composting of herbal and vegetable waste gave better quality compost in terms of temperature, moisture, nitrogen, Solvita maturity index and aerobic environment due to materials are complement each other, as vegetable waste have higher moisture and herbal waste functions as a bulking agent and moisture absorbent, resulting aerobic environment by increase molecular oxygen concentration.
- FT-IR also revealed that trial-1 (one rotation) and trial-4 (co-composting herbal & vegetable waste) gave quality compost in terms of high intensity peaks in the aromatic region and reduced intensity peaks in aliphatic region.

Chapter 3, part B

- FT-IR, TG, DTG and DTA techniques shall be used for aggregate organic matter transformation, stability and maturity evaluation of composted materials for their demand and acceptability.
- These techniques also determines an increase of the molecular complexity of compost by decreasing the aliphatic compounds such as polysaccharides and proteins while increasing the oxygenated group contents and the aromatic complex compounds during full-scale continuous rotary drum composting in different seasons.
- Some new functional groups are found during the study in IR bands such as 778, 722, and 560 cm^{-1} due to aromatic ring, halogen-compounds and some metal-halogen respectively.
- Higher degree of maturity was achieved in spring and summer seasons composting in terms of mass loss (TG), rate of mass loss (DTG), enthalpy change (DTA) in the final compost compared to winter full-scale continuous rotary drum composting.
- Correlation between temperature and CO_2 emission rate was shown using Andrews–Kambhu–Haug and Ratkowsky models. The Andrews–Kambhu–Haug model was found to be better model compared to the Ratkowsky model because optimum temperature (62.1°C) was obtained due to rapid microbial growth temperature while the later model gave 66.4°C as optimum temperature which is unfavorable for microbial growth.

6.2. Fate and degradation kinetics of trace hazardous organochlorine pesticides during household batch-scale rotary drum and comparison with conventional windrows composting

Chapter 4, part A

- About 70% removal of organochlorine pesticides can be achieved within 20-24 days by high rate household batch-scale rotary drum composting techniques due to better mixing, optimal temperature, pH and moisture contents.
- In conventional windrows technique, the removal of pesticides are possible only 50-60% in 30-36 days in which 40-45% removal of pesticides due to leachate generation.
- Temperature varied in household batch-scale rotary drum during the composting period is as shown in Fig. 6.1.

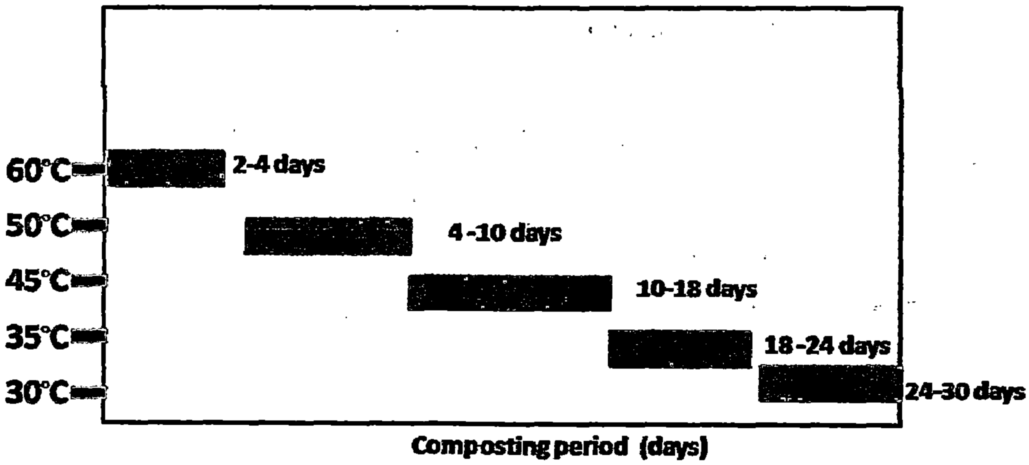


Fig.6.1. Temperature variation during the composting period in household batch-scale rotary drum composter

- Volume of waste material remained in household batch-scale rotary drum composter during composting period are given in Fig. 6.2.

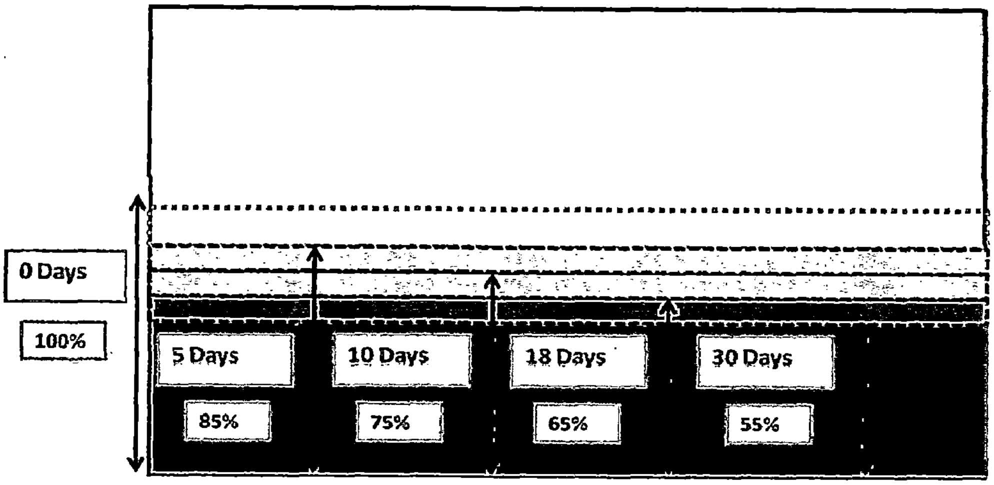


Fig.6.2. Material volume reduction during household batch-scale rotary drum composting

- Microbial community analysis in household batch-scale rotary drum and conventional windrows composting have revealed that major bacterial groups are mesophilic such as *Lactobacillus sp.*, *Clostridium sp.* and *Pseudomonas* sp.
- In thermophilic stage, gram-positive bacteria *Bacillus* sp., *Actinobacteria* sp., *Aspergillus* and *Rhizopus* sp. (major mycofloral) were dominant in household batch-scale rotary drum compared to conventional windrows composting.
- It is also confirmed that the identified bacterial and fungal genera are responsible for pesticides degradation.

- Biochemical degradation pathways of Aldrin, Endosulfan (α & β), and Lindane was proposed in aerobic condition. Aldrin after diol formation converted to 1-hydroxychlordene in four days at 55-60°C, followed by 4,7-methanoisobenzofuran in eight days at 45-50°C temperature. Finally it is converted to 4,5,6,7,8,8-hexachloro-1,3,3a,4,7,7a-hexahydro- in twelve days at 35-40°C due to oxidation and reduction reactions in the household rotary drum composting (Fig. 6.3). However, in conventional windrows, after aldrin epoxidation to toxic dieldrin it further converted to aldrindiol and no further degradation took place.
- Endosulfan α first changed to endosulfan β, subsequently converted to endosulfan sulfate (highly toxic intermediate) by oxidation process. By librating SO_3 gas, it further converted to endosulfan ether in four days at 55-60°C, followed by chlorendic acid and chlorendic anhydride in eight days at 45-50°C. Finally, it is converted to stable and less toxic 4,5,6,7-tetrachloro-3-hydroxy-3H-isobenzofuran-1-one in twelve days at 35-40°C during the household batch-scale rotary drum composting (Fig. 6.4). While in conventional windrows, Endosulfan α converted to endosulfan sulfate by oxidation process. Then, converted to Endosulfan ether by removal of SO_3 gas. Endosulfan acid was formed after hydroxylation process.
- Lindane gave some oxidative and reductive products, formed in both composting techniques under partially aerobic and anaerobic conditions as shown in Fig. 6.5.

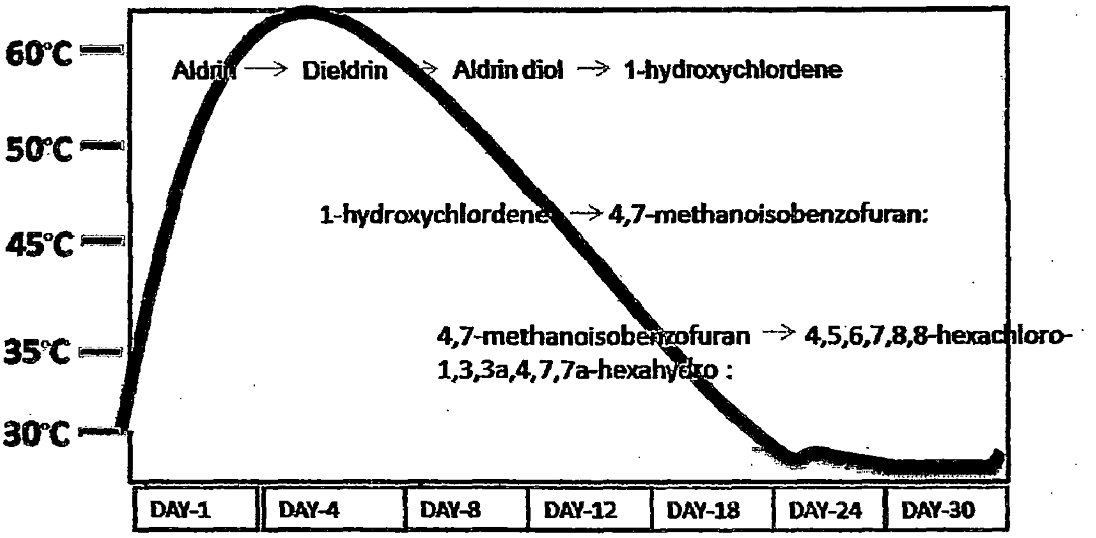


Fig.6.3. Degradation pathways of Aldrin with temperature during household batch-scale rotary drum composting

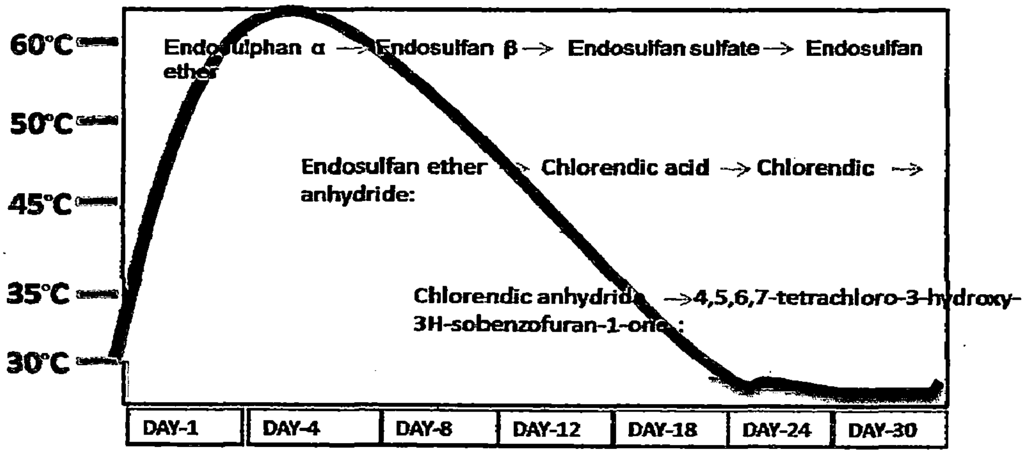


Fig.6.4. Degradation pathways of Endosulfan with temperature during household batch-scale rotary drum composting

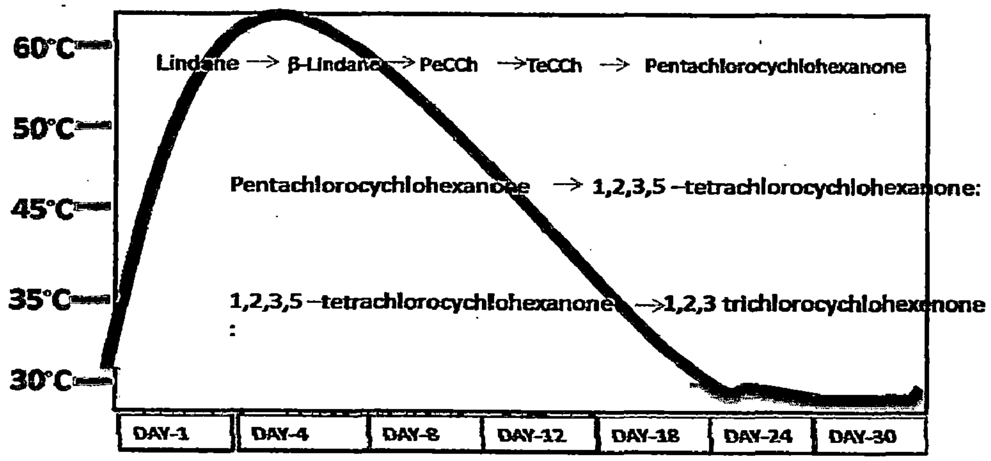


Fig.6.5. Degradation pathways of Lindane with temperature during household batch-scale rotary drum composting

- First order degradation kinetics was observed in pesticides and half life is reduced to 12-20 days from 1095 days, 9-17 days from 160 days, 11-30 days from 60 days and 9-11 days from 270 days in Aldrin, Endosulfan α, Endosulfan β, and Lindane respectively in household batch-scale rotary drum composting.
- First order degradation kinetics was observed and half life is reduced to 15-26 days from 1095 days, 13-25 days from 160 days, 13-59 days from 60 days and 95 days from 270 days in Aldrin, Endosulfan α, Endosulfan β, and Lindane respectively in conventional windrows composting.
- Household batch-scale rotary drum composting was also found suitable for the development of bacteria and fungi communities, efficient eradication of hazardous organochlorine pesticide residues in vegetable waste.

6.3. Fate and degradation kinetics of trace hazardous organochlorine pesticides and degradation kinetics during full-scale continuous rotary drum composting

Chapter 4, part B

- Removal efficiency of Aldrin, Endosulfan α, Endosulfan β and Lindane was calculated as 85.67, 84.95, 83.20 & 81.36% respectively in full-scale continuous rotary drum composting due to optimum temperature, moisture, pH conditions substrate availability, development of microbial activity causing depletion of dissolved and hazardous organochlorine pesticides in aqueous phase of composting material.
- Aldrin, Endosulfan α, Endosulfan β and Lindane was degraded around 20-30% in inlet zone of full-scale continuous rotary drum. Then, material moved and remained in the middle zone for four days where 30-40% pesticides depredated. Finally, material moved and remained in outlet zone for next four days where 5-10% pesticides degraded (overall 70-80%) might be due to variation of complex microbial communities.
- Temperature range varied from 20-70°C in different zones of the rotary drum. Inlet zone varied from 32-70°C in which temperature ranges 32-45°C near the opening of drum due to material contact to ambient air, 44-53°C bottom temperature due to more aqueous material present, 53-68°C upper layer of bottom temperature and 68-70°C core region of the inlet zone which showed the most active region of the drum. Middle zone varied from 30-50°C as shown in figure F. Similarly, outlet zone has also some variations 20-35°C as shown in Fig. 6.6. Due to temperature variations in different regions, full-scale continuous rotary drum composter has significance in the growth of microbial communities and so degradation of hazardous organochlorine pesticides.

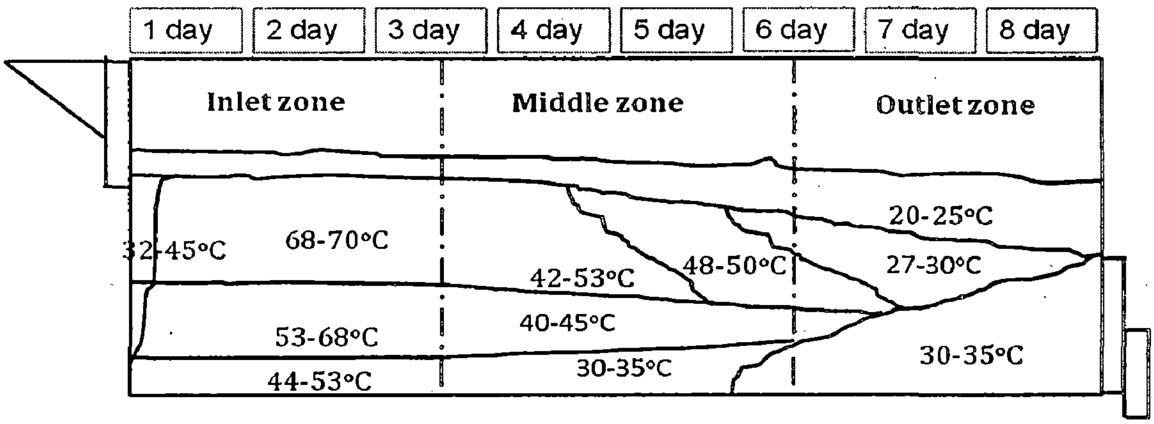


Fig.6.6. Temperature variations in different zones of full-scale continuous rotary drum composting

- Temperature also changed in different zones after feeding and rotation of full-scale continuous rotary drum. At inlet zone (active stage), temperature decreased from 60-65°C to 35-40°C and regained to 60-65°C in 7-8 hours. In middle zone, the temperature decreased from 40-45°C to 35-40°C and regained it in 7-8 hours. Similarly, in the outlet zone, the temperature decreased from 30-35°C to 25-30°C and regained it in 7-8 hours. Large temperature variation in inlet zone due to feeding and rotation might be changing a complex microbial population in full-scale continuous rotary drum composter where heterotrophic bacteria such as *Bacillus species, Pseudomonas sp. and Lactobacillus* species also varied during composting. However, no significant change was observed in the middle and outlet zone temperatures during feeding and rotation as shown in Fig. 6.7.

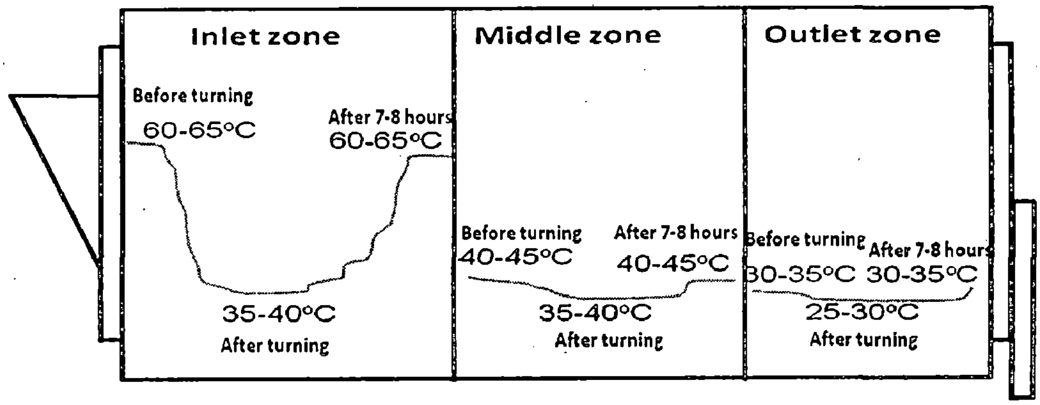


Fig.6.7. Temperature variations in different zones before and after turning during full-scale continuous rotary drum composting

- Aldrin, Endosulfan α, Endosulfan β and Lindane transformation was also observed during full-scale continuous rotary drum composting. In this, pesticides transformation path remained same as in household batch-scale rotary drum composting. But some new intermediates of each pesticide were found in different zones (inlet, middle and outlet zone) in full-scale continuous drum composter.
- Aldrin converted to dieldrin by epoxidation process using air oxygen. Dieldrin further converted to the Aldrin diol by the hydroxylation process in inlet zone. After four days, materials moved to middle zone and aldrin diol liberated one ethylene molecule to give 1-hydroxychlordene and its isomer. 1-Hydroxychlordene further oxidized to give two hydroxyl groups and oxidized to acidic and aldehydic compounds. Finally, aldehydic compounds of aldrin converted to 4,7-methanoisobenzofuran and 4,5,6,7,8,8-hexachloro-1,3,3a,4,7,7a-hexahydro- by the elimination of H_2O during next four days in the outlet zone as shown in Fig. 6.8.

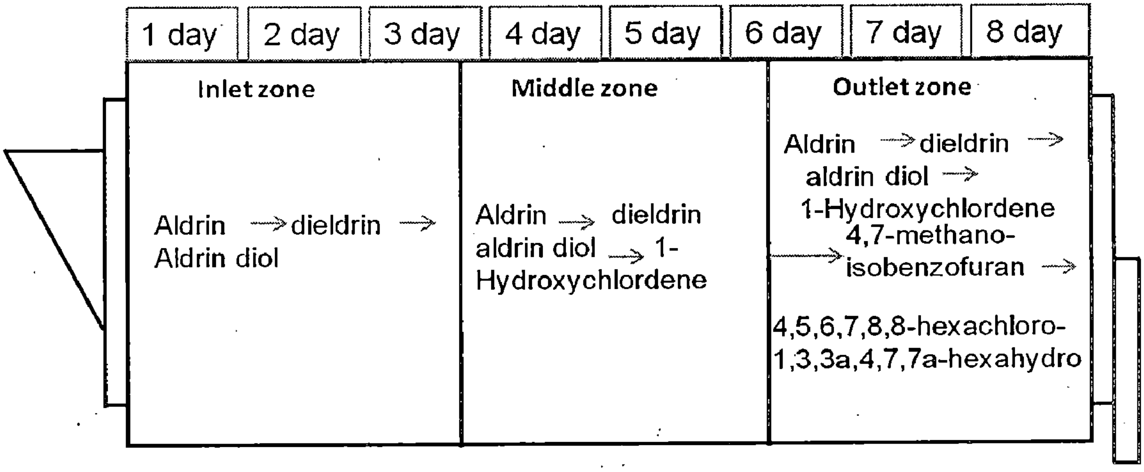


Fig.6.8. Aldrin degradation in different zones during full-scale continuous rotary drum composting

- Endosulfan isomerized to the endosulfan β, followed by converted to endosulfan sulfate in inlet zone. Endosulfan sulfate is highly toxic compound and persistent in environment. But, it was converted to endosulfan ether in the middle zone of rotary drum composting by liberating SO_3 gas in next four days. Finally, materials moved to outlet zone where Endosulfan ether converted to chlorendic acid using water molecule and converted to chlorendic anhydride by dehydration process. Chlorendic anhydride further converted to the 4,5,6,7-tetrachloro-3-hydroxy-3Hisobenzofuran-1-one due to microbials by taking out two chloride ions. 4, 5, 6, 7-tetrachloro-3-hydroxy-3H-isobenzofuran-1-one was not further degraded and persisted in the composting however less toxic in nature as shown in Fig. 6.9.

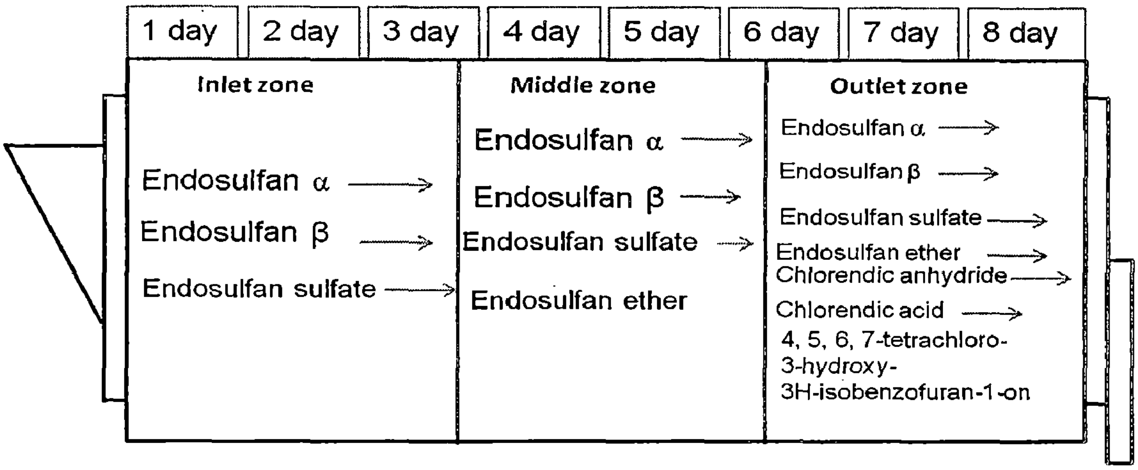


Fig.6.9. Endosulfan degradation in different zones during full-scale continuous rotary drum composting

- γ-Lindane was converted to β-Lindane in inlet zone of rotary drum composter, which is most persistent in environment. However, β-Lindane followed dehydrohelogenation and dehalogenation processes to afford pentachlorocychlohexene (PeCCh) and tetrachlorocychlohexene (TeCCh) respectively. Materials reached to the middle zone in next four days where PeCCh converted to pentachlorocychlohexanone by oxidation process, followed by 1,2,3,5-tetrachlorocychlohexanone and 1,2,3 trichlorocychlohexenone due to dehalogenation and dehydrogenation process respectively. Finally, in next four days materials moved to outlet zone where TeCCh converted to 1,3,5-trichloro-1,4-dihydroxybenzen by oxidation process. 1,2,3 trichlorocychlohexenone and 1,3,5-trichloro-1,4-dihydroxybenzen are less toxic than Lindanes as given in Fig. 6.10.

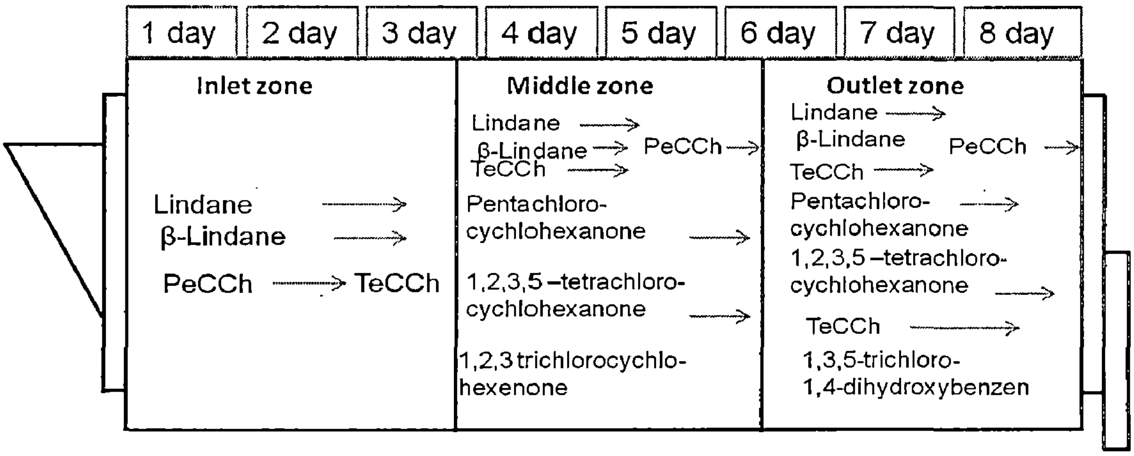


Fig.6.10. Lindane degradation in different zones during full-scale continuous rotary drum composting

- First order degradation kinetics of pesticides was observed during full-scale continuous rotary drum composting.
- Half life of the pesticides, Aldrin, Endosulfan α, Endosulfan β and Lindane was reduced to 25.54, 18.43, 18.43, and 27.43 days from 1095 days, 60 days, 270 days and 160 days respectively.
- Our observations in contrast of removal and degradation kinetics of organochlorine pesticides residue in vegetable waste, the full-scale continuous rotary drum composting has proved as the best suited technique for the removal of organic pollutants in full-scale composting plants used for various kinds of waste.

6.4. Effect of seasonal variation on trace hazardous organochlorine pesticides degradation during full-scale continuous rotary drum composting

Chapter 5

- Removal efficiency of the pesticides namely Aldrin, Endosulfan α, Endosulfan β and Lindane was calculated as 85.67, 84.95, 83.20 and 81.36% respectively during summer season in full-scale continuous rotary drum composting and found higher than the winter and spring seasons i.e. 69.31, 65.03, 69.84 and 71.94% and 64.33, 65.61, 63.28 and 68.23% respectively due to optimum temperature, moisture and pH conditions, which helped in develop the microbial activity during depletion of dissolved pesticides in summer season.

- In winter season, some of the pesticides (around 30-35%) removed through leachate generation (1-2L/day).
- Higher concentration of pesticides was found in winter season feedstock compared to spring and summer seasons full-scale rotary drum composting.
- Our observations in contrast of effects of seasonal variations on pesticides removal during full-scale high rate composting of vegetable waste have proved that the full-scale rotary drum is the best suited technique to check the performance of full-scale composting plants in different seasons and the factors affecting the composting of various kinds of waste.

6.5 Recommendations for future work

Based on our observations, we may recommend further studies be possible to improve the organic matter transformations including trace organics during composting process as follows:

- To study the effect of organochlorine pesticides degradation with waste material of different CN ratio i.e. 30, 36 and 40 during household batch and full-scale continuous rotary drum composting.
- To study the removal efficiencies and biochemical pathways of organochlorine pesticides with co-composting of vegetable waste with sewage sludge during household batch and full-scale continuous rotary drum composting.
- To study the determination of concentration of intermediates pesticides formed during the household batch and full-scale continuous rotary drum composting.
- To study the removal efficiency of biochemical pathways other than organochlorine pesticides i.e organophosphorus, nitrogenous and carbamates, etc during household batch and full-scale continuous rotary drum composting.
- To study the removal efficiency of biochemical pathways of personal care products (PCP), polyaromatic hydrocarbon (PAH) and endocrine disruptors (ED) during household batch and full-scale continuous rotary drum composting.
- To study the emission of green house gases (GHG) during household batch and full-scale continuous rotary drum composting.

- In cold weather conditions need higher blower capacity and blowing hot air to remove moisture condensation.
- To study increasing the rate of aeration for the elimination of anaerobic condition and check the biochemical pathways of pesticides during household batch and full-scale continuous rotary drum composting.
- To study isolation and identification of microbial consortium including bacterial, fungi and actinomycetes responsible for hazardous pesticides degradation at molecular levels.

References

1. Adani, F., Lozzi, P., Genevini, P., Determination of biological stability by oxygen uptake on municipal solid waste and derived products. *Compost Science & Utilization,* **2001,** 9, 163-178.
2. Aboulam, S., Morvan, B., Revel, J.C., Use of a rotating drum pilot plant to model the composting of household waste on an industrial scale. *Compost Science & Utilization,* **2006,** 4(3), 184-190.
3. Adrian, L., Szewzyk, U., Gorisch, H., Bacterial growth linked to reductive dechlorination of trichlorobenzenes, *Biodegradation.* **2000,** 11 73–81.
4. Allen, V., Barker and Gretchen, M., Bryson, Bioremediation of heavy metals and organic toxicants by composting, *J. The Scientific World.* **2002,** 2, 407–420.
5. Andrews, J., F., Kambhu, K., Thermophilic Aerobic Digestion of Organic Solid Wastes. EPA-670/2-73-061. PB 222 396; USEPA: Washington, DC, **1973.**
6. APHA, *Standard methods for the examination of water and wastewater.* 17th edition APHA, Washington DC, **1995.**
7. Arrebola, J., Martınez, Vidal, J.L., Mateu-Sanchez, M., Alvarez- Castellon, F.J., *Anal. Chemical. Acta.* **2003**, 484, 167
8. Barriada-Pereira, M., Gonzalez-Castro, M.J., Muniategui-Lorenzo, S., Lopez-Mahıa, P., Prada-Rodrıguez, D., Fernandez-Fernandez. E., *Chemosphere.* **2005,** 58, 1571.
9. Bishop, P.L., Godfrey, C., Nitrogen transformation during sludge composting. *BioCycle,* **1983**, 24, 34-9.
10. BIS, *Methods for analysis of solid wastes (Excluding industrial solid wastes),* Indian Standards Institution, New Delhi, **1982.**
11. Buyuksonmez, F., Rynk, R., Hess, T.F., and Bechinski, E. Occurrence, degradation, and fate of pesticides during composting, Part I. Composting, pesticides, and pesticide degradation. *Compost Sci. Util.* **1999a,** 7(4), 66–82.
12. Buyuksonmez, F., Rynk, R., Hess, T.F., and Bechinski, E. Occurrence, degradation, and fate of pesticides during composting. Part I. Composting, pesticides, and pesticide degradation. *Compost Sci. Util.* **1999b,7(4),** 66–82,
13. Buyuksonmez, F., Rynk, R., Hess, T.F. and Bechinski, E. The Occurrence, Fate, and Degradation of Pesticides during Composting. Part II. Occurrence and Fate of

Pesticides in Compost and Composting Systems. *Compost Science & Utilization.* **2000,** 8 (1), 61-82.

14. Brinton, W.F., An international look at compost standards methods used for evaluating compost quality in Europe are summarized in a new report. *BioCycle,* **2001**, 42, 74-77.
15. Chefetz, B., Hatcher, P.G., Hadar, Y., Chen, Y., Chemical and biological characterization of organic matter during composting of municipal solid waste. *Journal of Environmental Quality*, **1996**, 25, 776-785.
16. Chen, Y., Inbar, Y., Chemical and spectroscopic analysis of organic matter transformations during composting in relation to compost maturity. In: Hoitink, H. A. J., keener, H. M. (Eds), Science and Engineering of Composting; Design, Environmental, Microbiological and Utilization Aspects, Renaissance, Washington, OH, **1993**, pp. 551-600.
17. Chaney, R.L., Ryan, J.A., and O'Connor, G.A. Organic contaminants in municipal biosolids: risk assessment, quantitative pathways, analysis, and current research topics. *J. Sci. Total Environ.* **1996,** 185, 187–216.
18. Chen, Y., Inbar, Y., Chemical and spectroscopic analysis of organic matter transformations during composting in relation to compost maturity. In: Hoitink, H.A.J., Keener, H.M. (Eds.), *Science and Engineering of Composting: Design, Environmental, Microbiological and Utilization Aspects.* Renaissance, Washington, OH, **1993,** 551-600.
19. C.F. Chang, C.Y. Chang, K.E. Hsu, S.C. Lee, and Holl, W., Adsorptive Removal of the Pesticide Methomyl using hypercrosslinked polymers. *J. Hazard. Material,* **2008,** 155(1-2), 295-304.
20. C.F. Chang, C.Y. Chang, K.E. Hsu, W. Höll and P.C. Chiang, , Removal of Methomyl Pesticide by Adsorption Using Novel Hypercrosslinked Polymer of Macronet MN-100. *J. Environ. Eng. Manage.* **2007**, 17(5), 311-318.
21. CPHEEO, *Manual on municipal solid waste management.* Central Public Health and Environmental Engineering Organization, New Delhi, **2000.**
22. Dell'Abate, M.T., Benedetti, A., Sequi, P., Thermal methods of organic matter maturation monitoring during a composting process. *J. Thermal Anal. Calorimetry,* **2000**, 61:389–396.

23. Diaz-Burgos, M.A., Polo, A., Calcinai, M., Masciandaro, G., Ceccanti, B., Use of pyrolysis-gas chromatography to evaluate sludge humification. In: Senesi, N., Miano, T.M. (Eds.), *Humic substances in the global environment and implications on human health*. Elsevier, Amsterdam, **1994,** pp. 1285–1289.
24. Duff, S.J.B., Kennedy, K.J., Brady, A.J., Treatment of dilute phenol/PCP wastewaters using the upflow anaerobic sludge blanket (UASB) reactor. *Water Research,* **1995**, 29, 645–651.
25. Eekert, M.H.A., Van, Schroder, T.J., Stams, A.J.M., Schraa, G., Field, J.A., Degradation and fate of carbon tetrachloride in unadapted methanogenic granular sludge. *Appl. Environ. Microbiol.* **1998a**. 64, 2350–2356.
26. Eekert, M.H.A. Rasvan, N.J.P., Mentink, G.H., Rijnaarts, H.H.M., Stams, A.J.M., Field, J.A., Schraa, G., Anaerobic transformation of b-exachlorocyclohexane by methanogenic granular sludge and soil microflora. *Environ. Sci. Technol.* **1998b**, 32, 3299–3304.
27. Eekert, M.H.A. van, Stams, A.J.M., Field, J.A., Schraa, G., Gratuitous dechlorination of chloroethanes by methanogenic granular sludge. *Appl. Microbiol. Biotechnol.* **1999a,** 51, 46–52.
28. Eekert, M.H.A. van, Transformation of chlorinated compounds by methanogenic granular sludge. Ph.D. thesis, Wageningen University, Netherlands, **1999b**.
29. Eekert, M.H.A. van, Schraa, G., The potential of anaerobic bacteria to degrade chlorinated compounds. *Water. Sci. Technol.* **2001**. 44, 49–56.
30. Esaac, E. G., Matsumura. F., *Pharm. Thermodynamics,* **1980**, *9,* 1-26.
31. Fang, M., Wong, J.W.C., Ma, K.K., Wong, M.H., Co-composting of sewage sludge and coal fly ash: nutrient transformations. *Bioresource Technology,* **1999**, 67, 19-24.
32. Fathepure, B.Z., Vogel, T.M., Complete degradation of polychlorinated hydrocarbons by a two-stage biofilm reactor, *Appl. Environ. Microbiol.* **1991**, 57 3418–3422.
33. FAO, Available from http://www.fao.org/ag/AGP/AGPP/Pesticid/Disposal/index_en.htm> (accessed Dec **2002**.
34. Garcia, C., Hernandez, T., Costa, F., Characterization of humic acids from uncomposted and composted sewage sludge by degradative and non-degradative techniques. *Bioresourse Technology,* **1992**, 41, 53-57.

35. Garg, V. K., Kaushik and Priya, Vermistabilization of Textile mill sludge spiked with poultary droppings by an epigeic earthworm Eisenia foetida. *Bioresource Technology,* **2005**, 96 (9) 1063-1071.
36. Gea, T., Barrena, R., Artola, A., Sanchez, A., Monitoring the biological activity of the composting process, Oxygen Uptake Rate (OUR), Respirometric Index (RI), and Respiratory Quotient (RQ). *Biotechnology and Bioengineering,* **2004,** 88, 520-527.
37. Georgacakis, E., Khan, M.A.Q., Toxicity of the photoisomers of cyclodiene insecticides for freshwater animals. *Nature,* **1971**, 229, 120–121.
38. Goel, Jyotsna, Kadirvelu, K., Rajagopal, C. and Garg, V.K., Cadmium removal from aqueous solution by adsorption onto carbon aerogel using response methodology approach. *Indust. Engg. Chem. Resources*. **2006**, 45 (19), 6531-6537.
39. Gomez, X., Cuetos, M.J., Garcia, A.I., Moran, A., Evaluation of digestate stability from anaerobic process by thermogravimetric analysis. *Thermochim Acta,* **2005,** 426,179–184.
40. Gotaas, H.B., Composting-sanitary, disposal and reclamation of organic wastes. World Health Organization, Genewa, **1956.**
41. Gomez, R.B., Lima, F.V., Ferrer, A.S., The use of respiration indices in the composting process: a review. *Waste Management & Research,* **2006,** 24, 37-47.
42. Gupta, Pesticide exposure-Indian scene *J. of Toxicology*. **2004**, 198, 83–90.
43. Grossi, G., Lichtig, J., Kraub, *Chemosphere,* **1998**, 37, 2153–2160.
44. Grube, M., Lin, J.G., Lee, P.H., Kokorevicha, S., Evaluation of sewage sludge-based compost by FT-IR spectroscopy. *Geoderma,* **2006**, 130, 324-333.
45. Hassen, A., Belguith, K., Jedidi, N., Cherif, A., Cherif, M., Boudabous, A., Microbial characterization during composting of municipal solid waste. *Bioresource Technology,* **2001**, 80, 217-225.
46. Haug, R.T., *The practical handbook of composting engineering,* 1st Edition, Lewis publishers. **1993.**
47. Hendriksen, H.V., Larsen, S., Ahring, B.K., Influence of a supplemental carbon source on anaerobic dechlorination of pentachlorophenol in granular sludge. *Appl. Environ Microbiol*. **1992**, 58, 365–370.
48. He, X.T., Traina, S.J., Logan, T.J., *J. Environ Qual,* **1992**, 21, 318–329.
49. He, X.T., Traina, S.J., Logan, T.J., *J. Environ Qual,* **1995,** 24, 543–552.

50. Hoitink, H.A.J., Keener, H.M. (Eds.), *Science and Engineering of Composting: Design, Environmental, Microbiological and Utilization Aspects*. Renaissance, Washington, OH,.551-600.
51. Hsu, J.H., and Lo, S.L., Chemical and spectroscopic analysis of organic matter transformations during composting of pig manure. *J. Environ. Pollution*, **1999**, 104, 189–196.
52. Huang, G.F., Wu, Q.T., Wong, J.W.C., Nagar, B.B.,. Transformation of organic matter during co-composting of pig manure with saw dust. *Bioresourse Technology,* **2006,** 97, 1834-1842.
53. Iannotti, D.A., Pang, T., Toht, B.L., Elwell, D.L., Keener, H.M., Hoitink, H.A.J., A quantitative respirometric method for monitoring compost stability. *Compost Science & Utilization*, **1993,** 1, 52-65.
54. Iannotti, D.A., Grebus, M.E., Toth, B.L., Madden, L.V., Hoitink, H.A.J., Oxygen respirometry to assess stability and maturity of composted municipal solid waste. *Journal of Environmental Quality,* **1994,** 23, 1177-1183.
55. Inbar, Y., Hadar, Y., Chen, Y., Recycling of cattle manure: the composting process and characterization of maturity. Journal of Environmental Quality, **1993**, 22, 857-863.
56. Jackson, D.V., Merilott, J.M., and L Hermite, P., Eds. Commission of the European Communities, Luxembourg. pp. 227–236.
57. Jagnow, G., Haider, K., Evolution of $^{14}CO_2$ from soil incubated with dieldrin-^{14}C and the action of soil bacteriaon labelled dieldrin. *Soil Biol. Biochem.* **1972,** 4, 43–49.
58. Jimenez, E.I., Garcia, V.P., Determination of maturity indices for city refuse composts. *Agriculture Ecosystem & Environment,* **1992**, 38, 331-343.
59. Jouraiphy, A., Amir, S., El Gharous, M., Revel, J-C., Hafidi, M., Chemical and spectroscopic analysis of organic matter transformation during composting of sewage sludge and green plant waste. *International Biodeterioration & Biodegradation.* **2005**, 56, 101-108.
60. J.W.C. Wong and M. Fang, Lime amendment on availability of heavy metals and maturation in sewage sludge composting *Environ. Pollut.*, **1999**, 106: 83-89.
61. J.W.C. Wong and M. Fang, Effects of lime addition on sewage sludge composting process, *Water Research* **2000**, 34(15):.3691-3698.

62. K.E. Hsu, C.Y. Chang and C.F. Chang, Mass Transfer Aspects of Adsorption Removal of Pesticide of Methomyl from Water Using Novel Hyper cross linked Polymer of Macronet MN-100 and Its Regeneration. Bulletin of the College of Engineering, NTU, **2007,** No. 96, 15-30.
63. Kalamdhad, A.S., Kazmi, A.A., Mixed organic waste composting using rotary drum composter. *Int. J. Environ. Waste Management,* **2008a** 2, 24–36.
64. Kalamdhad, A.S., Kazmi, A.A., Rotary drum composting of different organic waste mixtures. *J. Waste management and research.* **2008b** 26, 1-9.
65. Kalamdhad, A. S., Kumar, Y.S., Ali, Muntjeer, Khwairakpam, M., Kazmi, A.A., Rotary drum composting of vegetable waste and tree leaves. *Bioresourse Technology.* **2009**, 100, 6442–6450.
66. Kearney, P.C., Roberts, T., (Eds.), Pesticide Remediation in Soils and Water. *John Wiley and Sons*, **2005**, 217–250.
67. Kiigemagi, D., Morrison, H. E., Roberts, J. E., Bollen, W. B., Biological and chemical studies on the decline of soil insecticides. *J. Econ. Ent*, **1958,** 51, 198-204.
68. Kim, M., Kang, T.W., Pyo, H., Yoon, J., Determination of organochorine pesticides in sediment using graphitized carbon black solid phase extraction and gas chromatography mass spectroscopy. *J. chromatography A.* **2008**, 1208, 25-33.
69. Knoepp, J.D., Vose, J.M., *Quantitative comparison of in situ soil CO_2 flux measurement method.* USDA Forest Service, Southern Research Station. **2002,** Research Paper SRS-28.
70. Kumar D., and Alappat, B. J., Evaluating leachate contamination potential of landfill sites using leachate pollution index. *J. Clean Techn Environ Policy.* **2005**, 7, 190–197.
71. Kumar, D. and Alappat, B.J., NSF Water quality index: does it represent the experts' Opinion? Practice Periodical of Hazardous, Toxic, and Radioactive. *Waste Management*, **2009**, 13 (1), pp 7579.
72. Kumar, M. and Philip, L., Enrichment and Isolation of a Mixed Bacterial Culture for Complete Mineralization of Endosulfan, *J. of Environmental Science and Health Part B*, **2006** , 41, 81–96.
73. Kunwar D., Yadav, Vinod Tare, M. Mansoor Ahammed, Vermicomposting of source-separated human faeces by Eisenia fetida: Effect of stocking density on feed

consumption rate, growth characteristics and vermicompost production. *Waste Management*, **2011,** 31, 6, 1162-1168.

74. Lardinois, I., Van de Klundert, A. (Eds.), *Organic waste-options for small-scale resource recovery*. Urban solid waste series 1, Technology transfer for development tool, WASTE Consultants, Amsterdam, **1993.**
75. Lazzari, L., Sperni, L., Salizzato, M., Pavoni, B., *Chemosphere,* **1999,** 38, 1925–1935.
76. Lee, W.Y., Iannucci-Berger, W., Eitzer, B.D., White, J.C., Mattina, M.J.I., *J Environ Qual,* **2003**, 32, 224–231.
77. Liao, P.H., Jones, L., Lau, A.K., Walkemeyer, S., Egan, B., Holbek, N., Composting of fish wastes in a full–scale in-vessel system. *Bioresource Technology,* **1996**, 59, 163-168.
78. Lichtenstein, E.P., Schultz, K.R., Epoxidation of aldrin and heptachlor in soils as influenced by autoclaving, moisture and soil types. *J. Econ. Entomol.* **1960,** 53, 192–197.
79. L.X. Zhou and J.W.C. Wong, Effects of dissolved organic matter from sludge and sludge compost on soil Cu sorption, *J. Environ. Qual.* **2001**, 30: 878-883.
80. Lyman, W.J., Reehl, W.F., and Rosenblatt, *D.H., Handbook of chemical property estimation methods:* American Chemical Society, Washington, D.C., **1990.**
81. Mathava kumar S and Ligy Philip, Bioremediation of Endosulfan Contaminated soils. Optimization of operating conditions under laboratory scale reactors. *Journal of Hazardous Materials*, **2006,** B-136, pp354-364.
82. Memon F.A., Butler D. Characterization of the pollutants washed off from road surfaces during wet weather, *Urban Water Journal,* **2005,** 2(3), 171-182.
83. Memon F.A., *Guidelines for composting toilets for inclusion in Part G (Building Regulations),* Office of the Deputy Prime Minster. **2003.**
84. Melis, P., Castaldi, P., Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process. *Thermochim Acta,* **2004,** 413:209–214.
85. McGrowin A.E., Adom K.K., Obubuafo A.K., *Chemosphere,* **2001,** 45, 857–864.
86. Miles, J.R., Moy P., Degradation of endosulfan and its metabolites by a mixed culture of soil microorganisms. *Bull. Environ. Contam. Toxicol.* **1979,** 23, 13-16.

87. Mohee, R., Mudhoo, A., Analysis of the physical properties of an in-vessel composting matrix, *Journal of Powder Technology,* **2005,** 155, 92-99.
88. Nakada, N., Kiri, K., Shinohara, H., Harada, A., Kuroda, K., Takizawa, S., Hideshige Takada, H, Evaluation of pharmaceuticals and personal care products (PPCPs) as water-soluble molecular markers of sewage, *Environmental Science and Technology,* **2008**, 42, 6347-6353.
89. National Solid Waste Association of India. *Urban Municipal Solid Waste Management*, Special Bulletin of the National Solid Waste Association of India (Inaugural issue), Mumbai, India, **2003**.
90. Otero, M., Calvo L.F., Estrada, B., Garcia, A.I., & Moran, A., Thermogravimetry as a technique for establishing the stabilization progress of sludge from wastewater treatment plants, *Thermochim. Acta*, **2002**, 389, 121–132.
91. Patil, K.C., Matsumura, F., Bousch, G.M., Degradation of endrin, aldrin and DDT by soil microorganisms. *Appl. Microbiol.* **1970**, 19, 879–881.
92. Patil, K.C., Matsumura, F., Bousch, G.M., Metabolic transformation of DDT, dieldrin, aldrin and endrin by marine microorganisms. *Environ. Sci. Technol.* **1972**, 6, 629–632.
93. Punyapalakul, P., Takizawa, S., Effect of Surface Functional Group on Adsorption of Organic Pollutants on Hexagonal Mesoporous Silicate, *Water Science and Technology,* **2006**, 63, 3, 17-25.
94. Pranab Kumar Ghosh and Ligy Philip, Environmental significance of atrazine in aqueous systems and its removal by biological processes: an overview. *GLOBAL NEST.* **2006**, 8, 2, 71-90.
95. Pietro, M., Paola, C., Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process. *Thermochimica Acta,* **2004**, 413, 209-214.
96. Pesce, S., Wunderlin, D., Biodegradation of lindane by a native bacterialconsortium isolated from contaminated riversediment. *Int. Biodeteration. Biodegradation.* **2004**, 54, 255-260.
97. Peter. M., Middeldorp, Marcojapers, Alexander, J. B., Zehnder, and Gosseschraa, Biotransformation of α, β, γ and δ-Hexachlorocyclohexane under Methanogenic Conditions, *Environ. Sci. Technol.* **1996,** 30, 2345-2349.

98. Rao, N., Grethlein, H.E., and Reddy, C.A., Mineralization of atrazine during composting with untreated and pretreated lignocellulosic substrates. *Compost Sci. Util.* **1995**, 3(3), 38–46.

99. Rao, N., Grethlein, H.E., and Reddy, C.A., Effect of temperature on composting of atrazine-amended lignocellulosic substates. *Compost Sci. Util.* **1996**, 4 (3), 83–88.

100. Ratkowsky, D. A., J. Olley, T. A., McMeekin, and A. Ball. Relationship between temperature and growth rate of bacterial cultures. *J. Bacteriology*, **1982,** 149:1-5.

101. Ratkowsky, D. A., R. K. Lowry, T. A. McMeekin, A. N. Stokes, and R. E. Chandler. Model for bacterial culture growth rate throughout the entire biokinetic temperature range. *J. Bacteriol.* **1983,** 154, 1222-1226.

102. Reungsang, A., Takizawa, S., Wirojanagud, W., Distribution of PCDDs/PCDFs in Sediments from the Pong River, Khon Kaen, Thailand, *Environmental Engineering Research,* **2006,** Vol. 43.

103. Saad, S.A.M., Processes and balance of organic matter turnover and transformation of mineral compounds during decomposition of biogenic material in the presence of soil material. Ph.D. Thesis, Georg-August-University Gottingen, Germany, **2001**.

104. Sanchez-Monedero, M.A., Roig, A., Paredes, C., Bernal, M.P., Nitrogen transformation during waste composting by the Rutger system and its effects on pH, EC and maturity of the composting mixtures. *Bioresources Technology*, **2001**, 78, 301-308.

105. Selent, B., Kombinierter anaerober und aerober Abbau von Chlorbenzolen mit immobilisierten Mikroorganismen, Dissertation, TU Berlin, **1999**.

106. Serpil Yenisoy-Karakas, Validation and uncertainty assessment of rapid extraction and clean-up methods for the determination of 16 organochlorine pesticide residues in vegetables, *J. of Analytica Chimica Acta*. **2006**, 571, 298–307.

107. Sikora, L.J., Benefits and drawbacks to composting organic byproducts. In *Beneficial Co-utilization of Agricultural, Municipal, and Industrial By-products*. Brown, S., Angle, J.S., and Jacobs, L., Eds. Kluwer Academic Publishers, Dordrecht, the Netherlands, **1998**, 69–77.

108. Smith, D.R., Cawthon, D.L., Sloan, J.J., Freeman, T.M., In-vessel, mechanical rotating drum composting of institutional food residuals. *Compost Science & Utilization,* **2006**, 14(2), 155-161.

109. Smidt, E., Lechner, P., Compost quality assessment and process control using Fourier transform infrared spectroscopy. *Proc. Int. Symposium Composting and Compost Utilization*. Columbus, Ohio, USA, **2002**, 1-11.

110. Smidt, E., Lechner, P., Study on the degradation and stabilization of organic matter in waste by means of thermal analyses. *Thermochim Acta*, **2005**, 438, 22–28.

111. Strom, P. F., Effect of temperature on bacterial species diversity in thermophilic solid-waste composting. *J. of Appl. Environ. Microbiol.* **1985a**.50, 899-905.

112. Strom, P. F., Identification of thermophilic bacteria in solid-waste composting. *J. of Appl. Environ. Microbiol.* **1985b**.50, 906-915.

113. Strom, P.F. Evaluating pesticide residues in yard trimmings compost. *J. BioCycle,* **1998,** 39, (11), 80.

114. Subrata Hait, Vinod Tare, Optimizing vermistabilization of waste activated sludge using vermicompost as bulking material, *Waste Management*, **2011a**,31,3, 502-511.

115. Subrata Hait, Vinod Tare, Vermistabilization of primary sewage sludge. *Bioresource Technology*, **2011b**, 102, 3, 2812-282.

116. Subrata Hait, Vinod Tare, Transformation and availability of nutrients and heavy metals during integrated composting–vermicomposting of sewage sludges. *Ecotoxicology and Environmental Safety*, **2012,** 79, 1, 214-224.

117. Suthar S., Potential utilization of guar gum industrial waste in vermicompost production. *Bioresource Technology*, **2006**, 97,18, 2474-2477.

118. Suthar S., Vermicomposting potential of Perionyx sansibaricus (Perrier) in different waste materials. *Bioresource Technology*, **2007a**, 98, 1231–1237.

119. Suthar S., Nutrient changes and biodynamics of epigeic earthworm *Perionyx excavatus* (Perrier) during recycling of some agriculture wastes Original Research Article. *Bioresource Technology*, **2007b**, 98, 8, 1608-1614.

120. Suthar S., Production of earthworm *Allolobophora parva* (Eisen) in cattle dung, *Ecological Engineering*, **2011,** 37, 4, 644-647.

121. Tam N F Y**.,** Changes in microbiological properties during *in-situ* composting of pig manure. *Environmental Technology*, **1995,** 16(5): 445-456) R: 57/126.

122. Tolvanen, O., Nykanen, J., Nivukoski, U., Himanen, M., Veijanen, A., Hanninen, K., Occupational hygiene in a finish drum composting plants. *Waste Management*, **2005**, 25, 427-433.

123.Terrance L., Miller, Ronald, R., Swager, Sue, G., Wood, Angela, D., and Atkins, Sampling compost sites for metals and pesticides. Sources: Illinois Department of Energy and Natural Resources. **1992.**

124.Tu, C.M., Miles, J.R.M., Harris, C.R., Soil microbial degradation of aldrin. *Life Sci.* **1968.**7, 311–322.

125.Tiquia, S, Tam, N. F. Y., and Hodgkiss, J., Microbial activities during composting of spent pig-manure sawdust litter at different moisture contents. *Bioresource Technology,* **1996a,** 55, 201-206. "P"; R: 23/11.

126. Tiquia, S., Tam, N. F. Y., and Hodgkiss, I. J., Effect of composting on phytotoxicity of spent pig-manure sawdust litter. *Environmental Pollution*, **1996b,** 93(3): 249-256 "P"; R: 25/129.

127. Tiquia, S.M., Tam, N.F.Y., Fate of nitrogen during composting of chicken litter. *Environmental Pollution*, **2000**, 110, 535-541.

128. Tomasz P. Baczynski, Tim Grotenhuis, Petronella Knipscheer, The dechlorination of cyclodiene pesticides by methanogenic granular sludge. *Chemosphere,* **2004,** 55, 653–659.

129. Troxler, W.L., Thermal desorption. In: Kearney, P.C., Roberts, T. (Eds.), Pesticide Remediation in Soils and Water. *John Wiley and Sons*. **1998**. 105–127.

130. Vogtmann, H. and Fricke, K., Organic chemicals in compost: how relevant are they for use of it. In: *Composting and Compost Quality Assurance Criteria*, **1992.**

131. Vuorinen, A.H., Saharinen, M.H., Evolution of microbiological and chemical parameters during manure and straw co-composting in a drum composting system. *Agriculture, Ecosystem & Environment,* **1997**, 66, 19-29.

132. Wang, T.C. and Hoffman, M.E., Degradation of organophosphorus pesticides in coastal water. *Journal of the Association of Official. Analytical Chemists*, **1991,** 74, 5,883-886.

133. Wiegel, J., Zhang, X., Wu, Q.Z., Anaerobic dehalogenation of hydroxylated polychlorinated biphenyls by *Desulfitobacterium dehalogenans*, *Appl. Environ. Microbiol.* **1999,** 5, 2217–2221.

134. Williams, R.T. and Keehan, K.R., Hazardous and industrial waste composting. In: *Science and Engineering of Composting.* Hoitink, H.A.J. and Keener, H.M., Eds. Renaissance Press, Worthington, OH. **1993,** pp. 363–382.

135. Wong, J.W.C., Li, S.W.Y., Wong, M.H., Coal fly ash as a composting material for sewage sludge: Effects on microbial activities. *Environmental Technology,* **1995,** 16, 527-537.
136. Yatish Kumar Singh, Ajay S. Kalamdhad, Muntjeer Ali, A.A. Kazmi., Maturation of primary stabilized compost from rotary drum composter, *Resources, Conservation and Recycling*, **2009**, 53, 386–392.
137. Zablotowicz, R.M., Hoagland, R.E., Locke, M.A., Biostimulation: enhancement of co- metabolic processes to remediate pesticide-contaminated soils. In: **1998.**

APPENDIX

Table.4.1. Physical and chemical properties of pesticides namely Aldrin, Lindane, Endosulfan- α and Endosulfan-β

Properties	**Aldrin**	**Lindane**	**Endosulfan-α**	**Endosulfan-β**
Formula	$C_{12}H_8Cl_6$	$C_6H_6Cl_6$	$C_9 H_6 Cl_6 O_3 S$	$C_9 H_6 Cl_6 O_3 S$
Molecular Mass, g/mol	364.93	290.83	406.95	406.95
Half life $t_{1/2}$	Five year*	15-20* weeks	1-2 *months	3-9 *months
Melting Point °C	104	112.5	106-109	207-213
Boiling point °C	132-150	288	449.7 °C at 760 mmHg	449.7 °C at 760 mmHg
Density, g/L at 20 ^{0}C	1.54	1.85	1.94g/cm^3	1.94 g/cm^3
Solubility in water, at 25°C, mg/L	0.011	7.3	0.33	0.32
Solubility in other solvents: (acetone, benzene, hexane, ethanol and ethyl acetate)	highly soluble in most of organic solvent	Soluble in organic solvent	Soluble in organic solvent	Highly soluble
Vapor Pressure , Pa , at 25 °C	1.87 E-07	5.6 E-06	1.9 E-03	9.2 E-05

* Half life $t_{1/2}$ at natural decay.

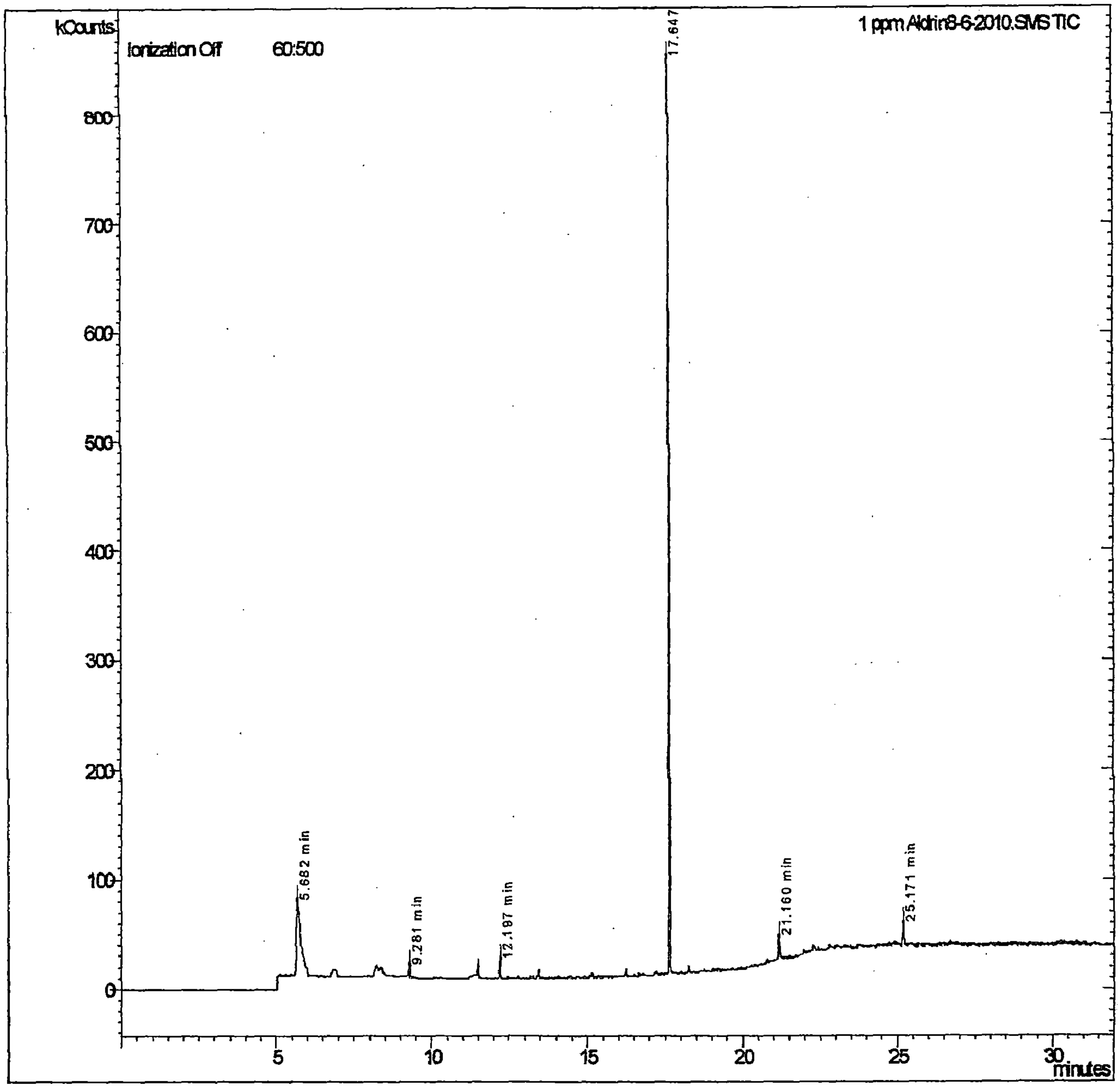


Fig.A1. GC spectra of Aldrin standard

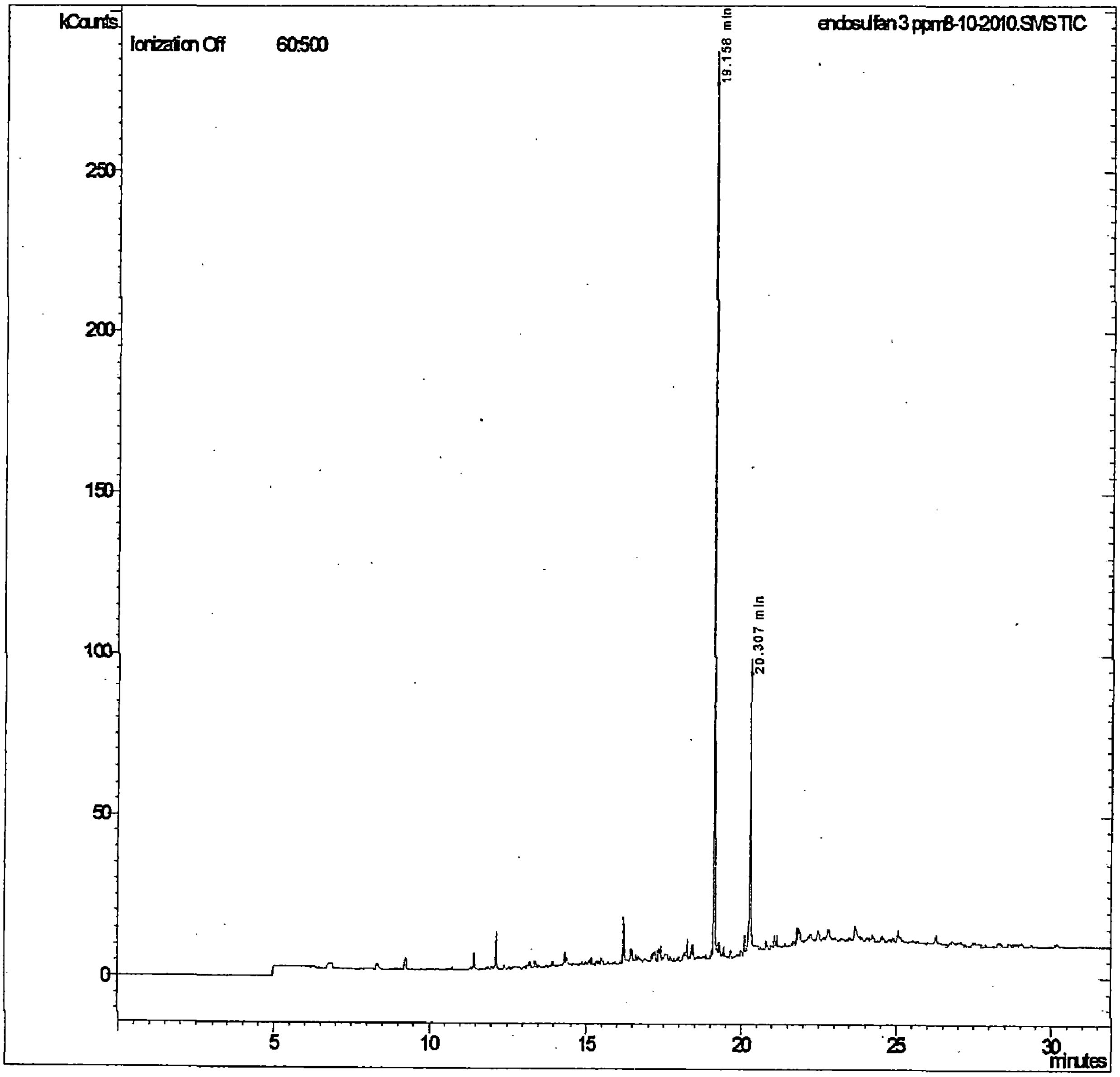


Fig.A2. GC spectra of Endosulfan α and Endosulfan β standard

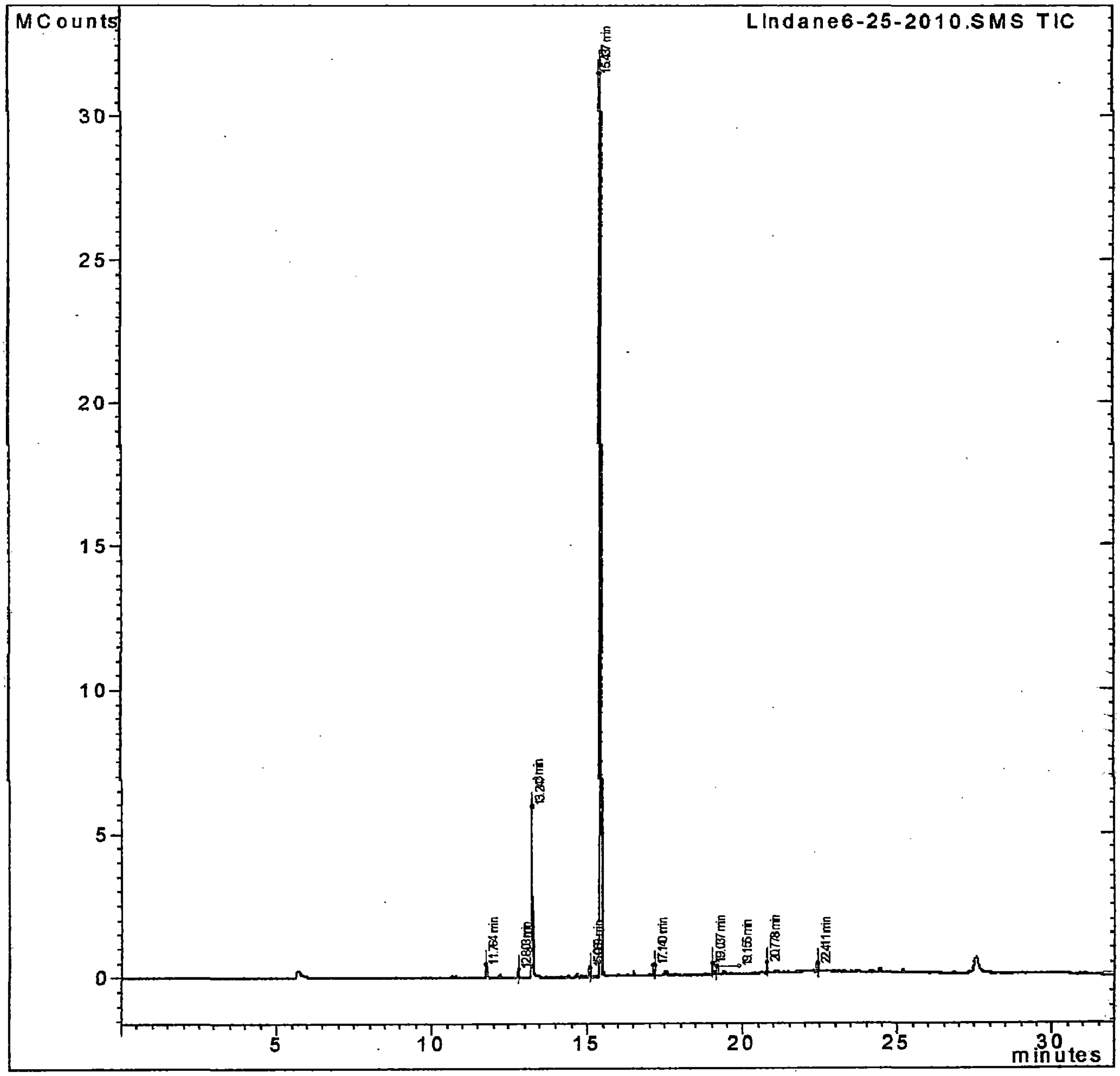


Fig.A3. GC spectra of Lindane standard

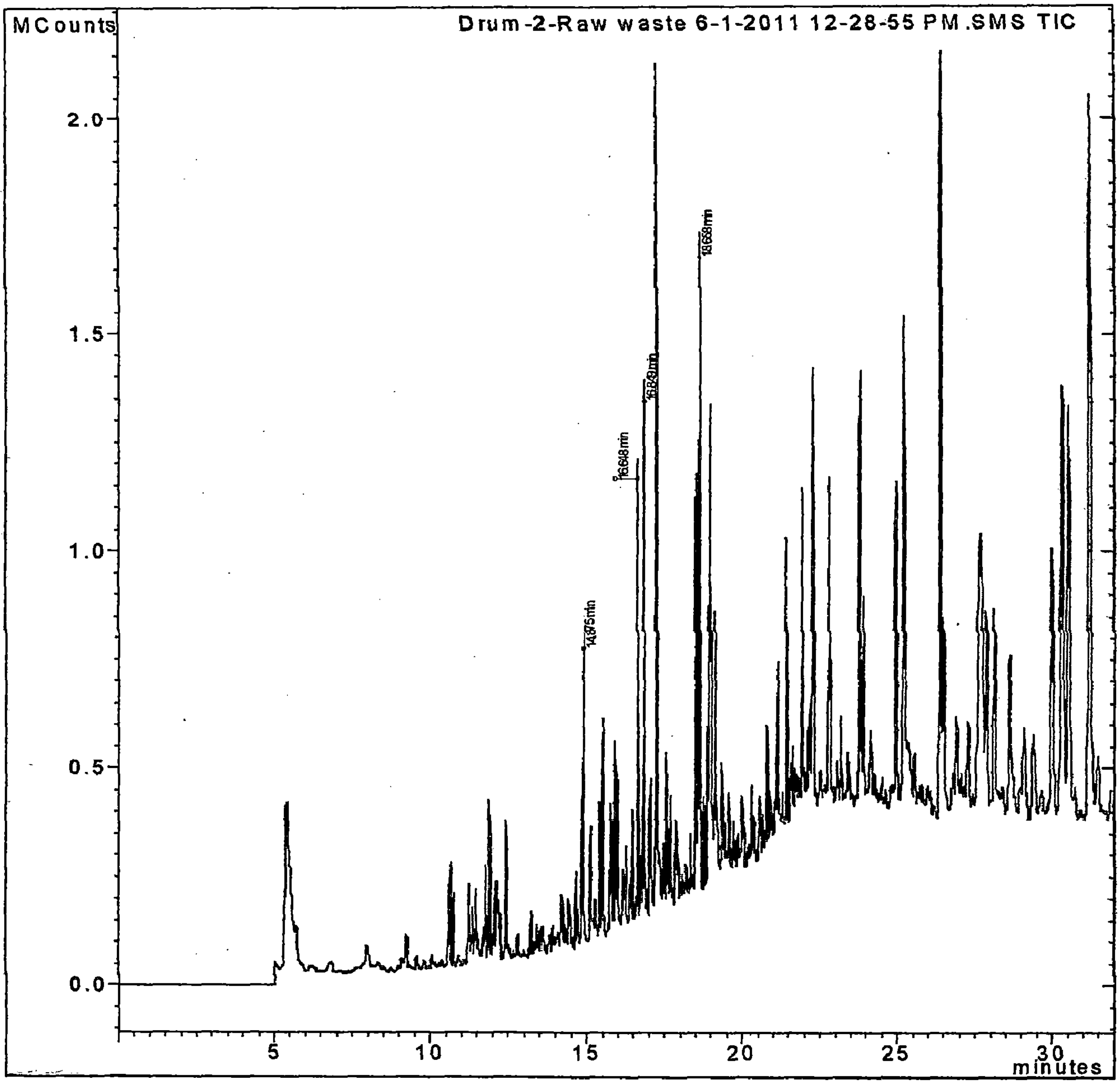


Fig.A4. GC spectra of waste material in house hold batch scale rotary drum composter

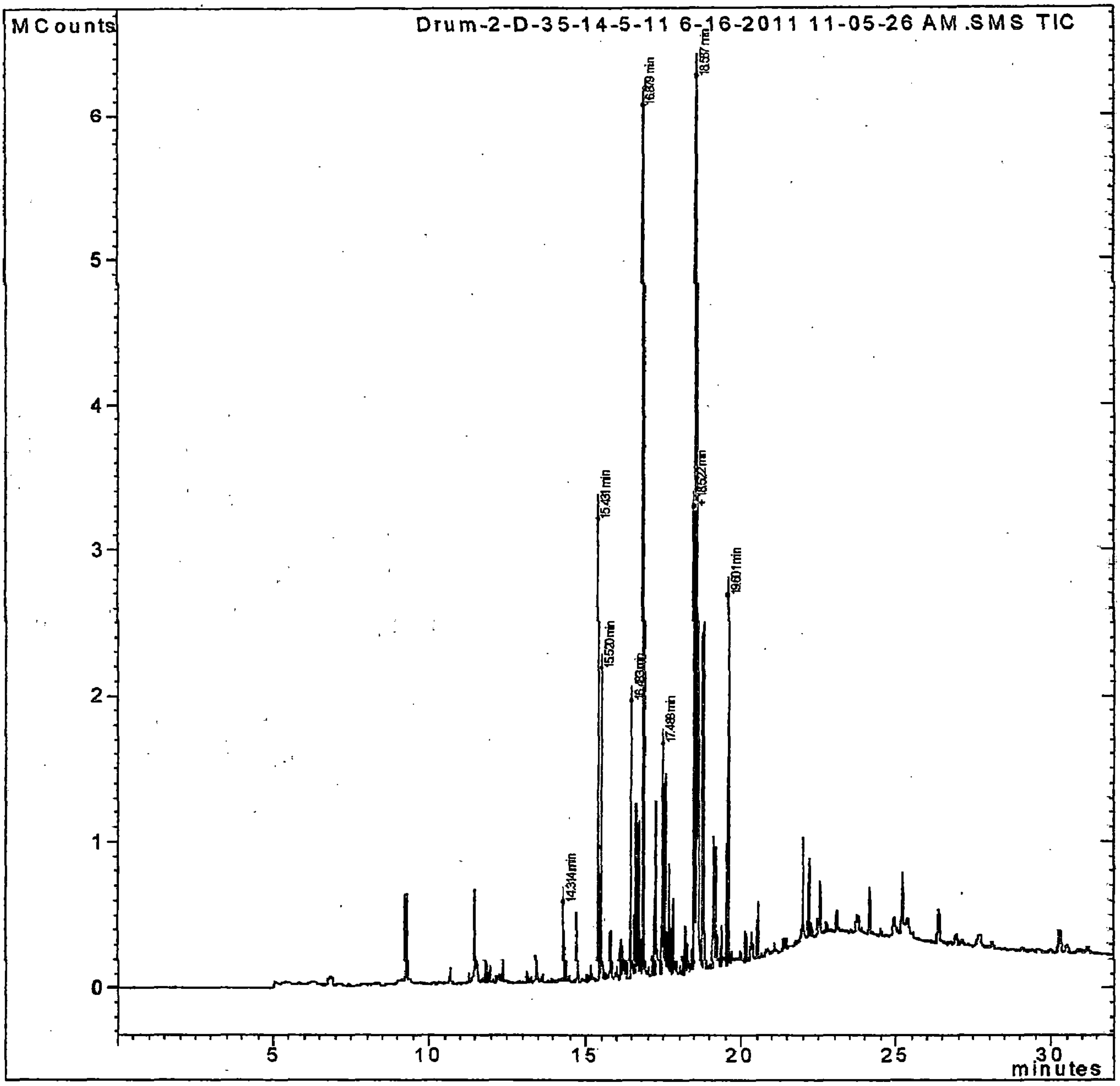


Fig.A5. GC spectra of compost sample in house hold batch scale rotary drum composter after 30 days.

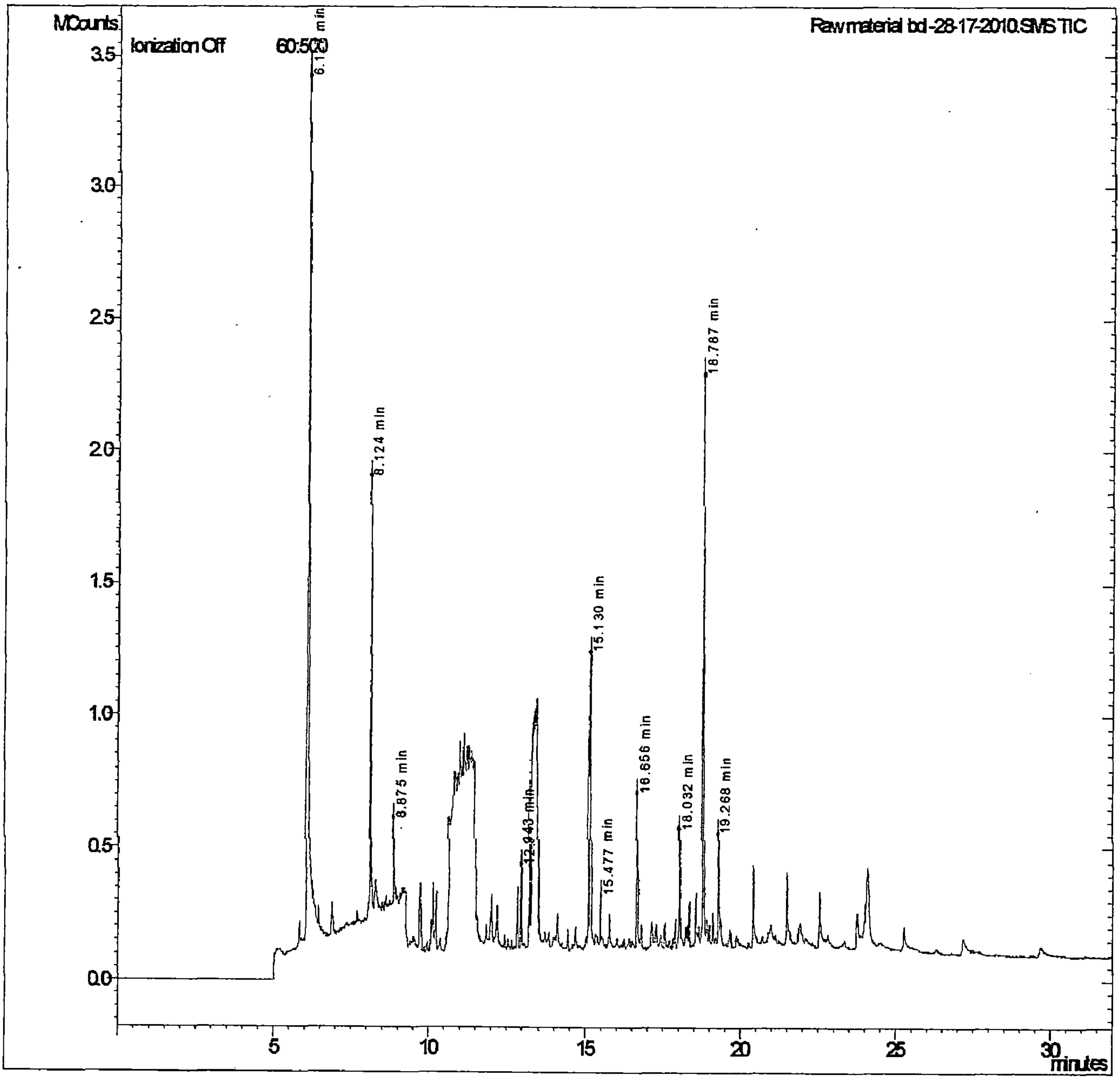


Fig.A6. GC spectra of waste material in full-scale continuous rotary drum composting

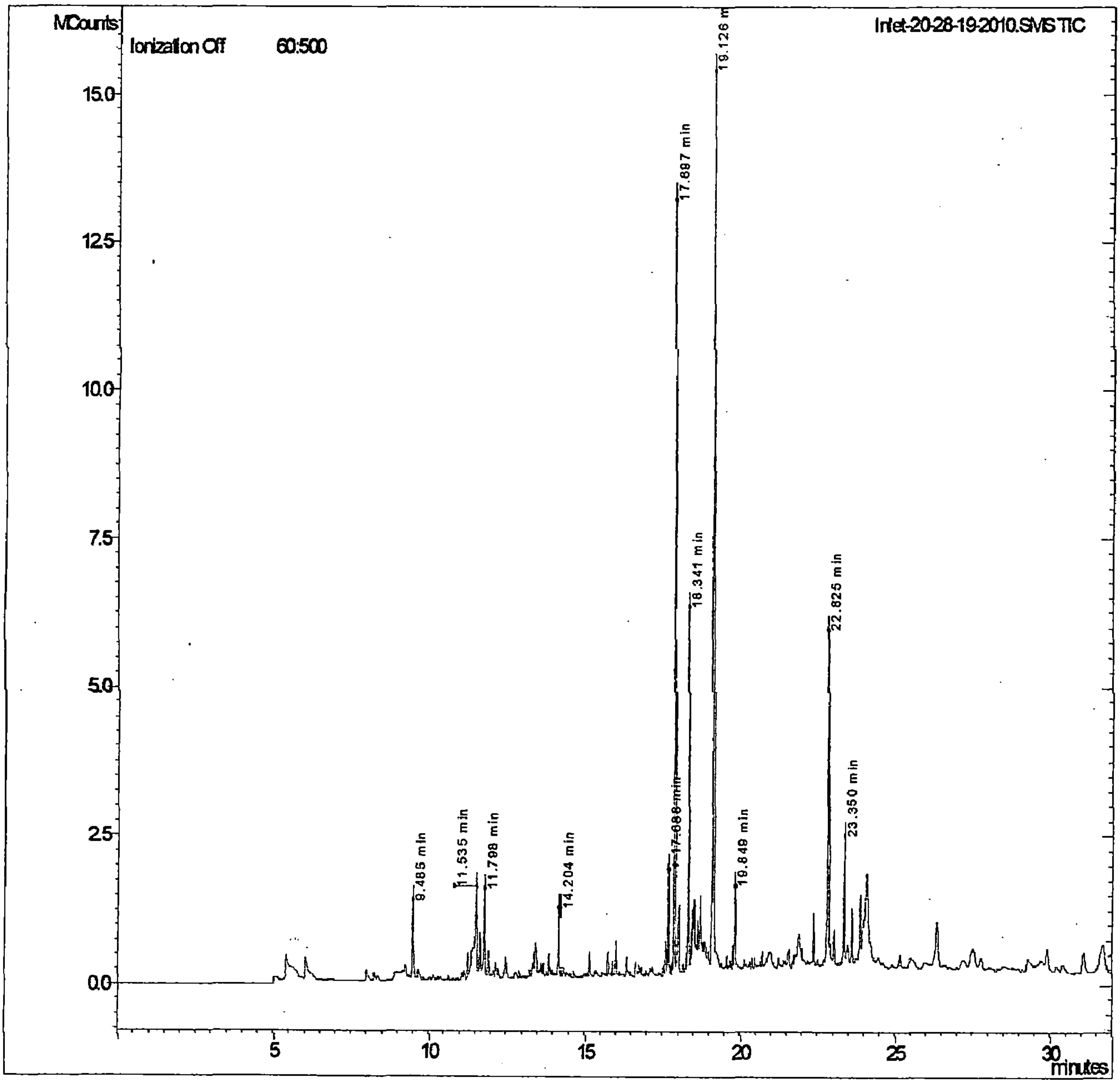


Fig.A7. GC spectra of waste material in inlet zone of full-scale continuous rotary drum composter

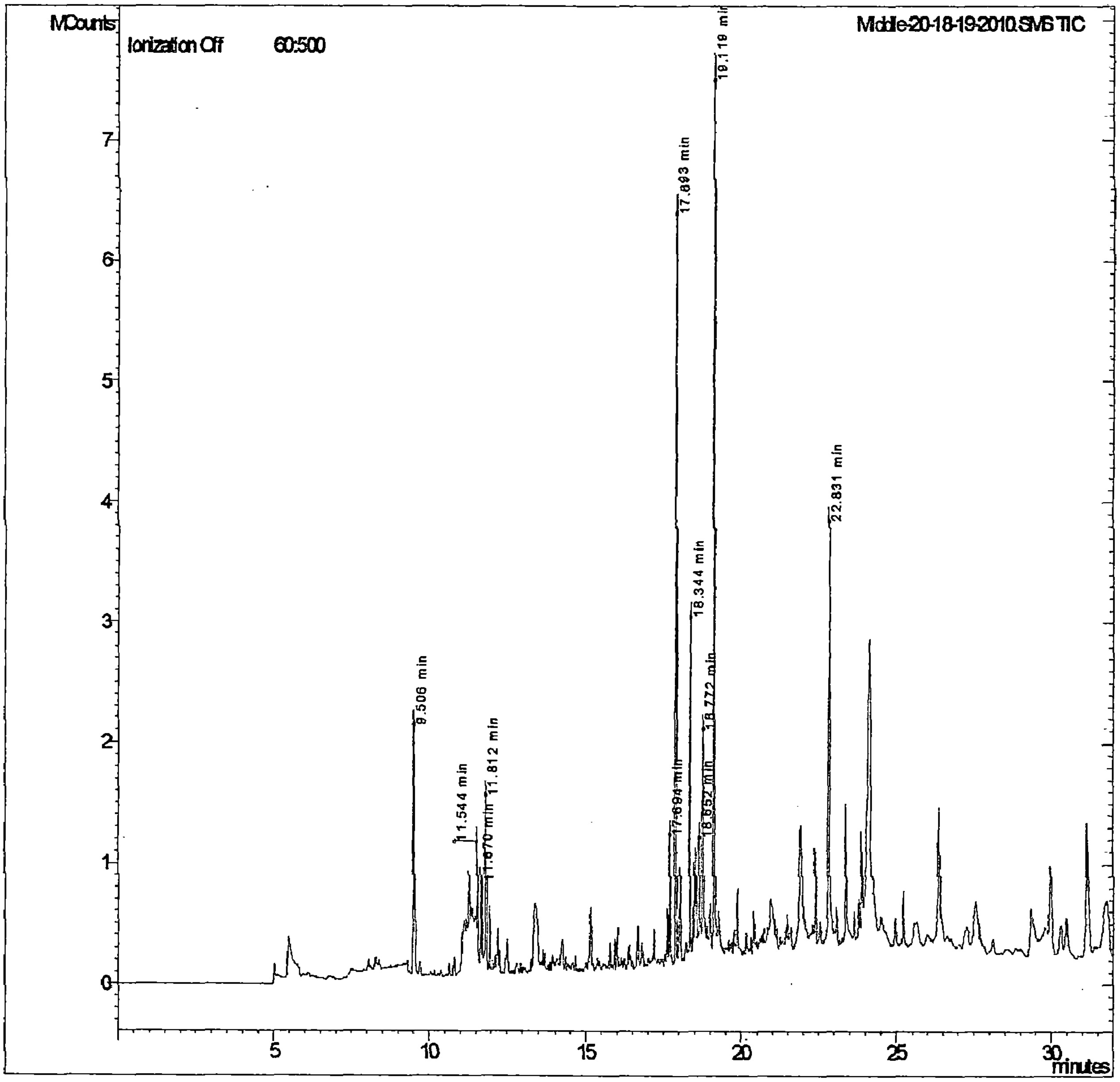


Fig.A8. GC spectra of waste material in middle zone of full-scale continuous rotary drum composter

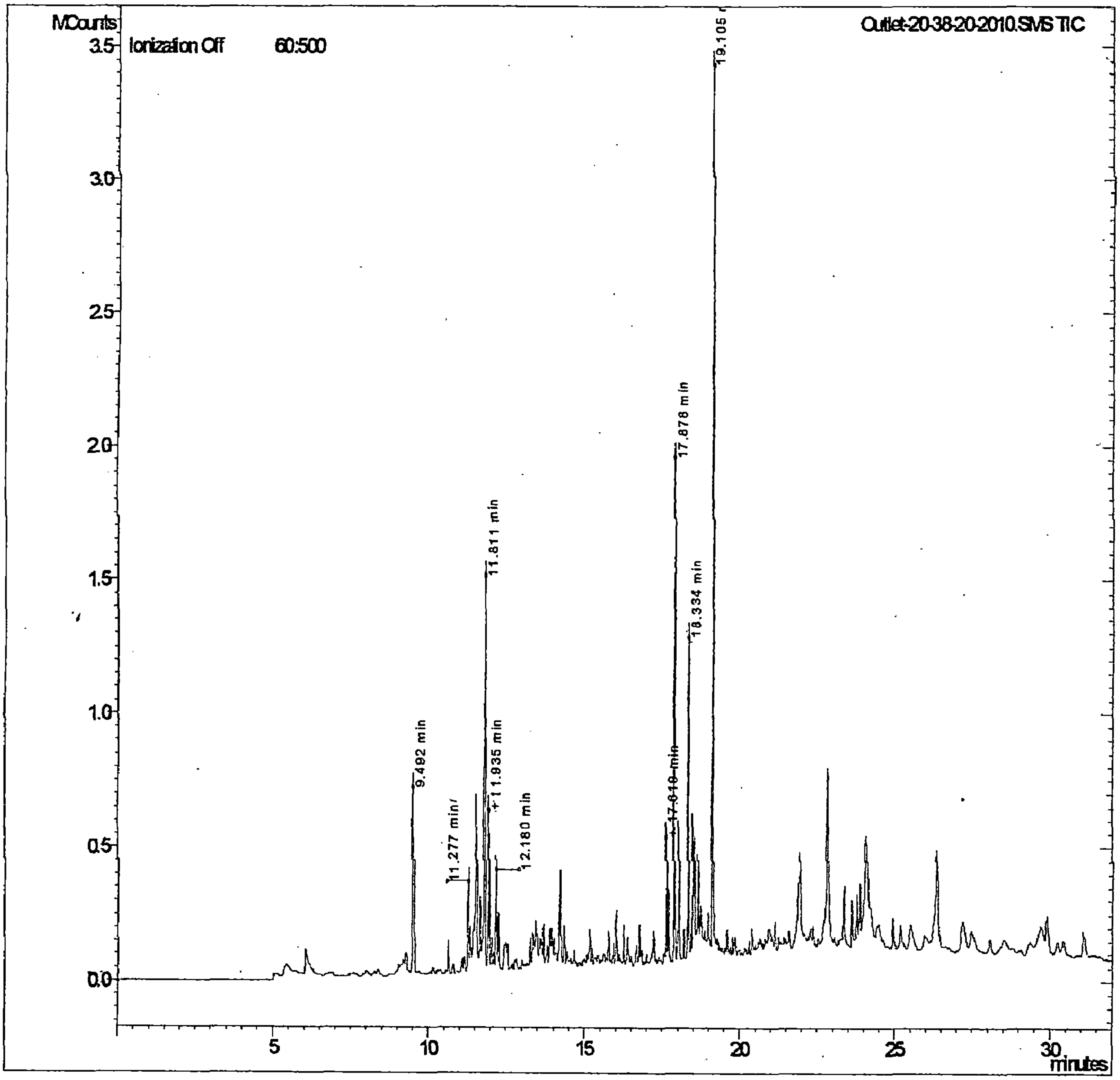


Fig.A9. GC spectra of waste material in outlet zone of full-scale continuous rotary drum composter

LIST OF PUBLICATIONS

- ***International Journals***

i) Muntjeer Ali, Akansha Bhatia, A. A. Kazmi, Naseem Ahmed, Characterization of High Rate composting of vegetable market waste using Fourier transform-infrared (FT-IR) and thermal Studies in three different seasons, *Biodegradation,* **2012**, 23, 225-237.

ii) Muntjeer Ali, K. Simon Duba, Ajay S. Kalamdhad Akansha Bhatia, Anwar KhursheedA. A. Kazmi, Naseem Ahmed, High Rate Composting of Herbal Pharmaceutical Industry Solid Waste, *Water Science and Technology,* **2012**, (In press).

iii) Akansha Bhatia, Muntjeer Ali, Jitendra Sahoo, Sangeeta Madan, Ranjana Pathania, Naseem Ahmed and A. A. Kazmi, Microbial diversity during Rotary Drum and Windrow Pile composting, *J. of Basic Microbiology,* **2011.** DOI: 10.1002/jobm.201100077.

iv) Yatish Kumar Singh, Ajay S. Kalamdhad, Muntjeer Ali, A.A. Kazmi, Maturation of primary stabilized compost from rotary drum composter, *Resources, Conservation and Recycling,* **2009**, 53, 386–392.

v) Ajay S. Kalamdhad, Muntjeer Ali, Meena Khwairakpam, A. A. Kazmi, Organic Matter Transformation during Rotary Drum Composting., *Dynamic Soil, Dynamic Plant,* **2009**, 3, 1, 93-98.

vi) Ajay S. Kalamdhad ,Yatish K. Singh, Muntjeer Ali, Meena Khwairakpam , A.A. Kazmi Rotary drum composting of vegetable waste and tree leaves., *Bioresource Technology,* **2009**, 100, 6442–6450.

vii) Muntjeer Ali, Akansha Bhatia, A. A. Kazmi, Naseem Ahmed, Study on fate of Aldrin, Endosulfan and Lindane Pesticides during Rotary Drum (RD) and Windrow (W) composting techniques, *J. of Environmental Science and Technology,* **2012**, (Under Review).

viii) Muntjeer Ali, A. A. Kazmi, Naseem Ahmed, Study on Effects of Temperature, Moisture and pH in degradation and degradation kinetics of Aldrin, Endosulfan, Lindane pesticides during full-scale continuous rotary drum composting, *Chemoshere,* **2012**, (Under Review).

ix) Muntjeer Ali, A. A. Kazmi, Naseem Ahmed, Effect of seasonal variations on degradation of organochlorine pesticides during full-scale continuous rotary drum composting. (Under preparation)

- ***International/ National Conferences Proceedings***

i) Muntjeer Ali, K. Simon Duba, Ajay S. Kalamdhad Akansha Bhatia, Anwar KhursheedA. A. Kazmi, Naseem Ahmed, High Rate Composting of Herbal Pharmaceutical Industry Solid Waste 8th Symposium on Waste Management Problems in Agro-Industries (Agro'2011), Ilıca (Çeşme-İzmir). Turkey, 21-24 June 2011.

ii) Muntjeer Ali, Akansha Bhatia, Ajay S. Kalamdhad , Sangeeta madam, Naseem Ahmed and A. A. Kazmi, Microbes in water and waste water IWA 22-26 March 2011, Goa, India.

iii) Muntjeer Ali, Akansha Bhatia, Ajay S. Kalamdhad, Sangeeta madam, Naseem Ahmed and A. A. Kazmi. Fate of Organochlorine pesticides and its associated microbial community in Rotary drum and Windrow composting 5TH UTTARAKHAND STATE SCIENCE AND TECHNOLOGY CONGRESS (10-12, NOVEMBER, 2010).