

**Risk assessment of contaminated sites:
science, public policy and social justice?**

Mr. Colin Ferguson
United Kingdom

RISK ASSESSMENT OF CONTAMINATED SITES: SCIENCE, PUBLIC POLICY AND SOCIAL JUSTICE?

*Presented by: Mr. Colin Ferguson
The Nottingham Trent University, United Kingdom*

INTRODUCTION

The US National Academy of Science report on risk assessment (National Research Council 1983) is often taken as a landmark document setting out clear definitions of risk assessment and risk management and their relationship. The NAS Committee recommended *risk assessment* to mean

the characterization of the potential adverse health effects of human exposure to environmental hazards. Risk assessments include several elements: description of the potential adverse health effects based on an evaluation of results of epidemiologic, clinical, toxicologic, and environmental research; extrapolation from those results to predict the type and estimate the extent of health effects in humans under given conditions of exposure; judgment as to the number and characteristics of persons exposed at various intensities and durations; and summary judgments on the existence and overall magnitude of the public-health problem. Risk assessment also includes characterization of the uncertainties inherent in the process of inferring risk.

The Committee used the term *risk management*

to describe the process of evaluating alternative regulatory actions and selecting among them. Risk management, which is carried out by regulatory agencies under various legislative mandates, is an agency decision-making process that entails consideration of political, social, economic, and engineering information with risk-related information to develop, analyze, and compare regulatory options and to select the appropriate regulatory response to a potential chronic health hazard. The selection process necessarily requires the use of value judgments on such issues as the acceptability of risk and the reasonableness of the costs of control.

The NAS Committee emphasized that risk assessment and risk management were to be separate activities. Indeed, one of its declared goals was to encourage scientists and policy makers to separate clearly the two processes. A recent conference to mark the 10th anniversary of the NAS Report has largely confirmed the paradigm established in 1983 (Barton et al 1994).

One purpose of this paper is to question whether it is really possible to separate risk assessment and risk management in the way set out in the paradigm. The other, and more central objective, is to explore the scope for integrating the various risk assessment practises into a coherent system that can be used internationally.

This is particularly important where risk assessments are partly based on standards or guidelines for contaminants in soil or groundwater. It is worth noting that this approach is now employed even in the U.S. Superfund programme. A study conducted by the USEPA in 1991 found that the risk assessment and remedy selection for National Priorities List sites typically took more than three years to complete. Subsequently the EPA has developed soil trigger levels (now known as

Soil Screening Levels or SSLs) for thirty chemicals in order to accelerate decision making for contaminated soils (USEPA 1994).

A REALISTIC BASIS FOR SETTING SOIL GUIDELINES & STANDARDS

Risk analysis is sometimes seen simply as a scientific exercise to determine what the risks "really are". The reality is more complex. The use of risk analysis to place limits on contaminant concentrations in food, water, air or soil cannot be divorced from social and economic considerations. Nor are the facts and the scientific methodologies that underpin standards and guidelines wholly divorced from these wider considerations. Jasanoff (1993) observed that "the principles by which we organise the "facts" of risk have to derive, at least in part, from underlying concerns of public policy and social justice: whom should we protect, against what harms, at what cost, and by foregoing what other opportunities?"

A key step in risk analysis is comparing estimated human intakes of soil contaminants with "safe" levels determined by toxicologists. It is an established principle of toxicology that, for many substances, there is a dose threshold below which no adverse effects are observed. Genotoxic carcinogens, however, are not believed to have such a threshold. In theory, then, it is easier to decide on a safe dose for threshold substances, ie determine the maximum dose at which no adverse effects occur - than for genotoxic carcinogens. But the information about dose-thresholds is not derived from controlled toxicity experiments on *human* subjects. Also, the effect of a dose depends on a number of factors, including absorption, distribution, biotransformation, retention or accumulation, and elimination. These considerations suggest that the adverse effect threshold for a toxic substance will depend on characteristics of the individual organism. Each member of a population in effect has its own threshold.

In practice these complexities are overcome by the convention of determining a *no observed adverse effect level* (NOAEL) from animal experiments, and then deriving a human *acceptable daily intake* (ADI) by dividing the animal NOAEL by a safety factor.

The factor used traditionally dates back to the 1950s when scientists from the U.S. Food and Drug Administration reviewed the literature on relative sensitivities of humans and test animals to chemicals used as food additives. Their conclusion at that time, that a safety factor of 100 was adequately protective, is still widely used not only for food additives but also now for other environmental media.

So the traditional method of determining a human ADI is a **convention**, as it is not solely the result of detailed scientific investigation. Therefore there is no exactness about an ADI, or about any soil guideline derived from it. It is therefore more appropriate to consider a soil guideline as a point within a broad zone of safety, rather than as a sharp dividing line between 'safe' and 'unsafe'.

There is a special difficulty with genotoxic carcinogens because the result of animal tests (cancer bioassays) is usually an increase in the incidence of tumours in the dose group relative to the control group. But the excess lifetime risk of cancer that can be detected and judged to be statistically significant depends on the number of animals used. In fact it is difficult to detect excess lifetime cancer risks less than 5 - 10%. But for almost all carcinogens in the environment, human exposures (and the resulting doses) are orders of magnitude smaller than those used in animal studies. Thus estimating excess cancer risks from such low levels of exposure involves not only applying animal test results to humans but also extrapolating to cancer risks thousands of times smaller than those for which dose-response data are available.

Numerous mathematical models for low-dose extrapolation have been proposed, but most fall into three general types as shown in Figure 1. A particular human dose from environmental exposure (say dose B, Figure 1) might be associated with no excess risk of cancer (threshold model) or with excess risks which differ by an order of magnitude depending on whether the linear or sublinear model is used. Accepted levels for contaminants in the environment are often determined using the reverse procedure. A level of excess lifetime cancer risk (say 10^{-4} , Figure 1) is set and then the maximum dose that would not exceed that risk is estimated. This procedure can be misunderstood and lead to the excess risk criterion (say, 10^{-4}) being treated as a *quantitative* statement about risk. This is not the case. The authors of pioneering work on extrapolating cancer bioassay data to low doses (Mantel & Bryan 1961) did not suppose that their procedure could be used to predict the actual risk associated with a given low dose. Rather, they saw it as a method for identifying the dose that would be unlikely to create a risk greater than some operationally-defined 'safe' level. From the outset quantitative risk assessment (QRA) for genotoxic carcinogens has been a **convention**, to express the concept of 'virtually safe'.

There is a reluctance in some countries to place too much emphasis on derivation of guidelines from laboratory studies of rats and mice because of the difficulty in extrapolation from high-dose results in animal tests to effects in people at very much lower doses. In the UK, for example, there is a preference for putting greater weight on studies of human populations, especially those exposed to chemicals in the workplace (e.g. Department of the Environment 1994). This approach also presents difficulties. Industrial workers may be exposed to higher concentrations of chemicals than the population at large, but usually do not include the more sensitive members of the population (children, the elderly, the sick, pregnant women).

Extrapolation from relatively high doses in healthy young and middle aged male workers to lower doses in the general population is rarely straightforward because of uncertainties over actual exposure levels, simultaneous exposure to other chemicals, differences in sensitivity, and different total exposures times. To overcome these difficulties safety factors are introduced, which again are no more than conventions chosen to provide reasonable confidence that certain very low levels of exposure are 'virtually safe'.

As well as toxicological safety factors, another type of safety convention is implicit in many risk assessments - that is the use of conservative assumptions in *exposure* assessments. Further conventions are involved in the selection of sampling regimes and analytical techniques to determine the actual concentration of contaminants on a particular site. Sampling regimes carry their own underlying statistical assumptions about the representativeness of a sample. Analytical techniques are also rarely absolute, and may not truly reflect the particular 'hazard' represented by the contaminant for which guidelines are being set.

SETTING SOIL CONTAMINANT GUIDELINES - A RISK MANAGEMENT PHILOSOPHY

It can be argued that the framework of guidance or regulation in which risk management decisions are taken, needs to balance the need to safeguard human health and the environment and the need to foster activities which will ultimately fund remedial works. The cost of risk reduction can be highly non-linear. If soil guidelines are set at levels which are prohibitively costly to achieve, redevelopment of many old industrial sites will not go ahead. The costs of untackled dereliction might include loss of new job opportunities or new amenities, and reduced local property values and quality of life. Failure to redevelop sites increases the pressures for greenfield sites to be converted to industrial or commercial use.

However, the risks to the public from contaminated land are involuntary and often not known or understood completely. Consequently the level of concern is typically much greater than might be expected from objective analysis of the risks. There is nothing irrational about this. Everyone expects a much higher level of protection against involuntary risks compared with risks from activities willingly entered into and bringing clearly identifiable benefits. The goal of risk management, then, is to select options that balance the costs of an action against protection from the real *and perceived* risks.

Soil guidelines should not be thought of as marking a sharp boundary between 'safe' and 'unsafe' concentrations in soil. It is more appropriate to think in terms of gradational zones from 'very safe' to 'not safe' with a diffuse boundary zone between them (Fig 2). Scientific risk analysis can aim to relate these zones to contaminant concentrations in soil. Choosing a *particular* value to act as a guideline is not, however, an entirely scientific decision. It is a risk management decision in which benefits and costs are also balanced.

THE HCH FORUM PROJECT PROPOSAL

In the EU there is no generally accepted method for assessing the risk from soils contaminated by chlorinated pesticides. Therefore it is virtually impossible to implement an economically sound strategy for the distribution of remediation funds. Methods and techniques for risk assessment of soils are often very expensive.

In order to make a Community-wide contribution to solving the risk assessment problem this project has two major objectives:

- to achieve a uniform, practical and transparent method for risk assessment of pesticides on contaminated sites using HCH as a demonstration pesticide. The method will be considered as a prototype for European use;
- to develop a modular decision support system that can be integrated with existing soil information systems to support the new evaluation method.

The products of this research can be expected to meet the following criteria:

- as far as possible the proposed method and support system should be applicable in all organisations responsible for the distribution and use of remediation funds; this is considered to be of the utmost importance and will be elaborated on in an initial definition study;
- the products will reflect the combined experience of several internationally leading groups which, in turn, will facilitate the spread of these advanced environmental decision support tools throughout the EU;
- it will be possible to adapt the system to the specific requirements of individual countries;
- the products will have been tested extensively by the partners in order to insure their utility and robustness.

The innovative aspects of the proposal can be summarised as follows:

- The unification of current investigation and risk assessment methodologies and computer techniques of the partners will lead to a more advanced and general tool for balanced assessment of waste sites and industrial land that is contaminated with pesticides.
- Due to the number of suspect locations and their likely complexity, the use of formal decision-support systems is essential in the long term if fair, consistent and practical support is to be provided to the authorities.

The partners plan to combine and to improve their current knowledge in this field and to address the problems involved in integrating computer-based support systems into complex environmental decision making.

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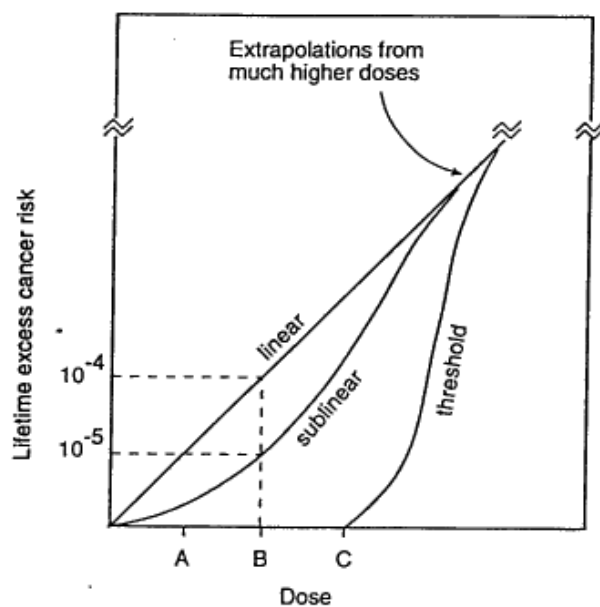


Figure 1. Hypothetical dose – response curves for chemically induced cancer at low doses.



Figure 2. Schematic illustration of 'safe' and 'unsafe' zones separated by a diffuse boundary zone.

**Biotransformation of β -HCH to monochlorobenzene
under methanogenic culture conditions**

Mr. Peter Middeldorp
The Netherlands

Biotransformation of β -hexachlorocyclohexane to monochlorobenzene under methanogenic culture conditions

PETER J.M. MIDDELDORP¹, MARCO JASPERS¹, THIJS KAPER¹, GOSSE SCHRAA¹,
AND ALEXANDER J.B. ZEHNDER²

Department of Microbiology, Wageningen Agricultural University, H. van Suchtelenweg 4, NL-6703 CT Wageningen, The Netherlands,¹ and EAWAG/ETH, CH-8600 Dübendorf, Switzerland²

Hexachlorocyclohexane (HCH) has been widely used as an insecticide for crop protection for over two decades. During production of the most active isomer γ -HCH (lindane) large quantities of by-products, like α -, β -, and δ -HCH were discarded at open air dump sites. This resulted in heavily contaminated soils, for instance in The Netherlands and Spain. Numerous laboratory and field studies on the biodegradation of HCH show that the α -, γ -, and δ -isomers are readily degraded under aerobic conditions. However, aerobic β -HCH degrading microorganisms do not prevail at effective levels, if at all, in contaminated soil. Therefore, during aerobic biological clean-up, this isomer will persist and leach to the aquifer.

In sediment column studies, we have achieved a quantitative dechlorination of β -HCH under methanogenic conditions with lactate as electron donor (see fig. 1).

Monochlorobenzene was detected as the end product in the column effluent by gas chromatography followed by mass spectrometry.

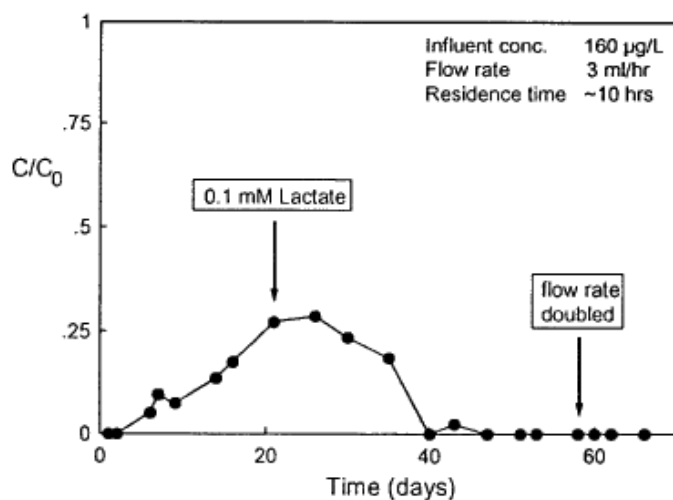


Fig. 1. Breakthrough and disappearance of β -HCH in the sediment column. The values on the vertical axis represent the quotient of the effluent and the influent concentration.

From this active sediment in the column, we have obtained a methanogenic consortium that is able to degrade β -HCH, but also α - and γ -HCH via the same pathway to

monochlorobenzene. The identification of the intermediate compound β -3,4,5,6-tetrachlorocyclohexene provides evidence for the biotransformation of β -HCH to proceed via two subsequent dihalo-eliminations and one hydrogenolysis reaction to form monochlorobenzene. This dechlorination sequence is consistent with that found in literature for α - and γ -HCH performed by different *Clostridia* species (see fig.2).

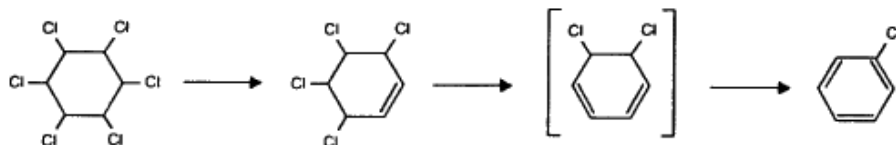


Fig. 2. Degradation pathway of HCH under anaerobic conditions as proposed by Ohisa et al. (1980)

We believe that β -HCH serves as an electron acceptor for dehalogenating microorganisms. As far as we know, this work is the first detailed description of the biotransformation of β -HCH under anaerobic conditions, including the identification of a key metabolite and the end product. Monochlorobenzene is persistent under anaerobic, but degradable under aerobic conditions. These results provide good perspectives for the application of a sequential anaerobic/aerobic biological treatment of soils and aquifers polluted with different HCH isomers.

In the presentation, we will discuss the stoichiometry of the transformation, the influence of alternative electron donors and acceptors, as well as strategies used for further enrichment of microorganisms responsible for the dehalogenation reactions.

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Solvent stripping experiments of packed HCH and mercury contaminated soil

Mr. Jos Brouwers
The Netherlands



SOLVENT STRIPPING EXPERIMENTS OF PACKED HCH AND MERCURY CONTAMINATED SOIL

*Presented by: Mr. Jos Brouwers
University of Twente, Enschede, The Netherlands*

INTRODUCTION

In the past, the pesticide hexachlorocyclohexane (HCH) has been produced on many different sites and in huge quantities all over the world [1, 2]. In the Netherlands, the production location at Hengelo (from 1948 until 1952) has become well known because of the soil pollution it has caused. Besides the contamination with HCH, this soil has also been polluted with mercury. The amount of excavated soil in Hengelo amounts to approximately 200,000 tons. In the future, there will still be substantial amounts of polluted soil in the Netherlands; in Hengelo once more 200,000 tons. Besides the contaminated soil in the Netherlands there is also a substantial amount of polluted soil in Saxony-Anhalt, the Basque Provinces, etc. HCH, including lindane, is a toxic substance which is very harmful to the public health and which also causes a lot of stench. Consequently, high priority has been given to the cleaning of HCH contaminated soil.

A commercially interesting remediation method is offered by solvent stripping and steam stripping, for convenience named two-stage steam stripping¹. In the first stage, an organic solvent is heated and led through the soil as vapour. In the soil, which is packed in a container, this vapour will condense. The soil is moistened and heated by which extraction and vaporization of HCH is promoted. Apolar organic solvents will particularly be effective as HCH is also apolar (as is also the case in PAHs, benzene, toluene, mineral oil etc.). In the second stage, steam is led through the soil in order to remove the solvent and pollutant left behind. Steam and solvent are separated by condensing and separation of the immiscible water and apolar solvent phases. The process can be operated both on-site as in-situ. In the following pages, the laboratory equipment used and the features of the treated soil are discussed and some of the experiments carried out are explained.

¹The University of Twente has applied for a patent covering this process.



TEST SETUP

At the department of Civil Technology and Management, University of Twente, a setup is available for treating both contaminated soil and water with heated air and/or steam (and other vapours). Here, the attention is restricted to the treatment of soil. The main components of the measuring equipment are (figure 1):

- a vertically placed thermally insulated glass tube with an inner diameter of 50 mm and a height of 1 m;
- a connection to the 6 bar compressed air network, fitted with a pressure reducer;

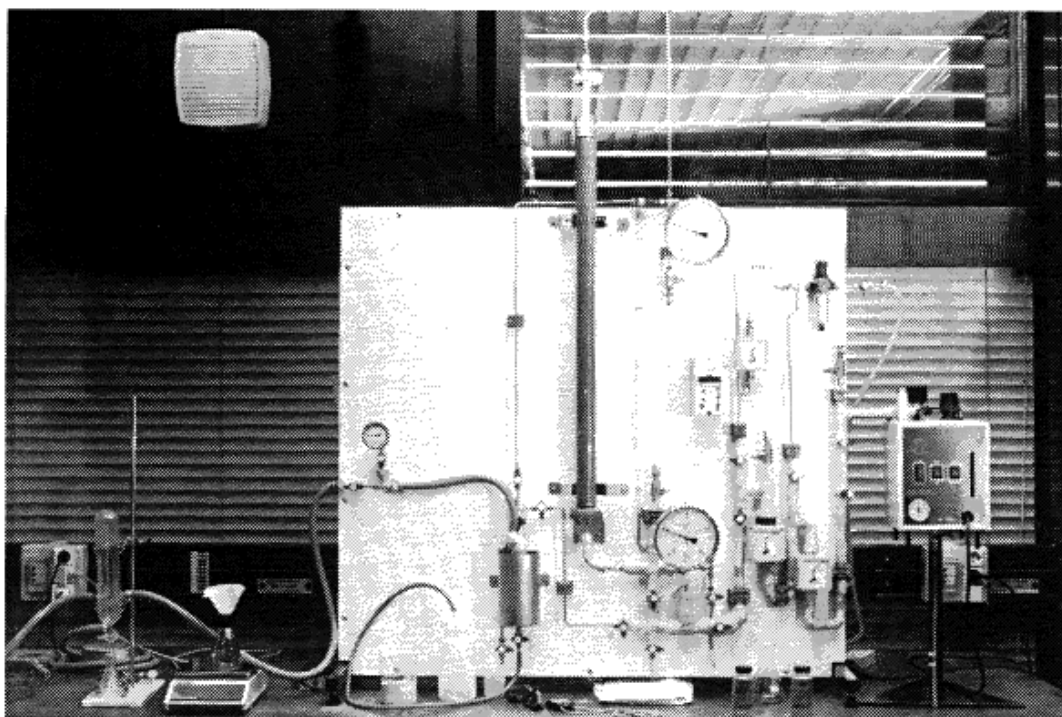


Figure 1 Picture of the test setup.

- a steam generator to create solvent vapour in the first stage and steam in the second stage, de maximal absolute pressure amounting to 5 bar, which can be reduced;
- electrical resistance heating to avoid premature condensation in supply channels - and/or heat the compressed air;
- a vacuum pump to create underpressure in the test tube;
- devices to measure pressure, flow and temperatures;
- a condenser to condense and separate solvent, water and pollutants.



The soil is brought into the test tube and tamped down. Preceding to experiment, the used soil is stirred manually and samples are taken to determine the initial pollution (idem after the experiment). Subsequently, the stripping media are injected at the bottom, led through the test tube and led from the exit at the top to the condenser. The condensate is led from condenser to one litre bottles for analysis after the experiment.

In the heated glass tube and in the first stage, the desorption and evaporation of volatile pollutants will be accelerated. In the second stage, injection of steam results in a removal of the solvent and the remaining pollutant. In the next sections experiments with HCH and mercury polluted soil will be presented.

TREATED SOIL

The treated soil is contaminated with HCH and mercury. It originates from the depot near the town of Beckum, near to the city of Hengelo (NL, the Province of Overijssel). In this depot, there are about 200,000 tons of polluted soil stored.

Dry weight (dw):	90.0 %
Organic fraction:	2.8 % of dw
Particle size distribution:	
$x > 2.000$	0.0 % of dw
$1.000 < x < 2.000$	0.0 % of dw
$0.500 < x < 1.000$	8.0 % of dw
$0.355 < x < 0.500$	19.3 % of dw
$0.250 < x < 0.355$	18.2 % of dw
$0.180 < x < 0.250$	14.0 % of dw
$0.125 < x < 0.180$	12.2 % of dw
$0.090 < x < 0.125$	7.6 % of dw
$0.063 < x < 0.090$	5.7 % of dw
$0.002 < x < 0.063$	11.9 % of dw
$x < 0.002$	0.3 % of dw

Table 1 Composition of treated soil (sizes in mm).

The soil is coming from sector 24, parcel Heideweg, and can be considered to be representative of most of the HCH and mercury polluted soil of the Province of Overijssel. The soil has been treated integrally, thus without preceding separation of the fine fraction.

In Table 1, the composition of the used soil is given. From this Table, it can be seen that 12.2 % of the dry weight of the soil consists of silt and clay fraction.

Several chemical analyses revealed that the soil contains $4.5 (\pm 1)$ mg HCH per kg dry weight (about 80% is -HCH) and $3.5 (\pm 1)$ mg mercury per kg dw. The initial pollution level is determined and given separately for each experiment.



EXPERIMENTS

During the first tests the entire test tube was filled with soil and flushed with an absolute entry pressure of 1.5 bar (this pressure is imposed for all experiments). Hexane is employed as organic solvent in the first stage. This apolar solvent has the advantages that it is able to dissolve HCH better than water does, it is inexpensive, relatively non-poisonous, reusable and can be processed with standard steam equipment. Moreover, the boiling point of hexane at 1 bar is 69 C and therefore in the second stage it can be stripped very well with steam.

It was noticed that, either immediately or after some time, the test tube became impermeable, both for steam, solvent and air. Furthermore, it was observed that the soil was compressed. The height reduction under the imposed pressure amounted to 2% of the initial height. These features can probably be attributed to the presence of the fine fraction and relatively high overpressure of 0.5 bar.

To reduce the pressure drop in the polluted soil and avoid consolidation, the treated polluted soil was less highly stacked. To this end, the lower three quarters of the test tube were filled with clean sand and the upper fourth part (about 25 cm) with polluted soil. The last experiments were performed in this way and the results are discussed in the following paragraphs. It was now noticed that the hexane progressed very rapidly through sand and soil. After 10 hours of hexane flushing the second stage was started. During the next 11 hours the soil was flushed with steam. The laboratory analyses after Experiment A reveal that the HCH and mercury concentrations in the soil are reduced to almost the detection limit (HCH: 0.01 mg/kg dw, mercury: 0.1 mg/kg dw) at the place where the stripping media enter the contaminated soil (at the boundary of sand and treated soil), see Table 2. It is not surprising that at this entrance the cleaning results are best, as the stripping media are still clean here. Higher up in the test tube the stripping media become contaminated with HCH and mercury and consequently the driving force for mass transfer between soil and vapours is less.

	HCH (mg/kg dw)	mercury (mg/kg dw)
before experiment	5.18	3.6
after experiment (bottom)	0.04	< 0.1
after experiment (top)	0.10	1.7

Table 2 HCH and mercury concentrations in treated soil before and after treatment (Experiment A).



On the basis of the obtained results, a second Experiment B was performed with 0.85 kg contaminated soil (about 25 cm high). During this experiment the soil was stripped 6.5 hours with hexane and subsequently 9.5 hours with steam.

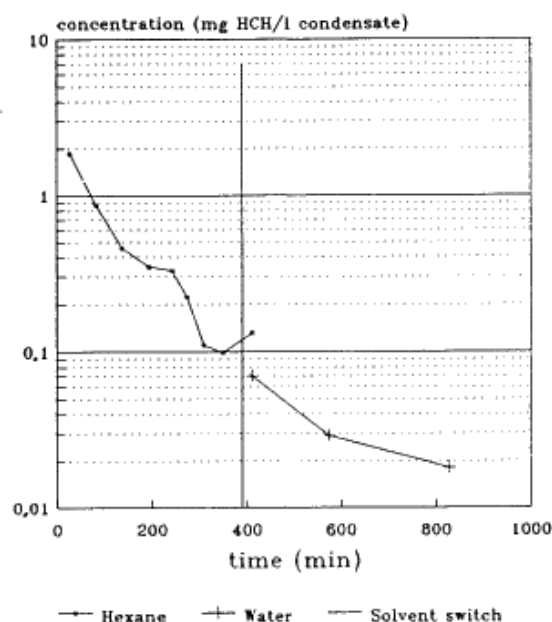


Figure 2 HCH concentration in the condensate during Experiment B.

In all, 8½ litres of hexane and 2.5 litres of water were used. This corresponds to 47 pore volumes of hexane and 14 pore volumes of water.

The soil analyses reveal that the HCH has been removed below the detection limit, see Table 3. This HCH removed from the soil has been found completely in the water and hexane condensate. Even more HCH (about 4.2 mg) has been found in the condensate than has been removed from the soil, which is about 3.8 mg. This difference can be attributed to the various inaccuracies of soil and condensate analyses. Figure 2 illustrates that most HCH has been removed in the hexane treatment of the first stage, although the steam stage also significantly contributes to the cleaning. Furthermore, in the soil practically all hexane has been removed in the second (steam) stage. The hexane concentration only amounts to 17 µg/kg dw. This content is below the A-level for mineral oil (10 mg/kg dw) from the Holland List (Hexane can be considered as a mineral oil). One can conclude from this result that steam is very well able to strip hexane from the soil.



	HCH (mg/kg dw)	mercury (mg/kg dw)
before experiment (bottom)	4.79	4.3
after experiment (bottom)	< 0.01	2.2
before experiment (top)	5.49	4.6
after experiment (top)	< 0.01	3.4

Table 3 HCH and mercury concentrations in treated soil before and after treatment (Experiment B).

Table 3 furthermore reveals that the mercury content during Experiment B, in contrast to Experiment A, is insufficiently reduced. It is expected that mercury is particularly removed in the second stage. Steam has a higher temperature than hexane and hence, an enhanced evaporation of mercury will take place. This is confirmed by Figure 3, in which the mercury concentration in the condensate is depicted as function of time. In the first three hours of the process, mercury is removed by the hexane to some extent. After this start, mercury is not transported anymore by the hexane.

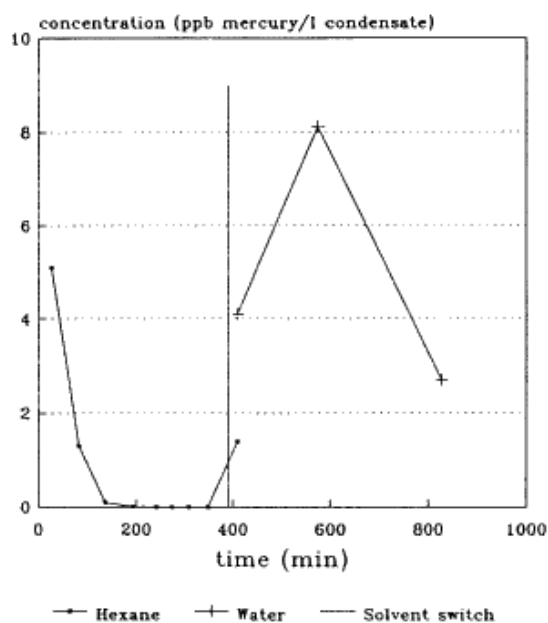


Figure 3 Mercury concentration in the condensate during Experiment B.

The moment that steam is introduced, after about 400 minutes (6.5 hours), one can see mercury is removed again from the soil and found in the condensate. It is found in the water in even greater quantities than in the preceding hexane stage. It is expected that if the steam stage is extended, the mercury removal will be considerably improved.



CONCLUSIONS

The first results of the two stage stripping method reveal the possibility of reducing the HCH and mercury levels below the detection limit. This innovative remediation method offers the following advantages:

- the process is relatively simple, no exhaust gas purification or classification fine soil fraction is needed;
- the technique is applicable to all volatile pollutants such as HCH, mercury, PAHs and so on;
- the soil is integrally treated, i.e. including the particles $< 63 \mu\text{m}$, so that classification and dump expenses are avoided;
- the technique is applicable both on-site and in-situ, so that costly transportation of polluted soil is not required;
- the chemical and physical properties of the soil are not affected;
- the process is applicable on a commercial basis. An indicative cost calculation of a mobile installation shows that treatment is possible for 120 NLG (105 DEM) per ton. The studied installation is based on static treatment in containers with a daily capacity of 50 tons [3].

The experimental results suggest further investigation of:

- the removal of mercury, in particular in the second (steam) stage;
- the stacking and permeability of the polluted soil and the susceptibility to the imposed entry pressure;
- the optimizing of the process, that is to say the minimizing of flushing time and amounts of flushing media.

The second item is not of interest anymore if the soil is classified before treatment or treatment in stirred containers is applied. For future research, therefore, two stage stripping experiments in a stirred container are planned.

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Thermal Hydro Dehalogenation

Mr. Wouter van der Meer
The Netherlands



THERMAL HYDRO-DEHALOGENATION

*Presented by: Mr. Wouter van der Meer
Koninklijke Schelde Groep, The Netherlands*

Dioxines formation a thing of the past:

THERMAL HYDRO-DEHALOGENATION

The environmentally friendly solution for halogenated hydrocarbons!

Recently a new efficient and environmentally friendly method has become available for the processing of waste streams containing chlorinated and other halogenated hydrocarbons: the Thermal Hydro-Dehalogenation (THD) process. This process provides for the recovery of both the halogen acids and the hydrocarbons for re-use. The major advantage is that no dioxines are formed. The process has a high thermal efficiency, and moreover, it is economically attractive.

Halogenated hydrocarbons have become known to a wider public because of their damaging effects on the environment. They create a problem in the atmosphere because of their attack on the ozone layer (CFCs), they create the conditions for the formation of photo-chemical air pollution (smog) and contribute to the greenhouse effect. Their persistence and toxicity form an acute problem in the soil and water. This may possibly lead to longer-term problems since halogenated hydrocarbons accumulate in the food chains (bio-accumulation).

Chlorinated and other halogenated hydrocarbons are used in a considerable diversity of applications, such as solvents and extraction agents, raw materials for plastics and/or as intermediates in the production of plastics. In addition they are used as pesticides, aerosol propellants, blowing agents and for fire extinguishers.

The halogenated hydrocarbons are attractive, since they are excellent solvents for oils, fats and resins. Some are toxic (and difficult to degrade) and are then used as pesticides. Other halogenated hydrocarbons, the chloro-fluoro carbon compounds (CFCs) are used because of their low toxicity.

In general halogenated hydrocarbons have very diverse physical, chemical, toxicological and other properties.



THE THD PROCESS

The fundamental research¹ for the Thermal Hydro-Dehalogenation process was carried out at the RU (National University) of Leiden under the leadership of Prof. Dr. R. Louw. Patents were applied for and granted².

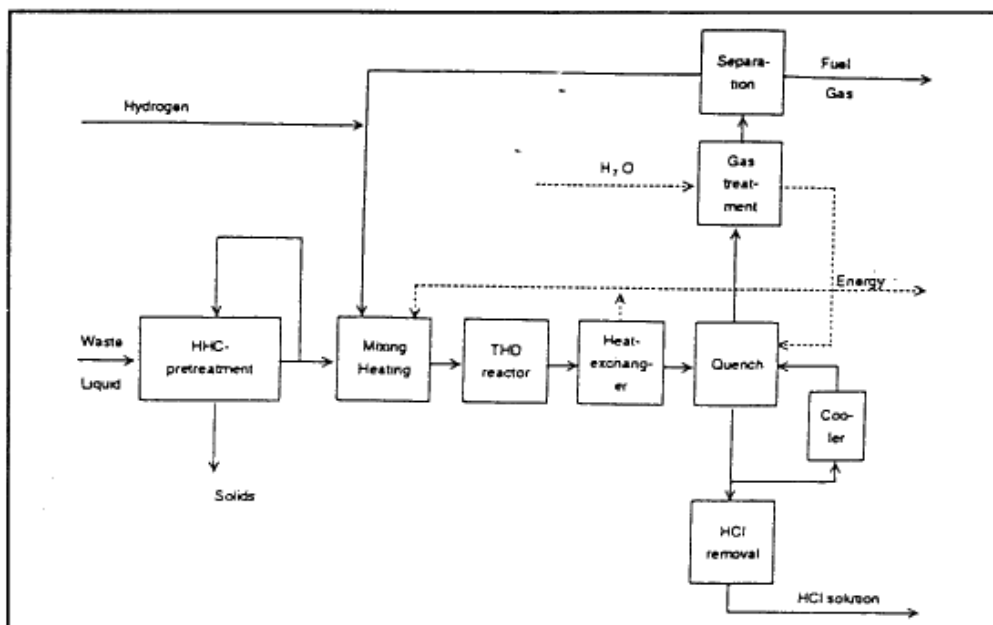
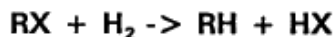


Figure 1 Schematic THD process flow diagram

The reactor technology research, using a mini-pilot plant, at the TU (Technical University) of Delft³, was led by Prof.ir.C.M.v.d.Bleek. The exclusive rights for production and commercialisation of THD installations have been acquired by the Royal Schelde, who have developed the process design into a commercially attractive installation - making use of the traditional areas of knowledge within the Royal Schelde.

In the THD process (Figure 1) the halogenated hydrocarbons are mixed either with hydrogen or a gas containing hydrogen. The mixture is then heated to about 850° C. At this temperature, in the reactor developed by the Royal Schelde, that does not require a catalyst, the reaction takes place between the halogenated hydrocarbon (RX) and hydrogen (H₂) to form a halogen acid (HX) and hydrocarbon (RH).



¹ Gas phase hydrogenolysis of ethene and benzene derivatives. Thesis J.A. Manion, 1989, presented by Prof. R. Louw.

² European patent no. 0 175 406 and US patent no. 4851600

³ Thermische hydrodechlorering, een alternatief voor de verbranding van gechloreerd chemisch afval, [Thermal hydro-dechlorination, an alternative to incineration of chlorinated chemical waste] M. Elderman, P.A.J. Mees, PT-procestechniek, January 1990



The gaseous halogen acid can be stripped out with water. The hydrocarbons can be returned to the process, or of course burnt. The product gas formed can be cooled, before it is washed, without the risk of formation of such undesirable byproducts as dioxines, making energy recovery possible.

The energy required for hydrogen production can thus be recovered from the process, following which an additional quantity of energy can be released by burning the hydrocarbons.

THD REACTION COMPARED TO INCINERATION

The overall reaction and energy balances of incineration and THD-process show that the THD process followed by combustion, in the ideal case, delivers as much heat of reaction as direct incineration.

For incineration the recovery of the halogen acid and of the heat of combustion have to take place in the same plant.

There can only be a partial recovery of heat (to a minimum temperature of about 500° C) because of the risk of dioxine formation. Removing the halogen acid first results in a temperature level that is too low for energy recovery.

After the THD process the temperature of the gas mixture can first be reduced and the thermal energy recovered, then the halogen acids can be scrubbed out and finally the residual gases (fuel gas) can be burned at a production location where the heat of combustion can be used.

Another important difference between incineration and THD is that, with an increasing halogen content, incineration becomes increasingly difficult (consider their use as flame extinguishers) while the THD process then works better.

The THD process places the emphasis on recovery of the halogen acid and the hydrocarbon. The hydrocarbons are not destroyed by the THD process.

Operation of the process is simplified considerably because of the high reaction rates without catalysis. The problems of stability and selectivity frequently encountered in catalytic processes do not arise. Another major advantage of the process is that it is robust, and suitable for a wide variety of halogenated hydrocarbons.



STUDY

Based on research results at Leiden university, a test reactor was built at Delft University of Technology in cooperation with the Royal Schelde. Using the results obtained from it a feasibility study was made for a commercial installation with an annual capacity of about 20,000 tons of halogenated hydrocarbons.

The feasibility study showed an attractive processing cost, after which the next step, the design and building of a pilot plant, could be taken. Companies interested in acquiring a THD installation can have the processing of their specific halogenated hydrocarbon streams demonstrated in the pilot plant. As well as being a demonstration unit the pilot plant will also allow any technical problems to be examined and solved. These could include the processing of any soot that might be formed and making the halogen acid suitable for the market.

Another research project was done by Leiden university and TAUW-milieu and Royal Schelde. In this study the effects of THD on the vapours that form when with HCH contaminated soil is heated to 250 °C under inert atmosphere. These vapours mixed with hydrogen are led through a bed of activated carbon at a temperature of ca 600 °C. The conversion to HCl is 100 %. Further studies are needed to convert this laboratory process to a commercial available plant.

DEVELOPMENTS

The pilot plant design is based on an annual capacity of 600 tons of halogenated hydrocarbons with a chlorine content of 65% (or other equivalent halogenated products).

The halogenated hydrocarbons and the feed gas are mixed in the specially-designed tubular reactor at about 850° C. The gas velocity in the reactor is such that the short residence time required is reached.

The halogenated hydrocarbon pre-treatment ensures that there is no polymerization and/or oxidation of the stored product, in addition solids are removed. The H₂ is brought in from outside and depends upon the chosen location. A gas control system ensures that the feed gas has the required composition, and also ensures that sufficient thermal energy is available to permit the reaction to start.

The pilot plant consists of two containers that accommodate the components of the THD process: Reactor, Quench, Liquid receiver and Gas receiver.



Thermal hydro-dehalogenation

Since it is not essential for demonstration purposes the energy liberated by the reaction will not be recovered in the pilot plant, neither will the hydrocarbons be re-used.

The reaction gas will be cooled in the quench by a recycle stream and the halogen acid in this gas will be neutralised. The reaction gas can then be burned.

First results from the demonstration unit, that has been built on the Royal Schelde site in Vlissingen, are expected in early 1993.

CONCLUSION

The Thermal Hydro-Dehalogenation process developed by the Royal Schelde will soon be tested on a commercial scale. The development from laboratory scale, via bench scale to commercial scale shows that this process offers promising prospects for the future.

An advantage of the THD process is that no dioxines can be formed. By placing a THD process unit before an incinerator expensive after-treatment will be made unnecessary, which means that the incinerator can be cheaper.

Because the chlorinated hydrocarbons have been removed the combustion chamber temperature can also be reduced and the formation of NO_x can also be prevented.

Because of the lower temperature and the presence of fewer corrosive gases, other materials of construction can be used, thus making the incineration installation even cheaper.

Moreover, more energy can be recovered from the flue gas, because the flue gas can be cooled to a lower temperature, this improves the economic feasibility of the incineration installation. In nearly all cases, both the halogen acids and the hydrocarbons can be re-used, which is better for the environment, and for the economic applicability of the THD process.

**Biological purification of HCH contaminated
waters by mixed cultures under aerobic and
anaerobic conditions**

Mr. Steffen Heinrich
Germany

BIOLOGICAL PURIFICATION OF HCH CONTAMINATED WATERS BY MIXED CULTURES UNDER AEROBIC AND ANAEROBIC CONDITIONS

*Presented by: Mr. Steffen Heinrich
Rathenower Anlagenbau GmbH, Germany*

SUMMARY

Waters saturated with Hexachlorocyclohexane can be biologically treated by using specific adapted mixed cultures isolated for instance from the area of a former Lindane producing plant near Magdeburg or a dump of waste of HCH near Bitterfeld. This also applies to the beta and delta isomers of HCH that are known to be persistent, but in that case treatment should take place favourably in an facultative anaerobic environment.

Satisfactory and stable effluent values could be achieved in continuous long-term experiments (over a period of more than 87 weeks) with model waters in a laboratory scale activated sludge plant.

Alpha- and gamma-HCH can be eliminated nearly completely under aerobic conditions.

With medium retention times of about 1,5 days under anoxic conditions the effluent concentrations of beta- and delta-HCH reached on average 0,039 mg/l or 0,023 mg/l at biological efficiencies of 78,2% or 96,5% respectively.

On average they could find 0,07 mg β -HCH/l and 0,06 mg δ -HCH/l at biological efficiencies of 62% or 91% respectively in an aerobic process condition under analogous conditions and realized space loadings of about 0,12 mg β -HCH/l*d and 0,4 mg δ -HCH/l*d (Fig.1).

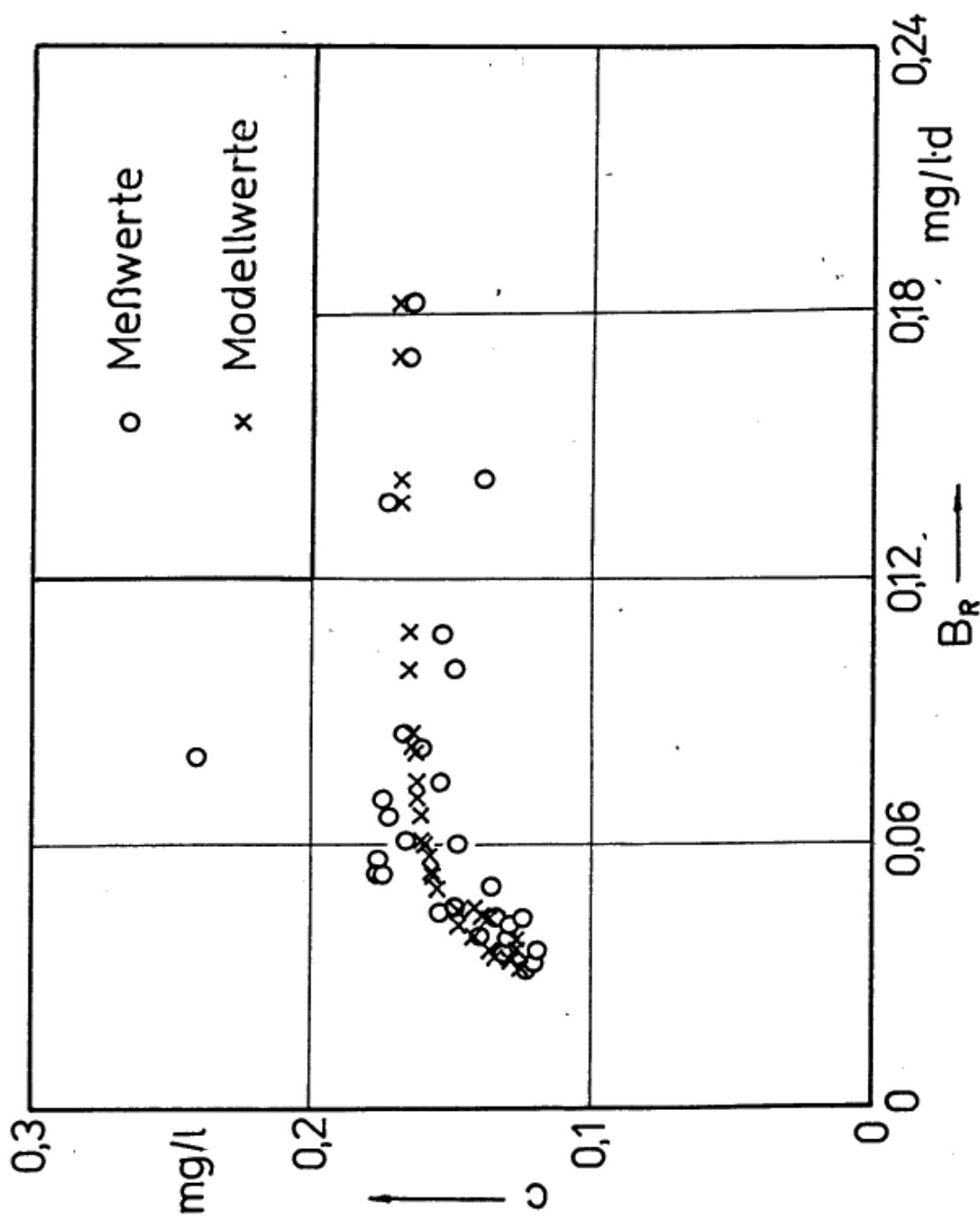
As expected the microbial growth was negligible. Nevertheless the processes remained stable. Increased biomass concentrations were observed with addition of Acetone as solvent assistant, but as experiments showed, it functions only as a competition substrate. Only in case of very low acetone concentrations, HCH was metabolised.

The organic chlorine content of the HCH that was feeded into the system was nearly complete found as free chloride in the effluents (Fig.2). Tests with various organisms demonstrated that the treated water was still toxic.

By combining ozonization with biological treatment the quality of the treatment plant effluents can be further improved.

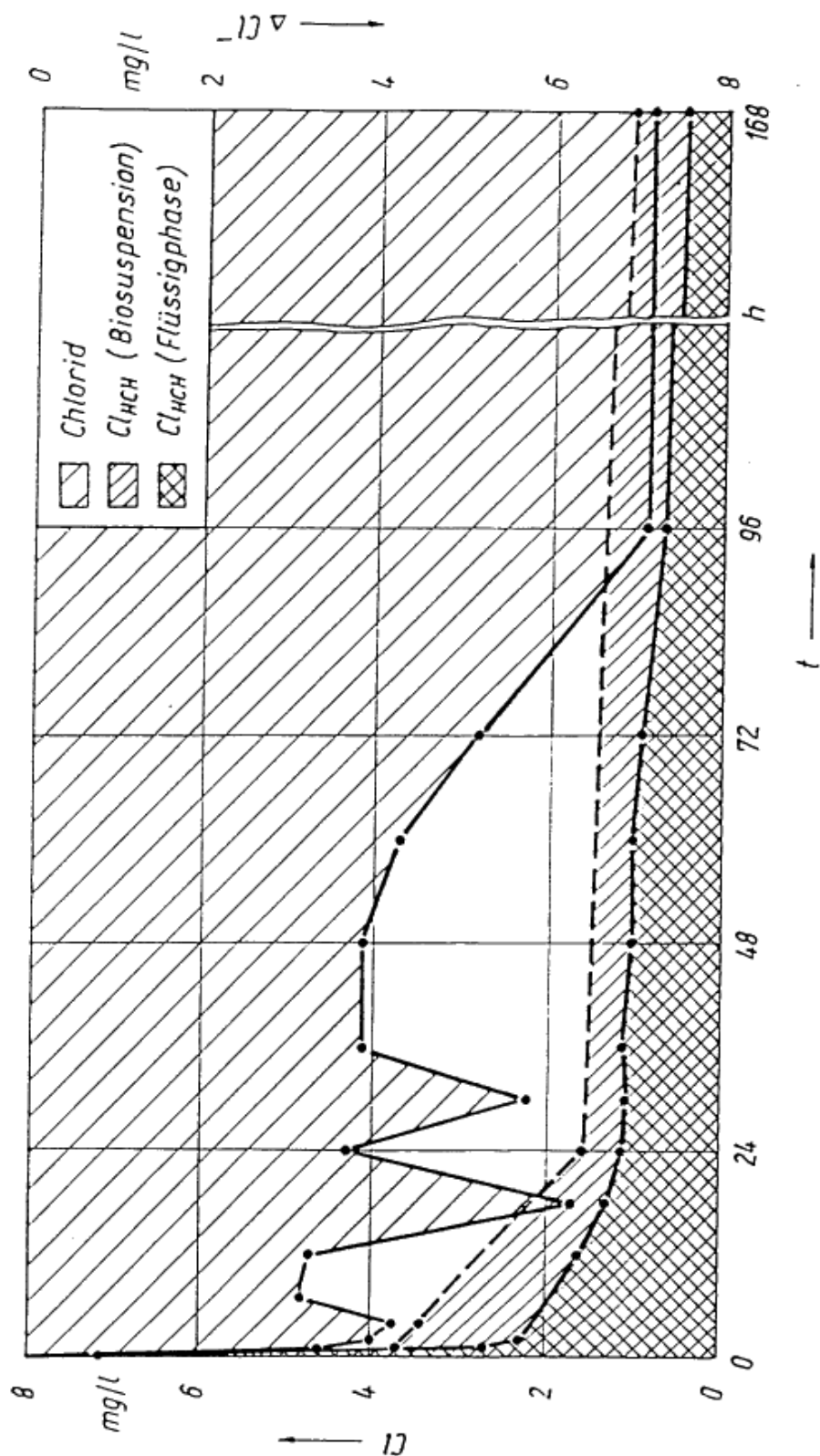
The next stage of investigation should deal with the microbial purification on semi-technical scale, of waters such as landfill leachates or waste waters of Lindane production.

Figure 1: Chloride balance (batch aerobic treatment)



Biological purification of HCH contaminated waters

Figure 2: Concentration of β -HCH in effluent as function of space loading (aerobic treatment)



Untersuchungen zur biologischen Reinigung von mit Hexachlorcyclohexan (HCH) belasteten Wässern

Grundlagen und vorbereitende Arbeiten

W. Meusel, St. Heinrich, Köthen

Zusammenfassung

Die biologische Reinigung von Wässern, die mit Hexachlorcyclohexan kontaminiert sind, ist unter Verwendung einer speziell adaptierten Mischkultur möglich. Dies gilt auch für die als persistent bekannten beta- und delta-Isomeren des HCH, wobei hier vor allem ein anaerobes Milieu von Vorteil ist.

Bei mittleren Verweilzeiten des Modellwassers von ca. 1,5 Tagen konnten in kontinuierlichen Langzeitversuchen zufriedenstellende und stabile Ablaufwerte erhalten werden. Durch Kopplung von Ozonierung und biologischer Reinigung ist eine weitere Verbesserung der Ablaufqualität erreichbar.

Schlüsselwörter: Abwasserreinigung, biologische Reinigung, Altlasten, Sanierung, Sickerwasser, Ingenieurwissenschaft

TESTS RELATING TO THE BIOLOGICAL TREATMENT OF WATERS POLLUTED BY HEXACHLOROCYCLOHEXANE (HCH)

Summary

Waters contaminated by hexachlorocyclohexane can be biologically treated by using a specific adapted mixed culture. This also applies to the beta and delta isomers of HCH which are known to be persistent, but in that case treatment should take place in an anaerobic environment.

With medium retention times of about 1.5 days for the model water, satisfactory and stable effluent values could be achieved in continuous long-term experiments. By combining ozonization with biological treatment, the quality of the treatment plant effluents can be improved further.

Key words: wastewater, treatment, biological treatment, contamination sites, rehabilitation, leachate, engineering science

EXAMENS RELATIFS À L'ÉPURATION BIOLOGIQUE DES EAUX CHARGÉES DE L'HEXACHLOROCYCLOHEXANE (HCH)

Résumé

L'épuration biologique des eaux chargées de l'hexachlorocyclohexane (HCH) est possible par l'emploi d'une culture mixte particulièrement adaptée. Cela s'applique aussi aux isomères beta et delta de l'HCH connues comme persistantes à quoi un milieu anaérobie est avantageux. Pour de moyennes périodes de séjour de 1,5 jours de l'eau sur modèle, on a pu arriver aux valeurs satisfaisantes et stables dans l'effluent aux essais continus de longue durée. En liant l'ozonisation et l'épuration biologique on peut arriver à une amélioration ultérieure de la qualité de l'effluent.

Notice-matière: épuration (f) des eaux usées, épuration (f) biologique, sites (m) contaminés, assainissement (m), lixiviats, ingénierie (f)

1. Einführung

Aufgrund des langjährigen Einsatzes technischen Hexachlorcyclohexans (HCH) als Insektizid in der Land- und Forstwirtschaft und infolge der Persistenz einiger Isomeren dieser Verbindung gelten entsprechend belastete Böden seit geraumer Zeit als Problemfälle.

Gleiches gilt für die bei der LINDAN (γ -HCH)-Herstellung anfallenden Prozeßabwässer sowie für die im allgemeinen freien Verkippungen von HCH-Abfallisomeren aus der ehemaligen LINDAN-Produktion (je nach Technologie sind LINDAN-Ausbeuten von nur 7–18 % erzielbar) und der damit verbundenen Gefahr der Kontamination von Sickerwässern. Letztere wird durch die geringe Löslichkeit der HCH-Verbindungen zwar etwas gebannt, jedoch im Einzelfall (z. B. bei gleichzeitiger Anwesenheit von Ölen) können erhebliche Konzentrationen auftreten.

Die Entfernung des gelösten HCH mittels verfahrenstechnischer Grundoperationen stellt im wesentlichen nur eine Problemverlagerung dar. Die biologische Reinigung dieser Wässer gilt hingegen als kaum praktikierbar. Am ehesten lassen sich nach Aussagen in der Literatur noch α - und γ -HCH biologisch abbauen.

Aus diesem Grund wurden an der TH Köthen, gefördert durch die A.I.F., systematische Untersuchungen zum Abbau der HCH-Isomeren in der wäßrigen Phase sowohl unter aeroben als auch anaeroben Bedingungen durchgeführt.

Ziel der Untersuchungen war es, festzustellen, inwieweit speziell adaptierte Mischpopulationen in der Lage sind, HCH-belastete Wässer zu reinigen. Darauf aufbauend sollten Möglichkeiten einer praktischen Realisierung abgeschätzt werden.

2. Stand des Wissens

Der Hauptteil der bisherigen Arbeiten befaßt sich speziell mit dem Verhalten des γ -Isomeren in betroffenen Umweltkompartimenten, um aus der LINDAN-Anwendung resultierende Risiken abzuschätzen bzw. Möglichkeiten der Sanierung zu finden [1–12].

Obwohl die Möglichkeit der mikrobiellen Umwandlung der vier relevanten HCH-Isomeren mehrfach behauptet wurde [13, 14, 15] und der Abbau von zumindest einigen Isomeren durch spezialisierte Mikroorganismen bereits nachgewiesen werden konnte [16, 17], war an eine biologische Reinigung entsprechend kontaminierter Wässer noch nicht zu denken.

Dafür werden im wesentlichen die geringe Wasserlöslichkeit, die geringe Bioverfügbarkeit und die hohe biochemische Stabilität des HCH, aber auch das breite Spektrum der beim mikrobiellen Abbau entstehenden Metaboliten sowie ungenügende Kenntnis der daran beteiligten Mikroorganismen und Enzyme bzw. begünstigende Milieubedingungen verantwortlich gemacht [17, 18].

Hinsichtlich der biologischen Abbaubarkeit ergibt sich für die HCH-Isomeren folgende Einstufung:

$$\gamma > \alpha > \delta > \beta \text{ [14, 16, 19].}$$

Bei den durchgeführten Abbaubersuchen kamen in den meisten Fällen aus kontaminierten Böden isolierte und anschließend angereicherte Bakterien zum Einsatz [5, 14, 16, 21].

Bakterien der Gattungen *ESCHERICHIA*, *ENTEROBACTER*, *CITROBACTER*, *CLOSTRIDIUM* und *BACILLUS* werden für die biologische Umwandlung von HCH unter anaeroben Bedingungen verantwortlich gemacht [4, 7, 9–12, 14, 16, 22, 23]. Auch Grünalgen (*CHLORELLA vulgaris*, *CHLAMYDOMONAS reinhardtii*) sollen in der Lage sein, HCH zu verstoffwechseln [24]. Dagegen sind eine Reihe von Bakterien der Gattung *PSEUDOMONAS* sp. und *XANTHOBACTER* sp. dazu befähigt, HCH unter aeroben Bedingungen abzubauen [4, 21, 25].

Die Biodegradation von β -HCH wurde erstmals durch SID-DARTHA et al. [21] in einer Schüttelkultur nachgewiesen, wobei jedoch über die langfristige Konstanz der Stoffwechselaktivitäten der Reinkulturen keine Aussagen vorliegen. Ebenso bleibt offen, ob diese Reinkulturen sich unter

natürlichen Bedingungen durchzusetzen vermögen. Versuche von z. B. mit genmanipulierten Mikroorganismen ergaben deren Verlust der Leistungsfähigkeit bezüglich der Verwertung von HCH nach ca. 3 Monaten [26]. Darüber hinaus ist bekannt, daß aus natürlichen Proben isolierte Reinkulturen infolge langfristiger Konservierung nicht mehr in der Lage waren, HCH abzubauen [27].

3. Vorbereitende Arbeiten

3.1. Gewinnung adaptierter Mischkulturen

Als Ausgangsmaterial zur Gewinnung von geeigneten Mischkulturen dienten mehrere Bodenproben von natürlichen Standorten, die bereits jene persistenten Substanzen enthielten. Es handelte sich dabei um eine Monodeponie von HCH-Abfallisomeren sowie um einen ehemaligen Produktionsstandort.

Die erhaltenen Eluate wurden in 3,2 l-Laborfermentoren unter aeroben und anaeroben Bedingungen behandelt. Die aerobe Anreicherung der Kulturen erfolgte unter nur schwacher Belüftung, um der geringen spezifischen Sauerstoffverbrauchsrate der spezialisierten Mikroorganismen Rechnung zu tragen. In Abständen von 2 bis 3 Wochen wurde erneut Substrat aus den Bodenproben bis zur Sättigung der Kulturbrothe mit HCH zugegeben.

Die Adaption der Kulturen konnte nach ca. 3 Monaten abgeschlossen werden, was u. a. durch eine deutliche Absenkung des pH-Wertes um etwa drei Einheiten zum Ausdruck kam. Von diesem Zeitpunkt an wurde ein Modellsubstrat mit folgender Zusammensetzung verwendet:

● Destilliertes Wasser + Nährsalze

KH_2PO_4	0,1700 g/l
K_2HPO_4	0,5700 g/l
$\text{Na}_2\text{HPO}_4 \cdot 12 \text{ H}_2\text{O}$	1,6840 g/l
NaHCO_3	0,0200 g/l
$\text{FeCl}_3 \cdot 6 \text{ H}_2\text{O}$	0,0020 g/l
NH_4NO_3	0,1855 g/l
$\text{MgSO}_4 \cdot 6 \text{ H}_2\text{O}$	0,0427 g/l
CaCl_2	0,0275 g/l

● Hexachlorcyclohexan (HCH), Fa. Riedel de Haën, Isomerenmischung

(α : β : γ : δ = 1:1:1:1) in unterschiedlichen Konzentrationen;

● gegebenenfalls Azeton als Lösungsvermittler bzw. Co-Substrat in unterschiedlichen Konzentrationen.

Innerhalb von wenigen Tagen war danach die Bildung von absetzbarer Biomasse feststellbar und somit die Möglichkeit gegeben, mit der eigentlichen Versuchsdurchführung zu beginnen.

3.2. Versuchsaufbau und -durchführung

Zur Umsetzung der eingangs formulierten Zielstellung wurden sowohl diskontinuierliche Abbaubersuche als auch kontinuierliche Langzeitversuche durchgeführt. Die Tabelle 1 enthält die jeweiligen Versuchsziele und -bedingungen:

Die versuchstechnische Realisierung der kontinuierlichen Versuche erfolgte in einer Laboranlage mit den Hauptbaugruppen Substratvorlage, Rührreaktor (3,2 l), Nachklärbecken, Schlammrückführung sowie Ablaufsammelbecken (Abb. 1). Die Zu- und Abläufe wurden zeitgleich beobachtet. Die

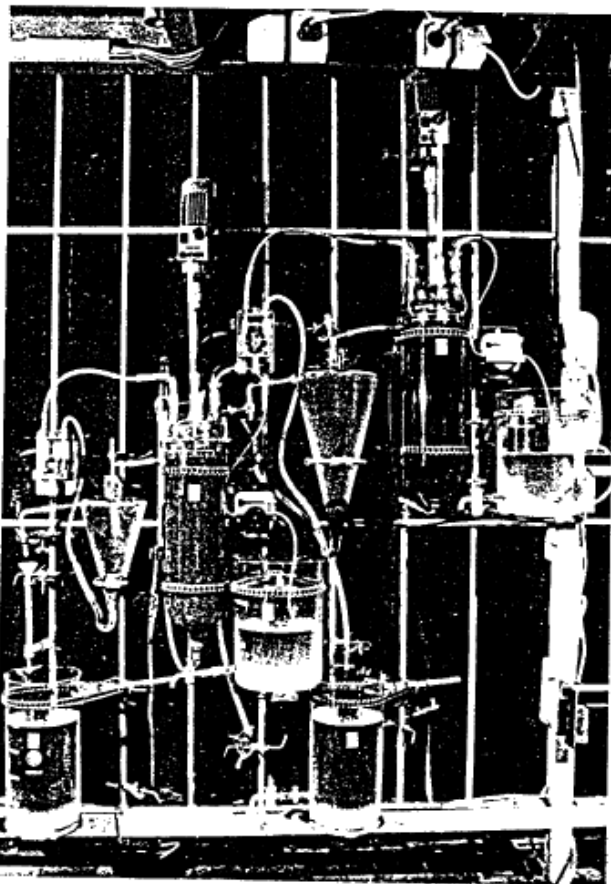


Abb. 1: Versuchsanlage zur Durchführung der kontinuierlichen Langzeitversuche

Proben blieben unfiltriert. Der Versuchszeitraum betrug mehr als 68 Wochen im Dauerbetrieb.

Zur Durchführung der Batch-Versuche dienten baugleiche Reaktoren. Zwecks Untersuchung etwaiger HCH-Emissionen durch Stripping kamen im Falle der aeroben Reaktoren

Versuchsreihe	Versuchsziel	Versuchsbedingungen
K 1	Nachweis der erfolgreichen Anzucht von adaptierten Mikroorganismenkulturen und des Abbaus von HCH	aerob/anaerob: $\dot{V}_{Luft} = 51/h$ $t = 1,5 d$ $c_{HCH} = 10 mg/l$ $c_{Azeton} = 0 ml/l$
K 2	Nachweis der Reproduzierbarkeit des Anzuchtverfahrens zur Gewinnung adaptierter Mikroorganismenkulturen	aerob/anaerob: $\dot{V}_{Luft} = 51/h$ $t = 1,5 d$ $c_{HCH} = 10 mg/l$ $c_{Azeton} = 0,1 ml/l$

Versuchsreihe	Versuchsziel	Versuchsbedingungen
K 3	Senkung der HCH-Konzentration durch Verminderung der Raumbelastung	aerob/anaerob: $\dot{V}_{Luft} = 51/h$ $t = 4 d$ $c_{HCH} = 10 mg/l$ $c_{Azeton} = 0,1 ml/l$
K 4	Quantifizierung der HCH-Eliminierung	aerob/anaerob: $\dot{V}_{Luft} = 51/h$ $t = 5 d$ $c_{HCH} = 10 mg/l$ $c_{Azeton} = 0,1 ml/l$

Kontinuierlich betriebene Versuche

Gaswaschflaschen zum Einsatz (Füllung: Raschigringe; Absorbens: n-Hexan; thermostatiert auf 4°C).

3.3. Verwendete Analytik

Die analytische Bestimmung der HCH-Isomeren erfolgte gaschromatographisch, nachdem sie mittels n-Hexan (ana-

Versuchsreihe	Versuchsziel	Versuchsbedingungen
B 1	Untersuchung des Einflusses der Konzentration der Testsubstanz HCH auf deren biologischen Abbau	aerob/anaerob: $\dot{V}_{Luft} = 51/h$ $c_{HCH} = 20 mg/l$
B 2	wie oben	wie oben $c_{HCH} = 10 mg/l$
B 3 (B 30)	Untersuchung des Einflusses der Konzentration der Testsubstanz HCH auf deren biologischen Abbau/Untersuchung der Wirkung von Azeton in unterschiedlichen Konzentrationen auf den biologischen Abbau von HCH	aerob/anaerob: $\dot{V}_{Luft} = 51/h$ $c_{HCH} = 5 mg/l$ $c_{Azeton} = 0 ml/l$
(B 31)	wie oben	wie oben $c_{Azeton} = 1 ml/l$

Versuchsreihe	Versuchsziel	Versuchsbedingungen
(B 32)	Untersuchung des Einflusses der Konzentration der Testsubstanz HCH auf deren biologischen Abbau/Untersuchung der Wirkung von Azeton in unterschiedlichen Konzentrationen auf den biologischen Abbau von HCH	aerob/anaerob: $\dot{V}_{Luft} = 51/h$ $c_{HCH} = 5 mg/l$ $c_{Azeton} = 5 ml/l$
(B 33)	wie oben	wie oben $c_{Azeton} = 10 ml/l$
B 4 (B 40)	Quantifizierung der HCH-Eliminierung (Adsorption, Emission, biologischer Abbau)	Blindversuch ohne Inoculum aerob/anaerob: $\dot{V}_{Luft} = 51/h$ $c_{HCH} = 10 mg/l$ $c_{Azeton} = 0,2 ml/l$
(B 41)	wie oben	wie oben Versuch mit Inoculum
B 5 (B 51)	Untersuchung der HCH-Eliminierung infolge Ozonbehandlung	$c_{HCH} = 10 mg/l$ $c_{Azeton} = 0,5 ml/l$ Füllkörperkolonne (Gegenstrom) $\dot{V}_{O_2} = 30 l/h$ $c_{O_3} = 0,1 g/l$
(B 52)	wie oben	wie oben Tauchstrahlschlaufenreaktor $\dot{V}_{O_2} = 20 l/h$ $c_{O_3} = 0,07 g/l$

Versuchsreihe	Versuchsziel	Versuchsbedingungen
B 6 (B 61) (B 62)	Untersuchung des Einflusses einer Ozonbehandlung auf den biologischen Abbau von HCH	aerob/anaerob: $\dot{V}_{Luft} = 51/h$ Produkte von B 51 bzw. B 52 als Substrat

Batch-Regime

Tabelle 1: Übersicht der absolvierten Versuchsreihen

log DIN 38 407, Teil 4) aus der wäßrigen Phase extrahiert worden waren.

Zur Quantifizierung des durch Adsorption an die Schlammflocken der Biosuspension gebundenen HCH wurde vor der analogen gaschromatographischen Bestimmung eine entsprechende Aufarbeitung der Proben durchgeführt. Sämtliche Analysenwerte resultierten aus dem arithmetischen Mittel zweier Spritzungen. Die Wiederauffindungsrate betrug mehr als 95 %.

Nach entsprechender Headspace-Probenaufbereitung erfolgte die Analyse der Azetonkonzentration ebenfalls gaschromatographisch.

Das Absorbens der Gaswäsche wurde mit dem COULOMAT 702 CL der Fa. STRÖHLEIN INSTRUMENTS auf EOX- und AOX-Bestandteile (DIN 38 409, Teil 8) untersucht.

Zur Bestimmung der Konzentration an freiem Chlorid sowie an CSB wurde das Photometer „CADAS 100 der Fa. Dr. Lange Industriemeßtechnik GmbH“ mit den entsprechenden Küvettentests verwendet.

Der Trockensubstanzgehalt der Biosuspension wurde nach Zentrifugation ($t = 20 \text{ min}$; $n = 6\,000 \text{ min}^{-1}$) und anschließender Trocknung bei 105°C bis zur Gewichtskonstanz und Abkühlung im Exsikkator gravimetrisch bestimmt. Aus Gründen der Meßgenauigkeit erfolgte auch hier jeweils eine Doppelbestimmung mit anschließender Mittelwertbildung.

Ergebnisse der Abbau- und Langzeitversuche

4. Ergebnisse der diskontinuierlichen Abbauprobversuche

Die Versuchsergebnisse aller durchgeführten Abbauprobversuche zeigen, daß α - und γ -HCH sowohl unter aeroben als auch unter anaeroben Bedingungen in vertretbaren Zeiträumen gut biologisch abbaubar sind (Abb. 2a, 2b), während bei β - und δ -HCH der Abbau vergleichsweise sehr langsam erfolgt und außerdem nicht vollständig stattfindet. Dabei erweist sich ein aerobes Milieu für den Abbau der α - und γ -Isomere und ein anaerobes Milieu für die β - und δ -Isomere jeweils als etwas günstiger.

Hinsichtlich der Konzentrationsabhängigkeit der Abbaugeschwindigkeit konnte für α - und γ -HCH keine und für β - und δ -HCH eine lineare Abhängigkeit im untersuchten Konzentrationsbereich ($0 \dots 20 \text{ mg/l HCH}$) ermittelt werden. Damit erklärt sich auch die Abnahme der Abbauraten letzterer bei insbesondere geringen Anfangskonzentrationen von HCH. Generell konnte festgestellt werden, daß HCH bis zu einer Konzentration von 20 mg/l in der wäßrigen Phase nicht inhibierend auf die adaptierte Mischkultur wirkte.

Das Biomassewachstum muß bei allen durchgeführten Versuchen als äußerst gering eingeschätzt werden. Diesbezüg-

liche Verbesserungen ergeben sich durch den Einsatz von z. B. Azeton als Co-Substrat insbesondere unter aeroben Bedingungen (Abb. 3). Eine Beschleunigung der Biodegradation von HCH konnte jedoch in Anwesenheit von Azeton nicht beobachtet werden, teilweise tritt sogar ein Rückgang der Abbauraten auf. Allerdings führte die stoffliche Verwertung des Co-Substrates nicht generell zum Verlust der Leistungsfähigkeit der Biozönose bezüglich des HCH-Abbaus.

Zu klären war vor allem auch die Frage, in welcher Relation die denkbaren Eliminierungsprozesse (biologischer Abbau, Adsorption, Emission) stattfinden. Diesem Problem wurde speziell die Versuchsreihe B 4 gewidmet.

Zunächst konnte eindeutig geklärt werden, daß HCH-Emissionen infolge Verflüchtigung bzw. Strippung nicht stattfinden. EOX- bzw. AOX-Gehalte konnten im Absorptionsmittel (n-Hexan), das von der Abluft durchströmt wurde, nicht nachgewiesen werden.

Deutlich wurde jedoch, daß der biologische Abbau von HCH in starkem Maße von Sorptionsprozessen überlagert ist. Das zeigen sowohl die starke Abnahme der HCH-Konzentration

Abfallbeseitigung im Sinne der TA-Siedlungsabfall:

§ 3.2. Vermeidung und Verwertung

Die Abfallvermeidung hat nach Maßgabe des § 1a AbfG Vorrang vor der Abfallverwertung, die Verwertung Vorrang vor der sonstigen Entsorgung

Die entsorgungspflichtigen Körperschaften haben darauf hinzuwirken, daß möglichst wenig Abfall verwertet werden muß. Sie sollen durch entsprechende Ausgestaltung ihrer Satzungen nachhaltige Anreize zur Vermeidung und Verwertung für die Abfallerzeuger schaffen.

§ 3.3. Vorbildfunktion der öffentlichen Hand

Die öffentliche Hand soll vorbildhaft dazu beitragen, daß das Ziel dieser Technischen Anleitung erreicht wird.

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bereits nach 0,5 Stunden Versuchsdauer als auch die ermittelten HCH-Gehalte der Biomasse (Abb. 4), die die zeitliche Überlagerung von Sorption und biologischem Abbau dokumentieren. Sichtbar wird, daß die gemessene HCH-Eliminierung aus der Flüssigphase nicht auf eine Bioakkumulation zurückzuführen ist. Dies trifft in analoger

Weise auch für die aeroben Versuche zu. Nicht zu vernachlässigen ist außerdem eine HCH-Adsorption an der Glaswandung der Reaktoren, die besonders beim β -HCH ausgeprägt ist. Hierüber gaben die durchgeführten Blindversuche (ohne Inoculum) eindeutig Aufschluß. Diese aufgeführten zusätzlichen Eliminationsprozesse für das HCH in wäßriger Lösung

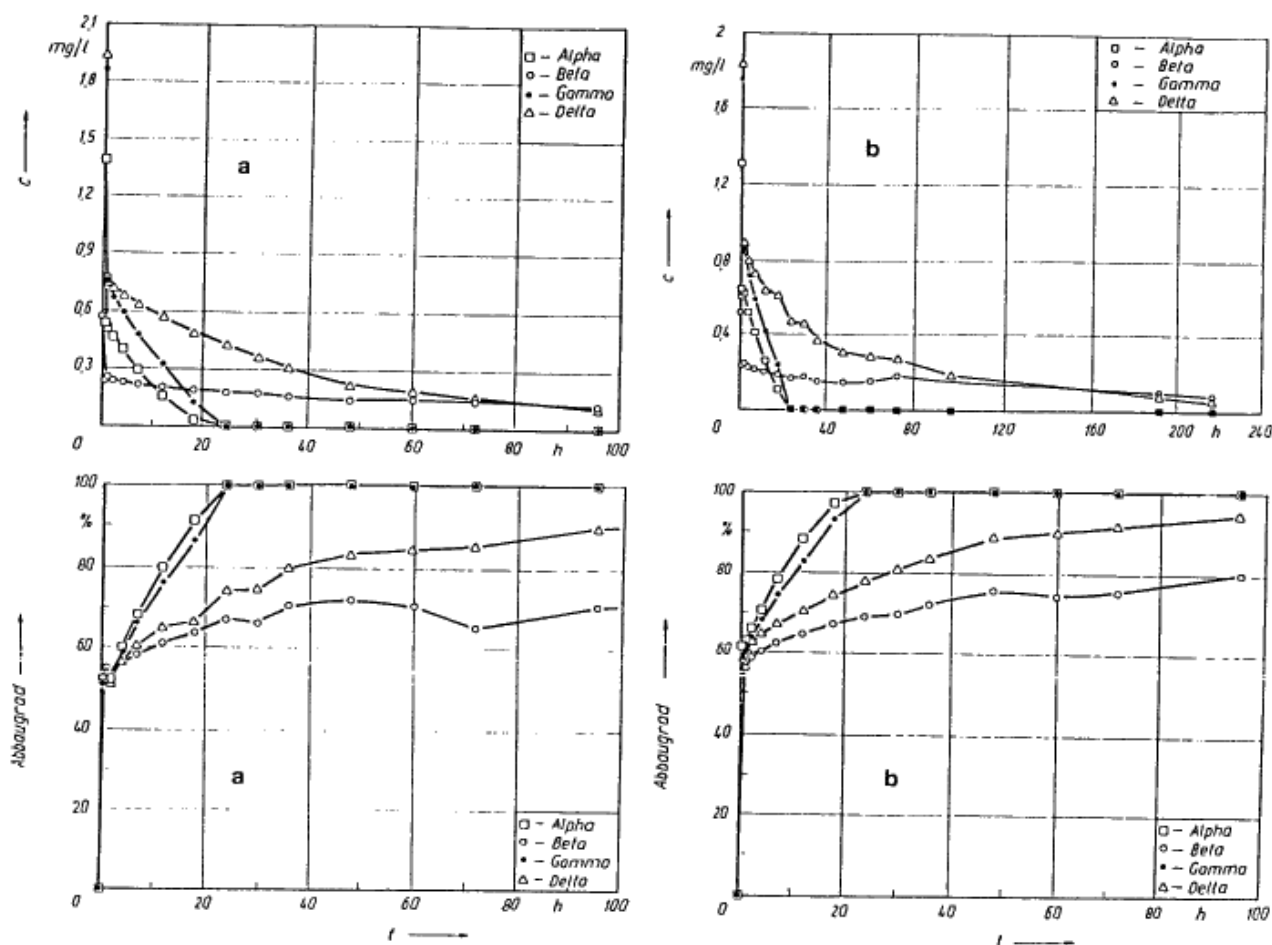


Abb. 2: HCH-Abbau bei unterschiedlichen Bedingungen (Versuch B 1); a = aerob, b = anaerob

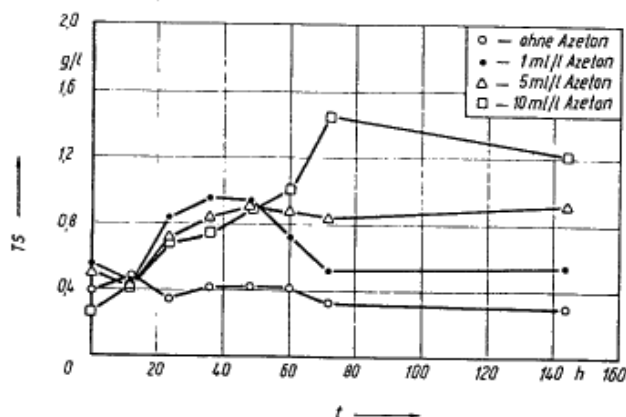


Abb. 3: Wachstum der Mischpopulation in Abhängigkeit von der Azetonkonzentration (aerob, Versuchsreihe B 3)

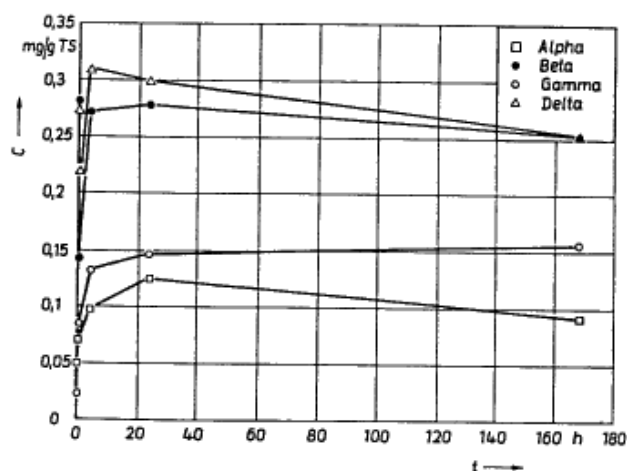


Abb. 4: Isomerenspezifische HCH-Gehalte der Biomasse in Abhängigkeit von der Versuchsdauer (anaerob, Versuchsreihe B 41)

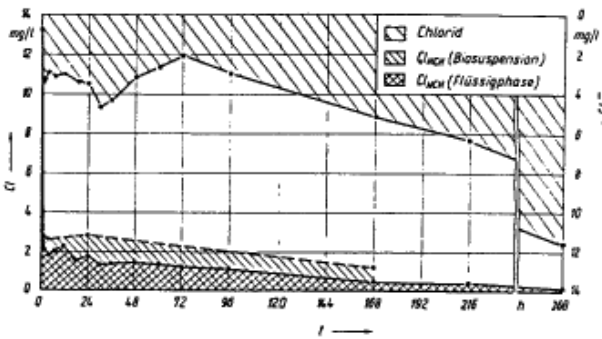


Abb. 5: Chlorbilanz (anaerob, Versuchsreihe B 41)

sollen jedoch nicht darüber hinwegtäuschen, daß die primäre Elimination durch den biologischen Abbau erfolgt.

Letztendlich belegen die aufgestellten Chlorbilanzen der Versuche mit Inoculum (B 41) eine weitgehende Dechlorierung des HCH infolge der Verstoffwechselung (Abb. 5). So ist u. a. eindeutig festzustellen, daß die Abnahme der HCH-Konzentrationen in der wäßrigen Phase und in der Biomasse mit der Zunahme von freiem Chlorid in der Flüssigphase korrespondiert. Offensichtlich kommen hier die Vorteile von Mischpopulationen im Vergleich zu Reinkulturen zum Tragen. Dadurch wird gewährleistet, daß die Abbauprozesse nicht frühzeitig zum Erliegen kommen und keine Anreicherung niedriger chlorierter Metaboliten im System stattfindet. Die aufeinander abgestimmten Mikroorganismen greifen demzufolge parallel zueinander alle im System auftretenden Chlorierungsstufen gleichzeitig an. Diese Beobachtung steht in sehr guter Übereinstimmung mit den Ergebnissen, die in [28] bei Untersuchungen zum mikrobiellen Abbau von polychlorierten Dibenzodioxinen und polychlorierten Dibenzofuranen in kontaminierten Böden erhalten wurden.

5. Einfluß von Ozonbehandlungen

Aus Abb. 6 wird ersichtlich, daß eine Behandlung von mit HCH kontaminierten Wässern mittels Ozon einen deutlichen, jedoch nicht vollständigen Abbau aller HCH-Isomeren in kürzester Zeit bewirkt. Erwartungsgemäß kristallisieren sich

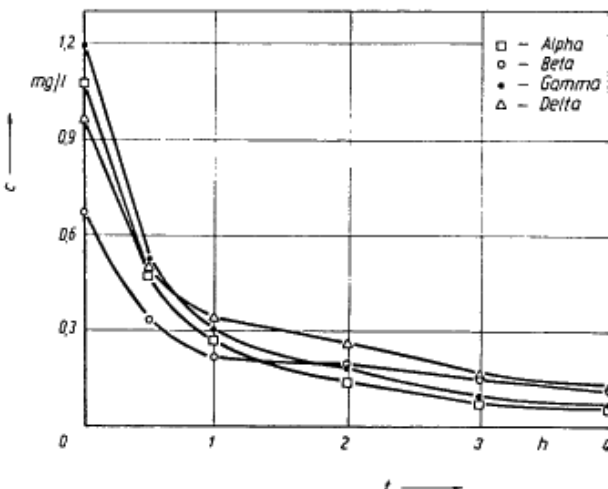


Abb. 6: HCH-Elimination durch Ozonbehandlung (Versuchsreihe B 51)

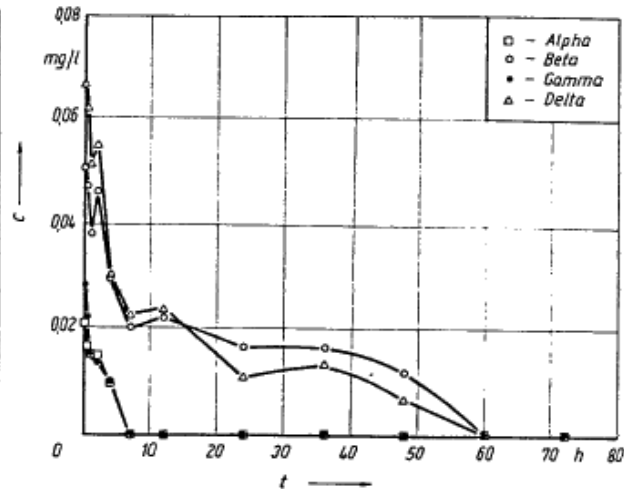


Abb. 7: Anaerober biologischer HCH-Abbau nach Vorbehandlung mit Ozon (Versuchsreihe B 61)

auch hierbei β - und δ -HCH als Problemkomponenten heraus. Eine Ozonbehandlung über den Zeitraum von 4 Stunden hinaus erscheint als wenig sinnvoll, da keine wesentlichen Konzentrationssenkungen mehr zu erwarten sind. Durch die Behandlung mit Ozon wird das zu eliminierende HCH weitestgehend dechloriert (ca. zu 85 %). Beobachtungen jedoch lassen vermuten, daß dieser Eliminierungsprozeß teilweise reversibel zu sein scheint, da insbesondere beim Versuch B 62 über einen Zeitraum von 3 Tagen nach der Ozonbehandlung eine leichte Zunahme der HCH-Konzentration bei deutlicher Abnahme des Chloridgehaltes in der Probe auftrat.

Führt man das mit Ozon behandelte HCH-haltige Wasser anschließend einer weiteren biologischen Behandlung zu, so ergibt sich insbesondere unter anaeroben Bedingungen ein Totalabbau aller HCH-Komponenten (Abb. 7). Die Gesamtabbauzeit (Ozonbehandlung + anaerober biologischer Abbau) liegt dabei mit $t \approx 4$ Stunden + 60 Stunden = 64 Stunden wesentlich niedriger als bei alleiniger biologischer Behandlung, die außerdem bei β + δ -HCH keinen vollständigen Abbau garantiert (vgl. Abb. 2). Diese Verfahrenskombination ist damit für β + δ -HCH eine echte Alternative zu anderen verfahrenstechnischen Grundoperationen.

6. HCH-Abbau im kontinuierlichen Langzeitversuch

Die Ergebnisse der über einen Zeitraum von mehr als 68 Wochen kontinuierlich durchgeführten Abbauprozesse zeigen, daß die adaptierten Mischkulturen unter aeroben und anaeroben Bedingungen in der Lage sind, sowohl α - und γ -HCH als auch die als hochgradig persistent geltenden β - und δ -Isomeren zu metabolisieren. Ein Verlust der Stoffwechselaktivitäten bezüglich der Metabolisierung von HCH und dessen Spaltprodukten konnte auch unter Einsatz von Azeton als Co-Substrat in Konzentrationen von bis 0,1 ml/l über den gesamten Versuchszeitraum nicht festgestellt werden.

In den Abbildungen 8 und 9 sind die Häufigkeitssummen der HCH-Isomerenkonzentrationen für die Zu- und Abläufe unter anaeroben Milieubedingungen bei mittleren Substratverweilzeiten von $t = 1,5$ d dargestellt. Es wird deutlich, daß im anaeroben Milieu auch der Abbau von β - und δ -HCH auf vertretbare Restkonzentrationen erfolgt. Darüber hinaus

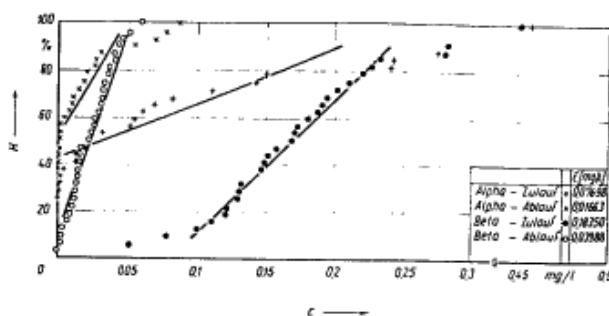


Abb. 8: Häufigkeitssumme der α - und β -HCH-Konzentrationen von Zu- und Abläufen bei den kontinuierlichen Langzeitversuchen (Versuchsreihe K 1, anaerob, Versuchsdauer: 68 Wochen)

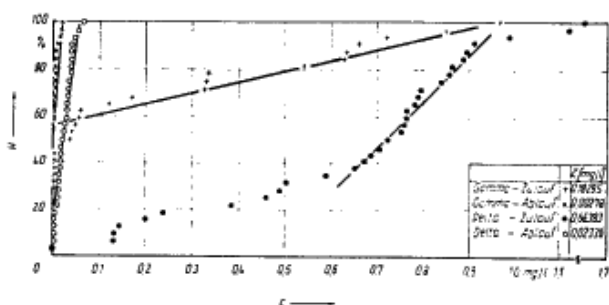


Abb. 9: Häufigkeitssumme der γ - und δ -HCH-Konzentrationen von Zu- und Abläufen bei den kontinuierlichen Langzeitversuchen (Versuchsreihe K 1, anaerob, Versuchsdauer: 68 Wochen)

bestätigen die Analyseergebnisse für den anaeroben Versuchsbetrieb wesentlich höhere Dechlorierungsgrade als unter aeroben Bedingungen. Insbesondere aus Abb. 9 geht hervor, daß selbst bei stark schwankenden Zulaufkonzentrationen (flach geneigte Kurve der Häufigkeitsverteilung) eine sehr stabile Ablaufkonzentration aller Komponenten eingehalten werden kann, d. h., daß das System eine gute Flexibilität gegenüber Zulaufschwankungen besitzt.

Eine weitere Senkung der Ablaufkonzentrationen ist durch eine Verminderung der Schlammbelastung (bei $t \approx 4$ d) möglich. Die damit verbundene Vergrößerung der Reaktorabmessungen erhöht dann natürlich die Behandlungskosten. Hier ist abzuwägen, ob nicht eine Vorbehandlung, z. B. durch Ozon, sinnvoller wäre.

Durchgeführte Toxizitätstests (Tab. 2) belegen eindrucksvoll die starke Abnahme der Giftigkeit der biologisch behandelten Wässer im Vergleich zu deren Ausgangszustand bei Verwendung von fünf Standardtests. Offensichtlich findet vor allem im anaeroben Milieu ein nahezu vollständiger mikrobieller Abbau der Chlororganika statt, so daß eine ökotoxikologische Unbedenklichkeit des Ablaufes der Anaerobstufe vorliegt, aber auch der Ablauf der Aerobstufe liefert unter praktischen Aspekten sehr brauchbare Werte mit z. B. einer Fischtoxizität von $G_F = 2$. Erinnert werden darf in diesem Zusammenhang daran, daß z. B. das Abwasserabgabengesetz den Schwellenwert für den Wegfall der Abgabe bezüglich Fischgiftigkeit mit $G_F = 2$ festlegt.

Der kontinuierliche Abbau von HCH war erwartungsgemäß nicht durch eine quantifizierbare Produktion von Überschußschlamm gekennzeichnet. Biomasseverluste (durch Absterben bzw. Ausschweben) werden durch die stattfindende

Probe/Parameter	Goldorffentest	Daphnientest	Paramecien-test	Leuchtbakterientest	Keimungstest
Zulauf					
GC	1 + 6	1 + 59	1 + 1		1 + 99
SC	1 + 5	1 + 49			1 + 49
LC	1 + 0	1 + 0	n.n.		n.n.
G	$G_F = 7$	$G_D = 60$		$G_L = 2$	
Ablauf, aerob					
GC	1 + 1	1 + 0	1 + 1		1 + 0
SC	< 1 + 1				
LC	1 + 0	n.n.	n.n.		n.n.
G	$G_F = 2$	$G_D = 1$		$G_L = 1$	

Probe/Parameter	Goldorffentest	Daphnientest	Paramecien-test	Leuchtbakterientest	Keimungstest
Ablauf, anaerob					
GC	1 + 0	1 + 0	1 + 1		1 + 0
SC					
LC	n.n.	n.n.	n.n.		n.n.
G	$G_F = 1$	$G_D = 1$		$G_L = 1$	

Tabelle 2: Toxikologische Untersuchungen, Versuchsreihe K 4

geringe Biomasseproduktion ausgeglichen. Dies muß bei der Konzipierung einer großtechnischen Anlage, vor allem bei der Reaktorgestaltung, berücksichtigt werden. Entsprechende technische Lösungen liegen aber bereits vor.

Die Zugabe von Azeton als Co-Substrat wirkt stabilisierend auf den Anlagenbetrieb bei Verminderung der HCH-Schlammbelastung infolge höherer TS-Konzentrationen im Reaktor.

Unter den realisierten aeroben bzw. anaeroben Bedingungen war die Entwicklung differenzierter Bioschlämme festzustellen. Im aeroben Fall bildeten sich kleine und kompakte Flocken, während die Flocken des Anaerobschlammes groß und diffus wirkten. Beide Schlämme sind durch das Auftreten von Mikroorganismen in relativ großer Artenvielfalt (vorwiegend CILIATEN, FLAGELLATEN und RHIZOPODEN) bei geringen Individuenzahlen gekennzeichnet. Im mikroskopischen Bild stellen sich einige Einzeller teilweise in enzystrierter Form dar.

Insbesondere in den lichtreichen Sommermonaten konnte eine intensive Grünfärbung der anaeroben Kulturbrühe durch Anwesenheit von Mikroalgen der Gattung CHLORELLA festgestellt werden. Die Reaktorzuläufe blieben jedoch über den gesamten Versuchszeitraum algenfrei (langfristige Algtoxizität bei HCH-Konzentration $C_{HCH} \approx 10$ mg/l).

7. Zusammenfassung und Ausblick

Der biologische Abbau persistenter zyklischer Chlororganika wie z. B. der β - und δ -Isomeren des HCH gelingt mit Mikroorganismenkulturen, die durch aerobes oder anaerobes Kultivieren in einem Mineralmedium, welches selbige Substanzen als einzige Kohlenstoffquelle beinhaltet, erhalten werden. Als Ausgangsmaterial zur Anreicherung der Mikroorganismen dienen vorteilhafter Weise Proben von natürlichen Standorten, die bereits jene schwer abbaubaren Substanzen enthalten. Es konnte gezeigt werden, daß ein derartiges Adaptionsverfahren reproduzierbar ist. Damit wird eine wesentliche Voraussetzung für die praktische Umsetzung der Versuchsergebnisse erfüllt.

Es konnte nachgewiesen werden, daß derartige Mischkulturen in der Lage sind, alle relevanten HCH-Isomeren sowohl unter aeroben als auch unter anaeroben Bedingungen abzubauen. Für die Metabolisierung von β - und δ -HCH ist ein anaerobes Milieu zu favorisieren, da hierbei die weitreichendste mikrobielle Mineralisierung von HCH erfolgt. Bei mittleren Verweilzeiten des Modellwassers (gesättigte wäßrige HCH-Lösung) von im Durchschnitt 1,5 Tagen konnten im kontinuierlichen anaeroben Betrieb für β - und δ -HCH mittlere Ablaufkonzentrationen von 0,039 bzw. 0,023 mg/l HCH erreicht werden.

Die Biomasseproduktion ist als äußerst gering einzuschätzen. Ein Co-Substrat (z. B. Azeton) in geringen Konzentrationen stabilisiert den Prozeß durch eine höhere Biomassebildung, hemmt jedoch den HCH-Abbau teilweise. Das bedeutet für den praktischen Betrieb möglicherweise einen zyklischen Wechsel der Zugabe von Co-Substrat und Substrat, um höhere Raum-Zeit-Ausbeuten zu bekommen.

Anderenfalls könnte den geringen Biomassewachstumsraten auch durch eine Immobilisierung der Mikroorganismen an Sand, Aktivkohle oder andere Träger (z. B. Kunststoffpakungen) Rechnung getragen werden. Hier würde sich ein vertikal durchströmter Festbettreaktor anbieten.

Denkbar wäre aber auch ein Kaskadenbetrieb im Submersverfahren, wobei die beiden biologischen Stufen durch eine Membranrennung gekoppelt sind. Infolge Aufkonzentrierung des Rest-HCH ließen sich in der nachgeschalteten biologischen Stufe höhere Umsätze erzielen, da vor allem die Abbaugeschwindigkeiten von β - und δ -HCH von der Konzentration dieser Isomeren abhängen.

Als eine weitere Möglichkeit der Verbesserung der Ablaufqualität bietet sich die Kopplung von Ozonung und anaerober biologischer Behandlung an. Die Eliminierung von HCH durch alleinige Ozonbehandlung erweist sich wegen des hohen Ozonverbrauchs als unökonomisch.

In zukünftig durchzuführenden Arbeiten ist nun vor allem zu klären, inwieweit die vorliegenden, an Modellwässern erzielten Ergebnisse, auf z. B. die biologische Behandlung HCH-kontaminierter Sicker- oder Bodenwaschwässer mit unterschiedlichen Relationen der HCH-Isomeren übertragbar sind.

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**Wet (classification/flotation) and thermal (desorption)
treatment of hch, drins and dioxin/furan-containing
soils - operational experience in the Netherlands**

Mr. Ton Honders
The Netherlands



WET (CLASSIFICATION/FLOTATION) AND THERMAL (DESORPTION) TREATMENT OF HCH, DRINS AND DIOXIN/FURAN-CONTAINING SOILS - OPERATIONAL EXPERIENCE IN THE NETHERLANDS

*Presented by: Dr. A. Honders
Centre for Soil Treatment (SCG), The Netherlands*

ABSTRACT

The performance characteristics of wet (classification/flotation) and thermal (desorption) processes for the treatment of soils contaminated with halogenated organics, and HCH in particular, were tested on a full operational scale. Wet treatment of HCH-contaminated soil yields HCH removal efficiencies in excess of 99 %. However, HCH concentrations below or near the reuse standard (100 $\mu\text{g/kg dw}$ total HCH) could not be consistently achieved. Thermal treatment of chlorinated hydrocarbons (HCH), pesticides (drins) and dioxin/furan-containing soils yields a product soil with virtually unlimited reuse options.

1 INTRODUCTION

The origin and presence of sites contaminated with HCH and other halogenated organics in The Netherlands; and the performance of a variety of bench and pilot scale treatment techniques has been extensively discussed in previous papers [1-3]. This paper deals with the performance aspects of full scale operational technologies. The performance characteristics of wet (classification/flotation) and thermal (desorption) treatment of HCH-containing soils are assessed.

2 BACKGROUND

2.1 Treatment technologies in The Netherlands

In The Netherlands, the following technologies are operational for the treatment of contaminated soils:

- 1) Wet (classification/flotation) treatment. General features:
 - * Suitable for soils which are contaminated with both heavy metals and organics, and cocktails thereof.
 - * Maximum amount of disposable residue (organic matter, < 63 μm fraction) < 20 %. This effectively limits the use of this technology to "sandy" soils.
 - * Operational costs = ca. 50 Fl/ton (= ca. 30 US \$/ton).
-

- * Residue disposal = ca. 150 Fl/ton (= ca. 90 US \$/ton).
- * Total treatment capacity = ca. 400 kton/yr over 6 plants.

2) Thermal (desorption) treatment. General features:

- * Suitable for soils which are mainly contaminated with organics.
- * Regulatory and technical limitations to treat soils contaminated with halogenated organics. Input tolerances are typically in the order of 8 mg/kg dw for total extractable organic halogens.
- * Non-volatile metals below reuse standards (in general 5 times the Dutch A-values).
- * Water content < 40 % (m/m).
- * Organic matter content < 30 % (m/m).
- * Operational costs = 75 - 100 Fl/ton (= 45 - 60 US \$/ton).
- * Total treatment capacity = ca. 600 kton/yr over 5 plants.

3) Biological technologies, which are abundantly operational, are not discussed within the context of this paper, because these technologies, at present, appear to offer little scope for large-scale treatment of soils contaminated with halogenated organics.

2.2 Centre for soil treatment (SCG)

The centre for soil treatment (in Dutch = Service Centrum Grondreiniging = SCG) handles the bulk of the soil decontamination processes financed with public (state, province, city) money. It assesses the treatability of soils, subcontracts the treatment process and warrants the proper reuse of the product soil. Some (approximate) basic figures are:

- * Soil assessment = 4 Mton/yr.
- * Soil treatment = 400 kton/yr.
- * Soil storage capacity = 750 kton.
- * Turnover = 60 M Fl/yr = 35 M US \$/yr.

The SCG is, within the context of its operational and regulatory duties, seeking for options to treat a lot of 250 kton of HCH-contaminated soil to a (tentatively) set reuse standard of 100 µg/kg dw for total HCH. It hereby focusses on proven operational technologies.

In the 1993 - 1994 period, several treatment trials were conducted in both wet and thermal plants. Some typical results are reported here. Technical details of the processes employed are withheld for confidentiality reasons.



3 TECHNICAL PERFORMANCE OF WET AND THERMAL TREATMENT PROCESSES

3.1 Classification/flotation of HCH-containing soil

The results described in this section are derived from a report by "Jaartsveld Groen en Milieu" [4]. A conceptualised process flow scheme of the wet plant is shown in Figure 1.

The following process steps can be distinguished:

- * Deagglomeration of sand agglomerates in a sol-clay washer.
- * Coarse sieving of +4 mm material.
- * Hydrocyclone classification in + and -25 μm fractions.
- * Dewatering and disposal of the -25 μm slimes.
- * Attrition of the 25 - 4000 μm slurry.
- * Slurry conditioning and froth flotation.
- * Hydrocyclone and sieve dewatering of the treated sand fraction.
- * Process water recycle.
- * If necessary, sand recycle for a polishing flotation.

In 1993, approximately 10.000 tons of sandy HCH-containing soil (project "Heideweg") were treated in the wet plant described above. Throughputs were in the order of 25 ton/h.

Process efficiencies fluctuated significantly. The maximum attainable HCH removal efficiencies are given in Table I. In the first process run the larger part of fully liberated HCH particles and the easier part of HCH associated with (e.g. adsorbed) organic matter and mineral particles are removed from the soil. Subsequent process runs (i.e. sand recycle) result in a polishing treatment with the efficiency effectively approaching zero after three runs. From these observations it is tentatively concluded that the efficiency of flotation treatment depends largely on the chemical and physical interaction of HCH with the soil matrix.

Fully liberated HCH can be easily removed, while HCH included in, for example, cracks or small pores in the mineral matrix (e.g. in the added lime particles) is not available for flotation. This latter hypothesis could not be unambiguously proven by Electronprobe Micro-analysis.

The HCH concentration in the input soil varied between 5 and 220 mg/kg dw. The product soil contained 100 - 1500 $\mu\text{g/kg}$ dw of HCH. Although attainable, HCH concentrations of 100 $\mu\text{g/kg}$ dw could not be consistently achieved.



3.2 Thermal treatment of HCH, drins and dioxin/furan-containing soils

The results described in this section are derived from a report by "Eco-technik" [5]. A conceptualised process flow scheme of the thermal treatment plant is shown in Figure 2.

The following process steps can be distinguished:

- * Coarse sieving.
- * "Indirect" heating of the soil by hot fluegas up to a temperature of 300 °C, and direct heating by the gas-fired burner up to a maximum temperature of 600 °C.
- * Direct water cooling of the treated soil to 75 - 90 °C.
- * Dust removal, and recycle, by multicyclones.
- * Organics destruction in an afterburner.
- * Heat recovery.
- * Additional dust removal by bagfilters.
- * Removal of acid components (e.g. HCl, SO₂) and organic components (e.g. dioxins, furans) from the fluegas by, respectively, lime and carbon adsorption.
- * Wet scrubbing.
- * Flue gas emission via chimney.

In 1993, 3000 tons drins-containing, 1200 tons HCH-containing and 800 tons dioxin/furan-containing soils were treated in the thermal treatment plant described above. Throughputs were in the order of 25 ton/h.

The treatment results for the soils are gathered in Tables II to IV. From these Tables it is concluded that drins and HCH are removed below the detection limit for chemical analysis. The concentration of dioxins and furans in the three product soils is minimal, and warrants a virtually unlimited (re)use, according to the German exposure limits [6].

The fluegas stream was sampled at five points in the process, and analyzed for dioxins/furans according to national and international guidelines and procedures [7,8]. The results for dioxin/furan stack emissions are given in Table V. The results demonstrate that consistently low levels, below the 0.1 ng TEQ/m³ regulatory limit, of dioxin/furan stack emissions are attainable, except for the HCH 1 run. No consistent correlation between afterburner temperature and dioxin/furan emissions levels was observed.



4 CONCLUSIONS

Wet treatment of HCH-contaminated soil yields HCH removal efficiencies in excess of 99 %. However, HCH concentrations below or near the reuse standard can not be consistently achieved. Thermal treatment of HCH, dioxins and dioxin/furan-containing soils yields a product soil which virtually unlimited reuse options. Full application of thermal treatment to soils contaminated with halogenated organics depends on proper licensing, mainly with respect to dioxin/furan stack emissions, by the regulatory authorities.

ACKNOWLEDGEMENTS

Jaartsveld Groen en Milieu and Ecotechniek are greatly acknowledged for their contributions to this paper.

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-



Wet (classification/flotation) and thermal (desorption) treatment of HCH

TABLE I

Maximum attainable HCH removal efficiencies for froth flotation.

Process run	HCH input, $\mu\text{g/kg dw}$ (*)	HCH output, $\mu\text{g/kg dw}$ (*)	Eff. per run, %	Total eff, %
1	69000	690	99	99.00
2	690	449	35	99.35
3	450	400	11	99.46

(*) = Sum of the 5 HCH isomers.

TABLE II

Treatment results for soil contaminated with drins.

Afterburner temperature	1200 °C		1050 °C	
Soil	Untreated	Treated	Untreated	Treated
Concentration	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Aldrin	53	< 0.1	70	< 0.1
Dieldrin	36	< 0.1	82	< 0.1
Endrin	240	< 0.1	320	< 0.1
Telodrin	15	< 0.2	24	< 0.2
Endrinaldehyde	74	< 0.2	510	< 0.2
Concentration	ng TEQ/kg dw	ng TEQ/kg dw	ng TEQ/kg dw	ng TEQ/kg dw
PCDD/F (*)	20	< 6 (**)	15	< 0.6 (**)

(*) = PCDD represents dioxins, PCDF represents furans. Analyses are given for the "dirty seventeen".

(**) = Summation over the detection limits of dioxin and furan isomers.



Wet (classification/flotation) and thermal (desorption) treatment of HCH

TABLE III

Treatment results for HCH-contaminated soil.

Afterburner temperature	1200 °C		1050 °C	
Soil	Untreated	Treated	Untreated	Treated
Concentration	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
alfa-HCH	2300	< 0.1	320	< 0.1
beta-HCH	550	< 0.1	190	< 0.1
gamma-HCH	< 1	< 0.1	6.3	< 0.1
delta-HCH	15	< 0.1	4.1	< 0.1
Total EOX (*)	2872	(**)	522	(**)
Concentration	ng TEQ/kg dw	ng TEQ/kg dw	ng TEQ/kg dw	ng TEQ/kg dw
PCDD/F (***)	1742	33	3284	28

(*) = EOX represents total extractable halogenated organics.

(**) = Below detection limit.

(***) = PCDD represents dioxins, PCDF represents furans.
Analyses are given for the "dirty seventeen".

TABLE IV

Treatment results for (gravel-type) soil contaminated with dioxins (PCDD) and furans (PCDF).

Afterburner temperature	1200 °C	
Soil	Untreated	Treated
Concentration	mg/kg dw	mg/kg dw
HCB (*)	5.2	< 0.05
EOX (**)	5.4	(***)
Concentration	ng TEQ/kg dw	ng TEQ/kg dw
Dioxins/furans	30280	60

(*) = HCB represents hexachlorobenzene.

(**) = EOX represents total extractable halogenated organics.

(***) = Below detection limit.

Dioxin and furan analyses are given for the "dirty seventeen".



Wet (classification/flotation) and thermal (desorption) treatment of HCH

TABLE V

Dioxin and furan stack emissions.

Run	Afterburner temperature, °C	PCDD/F emissions at 11 % O ₂ , ng TEQ/m ³
Drins 1	1200	0.04
Drins 2	1050	0.05
HCH 1	1200	0.35
HCH 2	1050	0.01
PCDD/F	1200	0.01

Dioxin and furan analyses are given for the "dirty seventeen".



FIGURE CAPTIONS

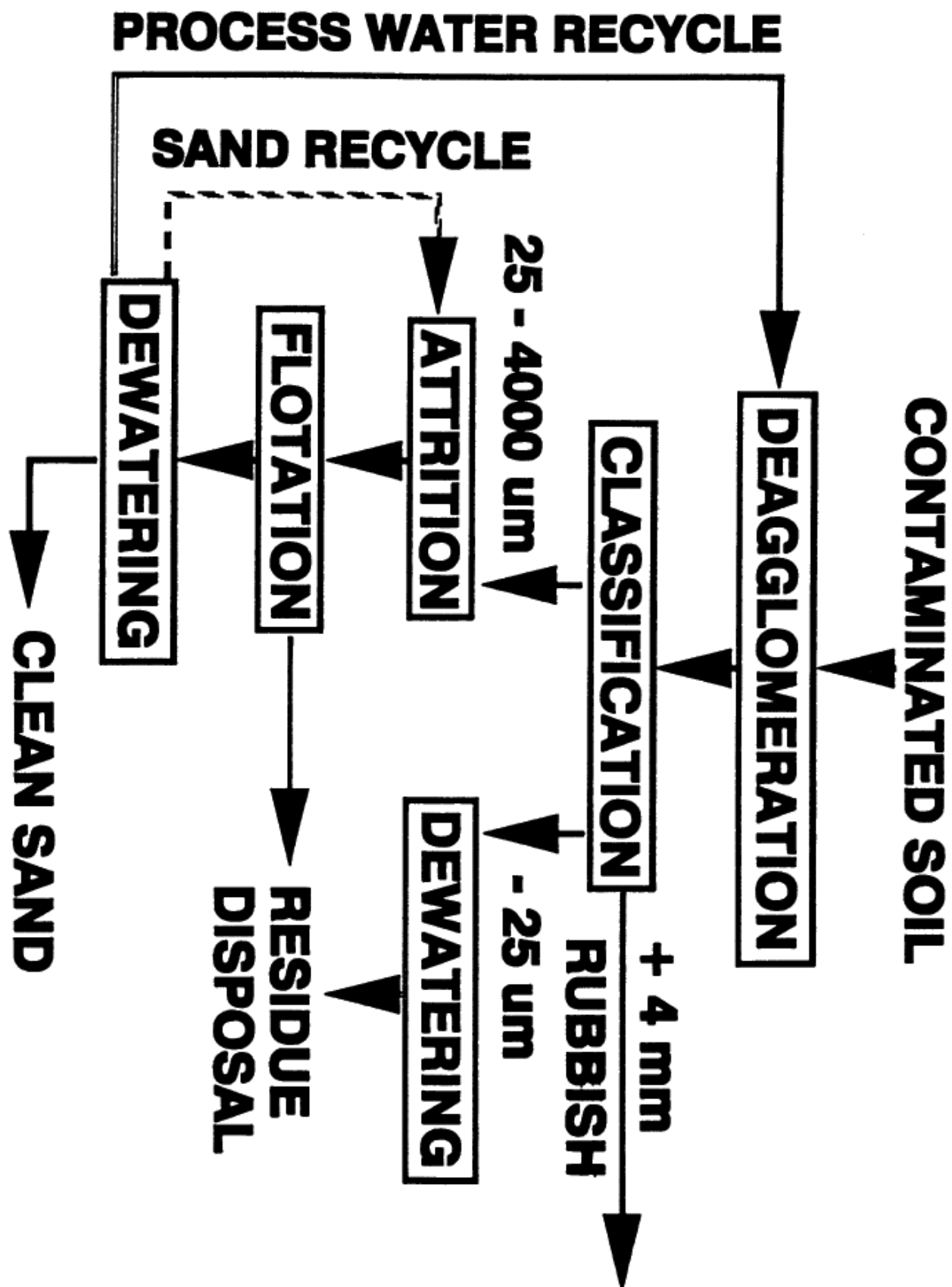
FIGURE 1

Conceptualised process flow scheme of a wet treatment plant
(Jaartsveld Groen en Milieu).

FIGURE 2

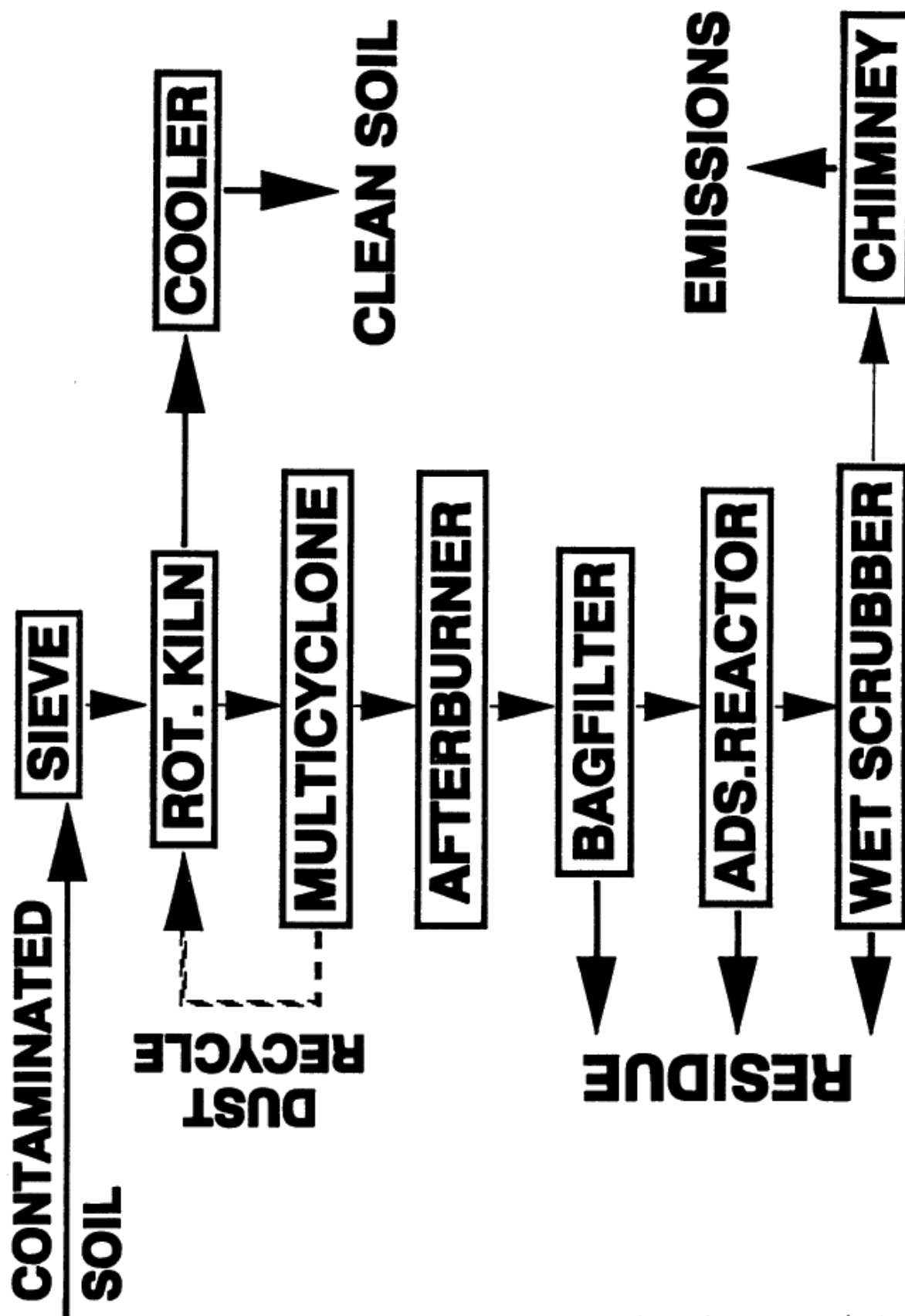
Conceptualised process flow scheme of a thermal treatment plant
(Ecotechniek).

FIGURE 1



Conceptualised process flow scheme of a wet treatment plant
(Jaartsveld Groen en Milieu).

FIGURE 2



Conceptualised process flow scheme of a thermal treatment plant

**Effect of desorption, temperature and soil
moisture content on the aerobic
bioconversion of α - and β -HCH in soil**

Mr. Huub Rijnaarts
The Netherlands

**Effect of temperature on mass-transfer and microbial activity
controlling the aerobic biomineralization of
 α - and β -hexachlorocyclohexane in soil.**

*Huib H. M. Rijnaarts, The TNO Institute of Environmental Sciences, Department
of Environmental Biotechnology, P.o. Box 6011, 2600 JA, Delft,
The Netherlands.*

A laboratory study was performed to investigate the effect of temperature on the aerobic biomineralization of α -hexachlorocyclohexane (α -HCH) in suspensions and water-unsaturated layers made from a calcareous waste site soil containing (240 ± 50) mg α -HCH and (220 ± 20) mg β -HCH per kg dry soil. Alpha-HCH mineralization was complete in suspensions but incomplete in the unsaturated system after 100 days of incubation at all temperatures tested (10°C, 15°C, 20°C, and 30°C). Upon decreasing the temperature from 30°C to 10°C, the first order rate constants for α -HCH biomineralization decreased by a factor of 10 for the suspensions and by a factor of 1.6 for the unsaturated soil layers. Alpha-HCH desorption tests indicated that the bioconversion rate in suspension is limited by intra-aggregate diffusion at temperatures between 30°C and 20°C and by microbial activity at temperatures lower than 10 °C. Mixed-slurry treatment appears to be a suitable technique to bioremediate α -HCH contaminated soil and can further be optimized by choosing appropriate temperatures and by taking measures to enhance intra-aggregate mass-transfer. In the unsaturated system, the residual α -HCH concentration after 100 days (expressed as the percentage of the initial α -HCH concentration) increased with decreasing temperature from 20% at 30°C to 68% at 10°C. Even at the highest temperature, mass-transfer processes are that slow that biomineralization already stops at high contamination levels. Hence, land-farming water-unsaturated soil is not a suitable method to bioremediate α -HCH contaminated soil. In all experiments, β -HCH completely resisted bioconversion. This persistence appears to be the primary bottle-neck for HCH-contaminated soil remediation and the solution of this problem should therefore be addressed in future research.

APPENDIX OF WRITTEN CONTRIBUTION

Water resources pollution with halogenated pesticides in Romania

Mrs. Marioara Ionescu
Romania

WATER RESOURCES POLLUTION WITH HALOGENATED PESTICIDES IN ROMANIA.

*From: Mrs. Marioara Ionescu,
Environmental Engineering Research Institute, Bucharest, Romania*

The use of synthetic chemicals has spread widely and has penetrated deeply into almost any human activity. This has created an unprecedented threat to the environment in general and to the very human life in particular. Among these synthetic chemicals the pesticides, and the insecticides in particular, which have been purposely created as toxic chemicals to be harmful to life in its natural environment, pose a high risk and raise a special concern. They are widely spread, in large quantities, over vast areas in agricultural use.

One of the most serious effects of this scattered use of toxic chemicals is the wide contamination of soil and water resources. Risk assessment should be used in any attempt at controlling and containing this pollution process, or at taking action to prevent its undesirable consequences, and this requires the knowledge of the actual dimensions and of the dynamics of contamination. The pesticide pollution problem, i.e. the contamination of soil and water resources, is therefore not confined to some limited areas in the vicinity of production and/or storage sites, but has already become an issue of global pollution with far reaching consequences.

The data presented in this paper shows concisely the dimension and the dynamics of water resources pollution with HCH and DDT, two of the most widely used insecticides. Given their persistence in the environment (although the use of DDT has been formally prohibited for years, its presence is still very high) associated with their high toxicity, these two compounds have raised special concern in the assessment of environmental pollution, and in particular that of water resources pollution.

Fig. 1 shows a hydrographical map of Romania with its main rivers. In Fig. 2 it is shown the dynamics of the use of pesticides (total pesticides and specifically the insecticides) over a period of 10 years. The use of pesticides in agriculture (including horticulture) accounts for most of the quantities shown. Figures 3 and 4 show the concentrations of HCH and that of the total (HCH+DDT), respectively, for the period from 1984 to 1993, in the main river courses. Values shown are the annual mean concentrations, averaged for the respective river basin or in the section with the highest concentration.

Water resources pollution with halogenated pesticides in Romania.

A first remark is that concentrations of the two compounds are higher in the southern and eastern regions; this can be related to the fact that these are the main agricultural areas. A second remark is that, although the variation of concentrations resembles the dynamics of the insecticide use, the concentrations in surface waters are also influenced by the hydrological regime (1990 was an excessively dry year).

A series of deficiencies in handling, storage and use of pesticides are factors that favor the environment pollution with these toxic chemicals. Thus it is observed that:

- (i) in spite of technical prescriptions and recommendations, pesticides continue to be used inadequately, in quantities larger than the recommended or needed doses;
- (ii) supervision and monitoring is inadequate and inefficient for all activities in the storage, handling and application processes;
- (iii) lack of proper equipment and of trained personnel for correct application of pesticides (proper timing and targeted spreading); incorrect applications are less effective and lead to repeated treatments, often with increased dosages. Although these deficiencies are well known, few improvements and little progress are observed.

Another issue of prime interest in the study of water resources pollution with pesticides, as well as in the associated risk assessment, is the bio-accumulation process. The halogenated pesticides, like other toxic pollutants existing in the aquatic environment, have a comparatively high bio-accumulation rate.

Studies carried out for the conditions of aquatic environment in the Danube Delta have shown that DDT has concentrated, as compared to its level in the river water, at the following rates: 200 times on sediments, 800 times in plankton and 3000 times in fish. Similar and more recent studies concerning bio-accumulation of HCH, carried out for the conditions of an impounding reservoir on the river Olt (which happens to be in the vicinity of a chemical plant for HCH synthesis) have shown similar results: from HCH concentrations, in the reservoir water, of few $\mu\text{g/l}$ much higher concentrations were found in the aquatic organisms (700 times in plankton and 3000 times in fish).

Studies have also shown that bioaccumulation occurs at a higher rate for aquatic organisms as compared to other organism in soil and plants. This points out the significance of this bioaccumulation process for the aquatic environment.

Water resources pollution with halogenated pesticides in Romania.

The combined process of concentration and transfer of toxic pollutants along the trophic chains and its end result, the bioaccumulation in the ecological pyramids (at the higher levels), suggests two remarks of significant practical interest:

- the human being, who according to its diet is a supper-predator, is threatened to take in, with food stuff, much higher quantities of toxic chemicals otherwise dispersed at low concentrations in the environment;
- the current practice of preventing the harmful effects of certain toxic pollutants through their dilution, down to small concentrations (bellow the "admissible" limits), should raise doubts that this can be a wise long-term strategy in pollution control, particularly for the case of persistent pollutants.

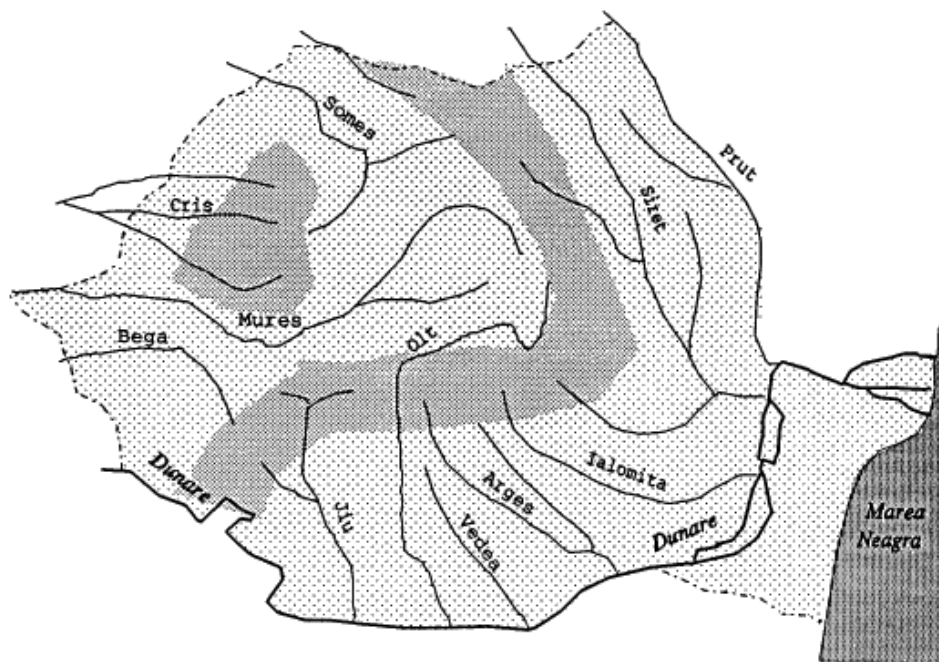


Fig. 1. Hydrographic Map of Romania.

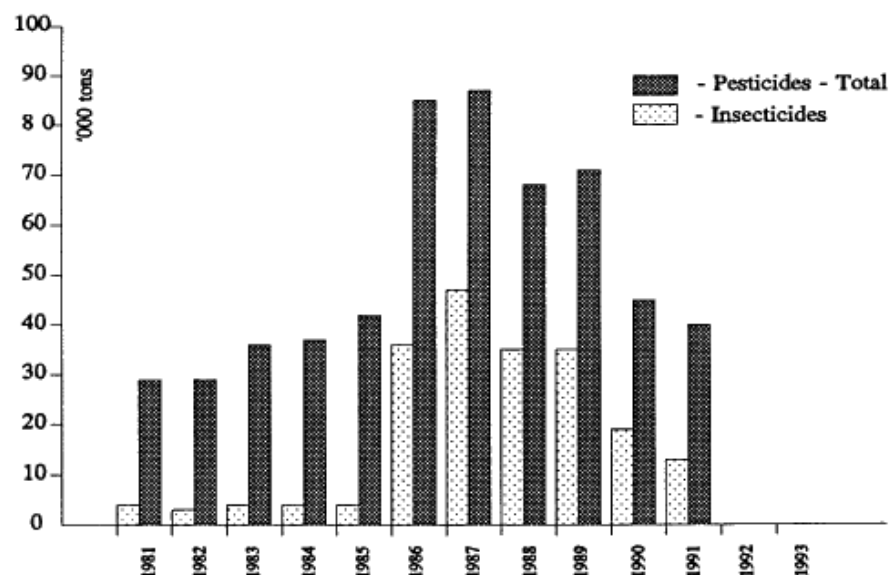
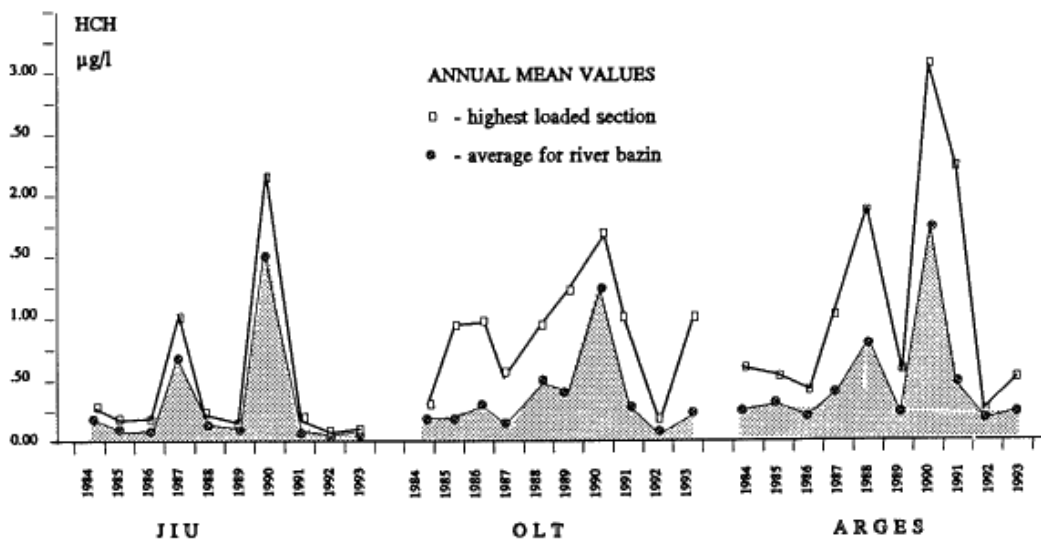
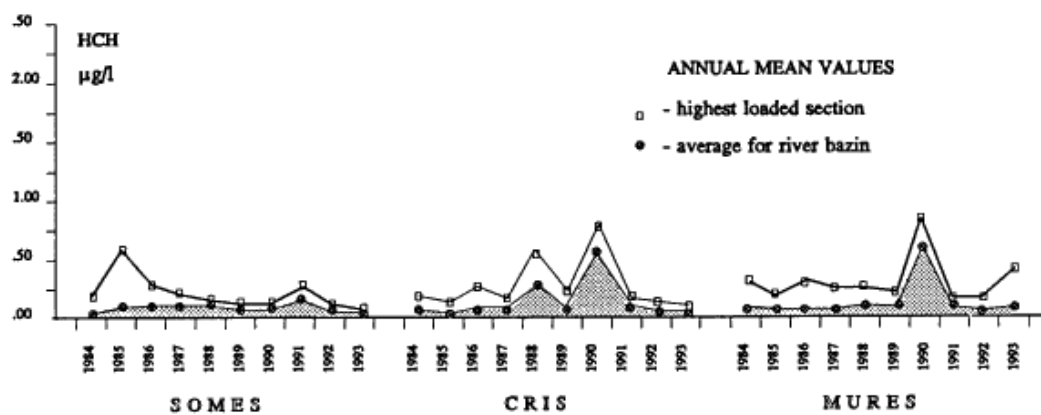


Fig. 2. Dynamics of Pesticide Use in Romania.

Water resources pollution with halogenated pesticides in Romania.



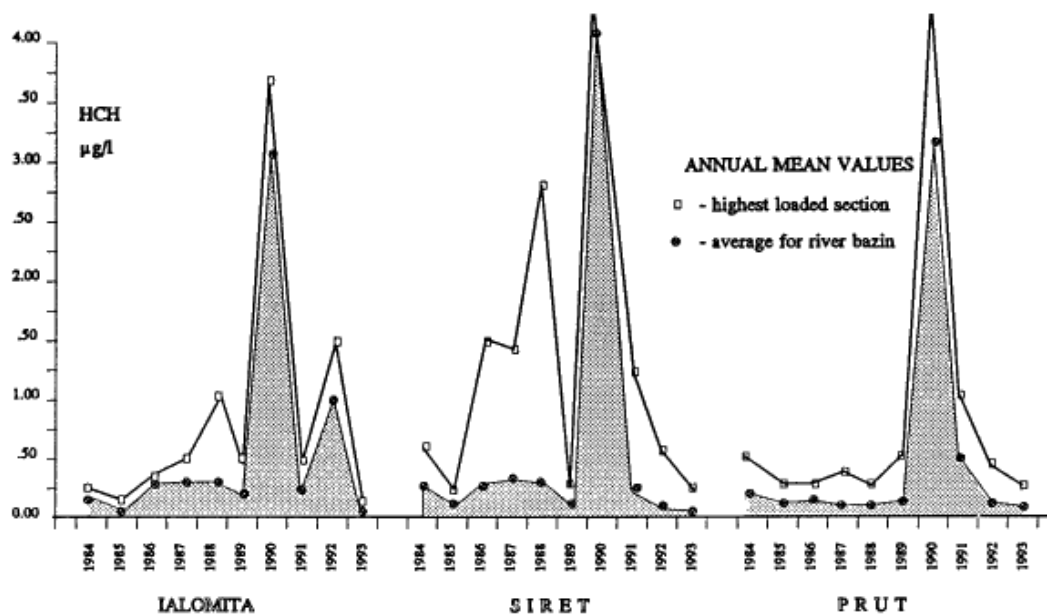
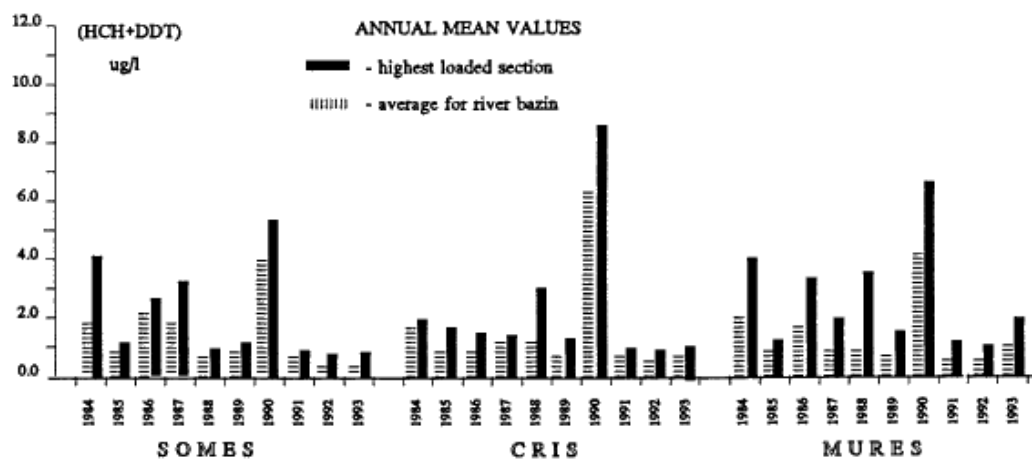


Fig. 3. Concentrations ($\mu\text{g/l}$) of HCH in Surface Waters.



Water resources pollution with halogenated pesticides in Romania.

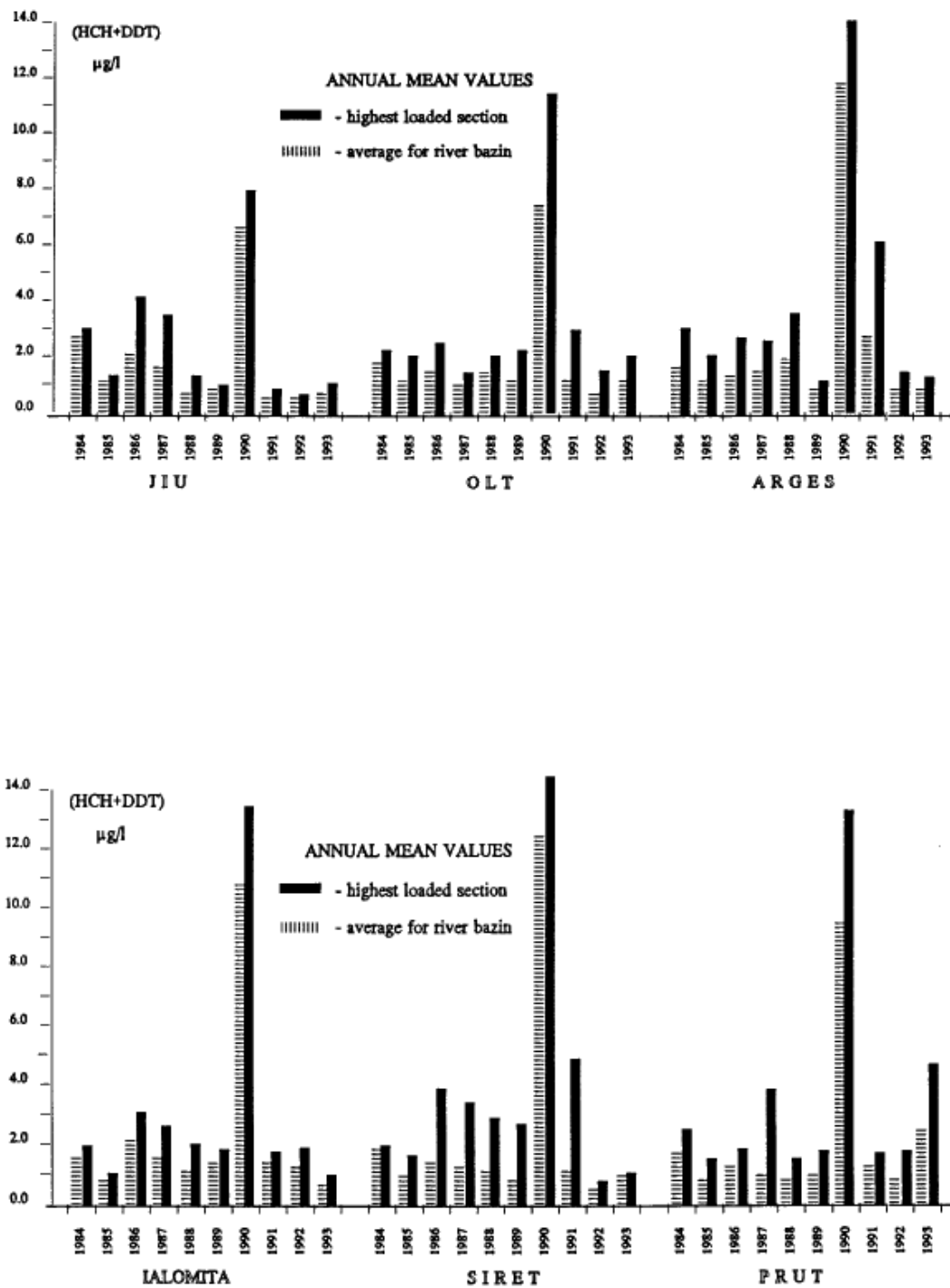


Fig. 4. Concentrations ($\mu\text{g/l}$) of HCH+DDT in Surface Waters.

APPENDIX OF WRITTEN CONTRIBUTION

BHC soil contamination in Sao Paulo metropoilitan region

Mr. Renato Pizzi Rossetti
Brazil

BHC SOIL CONTAMINATION IN SAO PAULO METROPOLITAN REGION

Biol. ROSSETTI, Renato Pizzi
CETEB, Sao Paulo, Brazil

Summary:

During public works undertaken by the state of Sao Paulo government in order to build a waterpipe for one of Tamanduateí affluents a huge BHC soil contamination was found.

Resumen:

Durante la realización de servicios de excavación por el gobierno del Estado de Sao Paulo objectivando la canalización de un afluente del río Tamanduateí se verificó una gran porción de suelo contaminado por el BHC.

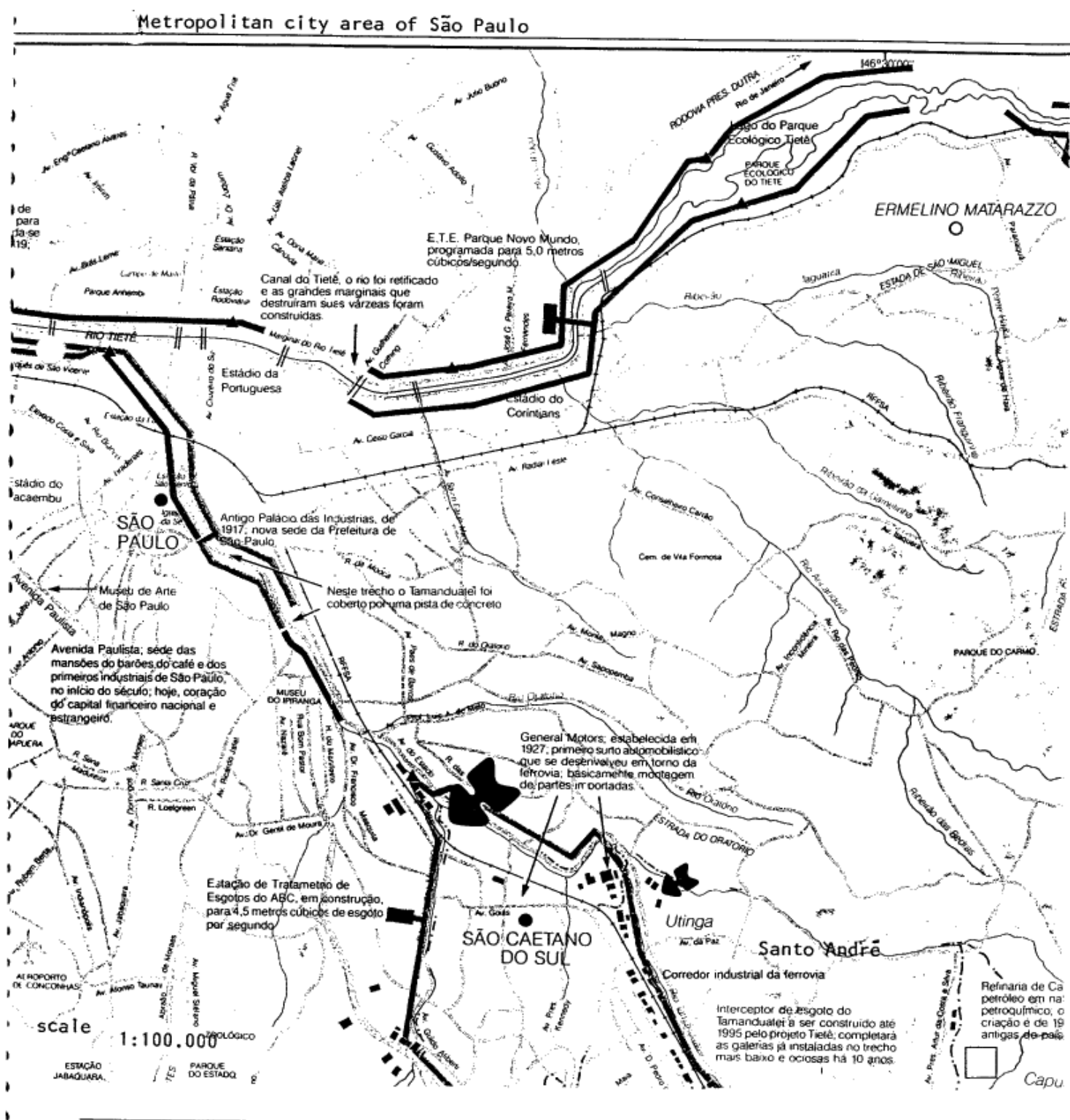
The metropolitan region of Sao Paulo city is the most important industrial set up in the country and also in Latin America, where one can find all kinds of industries. Sao Caetano and Santo Andre are cities that belong to this metropolitan region (in the southeast area). There one can find industries such as: metallurgy, iron and steel foundry, steel lamination, aluminum and steel forgery and a modern petrochemical industry. These cities are located in the Tamanduateí valley, one of the main affluents of Tietê River cutting this area.

As a consequence these cities also have great problems concerning all types of pollution and their rivers and streams are burdened with domestic and industrial sewage contamination. On the other hand, as this area faces frequent floodings of huge proportions, some civil works have been undertaken in order to minimize the problem.

In 1987, during the works for the canalization of a stream named "Corrego dos Meninos", an affluent of the Tamanduateí river, it was observed that the material removed from the excavations was contaminated as a result of the manufacturing of BHC- Benzene hexachloride. Nowadays the manufacturing of BHC is forbidden all over the country and its usage is restricted to endemic control.

CETESB, the Environmental and Sanitation State Agency that is responsible for the pollution control was then asked to interfere. (see Figure 1)

Figure 1 - Origin area of the BHC



Origin area of the BHC

Disposal place of the BHC

Map Source:

Santo André no Planalto
SEMASA/Pref. Santo André



CETESB

OS: 850000

Interessado/Programa: DAE/CETESB
Material declarado: Lodo
Local da coleta: Pto 08 - amostra de terra próximo a Av. do Estado
Origem da amostra: INDÚSTRIAS REUNIDAS FRANCISCO MATARAZZO
Data da coleta: 22-03-88
Data de entr. no Lab.: 22-03-88
Coletor: Anal.San.Amb. Fernando de Calres e Renato P. Rossetti

Amostra nº: 70581

TESTE DE LIXIVIAÇÃO

pH inicial 3,7
pH final 3,9
Volume de ácido acético gasto -

ANÁLISE NO LIXIVADO

BHC $2,80 \times 10^3$ µg/L

ANÁLISE NO SOLUBILIZADO

BHC $2,75 \times 10^3$ µg/L

São Paulo, 16 de maio de 1988.

QUIM. CACILDA JUNIO AIBA
Chefe Div. Química Orgânica
CRQ 04 204.017/4 - N.º Reg. 01.30610

QUIM. FREDERICO HORCEL
Gerente de Análises Químicas
CRQ 04 101.813/4 - N.º Reg. 01.0995.7

COMPANHIA DE TECNOLOGIA DE SANEAMENTO AMBIENTAL
Av. Professor Frederico Hermann Jr. 345 - CEP 05409 - PAIX - 2101100 - SÃO PAULO

V



CETESB

OS: 850000

Interessado/Programa: DAE/CETESB
Material declarado: Lodo
Local da coleta: Pto 01 - amostra de terra próxima ao portão
Origem da amostra: INDÚSTRIAS REUNIDAS FRANCISCO MATARAZZO
Data da coleta: 22-03-88
Data de entr. no Lab.: 22-03-88
Coletor: Anal.San.Amb. Fernando de Calres e Renato P. Rossetti

Amostra nº: 70580

TESTE DE LIXIVIAÇÃO

pH inicial 3,4
pH final 3,7
Volume de ácido acético gasto -

ANÁLISE NO LIXIVADO

BHC $1,65 \times 10^3$ µg/L

ANÁLISE NO SOLUBILIZADO

BHC $1,80 \times 10^3$ µg/L

São Paulo, 16 de maio de 1988.

QUIM. CACILDA JUNIO AIBA
Chefe Div. Química Orgânica
CRQ 04 204.017/4 - N.º Reg. 01.30610

QUIM. FREDERICO HORCEL
Gerente de Análises Químicas
CRQ 04 101.813/4 - N.º Reg. 01.0995.7

COMPANHIA DE TECNOLOGIA DE SANEAMENTO AMBIENTAL
Av. Professor Frederico Hermann Jr. 345 - CEP 05409 - PAIX - 2101100 - SÃO PAULO

V

The governmental branch DAEE-Water and Electrical Energy State Department- responsible for the canalization, decided to transport the hazardous waste to a wasteland in Santo Andre. The chosen place was located near a chemical industry- QUIMBRASIL- and a foodstuff industry - SWIFT. It is also located in the vicinity of residential and house development areas. (see Figure 2)

The estimated - 18.000 m³ - waste disposal has generated many claims and protests by the local community. To comply with their demands, CETESB asked to stop the waste dumping. CETESB also informed that the landfill would be temporary and indicated incineration as the method to eliminate the material contaminated by BHC.

In order to evaluate and monitor the quality conditions of groundwater during the period when the material was dumped there, CETESB proposed the isolation of the area. Thus, seen waterproof cells using protective covering made of PVC (polivinil choride) with size 30 x 15 x m each were built and four well were installed around the location in order to monitor the watertable. A system to collect eventual percolated liquids of the fill in order to treat then later won was also designed and established. (see Figure 3)

The system of rainwater flow was totally remodelled in order to gain security. The water would be retained if a leak happened.

As a matter of fact, a fresh water spring was found near this place. CETESB also defined parameters to be analysed in the gathered samples of the wells an soils, such as:

- pH
- conductivity
- total organic carbon
- B.O.C.
- B.H.C.
- Lyndane

Administrative procedures indicated in BSB- # 56 as of 7/13/1977, establishes the potability parameters and indicates as the maximum permitted value for Lyndane (BHC isomer gama), 4,0 microgram/liter. From 1992, the Brazilian Healthy Ministry indicates 3,0 microgram/liter. Further samples were taken from the four monitoring wells, where the values found ranged from 3.2 to 3.5 microgram/liter. (see Figure 3)

The recommendations set up by CETESB at that time were fulfilled and the BHC and Lyndane values found in the monitoring wells samples comply with the State of Sao Paulo environmental legislation. However, due to economic reasons the incineration of the waste has not yet been done. The waste is still confined in the seven cells of Santo Andre wasteland

Figure 2 - Disposal place of the BHC

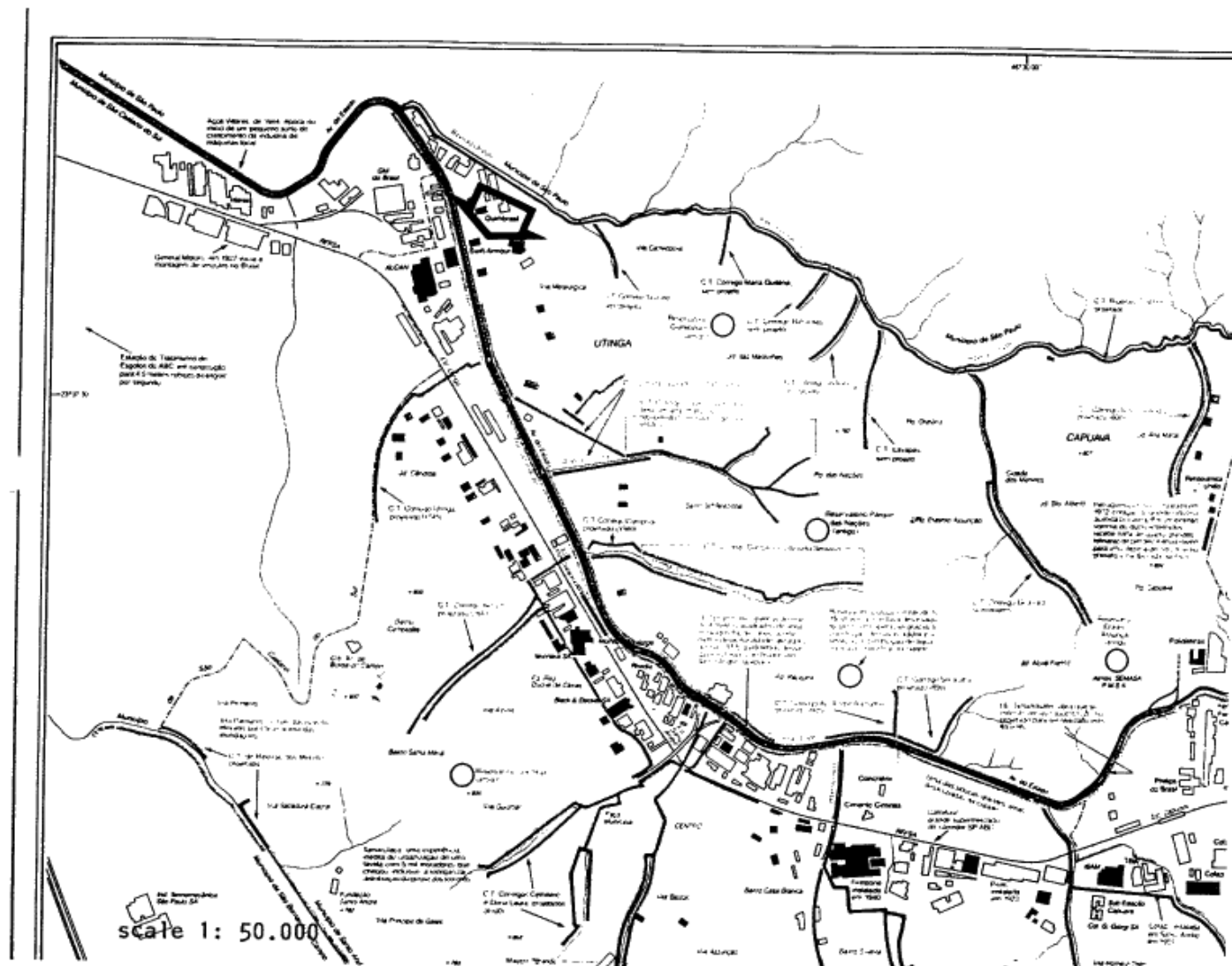
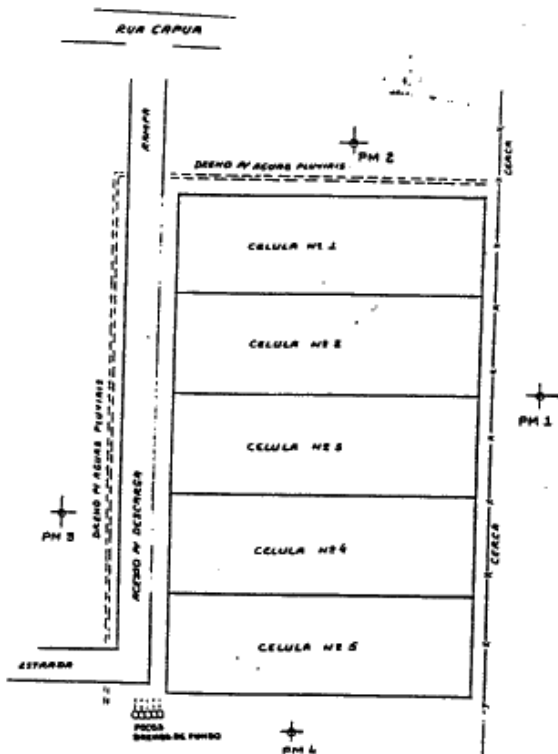
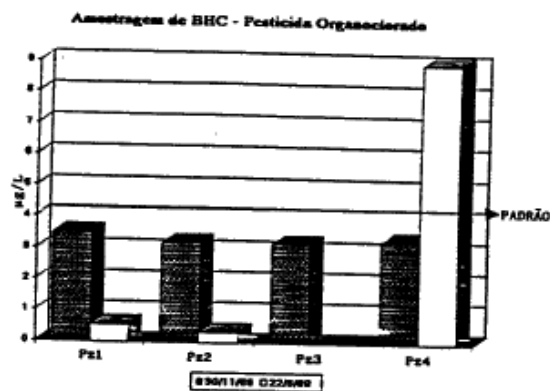



Figure 3 - Cells skeleton and pizometers sample sites


POÇOS DE MONITORAMENTO DO LENÇOL FREÁTICO
P.M.

	BOLETIM DE ANÁLISES COMPANHIA DE TECNOLOGIA DE SANEAMENTO AMBIENTAL	Nº de Análise: 850000 Nº da amostra:
	CLIENTE/PROGRAMA: _____	
ENDEREÇO:	Rua César - Botafogo	
MUNICÍPIO:		
COLETOR/CARGO:	Anal. San. Amb., Fernando de Calves e Arlindo J.B.	
LOCAL DA COLETA:	Vide procedimento (Inds. Reunidas Francisco Matias)	
GABARITO/ANEXO:	- - - - -	
CHUVA NOS ÚLTIMOS 24h:	<input type="checkbox"/> Sim <input checked="" type="checkbox"/> Não	TRATAMENTO: - - - - -
ASPECTO:	- - - - -	TEMPERATURA AMOSTRA: - °C - 22 - °C
DATA E HORA DA COLETA:	30-11-88	OCORR.: - - - - -
		DATA ENTRADA NO LAB.: 30-11-88

AMOSTRA Nº	PROCEDIMENTO	BHC mg/L
11167	Ponto 01 - Placimetro nº 1	3,5
11168	Ponto 02 - Placimetro nº 2	3,2
11169	Ponto 03 - Placimetro nº 3	3,2
11170	Ponto 04 - Placimetro nº 4	3,3
11171	Ponto 05 - Lagoa	0,25
<div style="border: 1px solid black; width: 100%; height: 100%; position: relative;"> <div style="position: absolute; top: 0; left: 0; right: 0; bottom: 0; border-left: 1px solid black; border-right: 1px solid black; border-bottom: 1px solid black;"></div> </div>		

RESERVAÇÃO: Cronograma nº 890047.

NOTA: MÉTODOS DE ANÁLISE BASEADOS NA - 2ª EDIÇÃO DO "STANDARD METHODS FOR THE EXAMINATION OF WATER AND ALLIANCE"

	BOLETIM DE ANÁLISES	FOLHA Nº 500106
	COMPANHIA DE TECNOLOGIA DE SANEAMENTO AMBIENTAL	DATA DE EMISSÃO 22-08-89

CLIENTE/PROGRAMA: CNEC

ENDEREÇO: Rua Capim

MUNICÍPIO:

COLETOR/CARGO: Fernando da Caldas, Renato F. Rossetti e Marcos Souza

LOCAL DA COLETA: -

MATERIAL ORGEM: - **TRATAMENTO:** -

CHUVA NAS ÚLTimas 24h: ☐ SIM ☒ NÃO **TEMPERATURA AMOSTRA:** - °C - AR - °C

ASPECTOS: - **ODOR:** -

DIA E HORA DA COLETA: 22-08-89 **DATA ENTRADA NO LAB.:** 22-08-89

PRESENTES ORGANOCLORES (µg/L)				
NOME do Biotipo	AMOSTRAS NÚMERO			
	60701	60703	60704	60705
	Ponto 01 Piscicultura 01	Ponto 02 Piscicultura 02	Ponto 03 Piscicultura 04	Ponto 04 Resumo
Aldrin	-	-	-	-
BHC	0,53	0,31	9,0	0,83
Chlordane	-	-	-	-
CYH	-	-	-	-
CCP	-	-	-	-
Dieldrin	-	-	-	-
Endosulfon	-	-	-	-
Heptachlor	-	-	-	-
Lindane	Traços	0,10	2,1	0,04
Methoxychlor	-	-	-	-
Polycy	-	-	-	-
Strobus	-	-	-	-
Tox	-	-	-	-
Triphenyl	-	-	-	-

OBSERVAÇÕES: Cromatograma nos 890569, 890568, 890547 e 890566.

NOTA: MÉTODOS DE ANÁLISE BASEADOS NA "Nº 1" EDIÇÃO DO "STANDARD METHODS FOR THE"

APPENDIX OF WRITTEN CONTRIBUTION

**The greatest chlorinated hydrocarbon problem of
Hungary**

István Bárczi
Hungary

The greatest chlorinated hydrocarbon problem of Hungary

Introduction:

For two years at the first HCH-Forum I have given account of the HCH production and usage in Hungary. At first I should like to summarize those information and then I make acquainted with one of the greatest environmental problem of our country.

In the past only one chemical plant produced HCH isomers in Hungary, but the separation of them was missed. This plant, located in Budapest, began the HCH production in 1953 and gave it up in 1964. The total produced HCH active ingredient amounted to 10 thousand tons and the rest of this amount was sold until the end of 1966. In 1966 the use of HCH isomers - except of gamma HCH - as insecticides, was banned. The onliest advance to produce and use unseparated HCH is, that the waste failed in the production.

Following the production ban, the above mentioned plant purchased 100 tons of lindane yearly from Eastern Germany and used it up in the production of 2000 tons of various insecticides. This practice lasted until the end of the last decade. Due to the economic difficulties of the Hungarian agriculture and relatively high price of lindane containing insecticides, these products are unmarketable.

As it was previously mentioned, the separation of HCH isomers, the production of pure gamma HCH was not solved in Hungary, and therefore no disposal problems of by-products emerged.

One of the typical environmental problems of our transforming economy is connected with other chlorinated hydrocarbon compounds.

This is caused by one of the greatest chemical factories of Hungary.

History:

It was manufacturing tetrachlor benzene from 1968 to 1987. In the process there were rising several mixed chlorinated benzene compounds as waste. They stored it in the factory until 1979 when the authority for public health banned it. The company had to look for a place in the vicinity which seemed to be suitable for landfilling waste. They took into account a few viewpoints only:

- the depth of soil water,
- the thickness of clay layer,
- soil permeability for water.

On the basis of these data had been choosen a site in the southern part of the country. According to their calculation the hazardous material would move 15 cm-s in 100 years. At this time there was not passed the governmental decree on the treatment of hazardous wastes and there was not authority for environmental protection. The local authority for building permitted to establish the landfill site. At first the steel barrels had been covered with soil. There had been placed here about 40 thousand barrels altogether. Most of them got rusty and the waste got to the soil and into the air. After the authority for environmental protection started to work, the covering of the barrels with soil had been banned and the factory had been compelled to put the rusty barrels into others. In 1992 the authority compelled the company to dispose the waste and clean up the soil. The deadline is the end of 1997.

Present situation:

There are 6.5 thousand tons of chlorinated benzene covered with 50 cm-s soil layer and 15.5 thousand tons without covering at the site, a part of them in new steel barrels.

The compounds of the waste are as follows: (according to a sample)

Components %	Fluid phase	Solid phase
chlorobenzene, otilbenzene, xilols	8.5	-
1,2-dichlorobenzene	1.2	-
1,2,4-trichlorobenzene	18.6	6.1
1,2,3,4-tetrachlorobenzene	5.5	52.8
1,2,4,5-tetrachlorobenzene	48.3	29.7
pentachlorobenzene	16.6	10.9
hexachlorobenzene	1.2	0.5

The compounds of the waste are dissolving into each others, the physical state of them alternates depending on the weather, they are evaporating and sublimating.

Several soil researches were performed at the site. According to them the mass of highly contaminated soil is more than 49 thousand tons. This soil contains more than 1000 ppm pollutant concentration. The depth of this highly contaminated layer is about 1.5-2.0 m-s.

The authority for public health gave local threshold value for chlorinated benzenes in soil. It is 2,8 ppm. According to this the estimated mass of contaminated soil is about 145 thousand tons. There is not national standard for the measuring of this pollutant in soil, so different institutes measure different concentration values depending on the extraction materials.

Luckily there hadn't been founded soil water in 20 meters depth.

The air pollution at the landfill is about 2000 microgramm/cubicmeters chlorinated hydrocarbon compounds, when the temperature is 3 centigrades plus. In the near villages the value of chlorinated benzene immission is sometimes more than 60 microgramm/cubicmeters. This value is the threshold value of this compounds.

Planned actions:

For the sake of the disposal of the hazardous waste the company decided to build a special incinerator. The implementation is feasible with initiation of international investor only. They decided about the investor company on the basis of an international tender. The implementation didn't started, because the inhabitants in surroundings oppose it.

The planned method of decontamination of highly contaminated soil is incineration. The lower pollutant concentration containing soil is planned to incinerate or clean up by biological method. For the sake of the biological decontamination there are experiments in progress. The researchers have found bacterias which are able to tolerate the tetrachlorobenzene, but there are a lot of technical problems with the usage of them.

- these are aerobic bacterias, so they demand ventilation. In the time of ventilation it is needed to prevent the gaseous pollutant from polluting the air.

- the product of biological degradation is not known.
We can't hope immediate solution on the basis of these researches.

The solution of this environmental problem is hindered by the economic problems of the company.
The estimated cost of the environmental reorganization is about 3 billion forints.
Today the company is owned by the state and it has other environmental problems at his other plants too. Now they are looking for investors in the sake of the privatization. There are two possibilities for the future:

1. The new private firm is able to solve the problems.
2. If the firm can't solve his environmental problem its going to be liquidate. In this case the state has to finance the cleaning up.

- 41 Institute of Ecology
Mrs. Milda-Zita Vosyliene
Akademijos st.2,
LT-2600 VILNIUS
LITHAUNIA
Tel: + 370-2-736237
Fax: + 370-2-159257
- 42 Gobierno Vasco
Departamento de Sanidad
Mr. Luis Gonzalez de Galdeano
VITORIA
BASQUE GOVERNMENT
- 43 Gobierno Vasco
Consejero
Mr. José Antonio Maturana
VITORIA
BASQUE GOVERNMENT
- 44 Gobierno Vasco
Vice-Consejero
Mr. Xabier Garmendia
VITORIA
BASQUE GOVERNMENT
- 45 IHOBE
Director
Mr. Raul Fernandez
Ibanez de Bilbao 28-8º
BILBAO
- 46 Ministry for Environment and Regional Policy
Department for waste Management
Mr. István Barczy
Fő u 44-50
H-1011 BUDEPEST
HUNGARY