Organochlorine waste management

Roger Papp

*Chairman of the Scientific and Technical Committee of CNEEIC (College National d'Experts
Environnement de l'Industrie Chimique France)
Professor of Chemical Engineering – Ecole Centrale de Paris*

Abstract: Sound environmental management includes the proper management of waste. This chapter reviews the basic rules of good management practice illustrated by some examples from chlorine derivatives production and gives the main considerations governing the Best Available Techniques for organochlorine waste thermal treatment. A review of the main degradation pathways of organochlorines—dispersal, distribution, degradation pathways, and environmental half-lives—demonstrates a very large range of characteristics, justifying the need for a separate study for each substance. Finally, the paper examines the latest developments in organochlorine contaminated site remediation technology.

1 – INTRODUCTION: THE THREE RULES OF GOOD WASTE MANAGEMENT

As a general rule the first step of waste management is the reduction of the waste and by-products created

As an example, the manufacture of chloromethanes initially used the thermal chlorination of methane. This process obviously created, due to the use of methane as raw material, a large amount of hydrochloric acid by-product.

To reduce the HCl by product formation, a second generation of processes produces methyl chloride using methanol and HCl as raw materials. In a second step, methyl chloride is chlorinated into methylene chloride and chloroform.

Furthermore, the thermal chlorination, which selectivity is poor, has been replaced by photochlorination or radical-assisted chlorination, permitting an overall raw material efficiency above 99.5%, and reducing the organics waste formation in a ratio of 10:1.

The second rule of waste management is the valorisation of the by-products

In the previous example, the use of methanol and hydrochloric acid in the first step, permits the recycling of part of the by-product HCl of the second step. Depending on the average degree of chlorination of the finished products, a nearly balanced process can be realized.

But most of the producers of chloromethanes are also producers of vinyl chloride-monomer. This important process implies a step of oxychlorination of ethylene to produce ethylene dichloride, using ethylene, air or oxygen, and HCl as raw materials.

It is therefore possible to recycle all HCl by-product—including that from chloromethanes production—in this process, provided the production units are on the same site and the suitable purity is obtained.

The vinyl chloride monomer process is another good example of waste management.

Historically, the old process starting from acetylene and HCl was very selective, having more than 99% efficiency on raw materials. This was due to the high reactivity of the triple bond of acetylene. Unfortunately acetylene production was less efficient and acetylene was replaced in the years 1960s, by ethylene.

Vinyl chloride manufacture uses 3 main reactions:
- a direct chlorination of ethylene to produce EDC ethylene dichloride. This reaction is highly selective;
- a pyrolysis of EDC to produce vinyl chloride and HCl. This step is selective provided there is a limitation of the transformation of EDC to less than 50–60%, as well as limitations of pressure and temperature;

- the third reaction is the oxychlorination of ethylene, using oxygen (from air or pure oxygen) and HCl as reactants. This reaction is conducted in fluidised or fixed beds, and represents the main source of organochlorine waste from the process, although the process has been continuously improved.

About 3% of the vinyl chloride production results in waste or by-products.

To valorize these waste, the producers are using different processes:

- an oxidation process using the waste as raw material, allows the recovery of at least the chlorine content as HCl, which is recycled;
- the TRI PER process, using the light fraction (50–60%) of the waste as raw material, transforms the waste into trichloroethylene and perchloroethylene for sale as marketable products, or raw materials.
- the Tetra-Per process, also using the light fraction of the waste as raw material, transforms the waste into perchloroethylene and carbon tetrachloride.

Since the Montreal Protocol for the protection of the Ozone Stratospheric layer, no longer allows CFC 11 and 12 production, (the main use of carbon tetrachloride), and since carbon tetrachloride itself is regulated by the Montreal Protocol, the uses of this product are now very limited.

The Tetra-Per process therefore has been modified to focus the production on perchloroethylene. In summary 50–60% of the vinyl chloride manufacture waste is recycled in marketable products.

The residual fraction, containing the most heavy parts, is thermally decomposed with recovery of hydrochloric acid, either recycled in the process itself, or as HCl commercial solution.

This treatment will be described later in this paper.

The third rule of waste management, after maximum reduction and recycling, is to dispose of the waste safely

The vinyl chloride process will be taken as an example for application in the next section.

2—WASTE MANAGEMENT IN THE MANUFACTURE OF VINYL CHLORIDE

The European Producers of VCM and PVC under the auspices of the European Council of Vinyl Manufacturers (ECVM) have conducted a two-year study on how to minimize the environmental impact of the manufacture of PVC and to define Best Available Techniques.

The study was issued in August 1994 [1].

All sources of impact were analysed: water, air, soil, waste.

With regard to the solid waste, the main sources are the heavy fractions from the 3 reactions mentioned in section 2 and specially the oxychlorination step.

The total amount is ≈ 0.03 ton per ton of VCM produced.

In some plants, the waste is subject to oxidation and transformed into CO_2, H_2O and HCl which is recycled in the process.

As already mentioned in section 2, other producers are using different techniques to recycle a large fraction of this waste. About 50–60% of the waste is transformed into marketable products or raw materials, such as trichloroethylene and perchloroethylene.

The fractions and residues not directly reusable are submitted to combustion under controlled conditions into water, carbon dioxide and hydrochloric acid. In this situation hydrochloric acid can be recovered from the off-gas and can be either recycled as feed stock to the oxychlorination plant for the production of more ethylene dichloride, or recovered as hydrochloric acid solution. A description of this process is given in section 3.

Spent catalyst, metal sludges and coke from EDC cracking is another source of waste obviously, in a quantity much lower than the previous one, e.g. a few tons per year. However, this waste requires attention because traces of furane compounds, mainly hepta and octochlorodibenzofuranes, are formed in the oxychlorination reactor, using a copper catalyst. These compounds are fixed on the catalyst.

As a result, the oxychlorination process water effluent, which contains the fine catalyst losses, is subject to adequate treatment.

Dissolved copper can be removed by precipitation and filtration together with the non dissolved particles.

When present in the aqueous effluent, the furane compounds are all adsorbed in the suspended solid particles which are present. This is the result of the very high value of the Koc coefficient of such compounds (i.e. the partition coefficient between water and organic carbon).

Therefore they can be removed from the effluent with traditional technology such as flocculation, settling, and filtration, with the addition of adsorbent material when necessary.

A third source of waste can be the biosludges from a classical aerobic biological purification of the waste water treatment plant.

With biological treatment, and depending upon the efficiency of the upstream physico-chemical treatments of the process water, some additional removal of the furane compounds may take place by adsorption. If contaminated, this sludge must be disposed of properly.

In summary, by a combination of appropriate and multiple technologies adapted to each individual situation, the impact of both atmospheric and water emission and waste disposal are reduced beyond the most stringent requirements of health-based and environmentally based regulating prescriptions and quality objectives. This is the main purpose of sound environmental management.

3—THERMAL TREATMENT OF ORGANOCHLORINE WASTE

The treatment, or destruction, of organochlorine waste by incineration has been the subject of a large number of studies.

Today, there is large agreement on the best available technique for such treatment.

The main considerations can be summarized as follows:
- The organochlorine waste contains sometimes more than 50% chlorine by weight. Therefore, the thermal treatment of such waste produces a large quantity of hydrochloric acid. It is advisable to recover it at a concentration permitting a chemical use.

  However, the HCl is diluted by the treatment off gases.
- The destruction must be complete and the chlorinated fractions transformed in the process into HCl, carbon dioxide and water.
- The exhaust gases must contain low levels of hydrochloric acid, chlorine and dioxin equivalents (ITEQ).

The European Union Directive requests for the last specification less than 0.1 nanograms per cubic meter.

In order to achieve the first condition, two methods are used:
- The HCl absorption can be made at a temperature low enough to permit an acceptable concentration of HCl solution, this is generally obtained in several steps.
- The absorption is conducted by a 20% azeotropic solution in an absorption stripping loop.

Temperature turbulence, residence time and oxygen concentration are the keys to a complete destruction and the final dioxin level concentration of the off gases. Typical temperatures of 1100 °C are used in combination with a residence time greater than 2 s.

However, good turbulence in the reactive zone or a higher temperature are compatible with lower residence times.

Specific burners have been developed to limit—or even suppress—the need for additional fuel even for low caloric waste, e.g. 2000–2500 kcal/kg.
- Specific steam boilers are also available to recover the heat of combustion after the reactive zone.
- In order to avoid any further chemical transformation in the off gases after the reactive zone and the eventual heat recovery boiler, a quench column is to provided quickly cool the off gas to an acceptable level of temperature, necessary for the absorption of the hydrochloric acid.

The environmental performance of these units is good and is already controlled under the regulations of most countries.* The United Nations Environmental Programme has also issued a specification for such units.

In summary all organochlorine waste can be treated and transformed into hydrochloric acid and off gas,

---

* TA Luft (1990), 17 BIMSCHG (Germany)—Arrêté du 1er Mars 1993 (France), etc.

that is not harmful for the environment. In particular the dioxin level ITEQ of the off gas is below the regulatory level of 0.1 nanograms per cubic meter.

The above description relates to incineration units which are devoted to the treatment of organochlorine wastes.

Some comments should be made on the impact of chlorine containing waste in modern municipal waste incineration units.

The awareness of dioxins in the environment is relatively recent. After the Seveso accident, is was not until the 1980s that it was recognized that the formation of dioxins results from many other activities and even natural events like forest fires.

Combustion of fuels, with or without chlorinated additives in engines and many other materials, like combustion of wood, coal, metallurgical processes, etc... have been shown to be major contributors of dioxin compounds into the environment (see Chapter D.5).

Municipal waste incinerators, if not properly designed and operated, may also be significant sources of dioxins.

At first, PVC was considered responsible for the formation of dioxins in municipal waste incineration, where the chlorine content of the feed stream can be as high as 1%. However, more than ten subsequent studies have demonstrated that the same amount of dioxin is emitted from incinerators burning municipal waste, with or without PVC [2].

A last study made by the American Society of Mechanical Engineers, based on results from 155 incinerators, has found no correlation between dioxin formation and the PVC content in the incinerators feed stream.

With respect to accidental PVC fires, several studies have been made to assess the dioxin compounds emissions.

As an example, an uncontrolled burning of 200 tons of PVC and 500 tons of PVC backed carpets in a wooden warehouse in Sweden gave 3 mg of dioxin in soot. If the production of dioxin from the wooden structure is not taken into consideration, this corresponds to 6.67 microgramme per ton of PVC.[†]

In comparison the uncontrolled burning of clean wood will give concentrations at nearly the same level. Wood contains 70–2100 p.p.m. of chloride. Dioxins will be formed in all processes where chlorine in some form is present, even in minor amounts.

4 — ORGANOHALOGEN COMPOUNDS — DEGRADATION PATHWAYS

Persistent and bioaccumulating chemicals such as PCBs, DDT, hexachlorobenzene, dioxin and dieldrin are often cited as examples implying that all chlorinated products have adverse effects. It is often suggested that the well established adverse ecotoxicological effects of these few compounds, which are now subject to strict regulatory controls, are also shown by all other chlorinated compounds. This is not scientifically justified and there is no reason to treat halogenated organic compounds any differently from other chemicals. Each substance must be evaluated separately on the basis of its individual properties.

There are different pathways to consider for degradation.

Many halogenated organic compounds with low molecular weight, have high vapour pressure, high Henry's Constants, and relatively low solubility in water. A MacKay partition model applied to the compartments of the environment may indicate that the major part of the emissions will reach the atmosphere.

Evaporation from water and subsequent atmospheric lifetime are important factors for such compounds. Biodegradation and metabolic degradation, hydrolysis and photolysis are other pathways to consider.

Table 1 gives an indication of the rate of evaporation from water of a number of halogenated organic compounds. The actual values of these rates in the natural environment depend on a number of parameters such as the depth of the water, its flowrate and the airspeed above it, the temperature of the water and the air, and the possibility of stratification caused by the salinity/density of seawater, freshwater or effluents.

Halogenated organic compounds may adsorb onto sedimentary solids or absorb into any organic phase present on these solids, and this may somewhat reduce their availability to evaporate into the atmosphere.

When an halogenated organic compound evaporates into the air, it is necessary to consider its potential effect in the troposphere and possibly in the stratosphere (rate of destruction by OH radical, atmospheric

---

† Source: Prof. Rappe.

Table 1 Evaporation from water (half-life time) [3,4]

Dibromomethane	18 min to 48 h
1.1.2-Trichloroethane	21 min
1.2-Dichloroethane	30 min to 4 h
1.2-Dichloroethylene	3 h
Trichloroethylene	Several minutes to several hours
Tetrachloroethylene	27 min to several hours
1.2.4-Trichlorobenzene	4.2 h
1.2-Dichlorobenzene	4.4 h
1.1-Dichloroethane	6.4 h
1.2-Dichloropropane	9 h
Monochlorobenzene	12 h
Hexachloroethane	15 h
Chloroform	36 h
1.1.2.2 Tetrachloroethane	3.5 days
1-Chloro-2-nitrobenzene	33.5 days
2-Chlorophenol	73 days

lifetime, possibility of migration to the stratosphere and consequent ozone involvement, global warming/greenhouse effect and possible formation of photo-oxidants). Compounds that evaporate do not normally bioaccumulate in the aquatic environment or accumulate on sediment solids unless their bioaccumulation factor is high and/or they are strongly adsorbed onto sediment solids (e.g. hexachlorobenzene). These effects are dealt with below.

The low molecular weight chlorinated hydrocarbons such as the chlorinated methanes (except tetrachloromethane), chlorinated ethanes (except hexachloroethane) and chlorinated ethylenes, some of which are widely used as industrial solvents, are degraded in the troposphere (lower atmosphere). This degradation occurs by oxidation through reaction with hydroxyl radicals and other naturally occurring oxidising agents, and forms carbon dioxide, water and inorganic chloride. There are significant differences in the decomposition rates (see Table 2).

Many studies have investigated the anthropogenic chlorinated and brominated organic compounds likely to be emitted into the atmosphere at the present time. These investigations conclude that the effects of the man-made substances are negligible with the exception of carbon tetrachloride, methyl bromide and 1.1.1-Trichloroethane.

The very long half-life of carbon tetrachloride makes it possible for this substance to contribute to the depletion of stratospheric ozone and has led to the strict control of this substance by the Montreal Protocol and its revisions in 1987, 1990 and 1992, similar to the chlorofluorocarbons (CFCs).

The Ozone Depletion Potential attributed to carbon tetrachloride is 1.018 compared to 0.7 for methyl bromide. Another halogenated organic compound, 1.1.1-Trichloroethane, has an Ozone Depletion Potential of 0.12 and is also controlled by the Montreal Protocol and its revisions.

Methylene chloride, perchloroethylene and trichloroethylene have no effect on the ozone layer in the stratosphere.

Ozone formation in the troposphere by chlorinated substances is marginal compared to other substances and can be ignored.

Biodegradation and metabolic degradation

Bacteria present in water are able to degrade organic substances by incorporating them into their metabolism. Like other organic substances, halogenated organic compounds undergo biodegradation. For many of them, however, the time required for this process can be long. The following products are known to be biodegradable,according to the criteria specified by the European Union for chemical substances classification:

Readily biodegradable
- 2-Chlorophenol;
- Benzyl chloride;
- 3-Chlorophenol;
- 4-Chlorophenol;
- 2.4.6-Trichlorophenol.

Table 2 Tropospheric degradation of some halogenated organic compounds

Compounds	Half-life (weeks)*
Vinyl chloride	≈ 0.3
1.2—Dichloroethane	≈ 4.0
Methyl chloride	≈ 50.0
Dichloromethane	≈ 15.0
Chloroform	≈ 23.0
Perchloroethylene	≈ 8.0
Trichloroethylene	≈ 1.0
1.1.1-Trichloroethane	≈ 296.4
Carbon tetrachloride	> 2000

* The half-life is the time necessary for 50% of the substance to degrade.

Inherently biodegradable (easily biodegradable by suitable organisms)

- 2.4-Dichlorophenol;
- 3.3-Dichlorobenzidine;
- Dichloromethane.

Biodegradable (biodegradable under specific conditions)

- 1.3-Dichloropropane;
- 1.2-Dichloropropane;
- Propanil;
- 1.1.2-Trichloroethane;
- 1.1.1-Trichloroethane;
- Trichloroethylene;
- Perchloroethylene;
- 4-Chloro-3-methylphenol;
- 1.2-Dichlorobenzene;
- 1.3-Dichlorobenzene;
- 1.4-Dichlorobenzene;
- Trichlorobenzenes;
- Hexachlorobutadiene.

Table 3 Degradation by UV light (see original reference for conditions) [9]

Compound	% Decomposition
Chlorinated organic compounds	
2.4.6-Trichlorophenol	65.8
Pentachlorophenol	50.0
Trichloroethylene	36.8
Chlorobenzene	18.5
DDT	5.4
1.4-Dichlorobenzene	5.1
Hexachlorobenzene	1.5
Carbon tetrachloride	1.0

Products such as DDT, PCBs and hexachlorobenzene (HCB) are at the other end of the scale. DDT shows 0% degradation in 7 days incubation followed by 3 weekly sub-cultures. In soils, some degradation ranging from 1.7–4.9% after one year is observed.

PCBs are biodegradable only when the degree of chlorination is less than 4 chlorine atoms. For higher levels of chlorination associated with very low solubility in water, the product is mainly associated with the organic components of soils and sediments and tends to accumulate in these media, thus having the capacity to bioaccumulate in aquatic organisms.

HCB shows 0% degradation in 7 days incubation followed by 3 weekly subcultures, but undergoes slow evaporation.

Many bacteria also dehalogenate halogenated organic compounds via special enzymes known as 'dehalogenases'. Here again some halogenated organic compounds are more easily degraded than others, depending on their structure. Microbiological systems have been applied successfully for many in-situ remediations where soil contamination has occurred [5].

For example, chloroform is degraded in the environment by natural microorganism populations [6]. Some halogenated organic compounds, for example, 2.4-dichlorophenoxyacetic acid (2.4-D), a chlorinated herbicide, are not persistent under most soil conditions because they are readily metabolized in plants, and by bacteria and fungi in soil and the aquatic environments, which use them as a food source. The persistence of 2.4-D is measured in days to weeks [Stevens & Summur 1991, MacEwen 1979].

Cometabolism and methanotrophic processes are presently beeing demonstrated to be successful for *in situ* remediation (see Section 5).

Hydrolysis

Another degradation pathway by which chlorinated organic compounds are removed from the environment and made less toxic is hydrolysis, the direct reaction of the substance with water. This type of reaction occurs with numerous halogenated compounds such as the chloro- and bromo-alkanes. The chloropropenes and epichlorhydrin, for example, are rendered non-persistent and non-accumulating by hydrolysis [7].

Photolysis

Many chemicals can be degraded by daylight in the upper part of the aquatic environment [8]. The rate of decomposition is highly dependent on the molecular structure of the individual compounds (see Table 3). Phenols are readily degraded while other compounds without functional groups are more stable. Halogenated organic compounds and non-halogenated organic compounds have decomposition rates in the same range.

Photomineralization, i.e. conversion into inorganic halide (chloride, bromide, etc.) is also a route by which 'dioxins' (PCDDs/PCDFs) can be degraded.

The above examples show that the environmental behaviour of chlorinated organic compounds differs greatly from one substance to another and that a large number of pathways exist for degradation in the environment.

There is no justification for treating all halogenated organic compounds in the same way. The dispersal, distribution, degradation pathways and environmental lifetime must be studied separately for each chemical.

5 — SOIL REMEDIATION

The large spectrum of physical, chemical, biological properties of organohalogens makes impossible a general assessment on the possible ways of soil remediation.

In the following section, we can only give some common examples, for chlorinated solvents and similar compounds.

The chlorinated organic compounds with low molecular weight, high vapour pressure, high Henry's constant, constitute a class of substances having large possibilities for soil remediation techniques.

Washing

With adequately designed wells, for water injection and water extraction from a contaminated zone, it is possible to remove the contamination by soil washing. The low solubilities of the substances imply a reasonable ground permeation permitting a significant and well dispersed flow of water. To remove the substance from the water, four techniques are available: air stripping followed by an activated carbon treatment of air, steam stripping of the water with heat recovery, activated carbon treatment of the water or chemical treatment of the water.

This process is very long. It may be useful however, to prevent any expansion of the contaminated zone, or an eventual ground water contamination out of the zone.

Air sparging — venting

Venting is a remediation technology applied to the removal of volatile organic compounds.

The concept of air sparging is simple: air is injected into the aquifer beneath the water table to induce mass transfer of contaminants to the vapour phase. This is usually performed in conjunction with soil vapour extraction to control the migration of sparged contaminants in the vadose zone.

This technology is generally applied in sandy soils and is not applicable with silts or clays, which require over pressures too high to achieve flow.

The same concept can be applied above the water table, or after lowering the water level if necessary. This technique (venting) is possible for substances having a high volatility such as chlorinated solvents.

Obviously, in all cases, the extracted air is subject to adequate treatment for contaminant removal.

Chemical techniques are also in development for in situ *remediation (destruction of the contaminant by a nontoxic reactant)*

Biological techniques

All chlorinated solvents could be biodegradable in specific conditions, more or less easy to realize.

In situ bioremediation exhibits serious advantages compared to the previous techniques based on mass transport and subject to pumps and outside treatment systems. The advantage of a contaminant being destroyed in place rather than extracted is obvious.

Most research studies on bioremediation of chlorinated solvents have focused on using *aerobic microbial metabolism* to achieve the contaminant transformation [10] with the exception of perchloroethylene which is transformed only by anaerobic processes.

A promising technique is to use cometabolism with another substance, using micro-organisms acclimated

for that substance for example toluene.

Several studies demonstrated that aerobic biodegradation of trichloroethylene is possible together with an aromatic compound, e.g. toluene, by using toluene-acclimated micro-organisms. Good results are obtained in several days [11].

However, the use of another contaminant even in small concentration, requires careful system control in the contaminated zone.

Bioremediation of chlorinated benzenes is also possible by aerobic microbial metabolism by using biostimulation (aeration and nutrient supplementation) or controlled composting [12].

In all cases where an aerobic system is used, care must be taken to avoid contaminant losses due to volatilization.

A large number of studies are in progress to develop *in situ* bioremediation of chlorinated solvents by *anaerobic processes*.

All chloroethenes can be degraded under anaerobic conditions [13,14]. Anaerobic transformation is obtained by sequential replacement of the chlorine atom by hydrogen. In this process perchloroethylene should be transformed sequentially into trichloroethylene, dichloroethylene and vinyl chloride and finally ethylene or ethane or carbon dioxide, and HCl.

However, the sequence is more or less complete and especially the last sequence requires much more time than the first ones. The addition of an electron donor which is fermented into hydrogen may be useful. Methanol has been proposed for this purpose [15].

In conclusion, it can be seen that there are promising ways to achieve remediation by biological techniques. When a substance natural biodegradation rate is too slow, when the proper microbial population is not present, or when the environmental conditions are not suitable, the best strategy is to change these conditions for a successful result [16].

The most cost-effective techniques are still to be developed into routine techniques. Such development needs studies, pilot plants, and research and, as a result, time must be given for their implementation.

REFERENCES

1   On the environmental impact of the manufacture of polyvinyl chloride. *A description of Best available techniques* (ECVM paper—August 1994).

2   E.W.B. de Leeren *et al.* TNO Report August (1990). *Environmental aspects of wastes incineration.*

3   *Environmental properties of organochlorines.* Report. Elf Atochem Solvay.

4   P.H. Howard. *Handbook of Environmental Fate and Exposure data of Organic chemicals.* Lewis Publishers (1991).

5   C. Tahon *et al. Synergetic behaviour of micro-organisms able to degrade halogenated organic substances.* EEC 6th European Symposium, Lisbon (1990). Kluer publisher.

6   Tabak *et al.* Biodegradability studies with organic priority pollutant compounds. *J. Water Poll. Control. Fed.* **53** (1981) no. 10.

7   K.R. Krijgsheld. ESF Report. *Assessment of the impact of certain organic compounds chlorophenols, chloropropenes and epichlorhydrin.* University of Leiden Netherlands (1984).

8   Lemaire *et al. Chemosphere* **14** (1985). D.F. Ollis. *Env. Sci. Technology* **19** (1985).

9   D. Frietag *et al. Chemosphere* **14** (1985). W. Klein *et al. Chemosphere* **13** (1984).

10   Mac Carty *et al.* (1994). *Ground water treatment for chlorinated solvents in Handbook of Bioremediation* Lewis Publisher, Ann Arbor, Michigan.

11   Chih-Jen. Lu *et al. Aerobic Biodegradation of Trichlorethylene by micro-organisms that degrade aromatic compounds in Bioremediation of chlorinated solvents.* Robert Hinchee, Lewis Semprini (Battelle Press (1995), Colombus).

12   Shields *et al.* (1994) In Hinchee *et al.* 'Bioremediation of chlorinated and polycyclic Aromatic hydrocarbon Compounds. Lewis Publisher'.

13   Vogel et Mac Carty. *Biotransformation of tetrachloroethylene under methanogenic conditions. Appl. Environ. Microbiology* 49 (5) (1985).

14   Barrio-Lage *et al.* (1986). Sequential dehalogenation of chlorinated ethenes. *Env. Sci. Tech.* (20) (1).

15   Bouwer (1994). Bioremediation of chlorinated solvents using alternate. electron acceptor. In Norris *et al. Handbook of bioremediation* Lewis Publishers.

16   Mac Carty (1991). Engineering concepts for in situ bioremediation. *Journal of Hazardous Materials* **29** (1991), 1–11.