TauwMilieu

Deventer

HCH

AND HALOGENATED PESTICIDES

– State of Art for Risk Assessment and Technology Development –

IWU

Institut für Weiterbildung
und Beratung im Umweltschutz e. V.
Magdeburg

IWU - TAGUNGSBERICHTE

Vorwort

Die Sanierung und der Schutz des Bodens sind langfristig angelegte Aufgaben des Umweltschutzes. Der Mensch und seine natürliche Umwelt können durch eine Vielzahl schädlicher Veränderungen von Böden beeinträchtigt oder gefährdet werden. Anreicherungen schwer abbaubarer organischer Verbindungen, wie des Hexachlorcyclohexans (HCH), gehören zu den schädlichen Bodenveränderungen, die für Sachsen-Anhalt von besonderer Bedeutung und Aktualität sind.

HCH wurde in Sachsen-Anhalt in großen Chemieunternehmen bis 1982 synthetisiert und verarbeitet. Die Entsorgung, aber auch die Produktion berücksichtigten kaum die Belange des Umweltschutzes, so daß es im Umfeld der ehemaligen Produktionsstätten erhebliche Belastungen des Bodens gibt. Auch über zehn Jahre nach der Einstellung der Produktion stellen die Kontaminationen aufgrund der Persistenz und der Tendenz von HCH, sich in Nahrungsketten anzureichern, eine Gefahr für Mensch und Umwelt dar. Die in den letzten Jahren, aber auch noch vor wenigen Monaten bekannt gewordenen Belastungen von Futter- und Nahrungsmitteln verdeutlichen dies.

Umso wichtiger ist es, für Sofortmaßnahmen zur Gefahrenabwehr und zur baldigen Sanierung ökologisch sinnvolle, effektive und möglichst kostengünstige Verfahren zu finden. Auf diesem Gebiet hat sich der internationale Austausch zwischen Wissenschaftlern als nützlich erwiesen. Der vorliegende Band faßt Vorträge von Tagungen in den Niederlanden und in Sachsen-Anhalt sowie die Ergebnisse von Arbeitsgruppen zusammen. Er bildet für Entscheidungsträger in den Verwaltungen ebenso wie für Ingenieurbüros oder Unternehmen der Umwelt-Technologiebranche ein wichtiges Arbeitsmaterial. Der Tagungsband ist sowohl dazu geeignet, die öffentliche Diskussion zu versachlichen, als auch zu mehr Effizienz bei den Maßnahmen zum Schutz von Mensch und Umwelt vor HCH-Belastungen beizutragen.

Heidrun Heidecke
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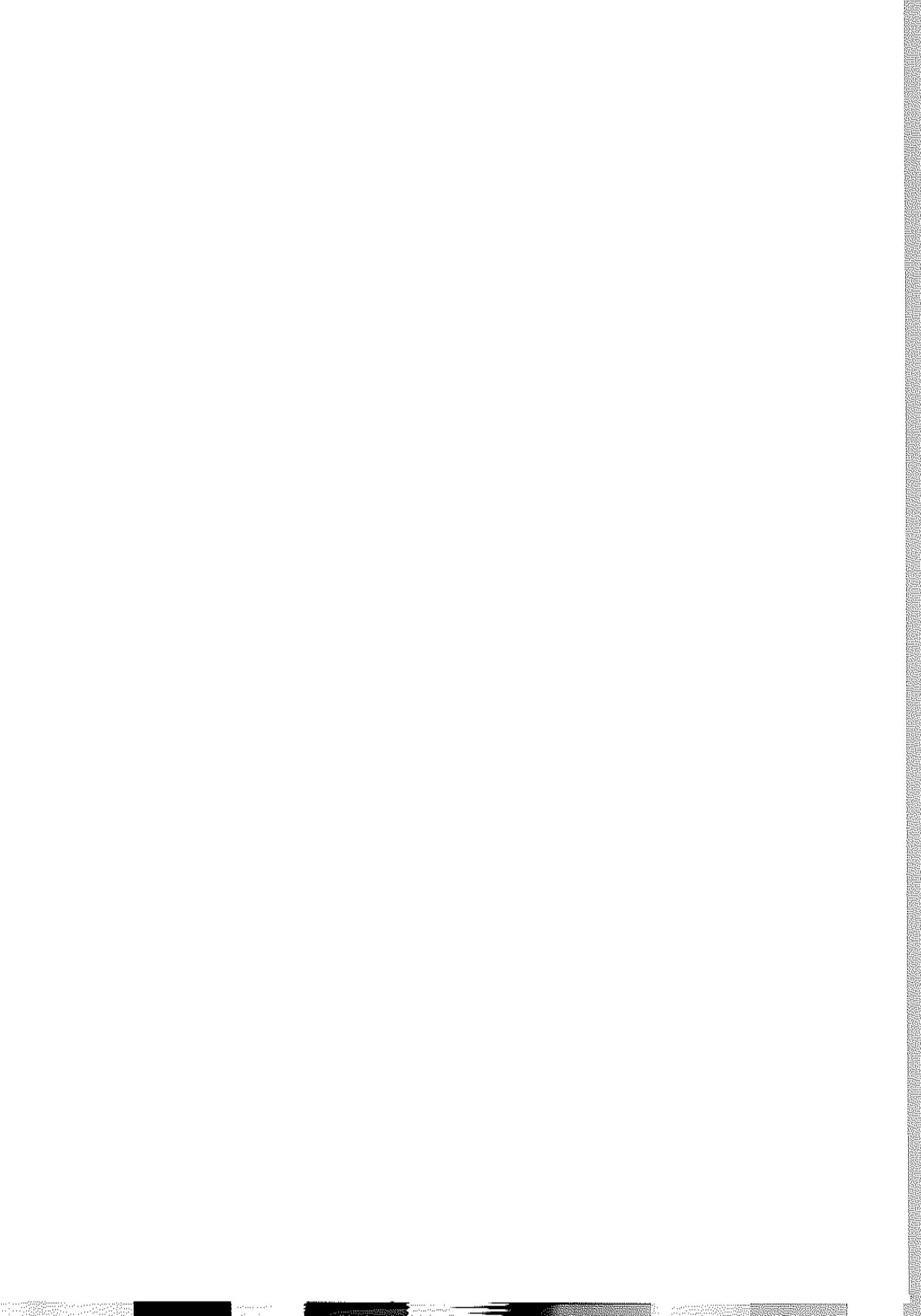
INTERNATIONAL HCH AND HALOGENATED

PESTICIDES FORUM

(COMPILATION OF 1ST AND 2ND HCH-FORUM)

CONTENTS

1   ACKNOWLEDGEMENT

This book is the result of a joint effort to tackle an international environmental problem: soil contamination by halogenated pesticides. Halogenated pesticides is a group of products like DDT, HCH, PCB, aldrin and dieldrin. Production and use of these compounds have caused severe soils contamination in many countries. Solutions for remediation are restricted to removal and storage of the contaminated soil. An international approach is required to achieve real solutions.

In order to join forces, two international forums have been held so far. To come to an appropriate approach, hexachlorocyclohexane (HCH) was selected as case or model for the pesticide problem. The first forum was held in 1991 in Zwolle, The Netherlands. The main objective was to create a framework for international discussions and exchange of knowledge. The second forum was held in 1992 in Magdeburg, Germany. Here, a broad consensus was found on the need for practical solutions and applications of risk assessment and the development of technical solutions.

Two working groups were formated whose task it is to design and execute programs for the further realization of the objectives. One group will deal with risk assessment, the other group with technology development. The forum claims to play a community wide demonstration role in the approach of an important worldwide problem. The forum has received support of various national governments, which have committed themselves to continue the activities and to find international support, like e.g. from the European Union.

This book gives an overview of a number of the presentations held at the two forums. The collected articles were supplied by the persons concerned. The objective of this book is to make the information more widely available. The articles were accepted as such, only a few limited attempts were made to upgrade the form and spelling.

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3. General Aspects and Risk Assessment

THE PRODUCTION AND USE OF HCH
By Ekkehard Amadori

1   INTRODUCTION

In German as well as in Anglo-America usage of HCH means the mixture of iso-
mers of hexachlorocyclohexane which is obtained from reacting benzene with
chlorine.

The commercial importance of HCH depends on its γ-Hexachlorocyclohexane con-
tent, which varies between 12% and 15%. γ-Hexachlorocyclohexane shows
strong insecticidal activity and is one of the most common pesticides; it is used
under the brand name Lindane. However, more recently, with growing ecological
and environmental awareness, the introduction of selectively acting insecticides,
and the fact that more attention is being paid to the negative aspects of pesticides
the use of this compound is declining.

Furthermore, it should be stressed that the production of HCH, especially that of
Lindane, leads to a large amount of by-products for which there are no applica-
tions yet.

2   HISTORY

The HCH-chemistry originated in 1825, when M. Faraday, just having discovered
benzene, reacted this solvent with chlorine in bright sunlight. What he finally held
in his hands was a white powder the molecular formula of which was found to be
$C_6H_6Cl_6$.

Neither Faraday nor the Dutch chemist Van der Linden, who in 1912 isolated the
pure γ-isomer from the mixture, realized the insecticidal potential of the com-
pounds they produced. This happened in 1933 in the US, but without any conse-
quences. After the introduction of DDT research was focused on other chlorinated
hydrocarbons. So the insecticidal properties of HCH became obvious in France in
1941 and in England in 1942. Finally, in 1943, the γ-isomer was identified as the
"active principle" and named "Lindane" after T. van der Linden, who had already
isolated it in 1912, as mentioned above.

A commercial breakthrough followed after World War II, when large-scale produc-
tion of HCH started in many countries.

3   THE USE OF HCH AND LINDANE

Due to their universal insecticidal properties, HCH and Lindane have rapidly been
introduced on a large scale. In contrast to DDT, Lindane has a rapid initial impact
(knock-down effect), but because of its volatility it is less persistent. It is applied
in the fields of agriculture and forestry and for sanitary purposes, and is active
against locusts as well as lice, fleas, ticks and worms.

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Another reason for the widespread use of HCH is that it is supposed to be only slightly toxic to mammalians. Its toxicological properties are considered well-known, though today studies are in progress on assumed neurotoxicological properties, and the effects of accumulation and storage in body fat have not yet been fully investigated and evaluated either. Because of this, but also due to an enhanced environmental concern, the use of these compounds is now diminishing, at least in the developed countries.

4 PRODUCTION OF HCH

As already mentioned above, the reaction of chlorine with benzene leads to a mixture from which seven hexachlorocyclohexane isomers can be isolated. The production process should be directed to the formation of pure HCH, and the formation of undesirable by-products such as chlorobenzene should be avoided. Attempts are also made to keep the portion of γ-HCH as high as possible.

Thus photocatalyzed addition of chlorine has been established as one of the standard procedures. In practice, first chlorine is dissolved in benzene, then this mixture passes the illumination tube where the reaction starts. This being an exothermal process, measures have to be taken to keep the temperature below 45 °C. Since benzene is used as a reagent as well as a solvent, the reaction is stopped as soon as sufficient chlorine has been taken up.

The residue obtained after removing the superfluous solvent contains about 12-15% of γ-HCH and may be used as a pesticide directly after formulation. In that case, however, all by-products and also the ineffective isomers are brought into contact with the treated crops. This may lead to a bad smell or taste, both being unwanted. Therefore, attempts have been made to isolate the active principle, i.e. the γ-isomer, from the by-products. This is easily achieved by fractionated crystallisation, using the deviant solubility of the isomers. It results in a nearly odourless γ-HCH the purity of which is > 99,5%. But also more than 80% of the initial materials are left as ineffective residues, more or less contaminated with solvents.

5 THE USE AND WHEREABOUTS OF HCH-RESIDUES

The unavoidable fact that there are no applications for about 80% of the reaction products has always been thought unsatisfactory. Unfortunately, until now no appropriate application or ingenuous use for the bulk of the residues has been found.

However, some methods exist to convert these by-productions, even though these methods are of minor importance. Dehydrochlorination leads to the formation of trichlorobenzene and hydrochloric acid, but for these compounds there is only little demand. Trichlorobenzene itself may be chlorinated further and then be hydrolysed to chlorophenols. The latter have been used to produce the herbicide 2.4.5-trichlorophenoxyacetic acid and the insecticide Bromophos, but meanwhile they have been banned or given up.

Consequently, most of the residues have been dumped over the last 50 years. For this purpose, state-of-the-art techniques were used. It should be noted that originally the residues were considered harmless and insoluble in water. So no objections have been raised to the practice of using them for filling up unwanted holes or pits wherever they were encountered. In some cases, however, residues were dumped in a proper way so as to recycle them in the future.

So today residues are found at many locations in the environment: in the soil of inundated regions, at places where the wind has spread flour-like residues which had been stored in the open air in large heaps, we find them on legal and illegal dumps, mixed up with household garbage, and in abandoned brown-coal mines and quarries.

Thanks to advances in the field of analytical chemistry, it has been discovered meanwhile that HCH-isomers are soluble in water to a certain extent (in the ppm-range). Also traces of solvents can easily be detected now. These advances led to the discovery of polluted groundwater, and certain crops were found to be polluted by the uptake of HCH, among other things.

Of course, these findings call for immediate measures to minimise harm to human health and welfare as well the ecosphere itself. But we always have to keep in mind than all our resources are limited. So neither inadequate claims nor inactivity fit in with the needs of the present.

With respect to HCH, we should look for measures to immediately stop further spreading, then define our aims, and finally start their achievement with a good sense of proportions.

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ASSESSING THE RISKS FROM SOIL CONTAMINATED BY CHLORINATED
PESTICIDES: DEALING WITH UNCERTAINTY
By Colin Ferguson

1   INTRODUCTION

Risk assessment has become an important component in environmental decision
making. The major objective of environmental risk assessment is to estimate the
likelihood of adverse effects on human health, wildlife or ecological systems from
specific levels of exposure to chemicals in the environment.   In addition, risk
assessments should also enable regulatory agencies and the public to gain a
proper perspective on the magnitude of risks posed by environmental contami-
nants. However, in each of the key components of the risk assessment process -
hazard identification, dose-response assessment, exposure assessment and risk
characterisation - there are major uncertainties. Achieving an acceptable balance
between adequate protection for human health and the environment, and the
economic and social costs associated with restoring (or not restoring) contamina-
ted land to beneficial use, is one of the major challenges facing environmental
professionals. An important part of that challenge is dealing with the scientific,
economic and political implications of uncertainty.

In the next section I describe a computer model in which many of the uncertain-
ties involved in risk assessment of contaminated land can be handled in a syste-
matic way. The Contaminated Land Exposure Assessment (CLEA) model (Fer-
guson & Denner 1993) has been developed as part of the UK Department of the
Environment research programme on assessing and managing risks from conta-
minated land.

2   THE CLEA MODEL

Trigger concentrations, and other generic guidelines for soil remediation, provide
nationally consistent guidance on the likely need for soil remediation without the
very substantial costs associated with site-specific risk assessment. CLEA is a
generic model in which site-specific and population-specific parameters are
replaced by probability density functions representing typical scenarios for the
chosen afteruse (residential, recreational or commercial/industrial). Soil type and
other relevant parameters (e.g. pH) can also be specified. A tentative guideline
value as input will then pass through a scenario to produce a risk or exposure
value as output. Multiple random trials will result in an output distribution of risk
or exposure. Guideline values derived with the assistance of the model will thus
have been chosen with knowledge of (a) the shape of the risk or exposure
distribution for each separate exposure pathway and for all pathways combined,
(b) separate analysis of toxic and carcinogenic effects, and (c) sensitivity to
scenario assumptions, exposure and media parameters, and physical -chemical
uncertainties.

CLEA can be run in inverse mode when previous work gives little guide to acceptable concentrations of particular substances in soil. In this mode, with a tolerable daily intake as input, the model produces an approximate soil concentration that could result in that intake as output. This approximation can then be used as a starting value for more detailed study using the model in forward mode. There are three forward-mode submodels as follows:

Background Submodel: This submodel allows the user to take account of background exposures which are unrelated to site contamination. It can accept a fixed background exposure if this has been determined by independent studies, and if necessary can adjust this to take account of age and body weight. Alternatively, it can compute a background estimate from exposures to public water supply.

Forward Submodel: This submodel calculates exposure via up to ten exposure routes as listed below.

* ingestion of outdoor soil
* ingestion of indoor dust
* consumption of home-grown vegetables
* ingestion of soil or dust attached to vegetables
* skin contact with outdoor soil
* skin contact with indoor dust
* inhalation of outdoor dust
* inhalation of indoor dust
* inhalation of outdoor vapours
* inhalation of indoor vapours

Average daily exposures are calculated incrementally so that the rate at which lifetime exposure accumulates, especially through the childhood years, is shown explicitly. Lifetime exposures computed by the model also take into account the removal of contaminants from soil by processes such as photolysis, volatilization and biodegradation as well as by run-off, erosion, leaching and crop offtake. Biodegradation is particularly important in determining exposure to organic contaminants, but the rate of degradation is highly site-specific depending on the types and growth rates of microbial populations, which in turn are influenced by moisture content, temperature, pH, Eh, nutrient availability and toxicity.

Several well-known models such as TOX-SCREEN (Hetrick & McDowell- Boyer 1984) and AERIS (Hosler et al 1991) provide no explicit means for modelling reduction of contaminants in soil over time. In contrast environmental models developed specifically for organics (Jury et al 1983; Melancon et al 1986), usually represent chemical and biological degradation of organic contaminants as a single first order process with rate constant specified by the user. This is the approach adopted for the CLEA model.

Monte Carlo Submodel: In this submodel variable values are replaced by probability density functions (PDFs) reflecting the uncertainties associated with environmental media, physicochemical properties, and exposure parameters. Each pass through the submodel involves random sampling from the relevant PDFs to produce a single estimate of exposure. Multiple passes thus allow a distribution of exposure to be built up. The Monte Carlo submodel can be used to test the sensitivity of output to the various input values and model assumptions.

The limitations of multimedia environmental transport and exposure assessment models are well known. In particular, there are serious deficiencies in our understanding of intermedia and multichemical transport and (even though the models are very data-demanding) a great scarcity of field data with which models can be calibrated or validated. Even fundamental properties are not always established. For example a range of solubility values for 2, 3, 7, 8 - TCDD at 25°C ranging from 0.0079 to 0.2 μg/1 has been reported (Shiu et al 1988). As environmental simulation models become more popular, there is a danger that the traditional close connection between theoretical development and experimental testing is weakened to an unhealthy degree. Even model components that have been laboratory-tested are often incorporated into field models without field trials or rigorous assessment of whether model assumptions are appropriate for field-scale application.

These problems affect all models, whether site-specific or generic. But parameters that are strongly medium-dependent need to be handled with particular care in generic models, and highlight the importance of designing models that include formal procedures for exploring the implications of data uncertainty. Indeed, the Monte Carlo submodel in CLEA was largely motivated by this need. In the next section we examine, in the context of lindane, a different type of uncertainty which does not lend itself to Monte Carlo modelling.

3   DOSE-RESPONSE RELATIONSHIPS FOR LINDANE

In spite of extensive research and a huge literature, it has proved difficult to reach consensus on an acceptable daily intake (ADI) of lindane for protection of human health. In the Netherlands (Janssen et al 1988; Leget 1992) a tolerable concentration level (TCL) in air of 0.25 μgm⁻³ has been derived. This is based on a No Observed Effect Level (NOEL) of 0.1 mgm⁻³ in a 90-day inhalation study of rats exposed for 6 hours per day. This corresponds to 0.025 mgm⁻³ for continuous (24 hour) exposure, and the human TCL is derived from this by applying a safety factor of 100. For a 70 kg adult inhaling 20 m³ of air per day, this gives an ADI of .07 μgkg⁻¹d⁻¹. This Dutch study needs to be interpreted with caution because the lindane concentrations in the exposure chambers were markedly higher at input than at exit, suggesting deposition of lindane from the aerosol and therefore the possibility of oral uptake. A 90-day rat study in the UK (ACP 1992) produced a higher NOEL, 0.6 mgm⁻³. Details are not available because the study was submitted "Commercial-in-Confidence" to the advisory body.

It is interesting to compare the Dutch TCL with the UK occupational exposure standard (OES) of 0.5 mgm⁻³ (8 hour time weighted average), corresponding to a TCL for continuous exposure of 120 μgm⁻³. This is nearly 500 times greater than the Dutch TCL. Part of the reason for this large discrepancy may be the UK decision procedure for setting OES's, which involves assessing all exposure data in a forum involving scientists, health professionals, regulators, industrialists, and worker representatives. Decisions are underpinned by detailed review and analysis of the toxicological literature. However, there seems to be a reluctance to place too much emphasis on particular animal studies combined with somewhat arbitrary safety factors; and more emphasis on occupational exposures that do not appear to result in adverse health effects.

For example, typical intakes of lindane for professional operatives applying lindane-based wood preservatives made up from concentrates are up to 0.05 mgkg^{-1}d^{-1} [ACP 1992]. This is close to the ADI that would be derived from an OES of 0.5 mgm^{-3} (8 hour TWA), assuming continuous exposure, 20 m^{3}d^{-1} inhalation and 70 kg body weight (viz. (0.12) * 20 ÷ 70 = 0.034 mgkg^{-1}d^{-1}).

The recent UK review [ACP 1992] includes a detailed assessment of the evidence for blood dyscrasias (including aplastic anaemia) related to lindane exposure. It concludes "that the weight of evidence suggests that exposure to γ-HCH does not cause aplastic anaemia in man. If a causal association exists it is probably not dose-related, and is a very rare idiosyncratic response. There is also no evidence of a link between exposure to γ-HCH and the development of other blood dyscrasias." This assessment concurs with that of the World Health Organisation [WHO 1991]. However, a number of court cases in the UK arising from exposure to wood treatment chemicals (almost all settled out of court without admission of liability), and similar concerns in the USA related to the possible link between blood dyscrasias and other chlorinated pesticides (especially chlordane and heptachlor) suggests that more detailed study of combined exposure (e.g. lindane and pentachlorophenol) might be warranted. It could be argued that the UK emphasis on occupational exposure takes into account, at least to some extent, possible synergistic effects from combined exposures. The animal studies conducted to date do not.

It should be noted that lindane is known to be an epigenetic carcinogen in rats and mice, where it acts by enhancement of tumorigenicity rather than causing neoplastic conversion. A NOEL for such effects can be determined from the dose-response for promotion of liver cells that have been transformed by exposure to a proven carcinogen. A NOEL of 0.5 mgkg^{-1}d^{-1} has been determined in this way (Schroter et al 1987), a somewhat higher exposure level than for some other endpoints.

In the United States the USEPA has derived a Reference Dose for lindane (also based on animal NOEL studies) of 0.3 μgkg^{-1}d^{-1}. In the past [USEPA 1991] it also used a no-threshold linear multistage model to derive a cancer potency slope of 1.8 (mgkg^{-1}d^{-1})$^{-1}$ which, assuming a tolerable lifetime cancer risk of 10^{-6}, would give a regulatory dose limit of 5 x 10^{-7} mgkg^{-1}d^{-1}. This approach is not appropriate for epigenetic carcinogens. It is believed that the USEPA is currently re-evaluating its carcinogenicity assessment for lindane.

Lindane is a compound with a history of use spanning half a century, and with a huge literature. Even so this brief review points to variations in acceptable daily intake spanning a factor of 500, which could easily extend to four orders of magnitude or more if recent USEPA models were included. The review has touched on the adequacy of animal studies, the appropriateness of extrapolation models, use of arbitrary safety factors, variations in the way disparate evidence is used, and lack of information about exposure to mixtures of compounds. It hardly needs to be emphasised how the uncertainties in this one key area alone might impact on the feasibility and cost of remedial treatment for lindane-contaminated sites.

Should we strive to eliminate these differences in handling toxicological evidence? Or is it better for each country to make its own science policy and risk management decisions, which can thus reflect the circumstances and scientific traditions prevailing in that country? These questions mirror the current great debate in Europe, the outcome of which, some would say, will determine the future of the Community.

4   HARMONISATION OR SUBSIDIARITY?

Harmonisation has been one of the major principles driving European Community legislation. Before 1987 EC environmental policy was mainly based on Article 100 of the 1957 Treaty which empowered the Council, acting unanimously, to adopt directives harmonising those national laws which directly affect the establishment or functioning of the common market. The essence of the argument is that differences in environmental standards are anti-competitive because they amount to a type of disguised subsidy. Since 1987 harmonisation has been accelerated by the Single European Act (SEA) which inserted Article 100A into the Treaty. This introduced qualified majority voting thus preventing one or two Member States from blocking measures agreed by the others. But, in Article 130R, the SEA introduced a new concept which can be illustrated by quoting two paragraphs in full.

1.   Action by the Community relating to the environment shall have the following objectives:

    (i)   to preserve, protect and improve the quality of the environment;
    (ii)   to contribute towards protecting human health;
    (iii)   to ensure a prudent and rational utilization of natural resources.

4.   The Community shall take action relating to the environment to the extent to which the objective referred to in paragraph 1 can be attained better at Community level than at the level of the individual Member States. Without prejudice to certain measures of a Community nature, the Member States shall finance and implement the other measures.

Paragraph 4 is a statement of the so-called principle of subsidiarity which, following the Lisbon and Edinburgh Councils, has taken on a much wider significance as the device used to hold the Community together in the face of a popular revolt against Eurocentrism.

The author's personal view is that it is impossible to harmonise something as complex as soil clean-up standards without imposing a cost burden on many sites which would be totally out of proportion to the benefits gained. Indeed, this seems to be recognised in paragraph 3 of Article 130R.

3.   In preparing its action relating to the environment, the Community shall take account of:

    (i)   available scientific and technical data;
    (ii)   environmental conditions in the various regions of the Community;
    (iii)   the potential benefits and costs of action or of
        lack of action;
    (iv)   the economic and social development of the Community as a whole and the balanced development of its regions.

However, it would save much time and money if the scientific and technical data used in risk assessments were available in common, even though interpretation and action on the basis of those data is probably best taken at a national or even local level.

The Organisation for Economic Co-operation and Development (OECD) has provided a lead by setting up a programme to undertake a Systematic Investigation of Existing Chemicals [OECD 1987, 1991]. This will reduce the volume of duplicative testing (a practice which wastes both animal lives and money) and provide a more complete scientific framework for decision making. In 1994 the programme will be extended towards harmonising risk assessment procedures for pesticides. It is particularly important, in the author's opinion, that the evidence used to reach risk management decisions is openly available, wherever possible, so that all can learn from the experience of others.

5 ACKNOWLEDGMENTS

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RISK ASSESSMENT AT HCH-CONTAMINATED LOCATIONS
By Alex Leget

1   INTRODUCTION

Why carrying out a risk assessment??

When considering and studying locations with contaminated soils, one might wonder why a risk assessment should be part of the research carried out.
It has long been recognised that people are prepared to take (high) risks on the basis of their own decisions. Driving a car at too high a velocity occurs very often, people go on skiing holiday in spite of the fact that braking one or more bones seems to be a normal risk. People tend to let the perceived advantages prevail over the disadvantages. Very often they feel confident about controlling the associated hazards. However, in many circumstances the risks are insufficiently known, as the inherent dangers only become apparent in the longer term (exposure to low radiation sources, smoking cigarettes causing cancer).
When environmental policies are concerned, they often seek to control risks that are largely of an involuntary nature and therefore difficult to observe or to control. The hazards involved may also have an unusually serious undesirable (side-)effect. Therefore these kind of risks are often regarded as being more serious. Gouvernements should (and in general do) take the responsibility to protect the population against these types of risks.
In order to be able to make sound policy decisions all possible alternative actions and solutions should be investigated and the risks of them, with regard to health as well as environment, be taken into account.
That's why!

2   SUSTAINABLE DEVELOPMENT

Sustainable development is a premis for (Dutch) environmental policy. Meanwhile the survival of man, animals, plants, ecosystems and property should be safeguarded. To achieve these objectives, two lines of policy could be followed:
I   source-oriented policy
         Within this policy line measures are introduced to deal with known sources
         of pollution; prevention of unnecessary environmental pollution is part of it
II   effect-oriented policy
         Within this policy line initiatives are introduced to adress the effects of
         contaminants; ensuring that the chance of deleterious effects on man,
         animals, plants, ecosystems, environmental functions and property is negligible: a risk assessment.

This paper focusses on the risk assessment, in particular of HCH and Hg contaminated sites (HCH and Hg often go together).

3 RISK ASSESSMENT IN GENERAL

3.1 General

For the evalutation of the contamination situation two approaches can be used. The first, and for this paper most important approach is the determination of the risks for human health of the contamination situation. However, existing data may be incomplete, and there is often great uncertainty in estimates of the types, probability, and magnitude of health effects associated with a chemical agent, of the economic effects of a proposed regulatory action, and of the extent of current and possible future human exposures. These problems have no immediate solutions, given the many gaps in our understanding of the causal mechanisms of carcinogenesis and other health effects and in our ability to ascertain the nature or extent of the effects associated with specific exposures. Because our knowledge is limited, conclusive direct evidence of a threat to human health is rare. Fewer than 30 agents are definitely linked with cancer in humans (Tomatis et.al., 1978); in contrast, some 1.500 substances are reportedly carcinogenic in animal tests (although they include substances tested in studies of questionable experimental design)(Nat.Res.Council, 1983).
A second approach is to evaluate the contamination situation (concentrations in soil, water, sediments and foodstuff) on the basis of existing legal standards, set by the government or the EEC. Independent of the risks for human health, concentrationlevels exceeding the legal standards give rise to remedial action or other measures, in order to end an illegal situation. Since in many countries no extensive legislative framework related to soil contamination exists yet, and no common applied standards have been set, this approach is not sufficient.

The model used for the risk assessment is discussed in paragraph 3.2. Paragraph 3.3. gives the most relevant exposure routes for certain uses (functions) an area can have. In this paragraph also relevant (legal) standards are summarized. The model is well elaborated for HCH, for mercury only for some relevant routes.

3.2 A model for human exposure routes

3.2.1 General

To determine the risks for man and environment caused by soil-pollution, it is necessary to analyse and quantify the different exposure routes. Figure 3.2.1 shows an exposure model containing the direct and indirect exposure routes by which soil and water pollution can reach man (Van den Berg, 1991). The extent to which exposure takes place depends on the ways of contact between the media (soil, water, air, biota etc.) and man, the transferfactors between the media and the amount of intake of media by man. They will be discussed in the next paragraphs.
Figure 3.2.2 shows the relation between various elements of risk assessment and risk management.
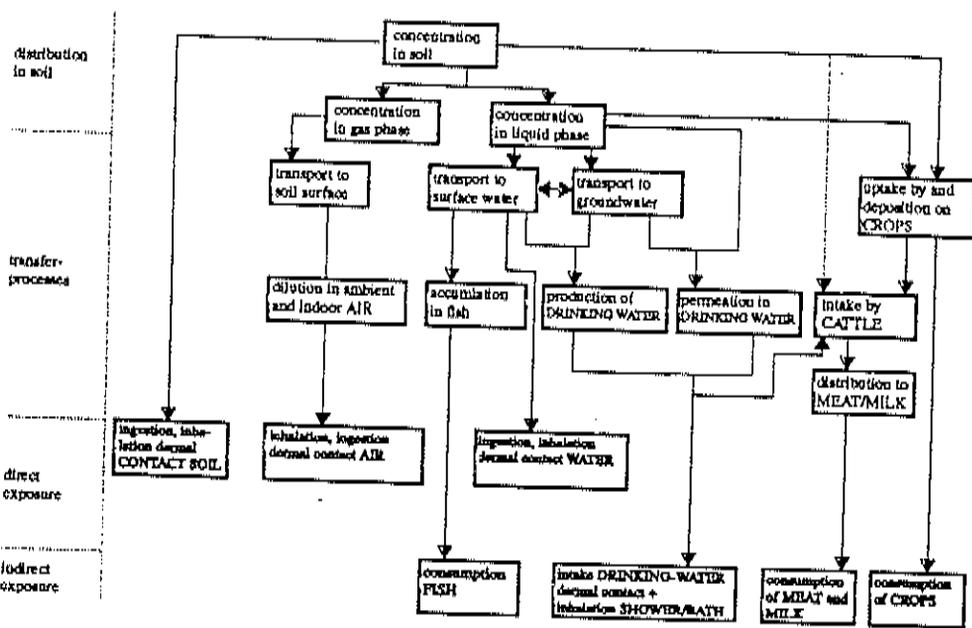
Figure 3.2.1: General model for exposure to soil and water pollution
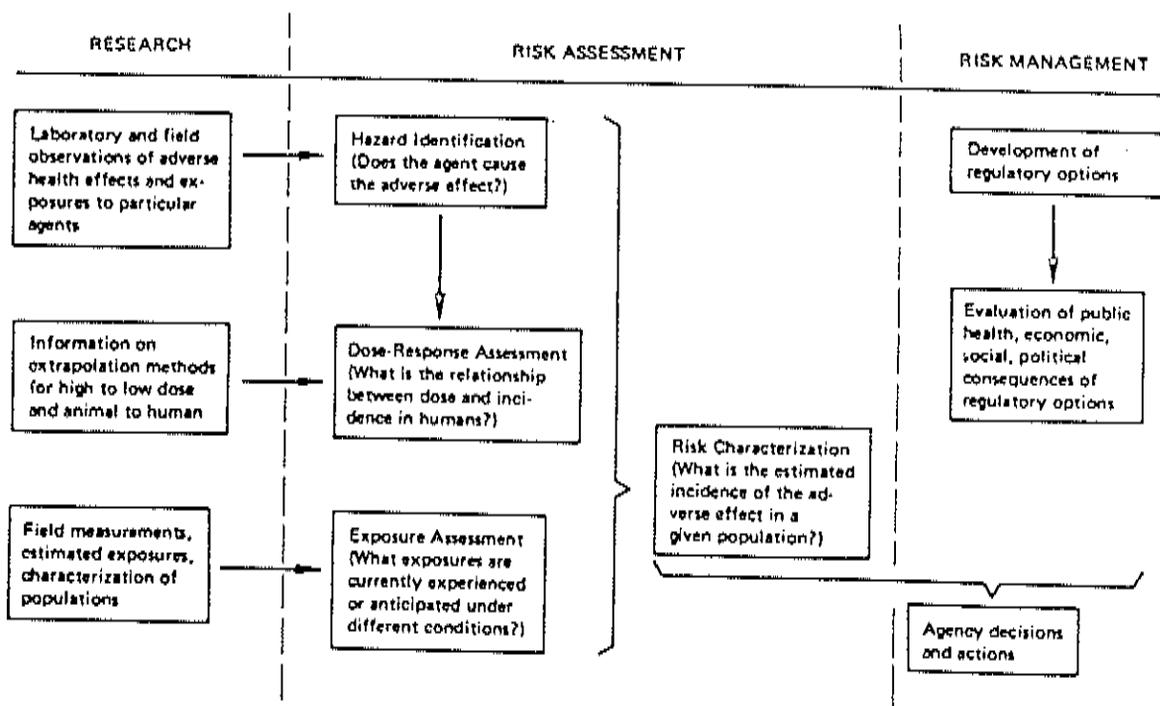
Figure 3.2.2: Elements of risk assessment and risk management

The transfermodels are mainly deduced from the CSOIL-model developed by the Netherlands National Institute of Public Health and Environmental Protection RIVM (Van den Berg, 1991). The choices made in this model are also based on an extensive study of the models HESP (Veerkamp, 1990), SOILRISK (Ten Berge, 1990) and a former RIVM-model (Linders, 1990).

3.2.2 Ingestion of soil

When the upper layer of the soil is contaminated, direct contact is possible and implies a health risk. Several activities on the ground, such as playing, digging or just sitting on it can cause a small ingestion of soil or dust containing soil particles. Soil dust is blown or walked in the houses, where ingestion can also occur. Especially for (small) children, who often play and crawl on the ground and have an intensive hand-to-mouth behaviour, this exposure route is important to consider. Dermal contact (uptake through the skin) in general is neglegible compared to the intake by ingestion of soil.

The intake of pollutants by ingestion of soil is:

$Is = Qs * Cs / W$

Is : intake pollutant by ingestion of soil (mg/kg/day)
Qs : daily amount of soil ingestion (kg/day)
Cs : concentration pollutant in soil (mg/kg)
W : body weight (kg)

In recent investigations on soil ingestion amounts were found ranging from 50 to 300 mg/day for children (Clausing et al, 1989). The average value can be estimated at 150 mg/day for children and 50 mg/day for adults (van den Berg, 1991). Assuming a body weight of 15 kg for children and 70 kg for adults, the following intakes can be calculated:

$Is,a = 0,8 * 10^{-6} * Cs$ (adults)
$Is,c = 10^{-5} * Cs$ (children)

3.2.3 Inhalation of air

Pollutants can evaporate from the soil and thus contaminate ambient and indoor air. In the ambient air a rather fast dilution will take place. In indoor air, however, pollutants can cause a significant exposure. For heavy metals, such as Hg, evaporation from the soil is assumed to be neglegible. For HCH the low vapor pressure and the low solubility are responsible for a rather low flux from the soil (Van den Berg, 1991). Therefore this exposure route can be considered as negligible.

Besides through evaporation, pollutants can come into the air by blowing up dust from the soil. The concentration of pollutants in the air connected to dustparticles is:

$Cda = SP * frs * Cs * 10^{-6}$

Cda : concentration pollutants in dustparticles in the air (mg/m³)
SP : amount of suspended dustparticles in the air (mg/m³)
frs : fraction soil in dustparticles
Cs : concentration pollutant in soil (mg/kg)

The RIVM (Van den Berg, 1991) estimates the average amount of suspended particles at 50 to 100 $\mu g/m^3$. In a dry, windy and dusty environment this can be much higher. A worst-case amount of 10 mg/m^3 is mentioned in the literature (TAUW, 1986). The fraction soil in the dust particles is 0,5-0,8.

Neglecting the rather small differences between concentrations in ambient and indoor air, the intake by inhalation of dust particles can be calculated by (adapted from Van den Berg, 1991):

$Ida = Cda * RV / W$

Ida :   intake of pollutant by inhalation of dust particles (mg/kg/day)

RV : respiratory volume (adults: 20 m^3/day; children: 7,6 m^3/day)
W   : body weight (adults: 70 kg; children: 15 kg)

The following intakes can be calculated with these parametervalues:

$Ida,a = 0,008 * 10^{-6} * Cs$ (adults)
$Ida,c = 0,013 * 10^{-6} * Cs$ (children)
In very dusty environments Ida can be up to $2.7 * 10^{-6} * Cs$.

3.2.4 Consumption of drinking water

Contamination of drinking water and subsequent health risks can occur by:

- extraction of drinking water from polluted surface water
- extraction of drinking water from polluted ground water
- permeation of pollutants from the soil into drinking water pipes.

An adequate purification and quality control on the drinking water production prevent the risk of exposure to pollutants. These measures are not possible in the case of private drinking water extraction.

The permeation of soil pollution through drinking water pipes is investigated by the Dutch Inspection Institute of Drinking water Articles (KIWA; see: Vonk, 1985). Permeation of inorganic compounds is assumed not to take place. For organic compounds it is proved that low pressure poly-ethylene pipes are much more permeable to organic compounds than other types of pipe, such as high pressure poly-ethylene, polyvinylchloride, concrete and iron.

The RIVM has deduced permeation coefficients based on the data of the KIWA. The average concentration in the drinking water as result of permeation is (Van den Berg, 1991):

$Cdw = Cpw * Dpe * 2\pi r * L / (d * Qw)$
      Cdw   : concentration in drinking water (mg/l)
      Cpw   : concentration in pore water (mg/l)
      Dpe   : permeation coefficient of pollutant (m^2/day)
      r   : radius of the pipe (m)
      L   : lenght of pipe on which permeation can take place (m)
      d   : thickness of the pipe-wall (m)
      Qw   : average daily water use from the pipe (m^3/day)

Assuming the following parameter values : $r = 1$ cm, $d = 2,5$ mm, $L = 100$ m, $Qw = 500$ l/day (these figures are applied for the situation in the Netherlands) and Dpe(poly-ethylene,HCH) $= 5 * 10^{-7}$ m²/day (Van den Berg, 1991), the concentration in the drinkingwater is:

$$Cdw = 25 * 10^{-4} * Cpw.$$

The intake of pollutants by way of consuming drinking water is:

$$Idw = Qdw * Cdw / W$$

  Idw : intake of pollutant by consumption of drinking water (mg/kg/day)
  Qdw : daily drinking water consumption
  W   : body weight (adults: 70 kg; children: 15 Kg)

By the WHO the drinkingwater consumption is estimated at 2 l/person/day. For children an amount of 1 l/person/day is assumed.

The following intakes can be calculated with these parametervalues:

$$Idw,a = 0,03 \ Cdw \ (adults)$$
$$Idw,c = 0,07 \ Cdw \ (children)$$

3.2.5 Consumption of agricultural food

Contamination of crops

Several pollutants can accumulate in crops. Therefore the cultivation of vegetables and fruit on polluted soil forms a risk for human health.
Contamination of crops can occur by:
- uptake of polluted pore water
- deposition from the air
- irrigation with polluted surface water.

The amount of pollutants in the pore water being accumulated in the crop is related to the properties of the component, the type of crop and the growing rate. Components with a low solubility, like HCH, tend to accumulate in the roots and are only slightly transported to the rest of the crop. Briggs et al (1982, 1983) have deduced empirical relations for the uptake of organic substances. The transfer pore water-root and root-stem is related to the octanol-water partition coefficient Kow of the component. The uptake is assumed to be independent of the type of crop.

The bioconcentration factors are:

$$BCFr = 10^{(0.77 * \log Kow - 1.52)} + 0.82$$
$$BCFs = [10^{(0.95 * \log Kow - 2.05)} + 0.82] *_2$$
$$[0.784 * 10^{(-0.434 * (\log Kow - 1.78)^2 / 2.44)}]$$

  BCFr : bioconcentration factor root (mg/kg fresh weight / mg/l pore water)
  BCFst : bioconcentration factor stem (mg/kg fresh weight / mg/l pore water)

The deduced concentrations are:

$$Cr = BCFr * Cpw$$

$$Cst = BCFst * Cpw$$

$$Cc = 0.5 * (BCFr + BCFs) * Cpw$$

Cr : concentration in root (mg/kg fresh weight)
Cst : concentration in stem (mg/kg fresh weight)
Cc : average concentration in crop (mg/kg fresh weight)

The RIVM has evaluated several soil-plant transfer factors and models. The given relations by Briggs et al were found to be the most practical (Van de Berg 1991). For HCH (because ß-HCH is the most cumulative, the calculation is made for this isomer, log Kow (HCH) = 3.72) the calculated bioconcentrationfactors are BCFr = 23 and BCFst = 5. The average concentration in crops is thus:

$$Cc = 0.5 * (23 + 5) * Cpw = 14 * Cpw$$

The results of the bioconcentration formulas correspond fairly well with the transferfactors as concluded in a study on crop concentrations in a ß-HCH polluted area in the town Hengelo in the Netherlands (Provinciale Waterstaat Overijssel, 1985). The transferfactors soil-crop for ß-HCH as found for different vegetables and the deduced transferfactors pore water-crop are shown in table 3.2.5.1. As shown in paragraph 3.2.1, in a soil with an organic fraction of 0.04 to 0.05 the concentration in the solid fraction is 100 times the concentration in pore water.

Table 3.2.5.1   Soil/pore water-crop transfer factors for ß-HCH

crop	transfer factor soil (mg/kg)-crop (mg/kg f.w.)	transfer factor pore water(mg/l)-crop(mg/kg f.w.)
potato	0.05	5
leek	0.13	13
carrot	0.34	34
other vegetables	0.05	5

The RIVM model shows that for most of the components including HCH the contamination of crops by deposition of particles from the air is neglegible compared to the uptake of polluted groundwater (Van den Berg, 1991).
For the assessment of the contamination of crops by irrigation with polluted surface water no model is available. An estimation can be made by using the model for uptake of pollutants from pore water and by substitution of the concentration of pore water by the concentration in the irrigation water.

Contamination of animal food

If cattle is grazed on polluted ground or fed with straw or corn from polluted ground, meat, milk and eggs can be contaminated. In the transfer of contaminants from fodder to animal the accumulation of HCH, especially of ß-HCH, becomes evident. The contaminent mainly accumulates in fat. The cumulative effect of ß-HCH is comparable to that of DDT and dieldrin (RIKILT, 1985). In table 3.2.5.2 transfer factors for fodder-animal products are given (Vreman et al, 1978, 1980; Provinciale Waterstaat Overijssel, 1985).

Table 3.2.5.2   Transfer factors fodder (mg/kg dry weight) - animal product (mg/kg on lipid basis)
for HCH-isomers

product	a-HCH	B-HCH	y-HCH
moat	6	15	1
milk	2	10	1
fatting-chickens	3	14	2
laying-hens	2	19	2
eggs	2	16	2

The concentration in fodder can be calculated by means of the estimated transfer factor soil (d.w.) - grass/corn (d.w.) of 0,05 (RIKILT, 1985). Assuming an organic fraction of 0,04 - 0,05 the soil (d.w.) is 100 times the concentration in pore water. The deduced concentrations in for example meat (fat) and milk (fat) are:

$$C_{me} = 15 * C_{fodder, fresh weight}$$
$$= 15 * 0,05 * C_s = 0,75 * 100 * C_{pw} = 75 C_{pw}$$
$$C_{mi} = 10 * C_{fodder, fresh weight}$$
$$= 10 * 0,05 * C_s = 0,50 * 100 * C_{pw} = 50 C_{pw}$$

C_{me} : concentration pollutant in meat fat (mg/kg)
C_{mi} : concentration pollutant in milk fat (mg/kg)
C_s : concentration pollutant in soil (mg/kg d.w.)
C_{pw} : concentration pollutant in pore water (mg/l)

Important to consider is the *direct intake of contaminated soil* in the case of grazing cattle. The amount is estimated at 0.5 kg/day. An example illustrates the relevance of this soil intake. Assuming a daily diet of 15 kg grass and 0.5 kg soil, and a transfer factor soil-grass of 0.05, the intake of HCH is 15 * 0.05 * C_{soil} = 0.75 C_{soil} by way of the grass and 0.5 * C_{soil} by way of the soil. It appears that almost half of the intake is caused by direct intake of soil (RIKILT, 1985).

Intake contaminated food

The extent to which man is exposed to pollutants by consuming agricultural products is, besides of the concentration in the crop or in the animal product, dependent of the amount of consumption and the fraction of the diet derived from polluted soil:

$$I_f = Q_f * f_{pf} * C_f / W$$

I_f : intake of pollutant by consuming food (mg/kg/day)
Q_f : daily consumption of crops/animal product (kg/day)
f_{pf} : fraction polluted food
C_f : concentration in the crops/animal products (mg/kg)
W : body weight (adults: 70 kg, children: 15 kg)

Personal and cultural nutrition customs vary, which makes it difficult to determine the daily consumption of food products. In 1989 for instance the National Institute of Statistics in Spain has sampled consumption quantities in 3200 households. The deduced daily food consumption is shown in table 3.2.5.3.

Table 3.2.5.3   Average daily food consumption in Spain (National Institute of Statistics, 1989)

food product	consumption (g/person/day)
potatoes	158
vegetables	148
fruit	264
milk products	328*
meat	112**
fish	47
eggs	35

*   assuming a fat percentage of 4% this means 13 g milkfat/person/day
**   assuming a fat percentage of 20% this means 22 g meatfat/person/day

Important for the assessment for the exposure of man by the consumption of food, is to determine which fraction of the food is derived from polluted area (fpf). In a local soil pollution case this means: the fraction derived from the own field or garden.

By means of the transfer factors soil-crop and fodder-animal product for HCH, the deduced concentrations in crops and animal products, and assuming an average daily consumption pattern as shown in table 3.2.5.3, the intake by consuming crops and animal products can be calculated. For this calculation the different crops are taken together and the daily consumption is estimated on 158 + 148 + 264 g/day is = 0,57 kg/day. The daily consumption of children is estimated to be roughly half the consumption of adults (adapted from Van den Berg, 1991).

Ccrops: $I_{c,a}$ = 0,57 * fpc * 14 * Cpw / 70
         = 0,11 * fpc * Cpw (adults)
      $I_{c,c}$ = 0,28 * fpc * 14 * Cpw / 15
         = 0,26 * fpc * Cpw (children)
      Ic : intake pollutant by consumption crop (mg/kg/day)
      fpc : fraction polluted crops
      Cpw : concentration pollutant in pore water (mg/l)

Meat: $I_{me,a}$ = 0,022 * fpme * 75 * Cpw / 70 = 0,02 * fpme * Cpw (adults)
      $I_{me,c}$ = 0,011 * fpme * 75 * Cpw / 15 = 0,05 * fpme * Cpw (children)
      Ime : intake pollutant by consumption meat (mg/kg/day)
      fpme : fraction polluted meat
      Cpw : concentration pollutant in pore water (mg/l)

Milk: $I_{mi,a}$ = 0,013 * fpmi * 50 * Cpw / 70 = 0,01 * fpmi * Cpw(adults)
      $I_{mi,c}$ = 0,007 * fpmi * 50 * Cpw / 15 = 0,02 * fpmi * Cpw (children)
      Imi : intake pollutant by consumption milk (mg/kg/day)
      fpmi : fraction polluted milk
      Cpw : concentration pollutant in pore water (mg/l)

3.2.6 Consumption of fish

Fish can take up pollutants from the surface water and accumulate in their tissue. The concentration in fish can be calculated as (Linders, 1990):

$$Cfi = BCFfi * Csw$$

Cfi : concentration in fish (mg/kg)
BCFfi : bioconcentration factor in fish (mg/kg fish / mg/l surface water)
Csw : concentration in surface water (mg/l)

The bioconcentration factor can be estimated according to Veith and Kosian (1983; see also Linders, 1990):

$$BCFfi = 10^{(-0.4 + 0.79 * \log Kow)}$$

With an average log Kow = 3,8 for HCH-isomers, BCFi can be calculated as 400. For heavy metals like Hg this approach is not appropriate, since for these contaminants a Kow cannot be determined. Apart from this, the situation in the case of Hg is further complicated by its speciation (methylmercury). For methylmercury bioconcentration factors of 10^4 - 10^5 have been reported. These factors seem considerably lower for other forms of mercury (IPCS, 1990). Therefore from scientific point of view for Hg determination of the concentration in fish by chemical analysis should be strongly advised, rather than by very uncertain calculations.

For HCH, the intake of pollution by fishconsumption is:

$$Ifi = Qfi * fpfi * Cfi / W$$

Ifi : intake of pollutant by consumption of fish (mg/kg/day)
Qfi : daily consumption of fish (kg/day)
fpfi : fraction polluted fish
W : body weight (adults: 70 kg; children: 15 kg)

Assuming an average fish consumption of 47 g/day for adults (see table 3.2.5.3) and 24 g/day for children, Ifi can be calculated as:

$$Ifi,a = 0,27 * fpfi * Csw \text{ (adults)}$$
$$Ifi,c = 0,64 * fpfi * Csw \text{ (children)}$$

3.2.7 Ingestion of surface water

By swimming and other water sports surface water can be swallowed. The amount of the water intake is estimated at 50 ml/swimming event (one or two gulps; see van Wijnen, 1982). Swimming is not an everyday activity. Linders (1990) estimates an amount of 30 swimming events a year (365 days), resulting in a time fraction of 0,08 (=30/365). The intake of surface water can be estimated as:.

$$Isw = Qsw * Csw * tf / W$$

Isw = intake pollutant by ingestion of surface water (mg/kg/day)
Qsw = daily amount of surface water ingestion (l/day)
tf = time fraction (0,08)
W = body weight (adults: 70 kg; children: 15 kg)

With these values, the following daily intakes can be calculated:

$$Isw,a = 0,06 \cdot 10^{-3} Csw \text{ (adults)}$$
$$Isw,c = 0,26 \cdot 10^{-3} Csw \text{ (children)}$$

3.3   Functions and legal standards

3.3.1   General

Soil and water fulfill several functions for man and nature. The functions relevant for human survival, health and well-being are:
- housing function: the soil serves as an underground for houses and all the involved human activities
- agricultural functions: crop-cultivation and cattle-breeding
- water extraction function: groundwater and surface water serve as stores for the supply of drinking water and water for agricultural or industrial use
- fishwater function: the surface water serves as a source of consumption fish
- recreation functions: on the soil and on or in the surface water several recreational activities take place, such as playing, sporting, diving, camping and swimming.

In the next paragraph the exposure routes relevant for certain functions of an area will be described. Also relevant legal standards will be given.

3.3.2   Drinking water function

Surface- and groundwater can be used as drinkingwater for human beings. Contamination of surface- and/or groundwater can make this potential function impossible if the contamination is beyond certain limits.

Formulas for risk assessment

The daily intake by drinkingwater is derived as:

$I_{dw,a} = 0,03\ C_{dw}$ (adults)
$I_{dw,c} = 0,07\ C_{dw}$ (children)

Legal standards

The EEEC has set quality requirements for drinkingwater quality and for surface water used as a source for the production of drinkingwater (EEEC, 1975a; EEEC, 1980; see table 3.3.2.1).

Table 3.3.2.1   Surface water and drinking water, EEC quality requirements

Type/use	Max conc. (μg/l) Hg	HCH	Remarks for HCH
Drinking water, source			
- simple purification	1	1	total-
- normal purification	1	2,5	pesticides
- thorough purification	1	5	
Drinking water, use	1	0,1	individual pest.
Drinking water, use		0,5	total pesticides

The EEC requirements for drinking water are adopted as Spanish standards. It must be noted that the values of the given standards are based on the ethical principle that pesticides should not be present in drinking water. Toxicological aspects did not play a role of importance in setting these standards. The detection limit of the best available analytical procedure at that time was choosen as the limit value of 0,1 μg/l. This value is therefore not adequate for a health risk assessment, since it was not set on a toxicological basis.

3.3.3 Fishing water function

Surface water can be used as a reservoir for consumption fish. Contamination of surface water can make this potential function impossible if as a result of this contamination fish is not suitable for consumption.

Formulas for risk assessment

In § 3.2.6 the daily intake of HCH by consumption of polluted fish is derived as:

$I_{fi,a} = 0,27 * f_{pfi} * C_{sw}$ (adults)
$I_{fi,c} = 0,64 * f_{pfi} * C_{sw}$ (children)

Legal standards

For consumption fish nor for fish water standards have been set for HCH or Hg in EEC directives or Spanish law. However, in the directive 84/491/EEC (on limit values and quality objectives for discharges of hexachorocyclohexane (EEC, 1984)), a quality standard for inland surface waters affected by HCH discharges is set on 100 ng/l. In the directive 82/176/EEC (on limit values and quality objectives for discharges of Hg from the chloralkali industry (EEC, 1982)), a quality standard for inland surface waters affected by Hg discharges is set on 1 μg/l. The concentration in fish may not exceed 0,3 mg/kg wet flesh. Furthermore it is not allowed that Hg concentrations of sediments increase significantly with time.

3.3.4 Recreation function

Areas can be used for recreation, like swimming, playing, etc. Contamination of an area can make this function impossible. Relevant exposure routes are: ingestion of soil, inhalation of dust particles and ingestion of surface water.

Formulas for risk assessment

In paragraph 3.2.2 for the mentioned exposure routes has been derived:
Ingestion:
$I_{s,a} = 0,8 * 10^{-6} * C_s$ (adults)
$I_{s,c} = 10^{-5} * C_s$ (children)
Inhalation:
$I_{da,a} = 0,008 * 10^{-6} * C_s$ (adults)
$I_{da,c} = 0,013 * 10^{-6} * C_s$ (children)
Ingestion of surface water:
$I_{sw,a} = 0,06 \cdot 10^{-3} \, C_{sw}$ (adults)
$I_{sw,c} = 0,26 \cdot 10^{-3} \, C_{sw}$ (children)

Legal standards

Nor for recreation areas or for swimming water standards have been set for Hg or HCH in EEC directives or Spanish law. In the directive 84/491/EEC on limit values and quality objectives for discharges of HCH (EEC, 1984) a quality standard for inland surface waters affected by HCH discharges is set on 100 ng/l. In the directive 82/176/EEC on limit values and quality objectives for discharges of Hg from the chloralkali industry (EEC, 1982) a quality standard for inland surface waters affected by Hg discharges is set on 1 μg/l. Furthermore it is not allowed that Hg concentrations of sediments increase significantly with time.

3.3.5 Agriculture function

An area can be used for agricultural purposes, like crop growing, cattle grazing, etc. Contamination of such an area can make this function impossible, because as a result of this contamination the agricultural products, like crops, meat and milk are not suitable for consumption.

Formulas for risk assessment

In § 3.2.5 the daily intake by food products has been derived as:

Crops: $I_{c,a}$ $= 0,11 * f_{pc} * C_{pw}$ (adults)
 $I_{c,c}$ $= 0,26 * f_{pc} * C_{pw}$ (children)

Meat: $I_{me,a} = 0,02 * f_{pme} * C_{pw}$ (adults)
 $I_{me,c} = 0,05 * f_{pme} * C_{pw}$ (children)

Milk: $I_{mi,a}$ $= 0,01 * f_{pmi} * C_{pw}$ (adults)
 $I_{mi,c}$ $= 0,02 * f_{pmi} * C_{pw}$ (children)

Standards for food products

For a number of pesticides limit values are set for the permitted residual concentrations in food products. To sell the product it must meet these requirements. These levels are based on the lowest residue concentrations that can possibly be achieved when 'good agriculture housekeeping' is practiced. In principle they are not choosen on toxicological basis. It must be emphasized that these values are not adequate for an assessment of health risks. The EEC has set maximal permitted lindane-concentrations for vegetables and fruit (EEC, 1976b).

Table 3.3.5.1   EEC maximal permitted concentrations in food for lindane

food product	concentration (µg/kg)
leaf vegetable	2000
carrots	100
other vegetables and fruit	150

In the Netherlands a more extended list of maximal permitted HCH-concentrations in food exists (The Netherlands Staatscourant, 1986; see table 3.3.5.2).

Table 3.3.5.2   Maximal permitted concentrations for HCH-isomers in food (µg/kg) in the Nether-
lands.

product	α-HCH	ß-HCH	γ-HCH
Milk	4	2	8
Meat *	300	100	2000
Cacao *	150	150	1000
Cereals	100	20	500
(remaining) vegetables and fruits	50	50	1000
Eggs *	500	200	1000
Tea	100		100
Coffee	100	100	1000
Poultry meat *	300	100	700
Tropical seeds	100	100	
Rabbit *	300	100	2000
Stone fruit, grapes and tomatoes			500
Whole meat			50
Leaf vegetables			2000
Winter carrots .			100
Potatoes			10
Remainder **	0 (10)	0 (10)	0 (10)

* calculated on fat basis
** no residues should be present, which is considered to be met at 10 µg/kg.

Using the transferfactors for animal fodder to milk and meat from
§ 3.2.4, the RIKILT institute in the Netherlands concluded that when cattle is
grazed on soil polluted with more than 0,05 mg/kg ß-HCH, a fair possibility exists
the milk will exceed the standards mentioned in Dutch legislation.

3.3.6 Housing function

The housing function is one of the most critical functions the soil can perform.
Relevant exposure routes are inhalation of dust particles, ingestion of soil par-
ticles, the intake of contaminated drinking water by permeation through drinking
water pipes and the cultivation and consumption of own crop. In a contaminated
area, the housing function may be impossible as a result of exposure to the
contaminants, or at least only be possible in a limited way, e.g. without the possi-
bility to cultivate own crop.

Formulas for risk assessment

A review of the amounts of intake is given:

Ingestion:
$$Is,c = 10^5 * Cs \text{ (children)}$$
$$Is,a = 0,8 * 10^6 * Cs \text{ (adults)}$$
Inhalation:
$$Ida,a = 0,008 * 10^6 * Cs \text{ (adults)}$$
$$Ida,c = 0,013 * 10^6 * Cs \text{ (children)}$$

Food products (a 100 % consumption of own crop means an fpc = 1):
Crops: $I_{c,a}$ = 0,11 * fpc * C_{pw} (adults)
  $I_{c,c}$ = 0,26 * fpc * C_{pw} (children)

Meat: $I_{me,a}$ = 0,02 * fpme * C_{pw} (adults)
  $I_{me,c}$ = 0,05 * fpme * C_{pw} (children)

Milk: $I_{mi,a}$ = 0,01 * fpmi * C_{pw} (adults)
  $I_{mi,c}$ = 0,02 * fpmi * C_{pw} (children)

Drinking water
  $I_{dw,a}$ = 0,03 C_{dw} (adults)
  $I_{dw,c}$ = 0,07 C_{dw} (children)
  C_{dw} = 25 * 10^{-4} * C_{pw}.

Legal standards

No legal standard in Spanish law or EEC regulation about a minimum soil quality for housing exist. In Holland in soil protection policy the multifunctionality of the soil is chosen as a basis for standard setting. This means that the soil must potentially be suited to fulfill all the originally existing functions (VROM, 1988). The housing function comes close to multifunctionality, because many relevant transferpaths for human exposure are involved.

In the Dutch 'Soil Protection Guide' a framework for evaluation of concentration levels for soil and ground water is given. Next to the reference values this framework contains action values for further investigation (B-level) and action values for cleanup investigation (C-level), (see table 3.3.6.1). Although not scientifically wellgrounded, the reference values are connected with multifunctionality.

Table 3.3.6.1   The Dutch reference-, B- and C-values for HCH, individual and total organochloropesticides

substance	Soil (mg/kg d.s.)			Groundwater (µg/l)		
	ref.	B	C	A	B	C
HCH	0,001	.	.	0,01	-	-
Individual chl.	.	0.5	5	.	0,2	1
Total chl.	.	1	10	.	0,5	2
Hg	0,2 + 0,0017 (2L + H) *	2	10	0,05	50	200

* L = lutum content; H = humus content

New, better founded human toxicological and ecotoxicological C-values are proposed by the RIVM (Van den Berg et.al., 1991). Probably they will replace the present C-values in future (Van den Berg, 1991; Denneman & Van Gestel, 1990).

For HCH these new proposed values (still under discussion at this moment) are (in mg/kg):

	C-hum.tox	r	C-ecotox.	r	C-integr.
alpha-HCH	21	6	2	6	2
beta-HCH	0,63	4	-	-	0,63
gamma-HCH	8	6	2	6	2
teta-HCH	24	6	2	6	2

where r = reliability

4   HEXACHLOROCYCLOHEXANES

This chapter contains data on Hexachlorocyclohexane (HCH) concerning production, physical and chemical properties, dispersion patterns, toxicity, exposure routes and health risks. It may form a helpful tool in the planning, execution and interpretation of investigations into possible contamination with HCH and its metabolites. Contamination may be the result of the production of Lindane and the disposal of HCH wastes. Most of the data are derived from the Basic and the Integrated Criteria Document Hexachlorocyclohexanes edited by Slooff and Matthysen, The Netherlands National Institute of Public Health and Environmental Protection RIVM, 1988 and 1990.

4.1   HCH, general aspects

HCH, a man-made organochlorine compound, has 8 stereo-isomers, of which the γ-isomer (lindane) is the best known. This compound is used as an insecticide.

Production of Lindane

Lindane is generally produced in two steps, a production step and an isolation step. In the first step, a mixture of benzene and chlorine gas is heated under luminisence and reacts to a mixture of HCH isomers, the so called technical reaction product (technical HCH). The technical reaction product mainly contains the α-, β-, γ- and δ-isomers. In the second step the technical reaction product is partly dissolved in methanole and then fractionally recrystallised in order to isolate γ-HCH from the other isomers. Only a part of the γ-HCH can be gained this way.

The production process leads to solid waste, waste water and emission into the air. The emissions into the water and the air can be controlled by filters, creating more solid waste.

Physical and chemical properties of HCH-isomers

The general structure of 1,2,3,4,5,6-hexachlorocyclohexane (molecular weight: 290,85) is shown below. Every carbon atom is connected with one H atom and one Cl atom. One bonding is directed in the equatorial plane, the other is parallel to the molecule axis.

Formula of HCH
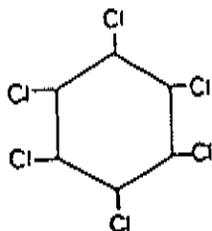
The difference between the isomers is caused by the combination of equatorial and axial places occupied by the Cl atoms. ß-HCH, which is thermodynamically the most stable, has all the Cl atoms on the equatorial positions.

Only the physical properties of the α-, ß-, γ- and δ-isomer are reasonably well known. Some of the most important values are given in Table 4.1.1. It must be noted that the values in literature vary considerably.

Table 4.1.1   Physical properties of HCH isomers

parameters	α-HCH	ß-HCH	γ-HCH	δ-HCH
melting p. (°C)	159	312	113	141
vapour p. (mm Hg, 20°C)	2.54×10^{-5}	2.85×10^{-7}	9.4×10^{-6}	1.7×10^{-5}
solubility (mg/l, 20°C)	1.5	0.2	7.3	9
Henry constant (dimless)	2.7×10^{-4}	2.0×10^{-5}	2.0×10^{-6}	3.0×10^{-5}
log(Kow)	3.81	3.72	3.85	-

Concerning the chemical properties the most important is the persistent character of HCH. At room temperature, all isomers are more or less stable, specially ß-HCH. The isomers do almost not react with acids. In alkaline environments however, heating causes dehydrochlorination, first to pentachlorocyclohexene, then to trichlorobenzene.

The smell of the crude reaction product is mainly caused by the presence of ß-HCH. Pure γ-HCH only has a weak odour. The odour threshold concentrations (Verschueren, 1983) are given in table 4.1.2

Table 4.1.2 Odour treshold concentrations of HCH-isomers in water

	α-HCH	ß-HCH	γ-HCH
odour treshold (mg/kg)	0.088	0.00032	12.0

4.2   HCH in the environment

The main emission of HCH to the environment can be divided in the following primary and secundary processes:
primary:
- disposal of solid and liquid HCH-wastes;
- chimney losses during the production process;
- usage of Lindane or technical HCH as insecticide.

secondary:
- leaching and subsequent transportation in ground- and surface water;
- transport by wind.

In the description of the dispersion properties of HCH in the environment , the following environmental compartiments can be discerned:
- soil (ground/groundwater/soilair);
- surface water
- atmosphere

Removal of HCH from the environment takes place by biodegradation and chemical degradation. It must be noted that these processes may cause the introduction of other possibly harmful substances.

4.2.1   HCH in soil

The flux of HCH to the soil is mainly caused by disposal of solid and liquid HCH-waste, by deposition of chimney losses during the production process and by use of Lindane or technical HCH as an insecticide.

Mobility

Based on the solubility of the different HCH-isomers (0.2-9 mg/l) it can be expected that diffusion of HCH in the soil by leaching and subsequent percolation is possible. However from different studies it is known that adsorption of HCH in the soil can be substantial.

For the description of adsorption processes, the empirically derived Freundlich equitation is often used:

$S = K * Cpw^{(1/n)}$ with:
S   : adsorption to soil particles in mg/kg;
K   : adsorption constant;
Cpw : concentration in pore water in mg/l.

For the adsorption of HCH to sediments and soils, different Freundlich relations have been found. It appears that adsorption mainly depends on the amount of organic material in the soil. The amount of clay particles is of much less importance. Assuming n = 1, the adsorption can be simplified as:

$S = Kp * Cpw$
   Kp : partitioncoefficient (l/kg)

For organic substances a strong relation exists between the partitioncoefficient Kp, the fraction organic material in the soil and the partitioncoefficient at 100% organic material (Koc). The Koc is estimated, following Karickhoff (1981), at 0.4 * Kow. The adsorption of organic components can thus be described as:

$S = 0.4 * foc * Kow * Cpw$
foc : fraction organic material in soil
Kow : octanol-water partitioncoefficient

For a typical soil with an organic material fraction of about 4 - 5 %, the following relation between S and Cpw can be calculated for HCH isomers (log Kow = 3.72 - 3.85):

$$S \approx 100 * Cpw$$

Generally, the adsorption of HCH-isomers is rather strong. Less than 1% of the soil load reaches the groundwater. With respect to applications in agriculture this has led to the assumption that lindane poses no threat to the groundwater. At the high concentrations occuring in local soil pollution (e.g. as a result of dumping), however, washing out of a small percentage of the initial amount may lead to unacceptable concentrations in groundwater.

On the subject of desorption, conflicting results have been found. Bowman et al. (1965), Adams and Li (1971), Bouchier and Lee (1972) and Wirth (1985) found considerable desorption, even in case of materials like peat, while Wahid and Sethunathan (979) observed a very strong adsorption hysteresis.

Degradation

Degradation of HCH isomers in soil mainly takes place by biological processes. The degradation patterns, mentioned in literature show a linear part, changing into an exponential part at low concentrations.
Probably, the degradation rate under anaerobic conditions is higher than under aerobic conditions. From research, it is known that Clostridium-, Bacillus- and Enterobacteria only degrade HCH under anaerobic conditions. In aerobic soils, however, micro-anaerobic zones (for example, pores filled with stagnant water) can occur (Haider, 1980). It must be stated however, that at very high concentrations as occurring in dumps, poisoning of bacteria and poor availability of HCH (in clods) can cause extreme lowering of the degradation rate.

Table 4.2.2.1 gives the most important metabolites of HCH isomers, mainly γ-HCH, mentioned in literature (Yule et al. 1967; Korte, 1980: Haider, 1980; Mathur and Saha, 1977; Kohnen et al., 1974; Haider, 1980).

Table 4.2.1.1 Metabolites formed under anaerobic and aerobic conditions

Environment / Metabolite	Source isomers
Aerobic	
γ-pentachlorocyclohexene chlorobenzenes (tri-hexa) chlorophenoles (penta)	all isomers all isomers (γ-HCH) all isomers (γ-HCH)
Anaerobic	
γ-tetrachlorocyclohexenes γ-tetrachlorocyclohexane trichloro-tetrachlorobenzenes σ-HCH (to 1 % of initial dose)	all isomers γ-HCH γ-HCH γ-HCH

It is not known to which level these metabolites can threaten the soil. It is known however, that in aerobic conditions, chlorobenzenes are very persistent (Bouwer, 1982).

4.2.2 HCH in surface water

The flux of HCH to surface waters is caused by direct input (mainly inflow of contaminated waste water from industries) or indirect input by wind action and by inflow of polluted surface- and groundwater (runoff- and percolatewater from dumping sites or treated agricultural land). The flux of HCH from surface water is caused by evaporation and adsorption to solid particles.

Evaporation

From experiments it is known that γ-HCH losses due to evaporation vary between 3 and 30% per day (Bowman et al., 1964; Büscher et al., 1964; Lichtenstein and Schulz, 1970), which is more than expected on the base of the Henry constant but is in accordance with thermodynamic calculations (MacKay and Walkoff, 1973).

Adsorption

HCH can adsorbe to particals: the more organic carbon the solid material contains the higher the adsorption. Investigations of the adsorption of HCH on active mud gave a 5-day accumulation factor of 1200 for ß-HCH and 800 for γ-HCH (Freitag et al., 1985). There are no data available on the adsorption hysteresis of HCH in sediments.

Degradation

Breakdown of HCH in surface water both takes place by biological and chemical degradation. From research into the biodegradation of α- and γ-HCH in surface water (a.o. Haider and Jagnow, 1975; Engst et al., 1979) it is known that the compounds break down fairly quickly in anaerobic environments, but are more persistent in aerobic environments. Biodegradation produces pentachlorocyclohexane, tetra- and trichlorobenzenes and chlorophenols (Portmann, 1979).

Chemical degradation mainly depends on alkalinity (Ullmann, 1972). In slightly alkaline environments like surface waters derived from calcareous regions as occurring in the area under investigation, a reasonably rapid degradation of HCH to trichlorobenzene could occur.

4.2.3 HCH in the atmosphere

The flux of HCH to the atmosphere is caused by evaporation of HCH from soils and from surface water, by wind action and by chimney losses. The flux of HCH from the atmosphere to the land surface is caused by dry and wet deposition. Because of the low vapour pressure and the high adsorption, HCH will evaporate slowly from the soil and the water. Higher concentrations in the air may occur as a result of emissions (use as insecticide, chimney losses) and by dispersion of dust from local soil pollution (such as dumpsites).

4.2.4   HCH in biota

HCH is added to organisms through ingestion of soil, food, groundwater, surface-water and drinkingwater.

In waterorganisms, the bio-accumulation factor amounts to 100-1000 with probably limited foodchain effects and rapidly reached equilibrium levels. In soil organisms, the accumulation/elimination process is slower (equilibrium levels reached within 5 weeks) and bioaccumulation is low. In plants HCH is mainly adsorbed by the roots. The transferfactor (concentration in plant divided by concentration in soil) depends on the soil type, the organic fraction and the plant type.

4.3   Effects of HCH

Experimental data on metabolism and toxicity are available for a-, ß-, γ- and δ-HCH and for the isomer mixture of technical HCH. HCH-isomers are readily absorbed in the gastro-intestinal tract: values of more than 90% of the dosages are reported. For γ-HCH substantial absorption through the skin was found for humans. After absorption the higest concentrations are present in fatty tissues. The extent of accumulation in these tissues can be given as ß- > a- > γ-HCH and is appearantly higher in females than in males.

The exact metabolic pathway of most HCH-isomers is not known. Animal experiments show that 2,4,6-trichlorophenol is the major metabolite for a-, ß- and δ-HCH. In addition biotransformation of γ-HCH yields substantial quantities of 2,4,5-trichlorophenol and 2,3,4,6-tetrachlorophenol.

a-HCH
Continuous accumulation of a-HCH has not been demonstrated in rats, but substantial accumulation may occur. In rats, excretions in milk were observed. Acute oral toxicity of a-HCH is slight to moderate. For rats LD50-values of 500 to 4674 mg/kg body weight were obtained. In a 90-day study on rats, effects (leucocytopenia and liver changes, indicating enzyme induction) were observed at 10 mg/kg feed and higher. The no-effect-level (NEL) was 2 mg/kg feed. This is approximatly 0.1 mg/kg body weight. Using a safety factor of 100, a tolerable daily intake (TDI) of 0.001 mg/kg body weight can be calculated. An acceptable daily intake (ADI) is not determined, a-HCH being considered an undesirable pollution.

a-HCH cannot be qualified as an initiating carcinogen (there is no evidence for genotoxic action), but hyperplasia, nodules and tumors developed at high dosage levels in mice and rats.

ß-HCH
In all studied species including man, continuous accumulation and slow elimination upon cessation has been found. Over several years the concentration in fatty tissues decreased to a small degree only. In The Netherlands, in recent investigations on humans, median concentrations of 100 μg/kg fat tissue were found. The levels found are markedly higher than those of the other isomers. This reflects the cumulative properties of ß-HCH.
Acute oral toxicity is low (LD50 values > 1500 mg/kg body weight for rats and mice). In 90-day toxicity studies on rats white blood abnormalities, liver hypertrophy, kidney damage and, at high dosage levels only, hormone-like changes, decreased activity and tremors were the most prominent effects. A tentative NEL derived from this studies is 0.4 mg/kg feed, this is 20 μg/kg body weight per day. This level may necessitate adjustment due to the results of additional reproduction studies.

Because of its cumulative properties, it is concluded that permanent exposure to this compound is not desirable. Therefore a tolerable dose at chronic exposure cannot be given. To estimate the toxicological risk in case of local pollution a TDI of 0.02 μg/kg body weight/day can be used. This value is derived from the NOAEL, using a safety factor of 1000 (Vermeire et al, 1991). In other studies a lower safety factor of 100 is used (Provinciale Waterstaat Overijssel, 1985). Vermeire et al. chose the safetyfactor of 1000, because only a NOAEL of a subchronical test is available and excretion of ß-HCH is very slow (Vermeire, 1991b).

Based on an unsufficient number of mutagenicity experiments, ß-HCH cannot be qualified as an initiating carcinogen. Carcinogenicity studies in mice showed similar results as those for α-HCH. These effects did not occur in rats.

γ-HCH

Absorption after oral intake is almost complete and dermal absorption is probably considerable. In rats, elimination is fairly rapid. In humans, no accumulation in fat was found. Acute oral toxicity is moderate. LD50 values ranged from 70 to 480 mg/kg body weight for mammals. In a 90-day study on rats, kidney and liver damage were observed at dosages of 4 mg/kg feed and higher. In a similar study on dogs, liver effects and kidney changes were found at dosages of 10 mg/kg feed and higher. The short-term NEL in rats is 2 mg/kg feed. This is approximatly 0.1 mg/kg body weight. With a safety factor of 100 this results in an ADI for the oral route of 0.001 mg/kg body weight.

In a 90-day inhalatory study, in which rats were exposed for 6 hours a day a short term inhalatory (NEL) of 0.1 mg/m³ was found. This corresponds with a NEL for continuous exposure of 25 μg/m³. With a safety factor of 100 this results in a tolerable concentration level (TCL) for continuous exposure of 0.25 μg/m³. Because of similarity in toxicity between α- and γ-HCH this value is applicable to the total concentration of this two compounds (Vermeire et al, 1990).

Based on mutagenicity experiments, γ-HCH cannot be qualified as an initiating carcinogen, but may cause cytogenic damage, induce C-mitosis and may cause chromosome abberations. Carcinogenicity studies in mice showed similar results as those for ß-HCH. At high dosages, tumors developed in mice but not in rats.

δ-HCH

No clear data on accumulation in fat exist. Acute oral toxicity of δ-HCH is slight to moderate (LD-50 values: 750-1000 mg/kg body weight for mammals).
Short-term and long-term studies are not available. Data on mutagenicity of δ-HCH are not available. Only two limited studies are available on carcinogenity, which were negative.

Technical HCH

No evidence for synergistic action of the isomers has been found. Because of the similarity beteen the toxicity of α- and γ-HCH the effects of this isomers can be considered as additive: one limit value for the sum of these two isomers is adequate. Vermeire et al. (1991) propose to consider δ-HCH as additive as well. This means for a toxicological evaluation the exposure to α-, γ- and δ-HCH can be taken together. The toxicological properties of ß-HCH differ from those of the other isomers. Therefore it is not possible to set one limit value for technical HCH or for the sum of all the isomers.

Review toxicological limit values

In table 4.3.1 a review of the toxicological limit values for human exposure is given.

Table 4.3.1 Toxicological limit values HCH-isomers for human exposure

isomer	TDI oral (µg/kg b.w.)	TCL inhalatory (µg/m³)
$\alpha + \gamma(+\delta)$-HCH ß-HCH	1 0.02	0.25

TDI = tolerable daily intake
TCL = tolerable concentration level

5 MERCURY

This chapter contains an overview of data on mercury concerning sources, physical and chemical properties, dispersion patterns, toxicology and other aspects. It may form helpful tools with the planning, execution and interpretation of investigations of possible contaminations with mercury. Most of the data are derived from the Exploratory document Mercury, edited by the Dutch National Institute of Public Health and Environmental Protection (RIVM). Another important source were the Environmental Health Criteria documents nr. 1, 86, 101 and 118 from the WHO/UNEP IPCS-series.

5.1 General aspects

Production and use

By far the most important source of mercury is mercury ore. This ore mainly consists of mineral mercury sulphide, named Cinnabar. Mercury is derived from Cinnabar by roasting it to about 500 °C, at which temperature it decomposes to mercury vapour. In 1980, the world production of mercury amounted 11.000 ton (Adam et al, 1980). This figure varies considerably from year to year, depending on the commercial value of the metal. Within the European Community, the Almaden mine in Spain accounts for 90 % of the EEC-production of mercury. The production in 1987 was expected to be 1380 tons (IPCS, 1990).

A major use of mercury is as a cathode in the electrolysis of sodium chloride in the chloralkali-industry. Quantities in the order of 10 tonnes or more of liquid metal are used in each manufactury plant. It should be noted that all the electrolytic products (like hydrogen, sodium hydroxide, sodium hypochlorite and chlorine) are contaminated with mercury. Their use in other industrial activities therefore may lead to a contamination of other products. The specific normal emission from a chloralkali plant is 450 g of mercury per ton of caustic soda produced (IPCS, 1991). The EEC has set monthly average effluent standards ranging from 0,5 to 5,0 grams of mercury per ton of installed chlorine production capacity (EEEC, 1982). Table 5.1.1 gives a review of the major other uses and anthropogen sources of mercury contamination (adapted from RIVM, 1991).

Table 5.1.1   Mercury contamination, sources and influenced compartiments.

Source	Air	Water	Waste
Chloralkaly industry	+ +	+	+
Dentists	-	+ +	+ +
Batteries	.	-	+ +
Thermometers	?	+	+ +
Electrical equipment	.	.	+
Crematory	+	-	-
P-fertilizer	-	+	.
Natural Gas, Purification and use	+	+	+ +
Fossil fuels, use	+	-	?
Smelting of ores and metals	+ +	+	?
Waste incineration	+	.	.

legend: + +, + : relative emission per source; ? : no data; · : no emission

Physical and chemical properties

Mercury (Hg) is a heavy metal, naturally occurring in the environment. It belongs to the same subgroup as zinc and cadmium, but shows such unique behaviour that it cannot be considered as homologous to those metals. In the univalent state, mercury occurs as Hg_2^{2+} (mercurous) and in the divalent state as Hg^{2+} (mercuric). The mercourous and mercuric states form numerous inorganic and organic compounds (IPCS, 1991). Organic forms are those in which mercury is attached covalently to at least one carbon atom. The most important organic form is methylmercury, which arises largely, if not solely, from the methylation of inorganic mercury. This transition is the first step in the bioaccumulation process in the food chain (IPCS, 1991). Some basic physical properties of mercury are given in table 5.1.2.

Table 5.1.2 Basic physical properties of mercury

Parameter	Value
density (g/cubic cm)	13,5
melting point (°C)	-49
boiling point (°C)	57
solubility (HgCl, mg/l, 25 °C)	2
solubility (HgCl2, g/l, 20 °C)	69
solubility (Methylmerc. mg/l)	ca. 6
vapour pressure (Pa, 273 °C)	0,0247
vapour pressure (Pa, 293 °C)	0,16

5.2   Mercury in the environment

In the description of the dispersion properties of mercury, the following environmental compartiments can be discerned:

- soil (ground/groundwater/soil air);
- surface water and sediments;
- atmosphere;
- biota (flora/fauna);

One of the most important changes in speciation of mercury is the transition from inorganic to methylated forms. This is the first step in a bioaccumulation process, which will be described in more detail in the paragraph on mercury in water and sediments.

5.2.1 Mercury in soil

Mobility
The mobility of mercury is mainly depent on the following factors:
1 Complexation with anorganic and organic agents.
   The most important anorganic agents enhancing solubility in groundwater are chloride and hydroxide. Important organic complexes are monomethyl- and dimethylmercury which are formed by a microbial methylation process that is is mainly limited to fluvial and marine sediments. The mobility of monomethyl-mercury is caused by its volatility while dimethylmercury is relatively soluble.

2 Evaporation after breakdown of Hg(II) compounds to Hg°.
   The breakdown of Hg(II) compounds is mainly caused by microbial activity while the dissociation reaction $Hg_2^{2+} = Hg^{2+} + Hg°$ plays an important role in the formation of Hg°.

3 Adsorption of mercury to soil compounds.
   The most important factor controlling the absorption of mercury is the availability of organic substance. Also, clay minerals and iron oxides play an important role in the demobilisation of mercury. However, the extractability with CaCl, indicating susceptability for chloride complexation, is much higher in case of clay and iron oxide then in the case of organic matter.

For metals no simple equation can be given for the relation between the soil and the pore water concentration. Empirical deduced partitioncoefficients (Kp) vary considerably. In the literature values are found from 12 to 110000 l/kg (v.d. Berg and Roels, 1990).

Natural background levels
Natural backgroundlevels of mercury in soils and sediments vary between 0,02 and 0,5 mg/kg, but are generally below 0,1 mg/kg (IPCS, 1989). These values tend to increase with the C_{org} content (Schachtschabel et al. 1989). In rocktypes that contain Cinnaber or other Hg-rich minerals, much higher concentrations can occur. Natural background levels in ground water are generally below 0,05 μg/l.

Levels in polluted soils
Most data on polluted soils concern river and lake sediments. In The Netherlands, mercury contents are recalculated to a 50% < 16 μm fraction because most of the mercury is bound to this fraction. In contaminated river sediments in The Netherlands, concentrations up to 6 mg/kg (Rhine) and in Germany up to 20-30 mg/kg (Elbe and Rhine) have been found (RIVM, 1991; Schachtschabel et al 1989).

5.2.2 Mercury in surface water and sediments

Behaviour

As in soils, the behaviour of mercury in surface water is complex. Generally, mercury tends to adsorb strongly to particulate matter, specially organic matter.

In well areated freshwater (Eh > 0.5 V), the main species of Hg are $Hg(OH)_2$, HgOHCl and $HgCl_2$, depending on pH and pCl (Stumm and Morgan, 1981, Salomons and Forstner, 1988). The adsorptive capacity of sediments was shown to decrease in the order HgOHCl > $Hg(OH)_2$ > $HgCl_2$ (Liu Ching and Tang Hongxiao, 1985).

In more reducing environments and in the presence of free-sulphide ligands, mercury is bound as extremely insoluble sulphide precipitates or as surface complexes with organic material containing sufphur donor atoms (Craig and Moreton, 1985). However, at very high sulphide concentrations, mercury concentrations may increase up to several $\mu g/l$ due to the formation of polysulphide complexes (Lindberg and Harris, 1974).

Methylation

Methylation takes place mostly on sediments in fresh and ocean waters. Methylation of inorganic mercury involves the non-enzymic methylation of Hg^{2+} by methyl cobalamine compounds (analogues of vitamin B_{12}) that are produced as a result of bacterial synthesis (IPCS, 1990). Methylmercury accounts for approximately 0,1-1,5 % of the total mercury in sediments. The rate of methylation is higher under anaerobic conditions than under aerobic conditions (Ferguson, 1990). Temperature affects methylation as a result of its effect on overall microbiological activity. The formation of new or enlarged artificial lakes is believed to increase the production of methylmercury (IPCS, 1989).

In aquatic systems, methylmercury is the most important species. In fish, about 80-90% of the mercury is present as methylmercury. The bioconcentration factor, i.e. the ratio of the concentration of methylmercury in fish tissue to that in water, is usually between 10^4-10^5 (CCCRX, 1986; IPCS, 1990).

Bioconcentration factors in other water organisms and related organisms are 400-700 (plankton), 1000 (macrobenthos) and 6000-7000 (waterbirds) (Liu Ching and Tang Hongxiao, 1985). It should be noted that these bioconcentration factors are not the result of partition between water and the tissue but of biomagnification through the food chain (IPCS, 1990).

Natural background levels

In aquatic systems natural background concentrations of about 1-3 ng/l have been reported, whereas in sediments concentrations range from 20 to 625 $\mu g/kg$ (IPCS, 1989).

Levels in polluted areas

Investigations of Rhine-, Meuse- and IJsselwater in the period 1971-1984 showed that about 60-80% of the mercury is adsorbed to particulate matter. This percentage is based on the assumption that analysis after filtering over a 45 μm filter represents the dissolved fraction (CCRX, 1986). The average concentration of dissolved mercury (i.e. fraction < 45 μm) in Rhinewater is about 1×10^5 times less than in particulate matter and sediments.

5.2.3 Mercury in the atmosphere

Washout in rainwater forms the main mechanism of removal from the atmosphere. The rate of washout depends on the speciation. Oxidised or methylised mercury compounds are more rapidly removed because of their relatively elevated solubility. As mentioned in the part on behaviour in soils, removal of mercury from soils to the atmosphere is mainly caused by evaporation after reduction of mercury to the native form or by evaporation after methylation.

5.2.4 Mercury in biota

In aquatic systems, methylmercury is the most important species. In fish, about 80-90% of the mercury is present as methylmercury. The bioconcentration factor, i.e. the ratio of the concentration of methylmercury in fish tissue to that in water, is usually between 10^4-10^5 (CCCRX, 1986; IPCS, 1990). Bioconcentration factors in other water organisms and related organisms are are 400-700 (plankton), 1000 (macrobenthos) and 6000-7000 (waterbirds) (Liu Ching and Tang Hongxiao, 1985). It should be noted that these bioconcentration factors are not the result of partition between water and the tissue but of biomagnification through the food chain (IPCS, 1990).

Because of the very low solubility in ground water, the uptake of mercury in plants is generally low. In two cases (7 and 27,5 mg/kg mercury in soil) mercury concentrations in salad were elevated to 0,08-0,12 and 0,32 mg/kg d.w. respectively. In another case with strongly contaminated golf courts (130 mg/kg in soil), concentrations up to 200 mg/kg d.w. were measured in grass (Schachtschabel, 1989). These values indicate that in strongly contaminated soils, significant uptake of mercury in plants may occur. The transfer of mercury to grazing cattle trough ingestion of contaminated food is generally low. Only in the liver and in the kidney, significant but not alarming elevations occur (CCRX, 1986).

5.3 Effects of mercury

Inorganic mercury
Results of both human and animal studies indicate that about 80 % of inhalated mercury vapour is retained by the body, whereas liquid metallic mercury is poorly absorbed via the gastro-intensinal tract (less than 1 %). Inhalated inorganic mercury aerosols are deposited in the respiratory tract and absorbed, the rate depending on particle size. Inorganic mercury compounds are probably absorbed from the human gastrointestinal tract to a level of less than 10 % on average, with considerable individual variation (IPCS, 1991).
Kidneys accumulate the highest tissue concentrations independent from the form of mercury. The most critical organ for exposure to inorganic mercury is the central nervous system (Vermeire et al., 1991). Occupational exposure may lead to tremor and other functional disturbance, whereas subacute disposal has given rise to reactions like delirium and hallucinations. There is no evidence that mercury is a carcinogen (IPCS, 1990). Elemental mercury vapour rapidly crosses the placenta. Infant suckling from heavily exposed mothers can cause dangerously high blood concentrations.

Methylmercury

It is estimated that after inhalation about 80% of the monoalkylmercury compounds is retained. Gastro-intestinal absorption of methylmercury is almost complete. Distribution of methylmercury to all tissues is completed within 4-6 days. The rate of excretion is proportional to the body burden and can be described with a biological half-time of about 40 to 70 days. In the case of continuous exposure a whole-body steady state (where intake equals excretion) will be reached after one year; the maximum amount accumulated will be about 100 times the daily intake. Also for methylmercury the most critical organ for exposure is the central nervous system. Methylmercury is teratogenic; it passes the placenta and causes growth delay of brain of the foetus, resulting in a mentally retarded child (Vermeire, 1991, IPCS, 1991).

Hair is a useful indicator for people exposed to methylmercury. Some average reference values for total mercury in commonly used indicator media are given in table 5.3.1

Table 5.3.1   Reference values for indicator media, total-mercury (WHO, 1990).

Tissue	Reference value
Blood	8 μg/l
Hair	2000 μg/kg
Urine	4 μg/l
Placenta	10 μg/kg fat weight

Toxicological limit values

The WHO Committee on Food additives (JEECFA) has established a provisional tolerably weekly intake for mercury of 300 μg/per person (43 μg/per person/day), of which 200 μg methylmercury (28 μg/per person/day). These values are mainly based on epidemologic studies in cases of high mercury intake as a result of consumption of fish contaminated with methylmercury (Ferguson, 1990; Vermeire, 1991). These values are believed to give sufficient protection against foetal damage. On the basis of an average body weight of 70 kg a TDI was derived of 0,61 μg/kg b.w./day for the sum of all mercury compounds and 0,4 μg/kg b.w./day for methylmercury. The background exposure is about 0,14 μg/kg b.w./day (Vermeire, 1991).

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HRGC-ECD AND HRGC-NICI SIM QUANTIFICATION OF TOXAPHENE RESIDUES IN SELECTED MARINE ORGANISM BY ENVIRONMENTALLY RELEVANT CHLOROBORNANES AS STANDARD.

By Li Xu, Dominik Hainzl, Jürgen Burhenne and Harun Parlar

ABSTRACT

The HRGC determination of Toxaphene[R] residues in fish tissues is often difficult because of the differing accumulation behaviour and decomposition rates of the individual Toxaphene compounds. This problem can satisfactorily be overcome by using purely isolated environmentally relevant chlorinated bornane derivatives (Parlar nr. 26, 32, 50, 42, 69). The method is highly selective for measuring Toxaphene residues in complex marine organism matrices.

1   INTRODUCTION

The chlorinated bornanes are known under several trade names such as Toxaphene[R], Strobane[R], and Melipax[R]. Two thirds of their production is used for cotton insect control, while other uses include soy beans, vegetables and control of external insects on livestock. It's annual production was about 50 million pounds in the last 25 years [1,3]. In the 1980's an investigation of the environmental relevance according to ecotoxicological criteria led to a ban on use and production first in the USA and later in other countries [4,5]. But even in recent years some typical cotton-growing countries and the former GDR have continued to manufacture chlorinated bornanes and to apply them intensively in agriculture[6]. The occurrence of volatilized residues of Toxaphene in the atmosphere was determined at various locations in the Unites state[7]. Toxaphene compounds were detected in air samples partly adsorbed on aerosols collected over the western North Atlantic[8]. In ocean surface water and in different soils chlorobornane derivatives occur very frequently, too[9].

Although some research groups have determined Toxaphene residues in various environmental samples such as fish, liver oil, fish oil, animal fat etc [10-15], the trace analyses of these compounds has not been paid the attention due to it in view of this distribution behaviour and toxicological effects in the biosphere [16-18]. This is because there are, on the one hand, problems in the separation of individual peaks in the capillary gas chromatography 19,20 and secondly, possible interferences with other chlorinated hydrocarbons with the same GC retention times. Therefore it is necessary to use environmentally relevant chlorinated bornanes as standards during the quantification of Toxaphene residues.

With the help of three purely isolated chlorinated bornane derivatives[21], namely 2-exo, 3-endo, 5-exo, 6-endo, 8b, 8c, 10a, 10b-octachlorobornane (Parlar No. 26), 2-exo, 3-endo, 5-exo, 6-endo, 8b, 8c, 9c, 10a, 10b-nonachlorobornane (Parlar no. 50), and 2, 2, 5, 5, 8b, 8c, 9c, 10, 10-nonachlorobornane (Parlar nr. 62) (see Fig. 1) it is possible to quantify Toxaphene residues in marine organisms.

The components Parlar no. 26, 50, and 62 constitute the major proportion of the total Toxaphene residues observed by GC-MS/NICI-SIM and GC-ECD analysis of aquatic biota extracts 14-16,22 (see Fig. 1). The total amount of Parlar Nr. 26, 50, and 62 constitute 25-30% of the chlorobornanes n cod liver oils, 8-12% in fish and 10% in caviar (see Tab. 1, attached). The first isolated and identified product from the Toxaphene mixture, the so-called Toxicant B[1,2] (Parlar nr. 32) could be found in very low quantities in fish and fish products.

Decachlorobornane, for example Parlar no. 69, cannot be determined in the extracts of fish products because of their instability under environmental conditions. But both compounds are detectable in technical Toxaphene at amounts between 0,1 and 1,1% of the total chlorobornane residues. This fact can be used to determine wether a direct fresh contamination with technical Toxaphene does exist or not. In this case the concentration of the compounds Parlar no. 32 and 69 are considerably higher than in ripe marine tissues as found in the samples after fish toxicity experiments, carried out with technical Toxaphene[22].

The presented data of the Toxaphene residues quantified by using the new standard mixture show that especially samples from the North Atlantic and the North Sea are highly contaminated by Toxaphene. In most of the investigated fish products the levels of Toxaphene exceed those of the PCB's. Therefore it is necessary to determine the residue levels of these substances in different marine samples to be able to compare the contamination of different organisms.

2   EXPERIMENTAL

Toxaphene (Camphechlor, standard mix with compounds Parlar nr. 26, 32, 50, 62, and 69, and aldrin reference standards were obtained from Ehrenstorfer, germany. The CB-standard was prepared by UV-irradiation ($\lambda = 254$ nm) of Toxaphene in n-hexane[2]. Organic solvents used were n-hexane, cyclohexane, dichlormethane, and carbon tetrachloride of purity grade for residue analysis. Na_2SO_4 and H_2SO_4 (95-97%) were from Merck, Germany. Standards and samples were analyzed on a Hewlett-Packard 5890/5988A GC-MS system equipped with a 25 m x 0,2 mm capillary colomn (HP-5, film thickness $= 0,33$ μm) with helium as carrier gas ($\approx$ 1 ml/min). The chromatographic time - temperature °C at 4 °C/min. The injectionport and transfer lines were maintained at 280 °C. The ion source temperature for the NICI mode was 100 °C. CH_4 was used as reactant gas. The emission current was approximately 200 μA.

HRGC-ECD routine measurements were performed with a Varian 3300 system, equipped with a 25 m x 0.2 mm capillary column (HP-5, film thickness $= 0,5$ μm) with nitrogen as carrier gas ($\approx$ 2 ml/mn); for better resolution it is recommended to use helium as carrier gas. The chromatographic time - temperature conditions were as follows: splitless injection - initial temperature 150 °C - to 250 °C at 5 °C/min.

The injection port was maintained at 250 °C. Detector temperature was 280 °C. HPLC experiments were performed with a Perkin-Elmer, Series 3B system, equipped with a Necleosil 120-5 C 18 column, mobile phase: acetonitrile/water gradient.

The analyzed fish and fish products were obtained from Iceland, Greenland and Germany. The samples were kept under -12 °C until used. 15-30 g fish or caviar tissue were minced with 60-120 g anhydrous sodium sulfate to fine powder and Soxhlet extracted with cyclohexane/dichloromethane (2:1) for 4 h. The extracts were reduced to about 30 ml by a rotary evaporator. Lipids were treated with conc. H_2SO_4 until H_2SO_4-phase remained colourless. The organic phases were collected, washed with tri-distilled water till neutral, dried with 10 g anhydrous Na_2SO_4 overnight, reduced to 0.5 ml and stored at - 12 °C until further fractionation on silica gel. Oil samples (2 g) were dissolved in 50 ml n-hexane, followed by a DMF/n-hexane distribution to separate the fat content of the samples. This method was favoured because of the excellent recovery rates of chlorobornanes (90-95%) by using a H_2SO_4.

A pre-separation of the chloropesticides was carried out by silica gel fractionation. The columns were prepared with 4.3 g silica gel 60 (70-230 mesh, activated at 140 °C for 25 h, and then deactivated with 5% water). For better reproducibility the use of 0.3 bar N_2 overpressure is advantageous. The resulting elution speed is about 7.1 ml/min. Impurities of the silica gel were eliminated by pre-elution with 30 ml n-hexane. Best results for the fractionation were obtained by eluting first with n-hexane (including 0.5 ml sample extract) and then with 9 ml of a mixture of n-hexane/dichloromethane (2:1). The first of the three resulting fractions contained PCBs, the second mostly DDE, and the third Toxaphene residues. Toxaphene reactions were reduced to approximately 1 ml and stored at - 12 C. The extracts were reduced to approximately 200 μl under gentle N_2-stream prior to the NICI-SIM analysis.

3   GC-MS/NICI-SIM QUANTIFICATION

The ions 340, 341, 342, 343, 375, 377, 411, 413, 447 and 449 are monitored for the quantification, which are common to both families of compounds, chloro-bornanes and bornanes. While many of the chlorinated hydrocarbon interferences are no problem when monitoring for selected fragments, there are several sub-stances that give the same ions as those of the standard. These include especially dieldrin, heptachlor, and technical chlordane, which contain cis- and trans-chlordane or cis- and trans-nonchlor, respectively, as major compounds. These substances, however can be satisfactorily eliminated by capillar gaschromato-graphy. They all have retention times different from those of the standards used in this work. In addition to that, these compounds yield a small molecular ion cluster and almost no (M-Cl) ion cluster in NICI. As a result, the main ions that are pro-duced by cyclodieninsecticides are different from those arising from the standards, and there are no mutual interferences.

Other potential interferences, including p,p'-DDT, p,p'-DDD and p,p'-DDE, show no signals in the traces of ions used for quantification of Toxaphene.
The NICI responses of the pure standards were linear over 4 orders of magnitude and the detection limits were between 0.3 and 7.0 pg absolute[21]. The fragmenta-tion of ions and their sensitivity of NICI are effected by the ion-source pressure and temperature and furthermore by the degree of chlorination.

Previous experiments in our laboratory have shown that a maximum of reprodu-cibility for the analyses of Toxaphene standards can be achieved at a pressure of 2×10^4 Torr and 100 °C. Therefore, our residue analyses were accomplished under these conditions. The NICI-SIM response factors for the chlorobornanes differ fundamentally from each other. They lie between 0.21 and 5.28[21] and point out the difficulties in the quantification of Toxaphene residues by negative-ion chemical-ionization mass spectroscopy using technical standards. In contrast to this behaviour, the relative ECD response factors of the hepta- tot nonachlorobor-nanes, present in the environmental samples, are almost similar and vary between 1.0 and 1.42.

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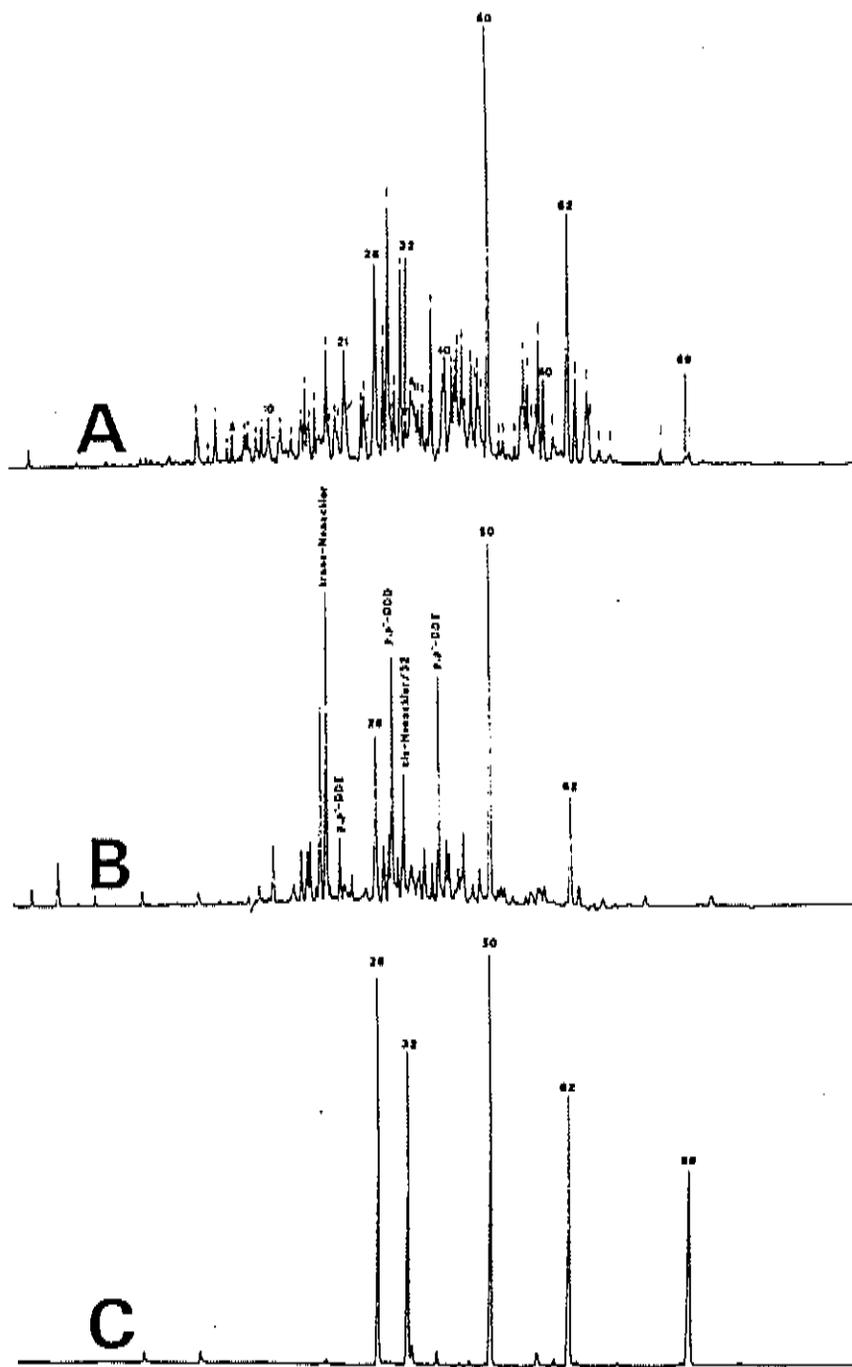
Fig. 1. HR-GC/ECD gaschromatograms of CB-standard "A", cod liver oil extract from Iceland "B", and standard mix "C" (Parlar No. 26, 32, 50, 62, 69). Conditions see exp. part.

Table 1. Concentrations (μg/kg) of the chlorobornanes and Toxaphene in samples of aquatic biota (I = HR-GC/ECD, II = HR-GC-MS/NICI-SIM). Total Toxaphene concentrations $[C_{Tox}]$ determined by using the CB-Standard . F (Conversionfactor) $= \dfrac{C_{Tox}}{C_{\Sigma 92,50,62}}$

Sample	Origin	Wet weight (g)	Fat (%)	Parlar No. 26 I	II	Parlar No. 32 I	II	Parlar No. 50 I	II	Parlar No. 62 I	II	Parlar No. 69 I	II	C_Σ 32,50,62 I	II	C_{Tox} I	II	F I	II
Caviar	Iceland	18	3.17	n.d.	< 0.10	2.50 ±0.80	2.40 ±0.80	3.70 ±1.00	3.35 ±0.90	1.22 ±0.40	1.01 ±0.40	< 0.10	n.d.	7.42	6.76	72-30	67-24	9.70	9.91
Caviar	Denmark	15	3.33	n.d.	n.d.	1.95 ±0.75	1.92 ±0.71	2.55 ±0.70	2.40 ±0.75	0.50 ±0.10	0.48 ±0.12	n.d.	n.d.	5.00	4.80	52±20	47±17	10.40	9.79
Caviar	Germany	15	5.10	n.d.	n.d.	1.95 ±0.80	1.90 ±0.75	2.76 ±0.74	2.50 ±0.85	0.79 ±0.22	0.25 ±0.10	n.d.	n.d.	5.50	4.65	54±20	44±17	9.81	9.46
Caviar	Germany	15	3.73	n.d.	< 0.10	2.00 ±0.75	1.80 ±0.65	3.00 ±0.70	2.84 ±0.76	0.60 ±0.20	0.20 ±0.10	< 0.10	n.d.	5.60	4.84	56±24	49±20	10.00	10.10
Caviar	Germany	15	9.47	n.d.	< 0.10	1.20 ±0.55	1.00 ±0.35	5.13 ±1.17	4.56 ±1.03	0.77 ±0.21	0.69 ±0.32	< 0.10	n.d.	7.10	6.25	70±30	60±20	9.86	9.92
Sea-eel	France	15	21.60	< 0.10	0.20 ±0.10	10.25 ±3.20	9.20 ±2.70	19.00 ±4.10	20.10 ±5.00	6.35 ±2.50	5.70 ±1.95	0.20 ±0.10	0.20 ±0.10	35.80	35.00	350±95	333±97	9.77	9.51
Sea-eel	Spain	15	11.27	n.d.	n.d.	10.00 ±3.30	9.80 ±2.85	18.45 ±4.05	19.20 ±4.00	1.65 ±0.75	1.27 ±0.53	n.d.	n.d.	30.10	30.20	315±85	300±75	10.46	9.93
Sea-eel	Germany	15	13.40	n.d.	0.20 ±0.10	7.25 ±2.05	5.90 ±1.20	10.20 ±2.70	10.40 ±2.50	3.70 ±0.90	3.70 ±0.90	n.d.	n.d.	21.15	20.00	200±60	190±55	9.46	9.50
Sea-eel	Italy	15	13.42	n.d.	n.d.	5.60 ±1.20	5.00 ±1.10	8.50 ±2.10	7.90 ±1.90	0.45 ±0.10	0.60 ±0.10	n.d.	n.d.	14.55	13.50	140±45	122±36	9.62	11.61
Cod fish	Greenland	18	0.05	n.d.	n.d.	50.00 ±24.00	40.00 ±16.00	82.00 ±32.00	86.00 ±36.00	50.00 ±24.00	54.00 ±24.00	n.d.	n.d.	182.00	180.00	1920 ±620	2010 ±700	10.55	11.16
Red fish	Greenland	30	0.90	n.d.	n.d.	7.00 ±2.00	9.00 ±3.00	15.80 ±8.00	27.00 ±15.00	8.00 ±4.00	17.00 ±5.50	n.d.	n.d.	30.00	53.00	310 ±120	425 ±180	10.33	8.02
Cod liver oil	Iceland	2		n.d.	<0.10	440 ±280	455 ±285	645 ±230	736 ±245	236 ±74	203 ±70	n.d.	<0.10	1320	1394	4810 ±1255	5020 ±1970	3.64	3.60
Cod liver oil	Germany	2		n.d.	<0.10	210 ±70	220 ±75	405 ±240	420 ±250	80 ±30	110 ±60	n.d.	n.d.	695	750	2730	2810	3.92	3.75
Salmon oil	Norway	2		n.d.	n.d.	33.00 ±13.00	21.01 ±7.02	60.03 ±28.03	75.09 ±29.05	9.05 ±3.01	14.01 ±5.02	n.d.	n.d.	102	110	1100 ±330	1250 ±325	10.78	11.36

4. Inventory of Sites Contaminated by Halogenated Pesticides

CASE STUDIES ON HCH WASTES AND CONTAMINATED SITES IN THE BASQUE COUNTRY
By Anton Azkona & Ignacio Quintana

1   FOREWORD

The Basque Country faces a serious environmental problem arisen from the lack of management of the wastes produced by the lindane industry for the last four decades. Two companies, Bilbao Chemicals and Nexana-Celamerk, located in the environs of Bilbao and decommissioned at present, have carried out this activity for over forty years producing in this period an approximate amount of 100,000 tons of HCH wastes.

Bilbao Chemicals, the oldest of these two firms, was founded in 1944 with the aim of producing pesticides, HCH in particular. Nevertheless it was not until 1953 when the system for extracting y - HCH, lindane, from the mixture of the HCH isomers was introduced in the factory, beginning at that moment the production of a huge amount of HCH wastes. From 1953 to 1987, when the Basque Authorities banned the dumping of this kind of wastes, their production was estimated at approximately 70,000 tons. This quantity of HCH wastes together with some other 5,000 tons brought by Bilbao Chemicals from another factory in Aragón were dumped in an illegal way.

Nexana-Celamerck was operating for thirty years. The amount of HCH wastes produced in this period is estimated at 14,000 tons. Half of this quantity was sent to Catalonia to be chemically converted into chlorobenzene and the remaining 7,000 tons were dumped in the surroundings of the factory.

According to this information the total amount of HCH wastes dumped in the Basque Country has been calculated in 82,000 tons. To date thirty dumping sites containing this type of wastes have been identified. These contaminated sites are basically spread out over the province of Biscay and in the surroundings of the above mentioned companies; fourteen of them are located on the left side of the river Nervión and in the mining zone, and some others along the right side (figure 1).

Apart from the problems of merely environmental nature, the sites where HCH wastes have been detected are affecting to a great extent the economic recovery plans designed for those areas, hindering at the same time important development projects. It should not be forgotten either that cases like the old pesticide plant Bilbao Chemicals mean an unacceptable risk for the inhabitants of the neighbourhood.

Although once the lindane production is over, the probability of new contaminated sites being generated is negligible, the inherited problem is of such a magnitude that requires an effort to find a final solution.

The strategy designed in the Basque Country to solve the problem caused by these thirty dumping sites containing HCH wastes focuses on the development of the so called BCD process (Base Catalyzed Dechlorination). This process should enable in the near future and with a reasonable cost, to decompose HCH wastes as well as remediate HCH contaminated soil.
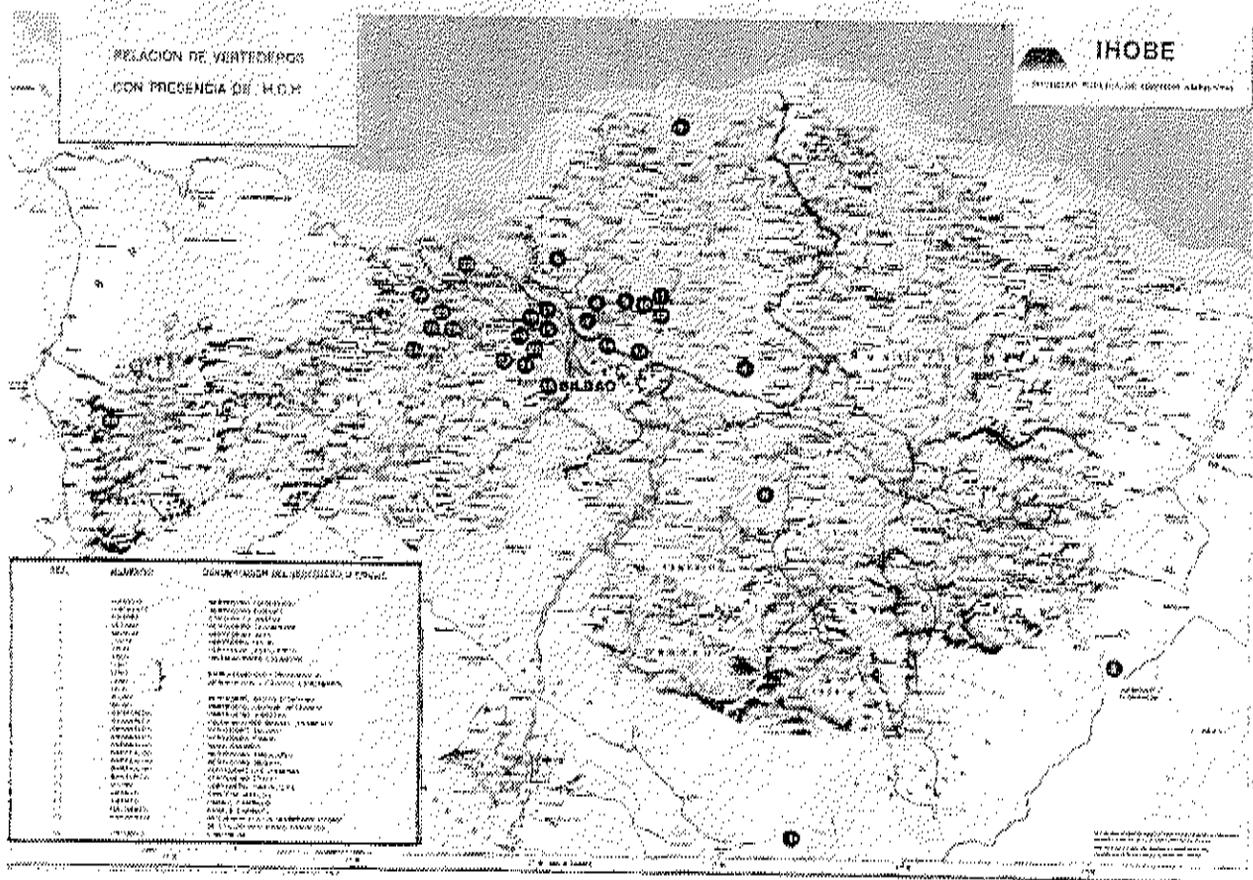
Figure 1 HCH dumping sites in the Basque country

The development of the BCD process has already started successfully in our region and in fact, the construction of a demonstration plant for soil treatment has already been planned within a short time. Nevertheless this process is not operational on a large scale for the moment. For this reason it has been necessary to choose a provisional solution according to which the HCH contaminated soil will be excavated and stored in two reversible safety landfills located each one on one side of the river Nervión (figure 2).

OLD FACTORY
UNCONTROLED LANDFILLS

HCH wastes   HCH contaminated soil

BCD Process   Two security landfills

BCD process + Other Pr.
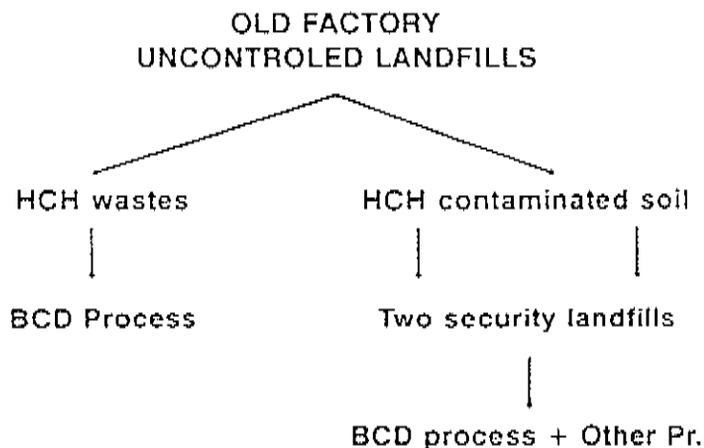
Figure 2   Strategy designed in the Basque country to solve the problem of the HCH dumping sites

2 THE PROBLEM OF HCH WASTES ON THE RIGHT SIDE OF THE RIVER NER-VION

Between 1966 and 1986 Nexana - Celamerck dumped on this side of the river Nervión, as already mentioned, 7,000 tons of HCH wastes spread basically in three municipalities: Loiu, Leioa and Bilbao. Up to now the most serious case of contamination in this area is represented by the land belonging to the Bilbao Airport.

2.1 The Bilbao Airport case

The case of the Bilbao Airport has become one of the most famous contamination events in the Basque Country due to the difficulties that the discovery of 75,000 tons of mixed industrial wastes of very different nature is imposing to the immediate plans to extend this infrastructure of vital importance for the whole area (figure 3).
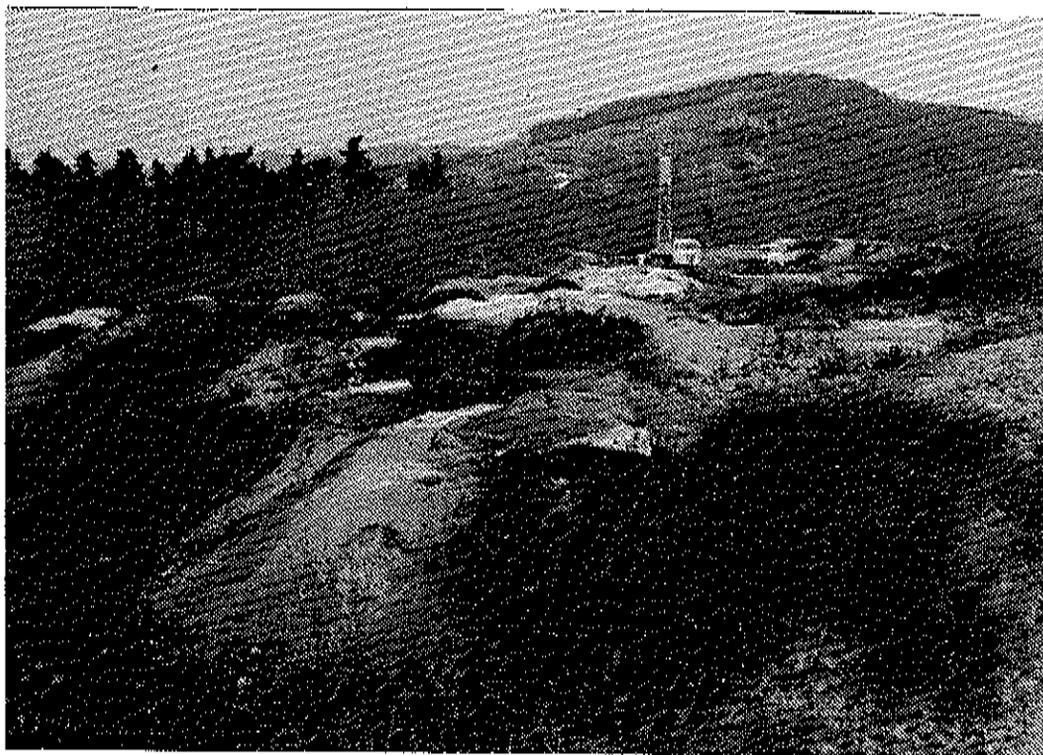
Figure 3 View of the airport dumping site

While the present conditions remain the same it is impossible to carry out the plans designed for this site. Therefore and in order to start the extension works forthwith an exhaustive investigation including soil characterization, risk assessment and evaluation of the possible technical solutions has already been concluded. Out of the soil investigation, the amount of pure HCH wastes was estimated at 2,554 tons in addition to approximately 45,000 tons of HCH contaminated soil.

According to the Dutch methodology applied in this study, 7 ppm has turned out to be the highest HCH concentration in soil that can be accepted for an industrial use of the soil. This conclusion leads directly to the necessity of remediating a total quantity of 190,000 m³ of wastes and contaminated soil.

After evaluating every possible technical solution only two options were finally considered:

a.- isolation of the hot spot area with a top cover controlling the water permeation by means of a perimetral trench;
b.- construction of a safety landfill designed to contain the soil excavated from the hot spots.

Only the second alternative was compatible with the extension plans of the Airport. Consequently the safety landfill option was chosen. Due to security reasons for the transport of wastes and contaminated soil, the safety landfill whose construction will probably start in 1994, will be located in the most favorable spot into the piece of land belonging to the Airport. The project of this safety landfill with capacity for 200,000 m³ was recently finished.

3 THE PROBLEM OF HCH WASTES ON THE LEFT SIDE OF THE RIVER NERVION

Fourteen out of the thirty dumping sites containing mainly HCH wastes identified in the Basque Country are located on the left side of the river Nervión and in the mining zone of Biscay. The design of an action plan for this area has already started with an investigation programme that is being carried out at this moment for every case under study. The programme developes the following issues:

- preliminary historical investigation
- topography studies
- characterization of the contamination
- risk assessment
- reclamation alternatives
- reclamation project and environmental integration project

In a first phase, five dumping sites considered of urgent reclamation because of their affection to important development plans have been investigated according to this scheme.

The construction of a safety landfill for the contaminated soil excavated from the dumping sites of the left side of the river Nervion is planned. This second landfill will have a capacity of 200,000 m³ and its location has not been decided yet.

However two cases have arisen which urgency has required a quick and specific solution: the old factory of Bilbao Chemicals and the construction of a commercial centre in Kareaga.

3.1 Bilbao Chemicals case

The old plant of the lindane producing company Bilbao Chemicals got attention when it was discovered that since the factory was decommissioned, one of its buildings stored 3,500 tons of pure HCH (figure 4). This circumstance together with the existence of a densely populated residential area in the surroundings of the plant and the passing of a very busy highway nearby has led to the conclusion, after a preliminary investigation, that the probability for the occurrence of a major accident is very high. Besides taking into account the way in which the HCH wastes are stored an additional risk of dispersion, basically by the wind, should be considered. Besides the 3,500 tons mentioned, 1,00 tons of soil mixed with HCH waste is involved. This quantity was dumped outside the Basque Country but transported back to the Bilbao Chemicals site.

Figure 4   Storage of pure HCH at Bilbao Chemicals

The solution for the specific problems caused by this HCH contaminated site has been planned in two phases. The first one has already been finished. According to a preestablished strategy the HCH wastes were packed in big-bags (figure 5) and transported from their location at that time to another building. This building is specially conditioned for the temporary storage of that kind of wastes, it is located at the factory site and far enough from the highway to minimize the risk of a major accident. To force this action, the Government Board had to release an order of urgent occupation of the old factory facilities due to the lack of cooperation lent by the owners. The second phase will consist in decomposing in situ the stored HCH wastes using the BCD process and transporting the contaminated soil to the safety landfill.
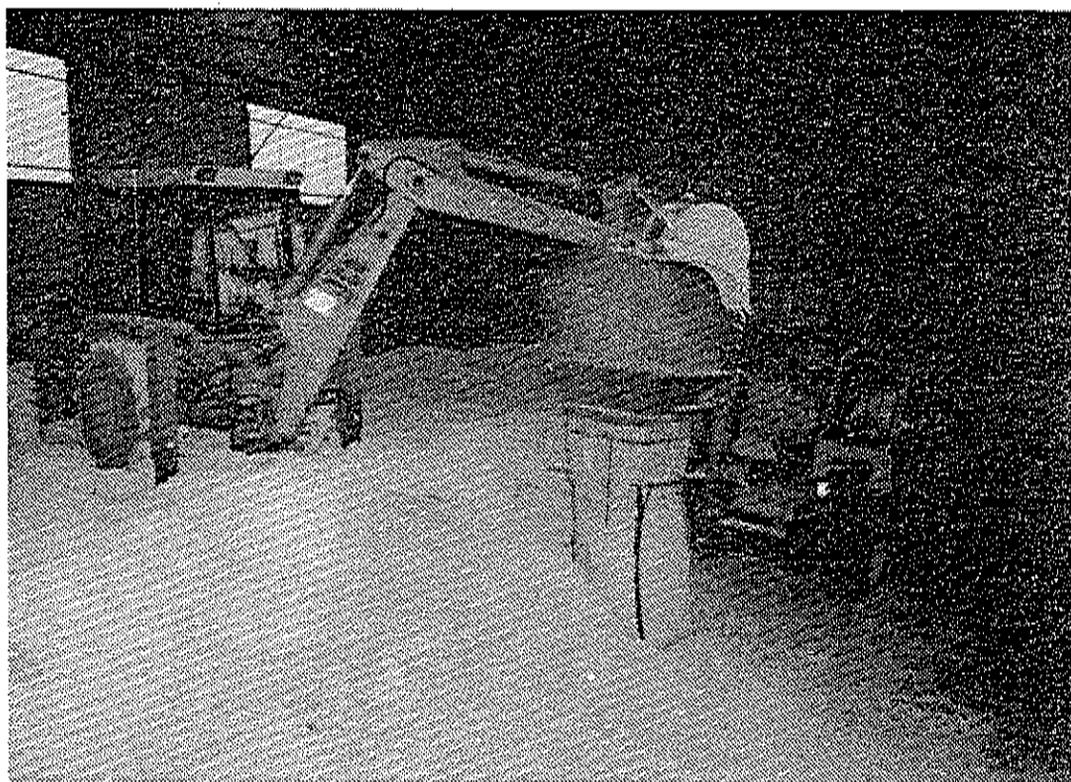
Figure 5   Packaging of HCH wastes in big bags.

3.2 Kareaga case

The construction project of a large commercial centre in Kareaga has been affec-
ted to a great extent by the finding in the future building site, during the ground
conditioning works, of a considerable amount of HCH wastes mixed with the
original soil as well as HCH wastes in nearly pure state. At this point it becomes
urgent to manage these wastes that hinder the execution of the project. Due to
the necessity of laying the building foundations within a short time an action plan
focused on the following subjects was designed:

- soil investigation
- risk assessment
- excavation and packaging of the contaminated soil in big-bags
- transport and storage of the big-bags in a suitable place until the safety landfill
  is constructed

The soil investigation showed that nine hot-spots with diametres under eight metres were spread all over the building site. In order to remediate this location 4,500 m³ of soil were excavated. Once the excavation works were completed, the material containing a high concentration of HCH was transported to the above mentioned pavilion of Bilbao Chemicals and packed in big-bags. The low content soil was stored, together with the material of the same nature excavated from Bilbao Chemicals in a provisional landfill. This contaminated soil will be transported to the safety landfill when constructed. At this moment the same investigation procedure and remediation project is being applied to the commercial centre accesses.

4 THE BCD PROCESS AND THE SOLUTION OF THE HCH WASTE PROBLEM IN THE BASQUE COUNTRY

As already mentioned the Basque Country has faced the solution to the HCH waste problem in two ways: the construction of reversible temporary safety landfills on the one hand and the development of the BCD process on the other.

The so called BCD (Base Catalyzed Dechlorination) process is a procedure for breaking down chlorinated organic compounds on which C. Rogers, A. Kornel and their group from the U.S. Environmental Protection Agency (U.S.E.P.A.) have been working for the last ten years. At the end of 1991 IHOBE got into contact with this research team checking the viability of the process for our needs, keeping in mind that the production of dioxines and other undesirable compounds during the process in negligible.

The process has been tested in a 50 litres pilot plant getting a conversion rate of hexachlorocyclohexane in trichlorobenzene of 99.9995% (figure 6). Furthermore the results of the experience have corroborated that the final products are free of dioxines.
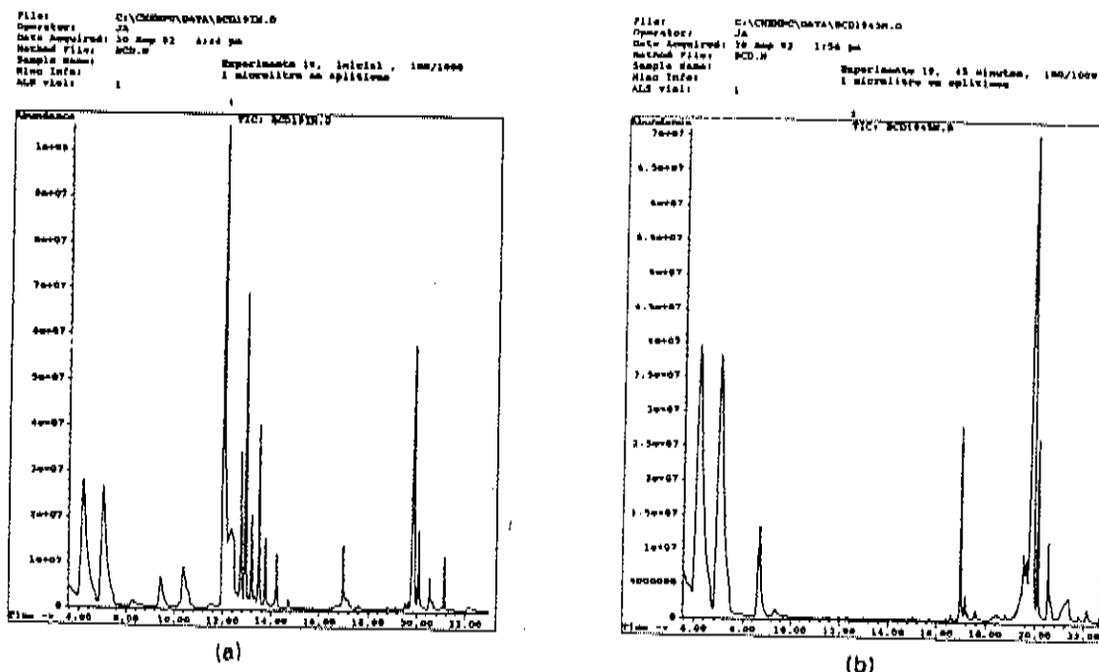
Figure 6   Chromatogram of HCH samples before (a) and after (b) treatment with the BCD process

Once a good performance of the procedure has been proved, the next step will be the design of a mobile large-scale plant with a capacity for 1 ton/hr. At first such a plant will be used for the destruction of the pure HCH wastes stored in Bilbao Chemicals, but afterwards, if feasible, some other pure chlorinated wastes will be treated.

At the present time our research group is busy in the development of a procedure for treating HCH contaminated soil using the BCD process in combination with a low temperature thermial desorption technique. This procedure has already been tested for PCB's in soil and sediments in the United States.

5   CONCLUSIONS AND FUTURE NEEDS

From the experience gathered in the soil projects carried out, it can be concluded that the used methodology is very suitable for our own purposes. The sampling as well as the investigation techniques have led to quite accurate results.

Regarding the specific behaviour of HCH wastes in the soils of the Basque Country, it has been proved that the dispersion rate of hexachlorocyclohexane through this medium is very low. This fact is also supported by the low affection to groundwater. Only in one case a serious pollution was detected and in the rest the contamination was easily controlled.

In order to find a final solution to the HCH dumping sites some questions on which we are already working must be solved:

- the urgent design of a pilot plant for the treatment of HCH contaminated soil
- the development of a separation/treatment technique for soil with a high con-
  centration of HCH
- the selection of the best available technology for treating the leachate seeping
  out from the safety landfill when they begin to operate.

ENVIRONMENTAL POLLUTION AS A CONSEQUENCE OF HCH PRODUCTION IN SACHSEN-ANHALT
- A SITUATION REPORT -
By Ekkehard Wallbaum and Wilfried Fuchs

1   INTRODUCTION

Hexachlorocyclohexane (HCH) was synthesised and processed as a raw material for the production of the insecticide lindane in Sachsen-Anhalt in the Bitterfeld (VEB Chemiekombinat Bitterfeld) and Magdeburg (VEB Fahlberg-List) chemical plants (see Table 1).

HCH was imported from the states of the former RGW (Rat für gegenseitige Wirtschaftshilfe; Council for Mutual Economic Aid), in particular from the former USSR and from Romania.

The synthesis of HCH leads to the formation of a mixture of isomers ("technical grade HCH"). As a rule, only 10 - 12% of the biologically active γ-isomer can be extracted from this mixture. This isomer has been used under the name lindane for the manufacture of a large number of plant protection preparations.

The mixture of isomers formed during HCH synthesis has also been used in smaller amounts for the production of sprays for military and agricultural applications.

Table 1   Production of technical grade HCH and lindane (in tonnes/annum) in Sachsen-Anhalt since 1967 (HEINISCH, KLEIN, JONAS 1992 - supplemented by data from Fahlberg-List Magdeburg - IMS/LUS 1993)

Year	FALIMA*		CKB**	
	HCH	Lindane	HCH	Lindane
1955-67	14766	2621	no data available	
1967	2970	383	4415	315
1968	3010	408	4914	351
1969	2946	336	5080	362
1970	1160	461	5058	361
1971	·	382	5390	585
1972	1624	322	5340	381
1973	1488	350	5300	378
1974	2366	340	5120	365
1975	3872	420	4578	327
1976	350	452	4598	328
1977	·	410	4550	325
1978	·	342	4620	330
1979	·	330	4343	310
1980	·	367	3752	268
1981	·	188	3786	270
1982	·	·	2110	151

(*FALIMA - VEB Fahlberg-List Magdeburg; **CKB - Chemiekombinat Bitterfeld)

In addition to the increasing indications of properties hazardous to the environment, the high proportion of unusable "waste" isomers obtained in lindane production (about 85% - 90%) was probably the deciding reason for the final cessation of HCH synthesis in the former German Democratic Republic in 1982.

Because of their toxic effects, their persistence and the conditions under which they are stored, as well as emissions during HCH production in the Sachsen-Anhalt region, the waste isomers (α, β, δ, ...) are one of the many inherited environmental problems which must be overcome.

2 HCH PROCESSING SITES IN SACHSEN-ANHALT AND THE RESULTING ENVIRONMENTAL PROBLEM

The Chemiekombinat Bitterfeld

About 73,000 t of technical grade HCH were synthesised between 1967 and 1982 in the former VEB Chemiekombinat Bitterfeld. However, HCH synthesis started as early as the second half of the 1950's. It is estimated that about 20,000 t of technical grade HCH were synthesised in the period between 1959 and 1967.

Some of the technical grade HCH synthesised in Bitterfeld was supplied to other companies (including VEB Fahlberg-List, Magdeburg) for further processing. However, the bulk of the product was used in the Chemiekombinat itself for the extraction of γ-HCH and, finally, the production of lindane.

HCH production and processing in Bitterfeld essentially led to two different environmental problems:

a) Pollution of soil in the flood plain of the Mulde and the CKB effluent system

Highly polluted effluent produced during the HCH synthesis was discharged largely untreated via the works effluent system into the River Mulde (see Figure 1).
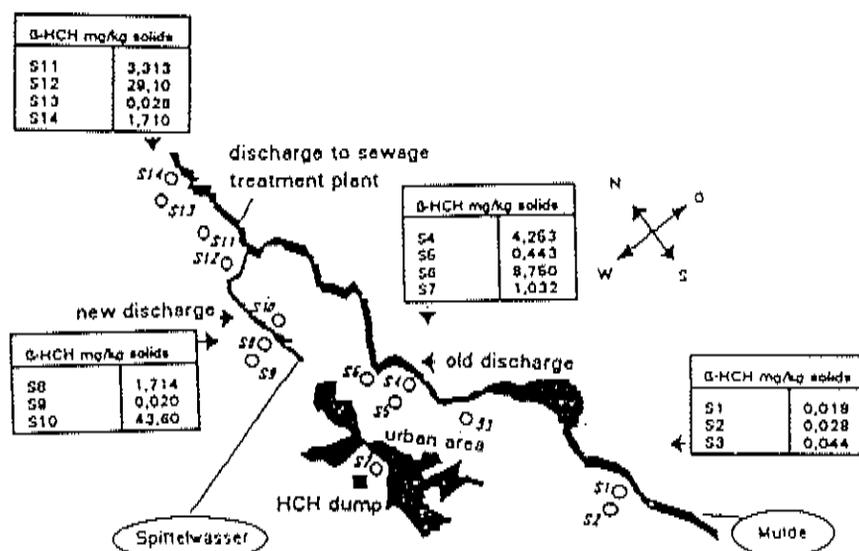
Figure 1: Sketch of the course of the Mulde and the CKB effluent discharge with data on the β-HCH concentrations found in the soil, in mg/kg solids (SCHOLZ, MAY, NOTHBAUM 1992, b)

As a result of the production technology used 200 g to 300 g of HCH per ton of HCH synthesised passed directly into the effluent.

The problem was exacerbated by HCH-polluted material which was washed out and drifted from the works site and the dump for HCH waste isomers which was located in the immediate vicinity. The consequence is enrichment of, in particular, the α, β and δ isomers of HCH over about 2,000 ha of land which hitherto was used predominantly for agricultural purposes and was periodically flooded.

To establish the causes of increased HCH levels in foodstuffs (SCHOLZ, MAY, NOTHBAUM 1992, a), research programmes were carried out to determine the extent of the pollution in these areas (SCHOLZ, MAY, NOTHBAUM 1992, b). It was found that the reference value for HCH of 0.2 mg/kg of soil (DFG 1982) was exceeded over about 650 ha in the area of the Mulde meadows and the Chemie-kombinat effluent system. The highest measured concentrations of HCH in the soil were between 3 and 6 mg/kg. The peak value found was a concentration of 43 mg/kg of ground. The soil studies carried out show a significant rise in soil pollution downstream of the CKB discharge.

It has been demonstrated that there is a direct relationship between the level of ground pollution in the flood plain of the rivers involved and the frequency of flooding (LAUER, HEYMANN, SCHNEIDER 1992) (see also Fig. 2).

β-HCH (in mg/kg solids)
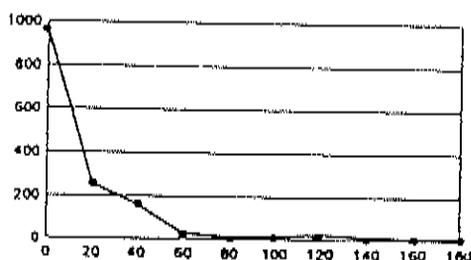
Height above normal water level
(in the Spittelwasser area)

Figure 2: β-HCH concentrations in the ground for 10 individual samples at different heights

Further trends found are: it was not possible to demonstrate the frequently described relative enrichment of the β-isomer in the soil in all cases. It was like-wise not possible to detect a significant decrease in soil pollution with increasing distance from the discharge point in the area examined (see Fig. 3).

β-HCH (in mg/kg solids)
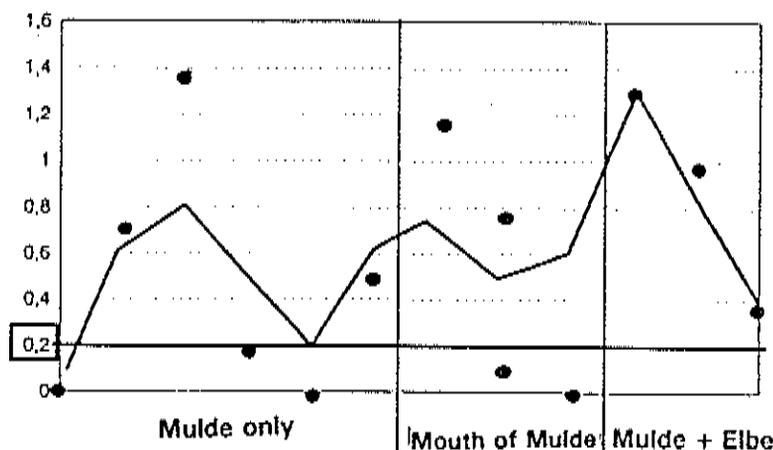
Figure 3: Pattern of β-HCH concentrations along the course of the Mulde and Elbe rivers

The causes of these unexpected results are taken to be the prolonged period over which the hazardous substance was discharged and the flow and sedimentation characteristics of the Mulde and of the CKB effluent system.

In addition to raised concentrations of chlorinated organic compounds, the HCH-polluted areas also show a large number of other pollutants (in particular heavy metals). The size of the areas affected, the fact that these have hitherto predominantly been put to extensive agricultural use (pasture) and the limited funds available demand an effective strategy for clean-up or making safe, in view of further environmental pollution to be dealt with in Sachsen-Anhalt. In accordance with the type of use of the meadow areas, various restrictions will result with regard to the further cultivation of the land.

The aim of a number of studies carried out at the request of the Environmental Authority is to draw up proposals for use in combination with targeted measures for the clean-up and making safe of the entire meadow land affected.

b)   Deposition of waste HCH isomers from lindane production

With the aim of subsequent utilisation, the waste isomers (α, β and δ isomers) produced during lindane production were selectively dumped in a separate area of the shut-down "Grube Antonie" brown coal opencast mine adjacent to the CKB site. Data on the amount of HCH isomers stored vary greatly. However, since no further deposition sites are known, we must work on the assumption of an amount of about 70 - 80,000 t. (This estimate is based on the amount of lindane produced, assuming a yield of 12%.)

In total just under 6 million cubic metres of waste, some of which is toxic, are stored in the Grube Antonie, including:

- -75,000 t neutral slurries
- - 975 t benzyl chloride residues
- -21,000 t waste sulphuric acid containing toluenes
- - 1,500 t tarry residues (cresidine, benzyl acetate)
- - 4,800 t distillation residues (tetrachloroethane vapours, trichloroethylene, perchloroethylene and hexachloroethane)(KRAPP, BOLCEK, BRAUN 1992)

The joint storage of HCH with other chemical waste has the associated risk of uncontrolled reactions as a result of mixing. This risk is intensified because the Grube Antonie has neither an artificially provided nor a natural base seal. If the groundwater rises to its original level, as is to be expected following the cessation of water retention measures taken hitherto for mining reasons, the foot of the Grube Antonie would lie about 12 m beneath the groundwater level to be expected. Reactions between the stored wastes can then not be ruled out.

The large volumes and the properties of the stored waste, as well as the geological characteristics, create problems when devising an affordable clean-up plan. Discussions on the clean-up or making safe of the existing "Grube Antonie" pollution have not yet been concluded. Figure 4 shows the geological characteristics and a proposal for making safe by the use of retention walls.
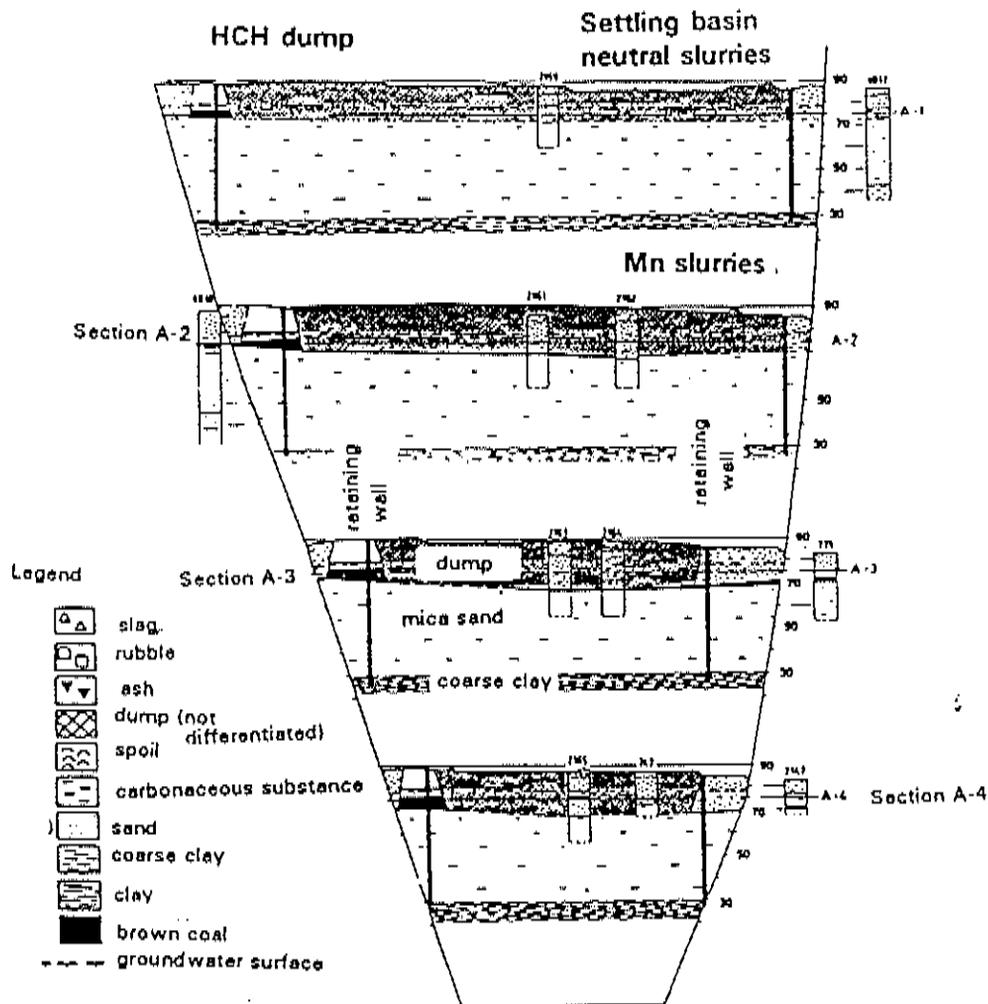
Figure 4: Sectional map of the "Grube Antonie" dump
(KRAPP, BOLCEK, BRAUN 1992)

The VEB Fahlberg-List-Magdeburg

The bulk of the HCH pollution in the Magdeburg region was caused by the former VEB Fahlberg-List which up to 1981 synthesised a total of 34552 t of technical grade HCH (14,766 t of which was synthesised prior to 1967) and produced 8112 t of lindane (see Table 1).

The figures show that (assuming a yield of 12%) it was necessary to buy in about 35,000 t of technical grade HCH from other producers (mainly Chemiekombinat Bitterfeld, but also imports from Romania and the USSR).

Essentially two sets of problems result from the HCH synthesis and processing in Magdeburg:

a)   Pollution of the ground in the vicinity of the production plants and in sediments of the Elbe downstream of the effluent discharge.

Detailed information on the pollution of the works site of the former VEB Fahlberg-List is not available at present. However, considerable soil pollution appears probable in the light of the prolonged period of HCH processing and the fact that it is known that waste isomers were temporarily stored on the works site.

According to the current state of knowledge, the soil pollution measured in the sediments of the Elbe downstream of the effluent discharge from the plant does not necessitate the design of a strategy for clean-up or making safe because of HCH pollution.

b)   Deposits of waste isomers from lindane production

Based on the volume of lindane produced, VEB-Fahlberg List had to dispose of about 60,000 t of waste HCH isomers in the period between 1955 and 1981.

In the period from 1964 to the time lindane production ceased, the isomers were exclusively dumped selectively in shut-down quarries in the municipalities of Emden and Bebertal in the Haldensleben region. Some of the filled quarries were covered with ceramic waste.

The dumps in Emden and Bebertal were authorised by the state authorities responsible at that time. The deposits were not considered to present a problem, as the quarries concerned are former sandstone quarries, the bottom of which is about 15 m above the groundwater level, it was assumed that there was an impermeable layer of clay between the bottom of the dump and the groundwater aquifer, the solubility of HCH in water is low and drifting was precluded after the dumps were covered. However, more recent studies on water sources in the region and on groundwater confirm that there is leaching from the dumps. The cause is considered to be crevice cracks in the surrounding rock (sandstone), through which precipitation water, which dissolves HCH as it passes through the body of the dump, but in particular entrains particles, passes into the uppermost groundwater aquifer. Studies to estimate potential hazards for the environment resulting from the dumps have not yet been concluded. However, a water-impermeable cover is generally shown to be an adequate option for clean-up or making safe.

Ground pollution in the vicinity of access roads, which was caused by carrying and drifting during transport, was already the subject of scientific studies at an early stage (HEINISCH, KLEIN, JONAS 1992). In this case, restrictions on use and, where appropriate, measures for making safe are considered to be necessary and achievable measures for combating the hazard.

For the period from 1955 to 1964 there are only fragmentary data on the whereabouts of waste isomers from HCH synthesis and processing in Magdeburg. The amount to be disposed of during this period was about 13,000 t of HCH. The fact that a series of discoveries and comments from the local population point to the presence of HCH deposits within the Magdeburg municipal area led the Ministry for the Environment and Nature Conservation in the Sachsen-Anhalt region to commission a study, based mainly on historical research, to ascertain the whereabouts and storage conditions of these amounts (IMS/LUS 1993).

Eleven sites of deposits in the Magdeburg municipal area were detected as a result of this study. The estimated amount of HCH isomers stored in these sites is 12,800 t. The pollution of further sites cannot be excluded. The potential hazard caused to the environment by the sites found has been assessed.

The results of the study are being taken into account when drawing up a list of existing pollution in the Magdeburg municipal area which is to be treated as a matter of priority. They will also be taken into account when planning future use.

3 ENVIRONMENTAL POLLUTION BY HCH IN SACHSEN-ANHALT - CONSIDE-RATIONS WITH REGARD TO MEASURES APPROPRIATE TO THE PRO-BLEMS

In the cases described, environmental pollution as a result of HCH processing can be subdivided into categories.

The main groups are **dumps** of larger amounts of waste isomers produced during lindane production and **areas/land** polluted by emissions from synthesis and processing plants.

Where hazards exist for the environment, engineering measures for clean-up or making safe are absolutely essential to make the dumps safe. For Sachsen-Anhalt, priority here is given to measures for making safe (covering, encapsulation, water retention and the like).

Polluted areas and land must be treated in accordance with the extent and severity of the pollution and the planned future use. "Off site" clean-up will be carried out only if measures for making safe are not able to prevent the discharge of hazardous substances into the environment, in particular into food chains. The rule will be measures for making safe, in particular ground utilisation suited to the conditions. In this context, ground utilisation which, if necessary, can be combined with "in situ" clean-up processes (for example stimulation of biological degradation processes by management measures) is to be preferred.

Finally, the measures to be taken to deal with environmental pollution caused by HCH must be specified for each individual case, as also applies in the case of many other potential hazardous substances. A balance must be struck between available funds and benefit, both for the environment in general and for future use of land.

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PROBLEMS CONNECTED WITH THE DISPOSAL OF UNDESIRABLE PESTICIDES IN POLAND

By S. Stobiecki, S. Pruszyński, A.Silowiecki, E. Czaplicki

1   INTRODUCTION

During 40 years in Poland a large amount of useless pesticides has been accumulated due to the defective, centrally governed system of production, import purchase, distribution and price policy. One of the reasons for such accumulation was also poor preparation of agriculture for chemization and, following the worldwide tendencies, withdrawal of DDT, mercuric seed-dressing and arsenic preparations from use in Poland.

At the beginning of 1970s an attempt was made to solve the problem through building of a network of tombs all over Poland. The tombs were concrete bunkers made of circles insulated with tar. The products stored in the tombs were mainly unwanted pesticides from 1950-1970. They were chlorinated hydrocarbons, organomercuric and organoarsenic compounds, nitrophenols and smaller amounts of carbamates and phosphoric acidesters. Many tombs also consist of other chemicals than pesticides, and empty containers.

Unfortunately, during the following years no steps were taken to solve the problem. Moreover, some new storage sites were built which made the situation even worse.

The problem of tombs and other places of storage has been purposely passed over and it is now that there are practical opportunities for the exact recognition of the problem.

Taking the opportunity, the Institute of Plant Protection in Pozna ± with its own specialists and experts invited from other institutions has developed the programme "Acquisition of Output Data for the Problem of Disposing of Unwanted Pesticides and Empty Containers". The programme was commissioned by the Ministry of Agriculture and Food Economy and executed within the PHARE programme and in co-operation with the Foundation FAPA from Warsaw.

Most of data presented in the paper mainly are the results of studies which were carried out within the above mentioned programme. The data has explicitly pointed to at least two problems which are very important, however not yet solved by worldwide science and practice, namely:
- hazard evaluation of places of storage to people and the environment.
- establishing a programme, methods and a course of problem eradication.

2   OUTLINE OF THE PROGRAMME AND ITS MAIN OBJECTIVES

Tombs, the subject of the programme studies, were built in 1970s according to the Instruction No. 1/71 of 21 May 1971 developed by the Centre of Horticulture Cooperatives, Centre of Agriculture Cooperatives "Peasants' Self Help" and the Ministry of Agriculture, Ministry of Health and Ministry of Chemical Industry. According to the information at the disposal of different institutions, the number of tombs in Poland is about 200 and there are about 6000 tonnes of unwanted pesticides stored in these tombs. Apart from the known and registered tombs there are many other tombs which were built without any appropriate documentation and inconsistently with the Instruction No. 1/71. In many cases they are simply ground pits. It is estimated that there are about 1000 tombs containing about 12000 tonnes of pesticides. A large amount of unwanted pesticides and empty containers is stored by distributors and users. The pesticides occupy stores and create hazard to the environment. The total amount of unwanted pesticides stored in different places is estimated at 25000 tonnes. The state of the majority of the tombs is unknown. A large number of them has no owner and any documentation that might have ever existed was distroyed. Lists concerning the location of tombs, their number and contents are at the disposal of different institutions or organizations and in many cases they are contradictory with one another. It is necessary to verify and arrange the data.

The programme "Acquisition of Output Data for the Problem of Disposing of Unwanted Pesticides and Empty Containers" includes:
-    acquisition of data concerning the tombs and other places of storage of unwanted pesticides which are at the disposal of different institutions.
-    verification of the acquired data and detailed scrutinies of five selected provinces.
-    developing database
-    drawing up a map of the tombs and other places of storage of unwanted pesticides and empty containers for five selected provinces.
-    developing a model system for the evaluation of the contamination level of the areas neighbouring the tombs
-    long-term plan of solving the problem of the disposal of unwanted pesticides.

The hazard to soil and water created by the emission of pesticides from the tombs constitutes a serious problem which requires broad and interdisciplinary approach. Its evaluation and creating the basis for its solution demands engaging experts representing different branches of knowledge like: plant protection, chemistry, toxicology, environment protection, analitical chemistry, pedology, hydrogeology, etc.

The primary objective of the programme was creating the basis for appropriate evaluation of the number and location of the tombs in Poland and estimating the amount and quality of stored pesticides. This was achieved by the acquisition of all data available from the official sources and by the detailed control of five selected provinces.
As the result of the actions carried out within the programme the most credible and extensive list of the tombs has been developed and the detailed maps of their location within the area of five provinces have been drawn up.

Another objective was to develop the model system for evaluation of the contamination level of the areas neighbouring the depots. Thanks to these studies it is possible to present results that clearly show the current dangers created by unwanted pesticides.

The acquisition and evaluation of the results obtained from the programme will contribute to the realization of its most important objective, namely creating a practical basis for:
- detailed inventory of the places of storage of unwanted pesticides all over the country
- evaluation of the present danger
- producing a schedule of actions leading to the limitation and liquidation of the danger and eventually to the disposal of unwanted pesticides and empty containers.

3   POTENTIAL RISK OF CONTAMINATION

Theoretically, assumptions concerning the construction and location of the tombs assured their tightness for a long but not specified period. In each of the provinces there is a number of tombs which with time were filled, concreted and appropriately marked. At the end of 1970s the department of environment protection issued a just ban on building new tombs. The sanitary authorities of the country also forbade to use this method of disposal of chemicals considering the fact that the tombs are only a temporary solution which potentially may be even more dangerous for the environment and in many cases directly hazardous for people. Inappropriate materials used for building the tombs and lack of recognition of hydrological conditions around them were additional elements intensifying misgivings.

In the majority of cases, Communal Offices are the owners of the depots. However in some cases, fences around the depots fail to fulfil their role, signs are destroyed and the place on which the depot has been located does not distinguish from neighbouring areas. Dangers resulting from such situations are very high. Pesticide waste after decomposition of containers contributes to gradual deterioration of tomb constructions, thus loss of their tightness is only a question of time. Independently on emission of toxic substances from the tombs, illegal places of storage of unwanted pesticides are a more serious problem. Without any appropriate protection pesticides were located in unadapted places or dug directly into the ground. In such cases, high level of danger should be assumed and its evaluation preceded by monitoring of the effects of harmful substances on ground waters should be one of prior actions.

Typical tomb is made of concrete rings of diameter 1-2m, its height is 1-3m. A tomb is located underground and both its top and bottom are covered with concrete lids. The whole tomb is insulated with tar outside and inside. Its capacity is 1-10m3 and the weight of stored preparations is 1-10 tonnes.

4   HAZARD TO HEALTH AND ENVIRONMENT

Evaluation of danger to health of people and animals created by pesticides emitted from the depots should include the following criteria:
- toxicity of pesticide
- stability of pesticide
- remote health effects resulting from long term exposure to relatively small doses of a pesticide, for example because of consumption of food containig pesticide residues, drinking water contaminated with pesticides or frequent handling with pesticides.
- potential effect of a pesticide on useful soil and water organisms.

There is also a danger of a direct contact of people and animals with poisons from the unprotected tombs or other places of storage. In extreme situations such contacts may result in serious poisonings. Equally dangerous for both people and animals may be inhaling of poisonous fumes emitted from the places of storage. The affected persons often are not aware of the actual cause of poisonings.

The highest danger of underground water contamination occurs in the areas where pesticide waste was dig directly into the ground pits. The scale of danger is difficult to estimate because waste is located under the ground, frequently in destroyed containers and without any protection against precipitation. Waste undergoes intensive erosion what poisons neighbouring grounds and underground waters. It is connected with a serious danger for the local people using wells into which the contaminated waters had permeated. The danger is not only dependent on the distance between a well and a tomb but also on the hydrogeological structure of the area and especially on the direction and degree of flow of underground waters.

Periodic intensification of surface and underground waters contamination may occur in case of flooding the tombs during spring thaws or intensive rainfalls. Especially dangerous may be flooding of the tombs during a flood evoking serious contamination of open waters.

Equally hazardous contamination may occur in case of fire, for example, of a forest where a pesticide depot is located. The process of thermal decomposition in the case of pesticide mixtures leads to an uncontrolled release of very dangerous toxic substances which may permanently contaminate the environment.

A potential hazard to health of people and animals is also created by consumption of plant products coming from areas contaminated by unwanted pesticides emitted from the depots. It becomes more dangerous as consumption often takes place unaware of the fact that the products are contaminated.

It should be emphasized that harmful effects of pesticides on men and the environment should not be treated separately. In the long run all the negative effects on the environment will affect people's health, life and feeling of safety.

In the case of a tomb failure considerable stability of pesticides should be taken into account. A few meters underground biological activity of microorganisms hardly exists and serious contamination coming from an untight tomb may weaken or even nullify biological processes within the contaminated area. In such situations a problem of underground waters occurs.

Variety of inland water functions indicates the necessity of their protection and maintaining of their good quality. Utilization of surface waters by people decreases, even after water treatment. It results from increasing chemical and micro-biological contamination. People are provided with water from underground resources. In this context the problem of tombs and their failures is especially dangerous. Among many contaminants, like heavy metals, mineral oils or detergents permeating into water, attention should be paid to pesticides containing substances of high toxicity and biological activity.

Even relatively small water contamination by pesticides may evoke considerable disturbances in functioning of ecosystem. Ecosystems of stagnant waters (lakes, ponds) are far more sensitive and their pesticide contamination may result in biological balance disturbances. For example, a release of a herbicide to stagnant waters may cause breakdown of the trophic chain on its initial stape contributing to a size drop contributing to a size drop of all living oranisms within a given ecosystem. Next, size drop within the planktonvorous organisms may cause entrophication of a reservoir because of plant organisms dominance.

Water and soil contamination by pesticides coming from untight tombs may, in extreme circumstances, lead to the necessity of exclusion of whole areas from agricultural exploitation. In the case when there is no information on toxic substances emitted from the depots, agricultural products may be a subject of commercial turnover and consumption what equals an obvious-without-comment danger.

Forests where the depots, especially illegal ones, have been located are exposed to their negative influence. The effect may be direct (on the whole ecosystem) or indirect (through consumption of forest ground cover).

5   NEED FOR LONG TERM ACTIONS

The need for the solution to the problem of unwanted pesticides results from:
- large amount of both registered and illegal places of storage
- observing untightness in many of these
- gathering of unwanted pesticides in different kinds of stores
- lack of the disposal method

Earlier actions leading to disposal of unwanted pesticides were fragmentary and not complete.

The programme constitutes a necessary introductory part to undertake further actions on a larger scale. The actions have to be multi-stage. In the first stage a complete inventory of all the depots in Poland should be carried out. In the second on the basis of local scrutines, the most hazardous places for people and animals should be determined. The depots should be monitored and protected against further emission. The third stage should result in full protection against untight depots and decontamination of soil from nieghbouring areas. The last stage should include disposal of unwanted pesticides through incineration.

The all-Polish realization of the presented plans requires complete coordination, management and sufficient financial support.

6   RESULTS - ALL-POLISH INVENTORY

In order to develop a database concerning tombs the following institutions were supposed to provide information:
- State Inspectorate of Environment Protection
- Ministry of Agriculture and Food Economy
- Voievodship Quarantine and Plant Protection Stations
- State Inspectorate of Hygiene
- Sanitary - Epidemiological Stations
- Chief Board of Supervision
- State Inspectorate of Labour
- Agricultural-Trade Chamber of Commerce
- State Forestry Managements
- former Association of State Farms
- former Horticultural - Apiarian cooperatives
- Agricultural Productive Cooperatives
- former State Association of Agricultural Cooperatives and Organizations

From among the members of the panels of experts persons responsible for obtaining data from the above mentioned institutions were appointed.
The database consists of 1999 items. Each item corresponds to one place of storage.

7   RESULTS - INVENTORY IN FIVE SELECTED PROVINCES

Five provinces were appointed for detailed scrutinies
- Province of Kalisz
- Province of Katowice
- Province of Kraków
- Province of Poznań
- Province of Toruń

A database was developed and it includes 189 items. There are divergences between data obtained from different institution and data resulting from our own scrutinies. For example, in the Province of Pozna± one institution informed about 6 tombs, another one estimated that there are 12 tombs and their actual number was 10 as it was found out during visits and scrutinies.

8   MAPS OF TOMBS

On the basis of information obtained from the field trips to the selected provinces, maps of the tombs and other places of storage were drawn up. The maps include symbols referring to containers and pesticides stored in the tombs. The size of a symbol depends on the amount of stored materials. Each map includes a legend locating a given province within the map of Poland and stating the tonnage of the stored products.

9 RESULTS - SYSTEM OF SAMPLING SOIL AND WATER FROM AREAS ADJACENT TO TOMBS

Actually, studies were carried out around 3 tombs. Soil samples taken from 25m underground and water samples were analyzed. Main analytical methods were gas chromatography and mass spectrometry. Two tombs turned out to be untight. In one of them presence of DDT, DMDT, fenitrotion and DNOC was determined in concentration from 10-100ppm, the other one contained chlorinated hydrocarbons up to a few ppm.

The studies resulted in a model procedure. It helps to determine contamination of areas adjacent to the places of unwanted pesticides and includes the following stages:
- tomb location
- geodesic studies
- hydrogeological studies
- sampling
- methods of sampling
- interpretation of results
- estimated costs of studies for one tomb
- time of studies

10 CONCLUSIONS - RECOMMENDATIONS

1. The actions carried out within the programme and the results which have been obtained and presented in the report indicate the absolute demand for immediate taking steps to limit and liquidate dangers resulting from the existence of tombs and other places of storage of unwanted pesticides and empty containers.

2. The programme concerning disposing of tombs and other places of storing unwanted pesticides and empty containers will constitute a long-term and multi-direction goal which demands appropriate organization, financial support and participation of the qualified local experts and foreign consultants.

3. On the basis of the studies, their results, recognition experience and consulting the foreign experts, the executors of the programme suggest the following order of further actions:

    First stage - immediate commencement of realization
    a). carry out a detailed inventory in the remaining 44 provinces and draw up an up-to-date list of tombs and other places of storage of unwanted pesticides and empty containers located all over the country.
    b). carry out local inspections to all tombs and other places of storage, determine institutions responsible for them, make the existing documentations available, evaluate the level of protection and estimate possible danger.
    c). carry out tests for contamination of areas adjacent to tombs and other places of storage according to the established model.

      d).   develop recommendations for taking immediate preventative actions and deliver them to local authorities.

      e).   establish a list of preferential actions on the basis of potential danger.

Second stage   - immediate commencement of preparations for this stage realization and taking some actions in the course of the first stage

      a).   take preventative actions to dispose of existing contaminations

      -   appoint and prepare a place for storage of unwanted pesticides, empty containers and contaminated soil

      -   technical preparations for transfer of materials to new storages (empting and transport).

      b).   analyse in detail the ways and possibilities of use of the available methods and installations for the disposal of unwanted pesticides and empty containers.

      c).   control constantly the level of danger around tombs and other places of storage

      d).   analyse in detail the state of tombs and other places of storage from the engineering point of view.

Third stage   - organizational and financial preparations for the commencement of this stage should be made as soon as possible

      a).   work on adaptation of different methods of disposal of unwanted pesticides and their gradual use:

      -   composting

      -   biodegradation

      -   combustion by means of existing installations.

      b)   appoint and prepare a central storage of unwanted pesticide and empty containers.

      c)   empty the tombs and other places of storage and transfer their contents to the cenral storage(s).

      d)   purchase or build installations for the disposal of unwanted pesticides and empty containers.

      e)   dispose of unwanted pesticides in the central storage.

11   GENERAL CONCLUSION

It is possible to limit the costs of disposal of unwanted pesticides and empty containers on the condition that complex decisions would be taken on the realization of the whole programme and it would be committed to the the qualified panel of experts cooperating with foreign consultants.

The costs of the programme should be shared between the following:
-   Ministry of Environment, Natural Resources and Forestry Protection
-   Ministry of Agriculture and Food Economy
-   Ministry of Health and Social Welfare
-   Committe of Scientific Studies
-   Foundations
-   Ecoconversion
-   International programmes
-   Goverments of different countries
-   Local authorities
-   Producers and distributors of pesticides
-   Economic subjects
-   Other institutions and private persons interested

The overall realization of the programme exceeds the organizational possibilities of the institutions with their present staff, thus it is suggested to establish a company to deal with the task.
The total cost of the solution to the problem of tombs and other places of storage of unwanted pesticides and empty containers should be estimated at $ 100 mln.

AN OVERVIEW ON HCH APPLICATION IN TURKEY

By Aysen Türkman, Nuri Azbar and Nermin Arikan

ABSTRACT

HCH has been one of the pesticides that has been commonly used in 1970's. Many studies have been conducted to determine its residue in foods. Although aldrin, dieldrin and lindane are forbidden to be used since 1985, all of them appear in food and in the environment. This may be explained by the use of pesticides still in stock at the time of prohibition. In this study, some information is given about the pesticide use in general, the extent of lindane use, its residue levels in food and the environment and the legal aspects of pesticide use in Turkey.

Lindane use has been increased from 200 tons/year in 1982 to 1458 tons/year in 1985. In 1978, Council of Agriculture has decided to limit the use of chlorinated hydrocarbon pesticides. After alternative, less harmful pesticides were found, the use of more dangerous ones was prohibited. In 1985, Ministry of Agriculture and Rural Affairs has forbidden the use of DDT, BHC and Lindane by Law number 6868 (Official Gazzette dated 17 June 1985), on the grounds that they have oncogenic, teratogenic and toxic effects on organisms.

Pesticide research studies are very limited in Turkey. Food analysis cannot be performed on routine basis. The analyses are generally conducted by Universities for research purposes. According to research studies given in this paper, lindane concentrations varied between 0.014 and 0.048 mg/kg in oil, n.d. and 0.051 mg/kg in groundwater, n.d. and 0.154 mg/kg in sunflower seed oil, n.d. and up to 0.08 mg/kg in fruits. Lindane contamination has, along with other chlorinated pesticides, been an important problem in the past. It is not included in routine food analyses on the ground that it is not used anymore. Recent analysis indicate that in some areas, foodstuff contain lindane residues.

1   INTRODUCTION

$C_6H_6Cl_6$, Gamma HCH or Gamma BHC; 1,2,3,4,5,6-hexachlorocyclohexane has been found in 1940. When gamma isomers content of HCH/BHC is at least 99%, they are called Lindane. Lindane is a broad spectrum insecticide of the group of cyclic chlorinated hydrocarbons called organochloric insecticides and is used in a wide range of applications, including treatment of animals, buildings, man, clothes, water, plants, seeds and soils. In a survey of finished drinking water in the USA, the highest reported level of lindane was 0.1 μg/l (WHO, 1984). It is a moderately persistent pesticide as can be seen from Table 1.

Table 1: Relative Persistence of Some Pesticides in Natural Water (McEwen, 1979)

Non Persistent ($t_{1/2} \leq 2$ weeks)	Slightly Persistent ($t_{1/2} = 2$-6 weeks)	Moderately Persistent ($t_{1/2} = 6$ weeks to 6 months)	Persistent ($t_{1/2} \geq 6$ months)
azinphosmethyl	aldrin	aldicarb	benomyl
captan	amitrole	atrazine	dioldrin
carbaryl	CDAA	ametryne	endrin
chlorpyrifos	CDEC	bromacil	hexachlorobenzene
demeton	chloramben	carbofuran	heptachlor
dichlorvos	chlorpropham	carboxin	isodrin
dicrotophos	CIPC	chlordane	monocrotophos
diquat	dalapon	chlorfenvinphos	
DNOC	diazinon	chloroxuron	
endosulfan	dicamba	dichlorbenil	
endothal	disulfoton	dimethoate	
xenitrothion	DNBP	diphenamid	
IPC	EPTC	diuron	
malathion	fenuron	ethion	
methiocarb	MCPA	fensulfothion	
methoprene	methoxychlor	fonofos	
methylparathion	monuron	lindane	
mevinphos	phorate	linuron	
parathion	propham	prometone	
naled	Swep	propazine	
phosphamidon	TCA	quintozene	
propoxur	thionazin	simazine	
pyrethrum	vernolate	TBA	
rotenone		terbacil	
temephos		toxaphene	
TFM		trifluralin	
2,4-D			

2   HCH USE IN TURKEY

Although the average pesticide application per hectare is lower than in many developed countries, it is increasing continuously, for example pesticide use has increased from 498.3 g/ha to 644.92 g/ha during 1980-1987 period. But these amounts are not equally distributed among all the agricultural areas in Turkey. For example in Mediterranean Region alone, more than half of the total pesticide consumption is practised (Delen et al, 1990). Thus, in some areas a dense pesticide application can be seen while in some other areas almost no application is achieved. Total pesticide use in Turkey is given in Table 2.

Table 2: Pesticide use in Turkey (Delen et al. 1990)

Years	Consumption (ton)	Number of Licensed Pesticides
1960	23 425	4
1961	23 795	7
1962	38 298	12
1963	37 442	13
1964	35 265	29
1965	36 656	22
1966	38 129	22
1967	40 195	37
1968	32 327	20
1969	61 385	24
1970	50 804	23
1971	48 362	25
1972	50 344	28
1973	66 350	49
1974	54 638	39
1975	48 132	27
1976	54 844	48
1977	73 508	30
1978	81 760	68
1979	81 214	120
1984	67 703	
1985'	36 660	191
1986	39 115	350
1988	34 152	391
1990	34 055	400

CuSO$_4$ and Powder Sulfur are excluded from the pesticide records although they are still in use.

There are several problems that should be mentioned related to the use of pesticides which results in environmental pollution:

i) The pesticides are applied in greater quantities than required amounts (Delen, 1990). The fruit and vegetable farmers are not well trained and pesticides are used without regard for pesticide population levels. Besides that in preparing solutions or applying pesticides, the concentrations or doses may not be exact due to the shortage of information and/or close control.

ii) Another problem is that although aldrin, dieldrin and lindane are forbidden to be used in 1985, all of them appear in foods and the environment. This may be explained by the use of stock pesticides that were in huge amounts at the time of prohibition. The use of prohibited pesticides is a very important problem related to the environmental pollution.

iii) Because of the organizational problems in the control mechanism related to the type, quantity and application period of pesticides, they are not applied properly. Thus, not only the beneficial effects are decreased, but also harmful effects appear.

64.4% of total exportation in Turkey originates from agricultural products. Turkey is selling agricultural products of EC member countries as well as other developed countries. This is why in sixth five year development plan which covers 1990-1994 period, this subject has been specifically taken into consideration. In the plan, it has been mentioned that the Turkish Agricultural activity will be in line with EC Agricultural policy.

If the pesticides that are registered in Turkey are compared with those in European countries, it can be seen that some pesticides registered in Turkey to be used for the diseases and pests are not permitted in other countries (Delen, 1981).
Lindane use has been increased from 220 tons/year in 1982 to 1458 tons/year in 1985. Lindane consumption in Turkey may be summarized as follows.

Table 3: Lindane consumption in Turkey, ton/year (Tisit, 1992)

Type of formula	1982	1983	1984	1985
2.6% Powder	.	.	875	1250
25% WP	200	185	175	200
20% EC	.	14	3	8
Total	200	199	1053	1458

WP: Wettable Powder
EC: Emulsion Concentrate

According to the data obtained from the records of Ministry of Agriculture related to the production and sale amounts of pesticides in 1986, it has been found that Lindane has been continued to be applied for one year after the prohibition in 1985 in amounts given in Table 4.

Table 4: Lindane consumption after 1985

	Amount (kg)	Year of Selling
2.6% Lindane	28644	1986
25 % Lindane	12839	1986

But after 1986, any record related to the importation or selling of Lindane has not been found in these documents (Tarim Bakanligi 1986 Yiliilac Imatat ve Stais Miktarlari Verileri).

Five pesticide manufacturers had been producing lindane until May 1982, namely: Hektas, Kimyagerler, Koruma, Midiltipi and Agrosan. All these manufacturers have been localized in Instanbul and Kocaeli. After the prohibition of use in 1985, most of these manufacturers have continued their activities by producing other pesticides.

3   HCH RESIDUES IN FOOD

3.1   HCH Residues in food

In this section, HCH residues determined in foods and drinking water in Turkey are given. Maximum allowable dose that can be taken for Lindane, is 0.01 mg/kg body weight.

The vegetative oils (olive-oil, cotton-oil etc.) may carry also organic chlorinated pesticides in their structures. Since organic chlorinated pesticides can be dissolved in oil, chlorinated pesticides can get into the oil easily. Pesticide concentrations determined in olive-oil samples are given in Table 5, in sunflower seed samples in Table 6, in corn oil samples in Table 7 and cotton seed oil samples in Table 8.

Table 5: Pesticide concentrations in olive-oils (mg/kg) (Hisil, 1987)

BHC	DDT	Lindane
0.030		0.048
0.005	0.203	
0.026	0.063	
0.004	0.077	
0.050	0.441	
0.155	0.008	
0.0004	0.015	
0.030	0.353	
0.048	9.975	
0.066	0.319	
0.048	0.239	0.014

Table 6: Pesticide residues determined in sunflower seed oil samples (mg/kg) (Hisil, 1987)

BHC	Lindane
0.153	0.154
0.017	0.053
n.d.	n.d.
n.d.	n.d.
n.d.	n.d.
n.d.	n.d.
n.d.	n.d.
n.d.	n.d.
0.010	

Table 7: Pesticide residues determined in corn oil samples (mg/kg)
(Hisil, 1987)

BHC	Lindane	DDT
0.015	0.008	0.048

Table 8: Pesticide residues determined in cotton oil samples (mg/kg) (Hisil, 1987)

BHC	DDT
0.009	
0.022	0.223

Lindane concentrations determined in oil samples vary between 0.014 to 0.048 mg/l. According to Codex Alimentarius (FAO, 1985) regulations, the allowable limit for oil is 1.5 mg/kg. Thus according to international regulations, lindane concentration does not exceed the limit value. Although allowable pesticide residue limits in food has been determined and published in Official Gazette (1990), lindane is not include in the list, possibly because it was forbidden.

HCH, Lindane and DDT residues have been determined in the samples of two corn oil and three cotton oil samples. Since the amount of Lindane up to 1.5 mg/kg is permitted in seed oils according to German standards, a pesticide concentration of 0.008 mg/kg of a corn oil sample is quite acceptable.

During 1975-1976 season fruit and vegetable samples were taken at irregular times from gardens and markets around Istanbul and analyzed for pesticide residue (Table 9 and 10).

The experimental results obtained from analysis of samples are given below:
a)   In citrus samples: 0.01-0.02 ppm DDT isomers, 0.006 ppm Lindane;
b)   On the cherry and sour cherry samples residues of 0.07-0.08 ppm DDT, 0.01-0.08 ppm BHC and isomers were detected;
c)   On the various vegetable samples 0.03-0.80 ppm of DDT 0.001-0.01 ppm of Lindane were detected.

Table 9: Lindane residue levels in apple and pear (Yigit, 1977)

Production Year	Name and type of fruit	Pesticide (ppm)	Residue
1975	Apple (Golden)	Lindane	<0.001
1975	Pear (Yalova)	Lindane	0.02
1975	Orange (Pea)	Lindane	0.062
1976	Dried grape	Lindane	0.007
1976	Apricot (Juice)	Lindane	0.003

Table 10: Pesticides residues in vegetable samples (Yigit, 1987)

Production Year	Name and type of ve-getables	Pesticide (ppm)	Residue
1975	Cabbage (Black)	Lindane	0.26
1975	Cabbage	Lindane	0.83
1975	Lettuce	Lindane	0.01

These residue levels are acceptable according to maximum residue limits (MRL) given by WHO.

In a research study conducted in Taris Research and Development apricots have been analyzed for gamma BHC residues and it has been determined that alpha BHC = 0.0413 ppm, gamma BHC = 0.0678 ppm (Arikan, 1992).

Lindane has been determined in fruits and vegetables like spinach, cow pea, pepper, egg plant, apple, although generally at acceptable concentration some of these residues are higher than the tolerance limit for Lindane (Hisil, 1984).

In a study conducted by Ege University Department of Food in 1987, carrot samples taken from market have been analyzed for pesticide residues. Alpha BHC and Lindane concentrations determined in carrot samples are given in Table 11.

Table 11: Pesticide residues determined in carrot samples (mg/kg) (Hisil, 1987)

α-BHC	Lindane
0.019	0.002
-	0.003
-	0.002
0.010	0.030
0.003	0.010
-	0.001
0.004	0.007
0.001	0.002
-	0.001
-	0.001

Lindane concentrations which were determined in carrot samples were below the maximum permisable limit (0.2 mg/kg) which were determined by Codex Alimentarius Commission (CAC). But it was interesting to observe that lindane concentrations between 0.001-0.0030 mg/kg have been determined after the prohibition of this chemicals in 1985. It is obvious that lindane has not been completely destroyed during this two year period.

In a study conducted TARIS Research and Development Center in Izmir in 1992, 0.0413 ppm alpha BHC and 0.0535 ppm gamma BHC has been determined in carrot samples. According to the conversation with the chemical engineer working in establishment in question, it has been pointed out that it has not been deter-mined any lindane in the analysis conducted in last five years.

In a study conducted to determine the pesticide concentrations at the Egean Sea and Büyük Menderes River (a river discharging into Egean Sea), lindane concentra-tion at Candarli Bay seawater was found as 0.05 ng/l, in sediment between 0-24.96 ng/g and in Büyük Mendedes River sediment 0.86 ng/g (Türkiye Cevre Sorunlari Vakfi, 1989).

3.2 HCH residues in water

A considerable portion of total pesticide consumption in Turkey is spent in cotton fields in South Anatolia. According to the activity reports published by Adana Regional Agrochemicals' Institue, active ingredient of pesticides per dekar cotton field is 1000 g in Antalya and 1200 g in Cukurova. Chlorinated insecticides that were used in the area amount to 1066 tons in 1972, 1081 tons in 1973 and 977 tons in 1974 (Temizer, 1979). In fact, the studies indicate that groundwater in Cukurova has been polluted by pesticides (Table 12).

Table 12: Pesticides concentrations determined in the water samples take from Cukurova region and Produk stream (Temizer, 1979)

Sampling points	Lindane concentrations (μg/l)
Seyhan Regulator	0.06
Yüzbaşi Village Drainage Channel	0.05
Yüzbaşi Village Irrigation Channel	0.09
Sirkenli Village Drainage Channel	0.08
Kamişli Village Well Water	0.16
Paşa Village Well Water	0.22
Kilise Village Well Water	0.31
Çiçekli Village Irrigation Channel	0.13
Çiçekli Village Well Water	0.37
Porsuk Karacaşehir Regulator	0.10

Izmir is the third biggest city of Turkey with three million inhabitants. In Izmir, mainly groundwater and spring water is used for drinking. Groundwater is abstracted from Bornova Plain which is recharged from 215 km² drainage area (Türkman, 1981). The depths of the wells used for sampling vary between 40 m and 140 m. In the area both industrial and agricultural activities are conducted.

In order to evaluate drinking water quality with respect to pesticides, groundwater samples from various parts of the Bornova Plain have been analyzed. Since it is known that considerable amounts of chlorinated pesticides have been used in the near past, this group of pesticides have been chosen for analysis. Lindane concen-trations are given in Table 13.

Table 13: Lindane concentrations in groundwater of Bornova plain (Türkman, 1991)

		Pesticide	Concentration (mg/l)
Sample number	Well	Date	Lindane
1	Fac. of Medicine	March 1991 July 1991 November 1991 May 1992 June 1992	- 0.004 -
2	Pinarbaşi Springs	March 1991 July 1991 November 1991 May 1992 June 1992	- - 0.017
3	Beer factory	March 1991 July 1991 November 1991 May 1992 June 1992	0.006 0.004 0.013
4	Izsu Bornova	March 1991 July 1991 November 1991 May 1992 June 1992	- - -
5	Motor factory	March 1991 July 1991 November 1991 May 1992 June 1992	0.006 0.004 0.051
6	Private well	March 1991 July 1991 November 1991 May 1992 June 1992	- - -
7	Fac. of Agriculture	May 1992 June 1992	
8	Standard value (EPA), 1991)		0.0002 (MCL)

MCL: Maximum Contaminant Level. Maximum permissible level of a contaminant in water which is delivered to any user of a public water system.

4   DISCUSSION

Although the pesticides are indispensable, their application poses many environmental problems. Especially in areas where the control mechanism does not work properly, the environmental pollution is almost impossible to avoid. Consequently, not only the fruits and vegetables to which the pesticides are applied are polluted, but also air, soil and water sources are contaminated, bringing health problems.

This study shows the importance of control mechanism starting from the registration of pesticides to their application. Otherwise, the appearance excessive concentrations in the environment is inavoidable. Although the legal framework related to permission procedure of pesticides and the limits on food in very well established in Turkey (Annex 1), it is difficult to say that these regulations are applied strictly.

According to the decision taken by Agricultural Research Council in 1978 chlori-
nated hydrocarbon pesticides like DDT and BHC are forbidden to recommend
except some special pests. After this decision Ministry of Agricultural and Rural
Affairs has started a research an evaluation as a result of which the permits for
production, importation, commerce of chlorinated hydrocarbon pesticides like
DDT, BHC and lindane. These pesticides have not entered into the market since
the end of 1985. The production and importation of these chemicals are under a
strict control.

In 1985, Ministry of Agricultural and Rural Affairs has forbidden the use of DDT,
BHC and lindane by law number 6868 (Official Gazzette dated 17 June 1985), on
the ground that they have oncogenic, teratogenic and toxic effects on organisms.

Other pesticides which are forbidden, are given below:
Aldrin, arsenic trioxide, BHC, calciumarsenate, chlordane, chlordimeform, chloro-
benzilate, copperarsenate, cyhexatin, daminozide, DDT, DDD, dieldrin, dinoseb,
zineb, endrin, kursurarsenate, lindane, mercury (CIVA), parathion-ethyl, silvex
2,4,5-T, sodiumarsenate, toxaphene, heptachlor.

Pesticides have not yet been included in Turkish Drinking Water Standards. This is
why EPA (Environmental Protection Agency of USA) standard values have been
taken as reference for groundwater which is used for drinking.

One interesting outcome of this study is the determination of prohibited pesticides
in fruits, vegetables, oil and groundwater. Private communication with the govern-
mental and private authorities reveal that some prohibited pesticides are still in
use. Food analysts who are conducting the pesticide analysis, indicate that the
presence of prohibited pesticides in food cannot be attributed to absorption from
soil only.

High pesticide concentration in drinking water despite their low solubility in water
indicate that the soil in contaminated to a considerable extent.

The pesticide pollution in Turkey may be considered as local for the time being.
South Anatolia and Egean Region are exposed to pesticide pollution as the studies
indicate. Larger areas may be involved within a few years after the completion of
South Anatolian Project. 1.1 Million hectar area will be irregated and dense agri-
cultural activities are expected in this region.

A closer control in every stage of pesticide use is a necessity in Turkey, starting
from manufacture till its application. A special consideration must be given related
to use of chlorinated pesticides.

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ANNEX 1: LEGAL ASPECTS OF PESTICIDE USE IN TURKEY

Registration of agrochemicals in Turkey

A- Registration of a new pesticide in Turkey which has a new active ingredient or in a new formulation type or new mode of action:

I- Company who wants a register a product will apply to Ministry with an application letter and will enclose below given document.
   a) Trade name of the product: This trade name should not be registered on behalf of another company or at least three letters should be different;
   b) Product specification which is prepared by manufacturer (4 set original) and its translation into Turkish. Both should be notary stamped;
   c) Biological data and trial reports (originals or copies);
   d) If the product is patent protected, notary stamped copy and translation of the agreement between patent owner and registrant company;
   e) Toxicological data: Long-term (two-years feeding test reports) toxicological study reports;
   f) Chemical and residue analysis methods;
   g) Label which is prepared in line with label regulation requirement;
   h) Registration certificate copies from other countries and dosage recommandations;
   i) Biological trial report obtained by the company from the trials done in Turkey. The trials to be carried out in two different areas which are ecologically different. These trials are going to be carried out by specialists* who are competent on their subjexcts. Officially approved trial methods are to be used and results to be written of proper forms**;
   j) Other information and documents which are going to be required by Ministry. After the submission of the above mentioned data and document, they will be studied by the commission which is formed by the general directorate.

   The commission may ask the company technical report to join the meeting.
   If the commission believes that the submitted data and document is sufficient, the product will be taken into analysis.
   If there are results in line with product specification at the of the analysis, registration is granted.

B- Registration of the products which the examples are available in Turkey (= norm basis registration, same a.i., same formulation type, same amount of the a.i. in the formulation):
   a) Locally produced products in this category will be registered, if the analysis result of the first batch sample which is taken by officials was found in line with specification values;
   b) Norm basis registration of readily imported products: Product sample will be analyzed: If the results in line with product specification, registration will be granted.

* 1 People who have a degree in entomology, phyopathology or herbology may carry out the trials in these three subjects;
  2 Persons who have worked minimum three years in plant protection institutes as researcher, may carry out the trials at their own branch only;
  3 Persons who have worked minimum 10 years at agrochemical companies as researchers, may carry out trial at their branch upon application the company and approval of the Ministry.

1 Trial reports will be signed by the person who made the trial. Also the company will approve them by signing and stamping;

2 Biography and copies of researcher diploma will be attached;

3 At the herbicide trials for registration and recommendation two different dosages can be given. (One for early, one for late season). At other pesticide trials one dosage will be given;

4 Trial reports will be given according to the attached form.

INFORMATION ABOUT ENVIRONMENTAL PROBLEMS

1 Contamination of air

Factors effecting residues and transportation of vapours and particles in the atmosphere and measure to be taken to prevent them, ppm value tolerated in the atmosphere is to be given.

2 Contamination of water

Information on above point are to be given:

a) Factors which effect transportation of a chemical in the water, on the surface or underground such as: volatility, penetration, washing on the surface, wind, soil type, topography, meteorology, pH, microbial activity, degree of effects of these factors and their interrelationships;

b) Residue disappearance curves for various types of waters (waters of different temperatures, hardness, pH, etc.);

c) Effects on concentration of soluble oxygen and biological oxygen demand (BOD), and the duration of this effect;

d) Dispersion, accumulation and results on living and nonliving materials;

e) Negative effects on planctons;

f) Bioconcentration in food cycle of aquatic environment;

g) Chronic and acute toxicity on fishes (LC_{60} or LC_{90} values at 2, 4, 6, 8, 24, 48 and 96 hours according to the decomposition rate);

h) Negative effects on water birds;

i) Effects on quality of drinking water and acceptable ppm level;

j) Herbicides used in water:
   - phytotoxicity of the water used for irrigation,
   - minimum time period between two successive applications,
   - period between application and time of irrigation;
   - changes on the vegetation where the chemical is used.

3 Contamination of soil

a) Factors which effect residues of chemicals of their by products in the soil, decomposition ways and speed, absorption, movement and decrease in residues:
   - formulation, dosage, application method,
   - soil type,
   - humidity of the soil,
   - cultivation of the soil,
   - vegetation,
   - micro-organisms;

b) Negative effects of chemicals on soil micro-organisms (ammonification, nitrification, nitrogen cumulation and total micro-organisms) and soil fauna;

c) Effects of the residue on soil structure and the effects the soil structure on plant and growth and quality;

d) Transfers of residues in the soil into the plant, accumulation spots in the plant and interrelationships between dosage and residues.

4 Effect on wild life

Trials and observations on acute toxicity on birds and other wild animals (feeding, behaviour, laying of eggs, hatching, life span of the chicks).

5 Effects on bees other beneficial insects

Negative effects seen in LD_{50} toxicity trials and field observations on bees through acute intake. If the chemical is going to be used in the whole treatment program, negative effects to be beneficial insects must be stated.

6 Time to enter sprayed field

Time to enter the sprayed area for harvesting, pruning, hoenging, etc., to avoid toxicity to humans and other warm-blooded animals, period that the animals should be kept away, atmospheric conditions on effects of toxicity.

7 Methods of destroying left-over products whose shelflives have expired

8 Methods of destroying empty containers and other measures to be taken for environmental protection

9 Literature

Sources of information about environmental protection.

5 Behaviour of Halogenated Pesticides in Soils

LONGTERM DEGRADATION AND MOBILITY OF DDT IN SOILS
By Ketil Haarstad

SUMMARY

Degradation and mobility of DDT in a landfill was studied in 1992—1993. The soil at the site was a homogenous sand (90 % sand) with a mean TOC of 2.5 % dry weight. Two vertical cross-sectional soil samples were analyzed, and the maximum concentration of DDT was 93 and 3302 mg DDT/kg at the two locations. Maximum concentration of DDT in filtered groundwater samples was 5.0 mg/l. Maximum concentration of DDT in unfiltered surface drainage water was 38.5 mg/l, at a distance of approx. 100 m from the landfill. The groundwater samples with high DDT concentrations were characterized by high pH, O_2, TOC, Cl and very high in HCO_3, relative to the «bulk» groundwater quality in the area. The same groundwater samples were low in NO_3-N, K, Ca Mg and Si, and very low in S. The piezometer with high DDT concentrations also had a high groundwater level with large fluctuations. The groundwater samples were low in DDE. Other pesticides found in groundwater samples from the site were Lindane (g-HCH), Tolylfluanide and Fenvalerate, with maximum concentrations of 3.31 mg/l, 1.80 mg/l and 0.20 mg/l, respectively. The degradation of DDT at the site seems to be extremely slow, if the maximum groundwater level is significantly below the level of polluted soil. Introducton of high water content in the soil seems to both benefit degradation and mobilize DDT into the water phase. The degradation of DDT seems to correlate with a reduction of S, possibly indication microbial S-reducing conditions. Surface transport of DDT due to runoff erosion has reached a distance of more than 100 m. The maximum distance of subsurface transport with groundwater has not yet been determined.

1   INTRODUCTION

DDT (see abbreviations for explanation) has been a widely used insecticide since 1945. It is a nonpolar (and in some countries even nonpopular) chemical substance, with low water- solubility and high affinity to dissolve in fats (lipofile). In Norway the use of DDT was restricted in the period 1969 — 1988, and totally banned after that. Typical use of DDT before 1970 was one or two annual sprayings of fruit orchards against apple fruit moth and other pests (Stenersen & Fristad, 1969). Measurements of soils from the upper 15 cm layer from orchards in the USA showed a mean DDT concentration of 34.5 mg/kg (Ginsburg, 1955). According to Stenersen (1970), the mean concentraion of soil samples from 55 orchards in Norway was 10,1 mg DDT/kg, with a maximum of 65,2 mg/kg. Nearly half of the applied DDT could be found as soil residues during use.

According to Lichtenstein (1957), more than 10 %' of the amount of DDT applied to several orchards in 1945 was found in the soil 10 years after. Table 1 shows that maximum concentration of DDT in the soil of a Norwegian apple orchard 2 and 4 years after application were 22 and 6,5 mg/kg, respectively (Kveseth et al., 1977). The ratio between DDE and DDT showed a small increase. According to Hitch and Day (1992), ratios of DDE to DDT in soils lower than 0.20 indicates «suspicious» soils where DDT use is expected to be of recent age. They also reported that soils with high water holding capacities and high contents of several metals (Al, Ba, Cd, Co, Cr, Fe, K and others) show extreme slow conversion of DDT to DDE. Oden and Ekstedt (1975) reported a slow increase in the ratio DDT/DDE in «natural soils» from 0.10 to 0.15 in Swedish soils from 1966 to 1975.

Technical DDT consists of approx. 75% pp-DDT, 25 % op-DDT and less than 3 % DDE (Oden & Ekstedt, 1975). The op-isomere is much less toxic as a biocide than the pp-isomere (Bhuiya & Rothwell, 1973). Half-life values of DDT from the literature varies between 40−122 (95 % CI) (Sims et al., 1988) to 1657 days (Overcash & Davidson, 1980). Typical metabolic or chemical reduction products are DDE under aerobic conidition, and DDD to DDA under anaerobic conditions (Oden & Ekstedt, 1975). Nash et al. (1973) showed that high pH (from 5 to 10), increased concentration of NH_4 and MgO, and high soil temperature could increase the reduction of DDT to DDE, and that reduction of DDT to DDD increased at high temperatures.

Table 1   The DDT-residues and distribution of DDT, DDD and DDE in an orchard from Sogndal with a slope of about 6 degrees. The orchard lies 50 −160 m from the shoreline. The samples are from 1972 and 1974. (Kveseth et. al, 1977)

Dist. [m] from shoreline	S-DDT [mg/kg] 1972	1974	%-DDE 1972	1974	%-DDD 1972	1974	%-DDT 1972	1974
-30a	0.005		100		0		0	
-10a	0.004		100		0		0	
10b	0.03		27		0		73	
30	0.39	0.08	32	32	0	10	68	58
60	22	2	23	19	5	12	72	69
70	11.2	6.5	23	31	10	10	67	59
90		0.63			37	2		61
110	2.8	2.1	36	27	13	12	51	61
130		1		42		2		56
150	3.1	1.5	24	26	5	3	71	71
200	0.06	0.04	21	24	24	0	55	76
230	0.04	0.07	22	24	0	0	78	76

a) The samples are taken 30 and 10 m from the shoreline into the water
b) Shoreline at tide

The use of DDT in Norway between 1970−1989 was restricted to treatment in the production of young tree plants. The annual application was less than 1500 kg. (as DDT) at approx. 35 location throughout the country. The persistence of DDT in soils at low concentrations and relative short time intervals (up to a few years) is well documented (Lichtenstein & Polikava, 1959; Nash & Woolson, 1967). Adsorption to soil particles is on the extreme high side (K_{oc} = 229 000, Torstensson, 1987) at normal soil pH, temperature, organic content and water content levels. We wanted to measure the persistence of DDT in soils where the pesticide had been applied at relatively high concentrations, after a relatively long time period. There was also a sewage outlet with high temperature and ionic strength near the landfill . The landfill at the study site was in operation until 1988, receiving annualy (about) 200 kg DDT-polluted sludge from 1960−1988. The hydrogeological conditions at the site (high groundwater table and hydraulic conductivity) favours groundwater contamination, though DDT mobility in water is extremly low.

3 MATERIALS AND METHODS

3.1 The study site

The study site is located at 9° 10 ′ longitude, and 59° 23 ′ N latitude, approx. 125 km west of Oslo and 30 m above sea level (see Fig. 1). The landfill of DDT-sludge is situated 150 m. from and 15 m above a river. It is deposited on sediments consisting mainly of medium to coarse grained sand. The sediments are glaciofluvial. A schematic view of the study site and sampling points is given in Fig. 2.
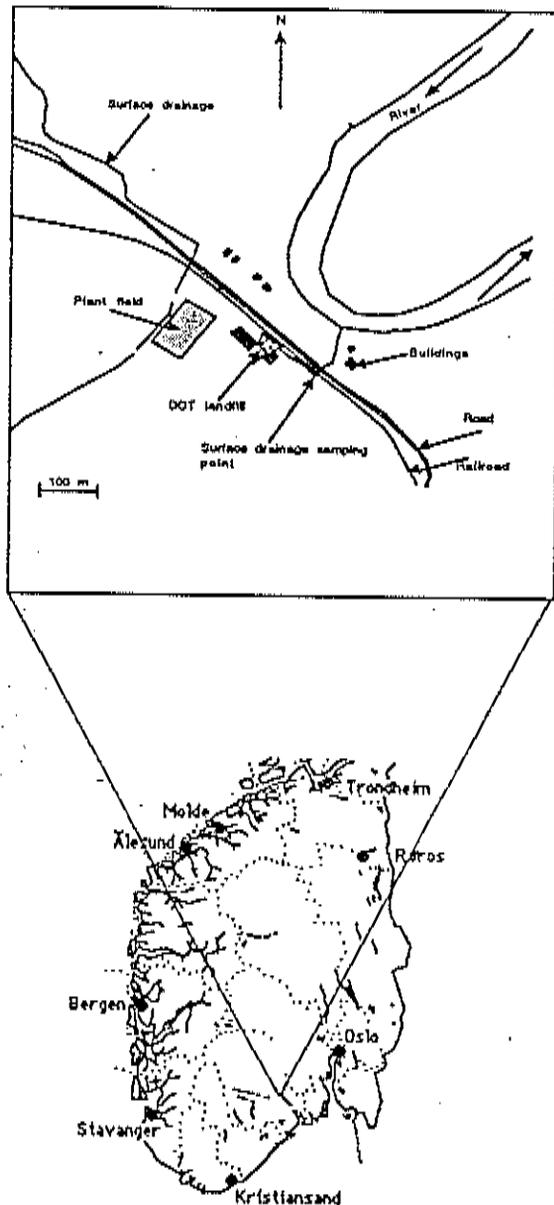
Figure 1. DDT Landfill site
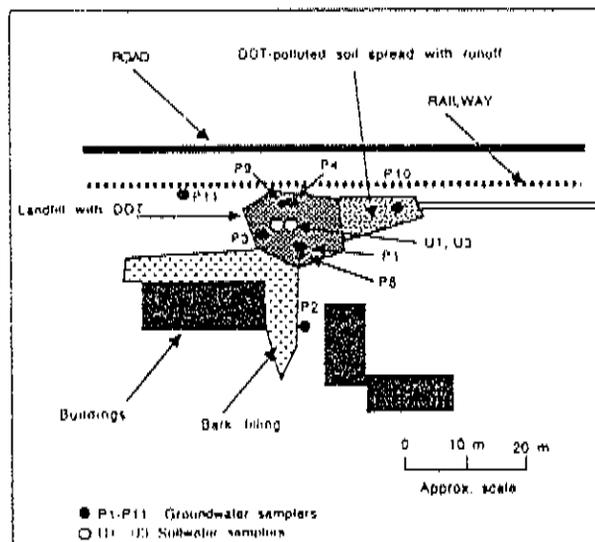
Figure 2. Location of sampling points

3.2 Soil samples

The soil structure and volume fractions were measured from GSD from 33 soil samples, and from 6 pF-analyses (Ejielkamp cat.no. 08.03). Soil samples were collected by drilling 2" open steel tubes to the selected depth. The mean soil composition was 0 % clay, 10 % silt and 89 % sand. The mean soil content of TOC, pH and EC were 2.5 % of dry weight, 5.3 and 5.6 mS/m, respectively. Maximum TOC in the soil was 8.7 % in the upper 0.5 m, and 6.2 % at 3.5 m depth. The detection limit for DDT measurements in soil samples was 0.02 mg/kg. Zoological material (earthworms and insects) will be collected from soil samples and analyzed for accumulated DDT and metabolic products. The collected material will also be analyzed for the enzymes ATP, ADP and AMP, in order to characterize the soil concentrations of DDT with respect to toxicity and level of pollution.

3.3 Water samples

Soilwater was sampled through 3 Prenart PTFE field lysimeters with pore size 5 mm and an air entry value of approx. 0.7 bar. Groundwater samples and level measurements were obtained from 4 5/4" PVC-tubes with 0,5 mm mesh openings, and 2 1/2" PE-tubes with 1.5 mm mesh openings. The depths and positions of the samplers are given in Fig. 3. Sample volumes of 0.5 litres were extracted after pumping at least 3 well volumes of water. The samples were stored dark and chilled in glass bottles. Water samples were analyzed for common ions and elements, DDT and other pesticides. DDT and metabolic products were analyzed on filtered and non-filtered water samples. The water samples (and soil samples) were extracted with dichlormethane and analysed for pp-DDT+DDD, op-DDT+DDD and pp-DDE on a HP 5890 with a Ultra 2 column and a EC detetctor. The detection limit for water samples was 0.1 mg/l. These analyses could not separate DDT and DDD, because DDD was produced from DDT during analysis. Three water samples were analyzed as parallells at two different laboratories. The alternative laboratory used a HP 5730 A gaschromatograph on samples extracted with cyclohexane. Detection limit was 0.005 mg/l. This method could separate between DDT and DDD.

Watertemperature, oxygen content, pH, EC and salinity were measured on site with WTW Oxi 96, ser.no. 2325170, sensor EO 96 ser.no. 29100154, WTW pH 96 ser. no. 2901265, sensor Sentix 96 ser. no. 163228 and WTW conductivity meter LF 95 ser. no. 2903191, sensor Tetra Con 96, ser. no. 29030055, respecitvely. «Standard» water chemicals were analysed at various intervals; NO_3-N, NH_4-N and Tot-N in an Autoanalyzer and HOC_3, Cl, S, K, Na, Mg, Ca, Fe, Mn, Zn, Al and Si were analysed on ICP. Measurements of TOC were conducted with a spectrophotometric method at 254 nm (Phillips PYE-UNICAM 8600). Detection limits on Autoanalyzer and ICP were 0.05 mg/l.

Figure 3. Soil profile, sampler posititons and soil content of DDT
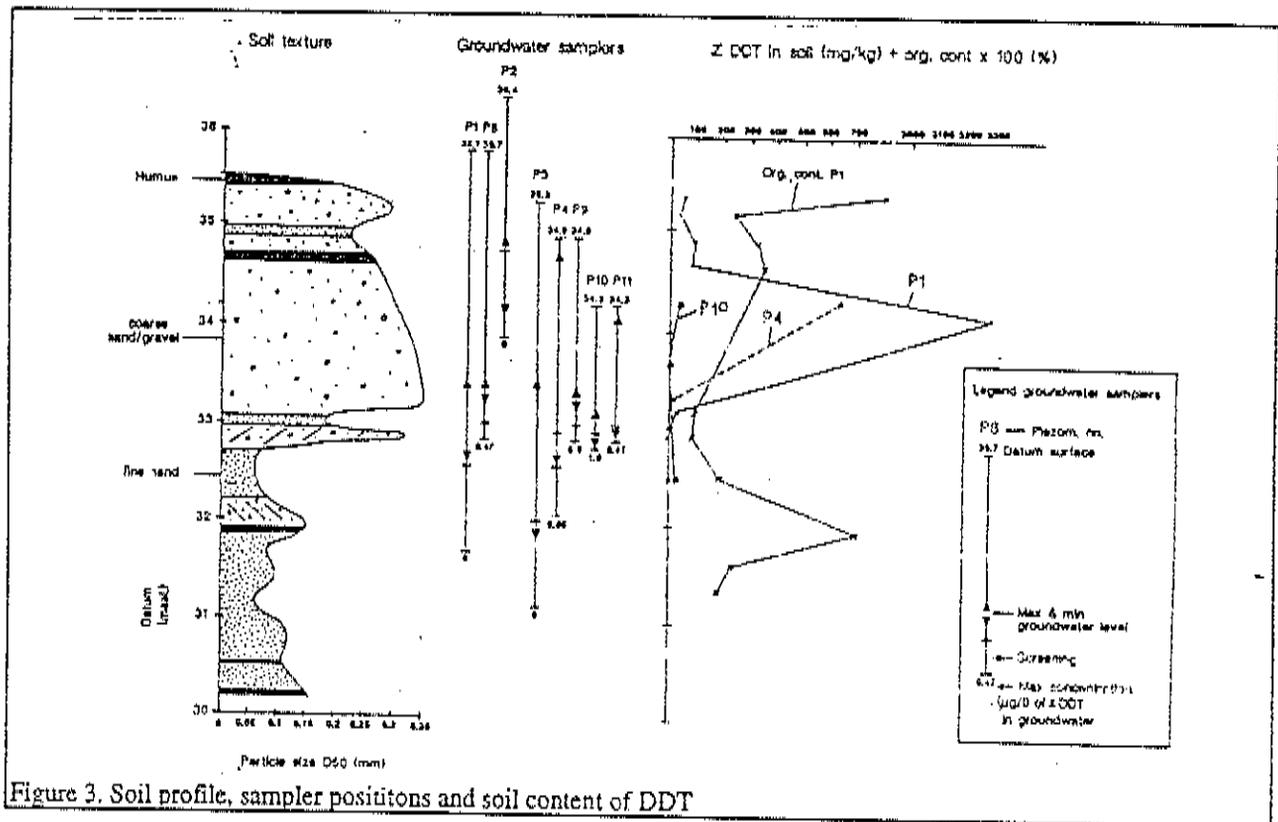
Figure 3   Soil profile, sampling points and soil content of DDT

3.4   Calculations

Soil- and groundwater balances were simulated with the model SWACROP (Feddes et. al, 1988). Statistics have been calculated with EXCEL (Microsoft Corp., 1992) and SYSTAT (Wilkinson, 1989).

4   RESULTS

4.1   Climate and hydrogeology

Total precipitation in 1992 was 687 mm. Fig. 3 is a schematic vertical cross-section of the watertable and sedimentologic units at the site. The characteristic elevated watertable at P4 can be explained by infiltration of drainage water, or a lowered hydraulic conductivity in this area. There is no evidence that the construction of the railway or road support might have changed the groundwater flow of the area. Table 2 shows that P4 has a high groundwater level as well as a pronounced difference in groundwater levels (Dh) compared to the other piezometers. This is a clear indication of soil with a low hydraulic conductivity, in contrast to P1 and P3. Mean groundwater level in P4 is 1.14 m below surface.

Table 2. Mean groundwater levels and filter depths

	P1	P2	P3	P4	P8	P9	P10	P11
				(m below ground)				
Am +	2.49	1.94	3.01	1.24	2.25	1.56	1.23	1.75
Max	2.77	2.19	3.47	2.19	2.39	1.66	1.62	1.48
Min	2.06	1.62	1.77	0.2	2.11	1.45	1.07	1.02
Dh	0.71	0.57	1.7	1.99	0.28	0.21	0.43	1 46
Fd	3.54	3.53	4.57	3.24	2.8	2 14	1.73	1.63
Datum gv-level (masl.)	3.3	34.6	32.4	33.7	33.5	33.3	32.9	33.6
Ground level (masl.) 35.7	36.4	35.3	34.9	35.7	34.9	34.4	34.4	

+Am = mean groundwater depht, Max & Min = highest and lowest measured ground-water levels, Dh = Max - Min,
Fd = distance to the middle of filter.

4.2   Soil samples

The soil content of DDT and metabolites at P1 and P4 is given in Figs. 4 and 5 Maximum S-DDT concentraion in P1 and P4 was 93 and 638 mg/kg, respectively. The concentration of DDT in the soil drops (to a background level) below 2.5 m depth in P1.
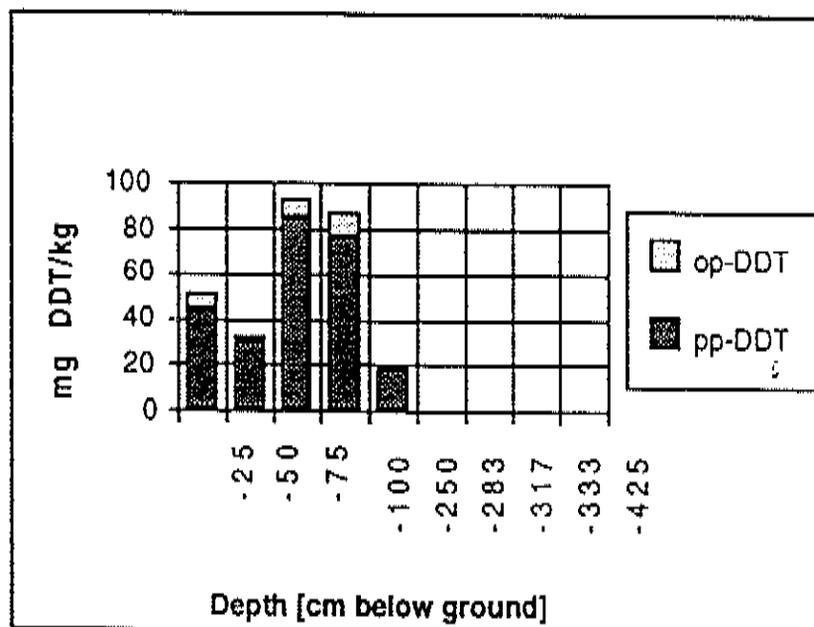
Figure 4. DDT in soil at P1

The DDT in P1 consisted of 95 % pp—DDT+DDD, and 5% op—DDT+DDD. The DDE content was not measured in P1. In P4 the DDT consisted of 88.7 % pp—DDT+DDD, 11.6 % op—DDT+DDD and 0.6 % pp—DDE at depth 0—1.5 m, and 89 % pp—DDT+DDD, 10 % op—DDT+DDD and 0.7 % pp—DDE at depth 1.5-3 m. The mean groundwater table in P1 is 2.43 m, which indicates that the groundwater is in contact with DDT-polluted soil in P1. In P4, the mean groundwater level is 1.14 m below surface, and the groundwater is in contact high DDT-concentrated soil.
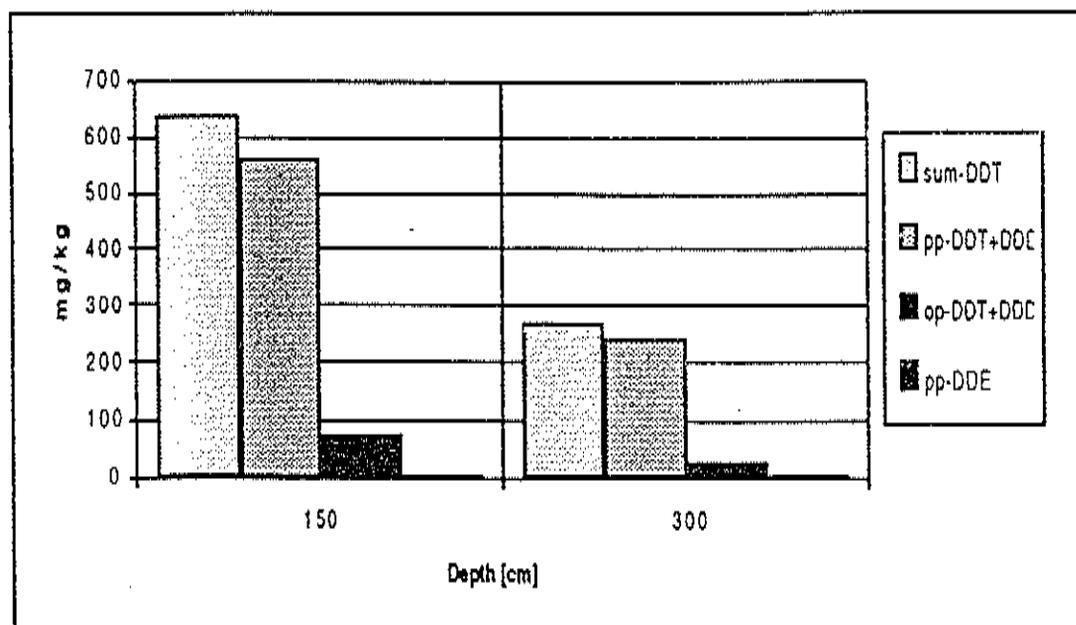
Figure 5. DDT in soil at P4

4.3 Water samples

Soil— and groundwater samples have been collected for two years. All measurements from groundwater samples were pooled, and the statistics are given in Table 3. Confidence intervals (95 % or greater) based on the significant frequency distribution for each type of analyses have been calculated. The groundwater was acidic, low in O_2 and TOC, Cl, Na and high in K, Fe,Mn, Zn, Al and Si relative to median values from Norwegian drinking waters.

Table 3 Batch groundwater quality statisties (+)

	pH [-]	EC [mS/m]	O_2 [mg/l]	TOC [mg/l]	NO$_3$-N [mg/l]	CL [mg/l]	HCO$_3$ [mg/l]	K [mg/l]	Ca [mg/l]	Mg [mg/l]	Na [mg/l]	S [mg/l]	Fe [mg/l]	Mn [mg/l]	Zn [mg/l]	Al [mg/l]	Si [mg/l]
Max	6.40	25.0	8.5	1.18	24.2	10.4	41.5	21.2	23.9	8.19	15.0	27.3	13.9	0.48	0.08	1.53	7.62
Min	3.60	6.20	1.50	0.00	0.00	1.77	0.00	1.01	5.48	0.86	1.67	0.85	0.23	0.03	0.00	0.00	2.57
Am	5.27	12.3	3.75	0.62	3.07	3.91	10.8	5.54	10.3	2.41	4.16	12.0	3.12	0.17	0.02	0.41	4.40
n	21	24	16	6	20	20	20	20	20	20	20	20	20	20	20	20	20
Dist.	N	N	LN	N	NP	NP	NP	LN	N	N	LN	N	LN	N	NP	NP	N
U	5.6	14.4	4.3	0.94	1.43	4.53	12.2	5.8	12.1	3.22	4.52	15.5	2.62	0.22	0.03	0.49	5.37
L	4.93	10.19	2.53	0.3	0.11	2.21	4.27	2.86	8.33	1.6	2.92	8.48	0.79	0.1	0	0.17	3.42
Norw.	7.3	11		1.65	1.5	5.7		0.74	8.66	1.86	5.5		0.01	0.0007	0.009	0.02	3.45

† Am = mean, n = number of obs., value 0 = lower than det.limit, Dist. = Significant Distribuion, N = normal, LN = log-normal, NP = non-parametric. U = upper value of 95 % confindence interval, L = lower value. Norw. = median value from 35 Norwegian groundwater works (Hatcn, 1985)

The groundwater quality for each location is given in Table 4. Piezometer P2 represents background levels compared to the DDT landfill. Compared to the confidence intervals in Table 3, P4 was high in pH, TOC, Cl, Mn and HCO_3, and low in K, Mg, S and Si. P1 was low in O_2 and Na, and high in Al. P2 was low in Cl, HCO_3, Na and Mn. P3 was low in EC, K, Ca, Mg, Na, S and Mn.

Table 4 Mean water quality

	pH [-]	EC [mS/m]	O₂ [mg/l]	TOC [mg/l]	NO₃-N [mg/l]	Cl [mg/l]	HCO₃ [mg/l]	K [mg/l]	Ca [mg/l]	Mg [mg/l]	Na [mg/l]	S [mg/l]	Fe [mg/l]	Mn [mg/l]	Zn [mg/l]	Al [mg/l]	Si [mg/l]
P1	5.1	10.5	1.8	0.59	0.06	2.44	4.58	4.36	10.5	1.67	2.19	13.2	1.45	0.08	0	0.42	4.53
P8	5.7	11.0	8.5	nd.	1.43*	5.82	9.76	4.56	8.87	1.64	6.13	12.7	1.64	0.09	0.03	1.46	7.6
P2	4.9	12.3	2.5	0.58	0.54	2	2.75	6.76	9.38	1.63	2.19	13.3	1.26	0.05	0.02	0.38	4.28
P3	5.1	7.1	2.4	0.57	0.06	3.29	4.38	3.11	5.9	0.91	2.47	7.74	1.12	0.06	0.03	0.22	3.29
P4	6.0	12.4	4.4	1.18	0.08	6.98	21.9	2.59	7.76	1.08	4.26	2.79	2.11	0.18	0.01	0.17	2.61
P9	6.1	7.8	4.9	nd.	1.35*	7.89	25.0	1.36	6.13	1.2	4.66	1.57	2.1	0.2	0	1.1	3.7
P10	5.4	8.4	2.7	nd	3.12*	4.5	12.7	1.86	8.35	1.39	3.69	2.84	0.22	0.12	0.03	0.67	3.5
P11	6.4	15	7.2	nd.	18.2*	6.89	41.5	4.04	7.43	2.38	15	15.5	1.06	0.12	0.08	2.34	6.55
11	5.9	10.5	nd	nd	1.02	3.61	11.4	1.59	8.35	0.97	2.53	5.38	0.15	0.04	0.05	0.19	3
U3	6	16.3	nd	0.84	5.04	2.52	11.3	3.81	14.0	1.4	2.17	4.31	0.04	0.02	0.11	0.11	3.8
Sew	7.3	11.6	nd.	1.36	8.75*	12.5	40.3	4.33	4.83	0.72	4.91	0.82	0.09	0	0	0.07	2.47
Drain.	6.9	30	nd.	nd.	5.26*	2.23	nd	0.13	0.28	0.07	2.46	0.03	0.29	0	0	0.05	0.04
P4/P2						3.5	7.97					0.22					
Sew./P4						1.8	1.8					0.29					
P1/P2						1.2	0.99					1.65					
Sew./P1						5.12	8.80					0.06					

† P1—P11; groundwater samplers, U1—U3; soilwater samplers. Sew = sewage-outlet, Drain. = surface drainage, value 0 = below det. limit, nd. = not determined * = Total N.

Table 4 shows that the mean Cl concentration in P4 is 3.5 times higher than in P2 (the «background»). This increase cannot be fully explained by infiltration of sewage water to P4, unless excessive amounts of sewage water is infiltrated, which is unlikely due to the consistent ratio of mean concentrations of Cl and HCO_3 in sewage water relative to P4. The concentrations of in P1 is fairly concistent with background levels.
The pesticide content in water samples is given in Table 5. The positions of the piezometers relative to the DDT landfill and the positions of the filter relative to the groundwater levels are given in Fig. 2 and Table 2. There were large differences in filtered and unfiltered water samples in P4, as expected. The DDT is however significantly dissolved in the groundwater at P4. The watersample in the surface drainage is taken approx. 100 m distance from the landfill (Fig. 1). The DDT in the water eroded from the landfill and was transported in suspension via surface water.

The compostion of DDT in the filtered water samples in P4 was 73 % pp-DDT+DDD, 26 % op- DDT+DDD and 1 % DDE. In the unfiltered water samples, the composition was 87 % pp- DDT+DDD, 10 % op-DDT+DDDand 3 % DDE.

Table 5. Mean pesticide concentration in watersamples (µg/l)

	Σ-DDT	pp-DDT	op-DDT	pp-DDD	op-DDD	pp-DDE	Σ Other pest.
P1‡	0.13	0.13	0	-	-	0	0
P2‡	0	0	0	-	-	0	0
P3‡	0	0	0	-	-	0	0
P4†	5.09	3.0	1.1	0.5	0.4	0.09	3.51*
P8†	0.47	0.06	0.02	0.01	0	0.009	nd
P9†‡	0.85	0.73	0.12	-	-	0	nd
p10†‡	1.0	0.86	0.14	-	-	0	nd
P11†	0.1	0.07	0.02	0.01	0	0	nd
U1‡	0	0	0	-	-	0	0
U3‡	0.05	0.05	0	-	-	0	0
Drain‡	38.5	34	0.5	-	-	0.5	nd

† Sample decantated ‡ DDT = DDT+DDD * Lindane + Fenvalerat, 0=below det.limit, nd=not determined

5   DISCUSSION

The risks from landfills of DDT are connected to direct uptake in zoological material, or pollution of surface— or groundwater. We have not discussed the risk concept here, but will concentrate on the probability of mobilizing DDT to water bodies. The probability will surely depend on the concentrations of DDT in the soil, together with the soil's physical and chemical properties. The soil at the site is a homogenous sand with organic rich layers (black layers in intersection in Fig. 2).
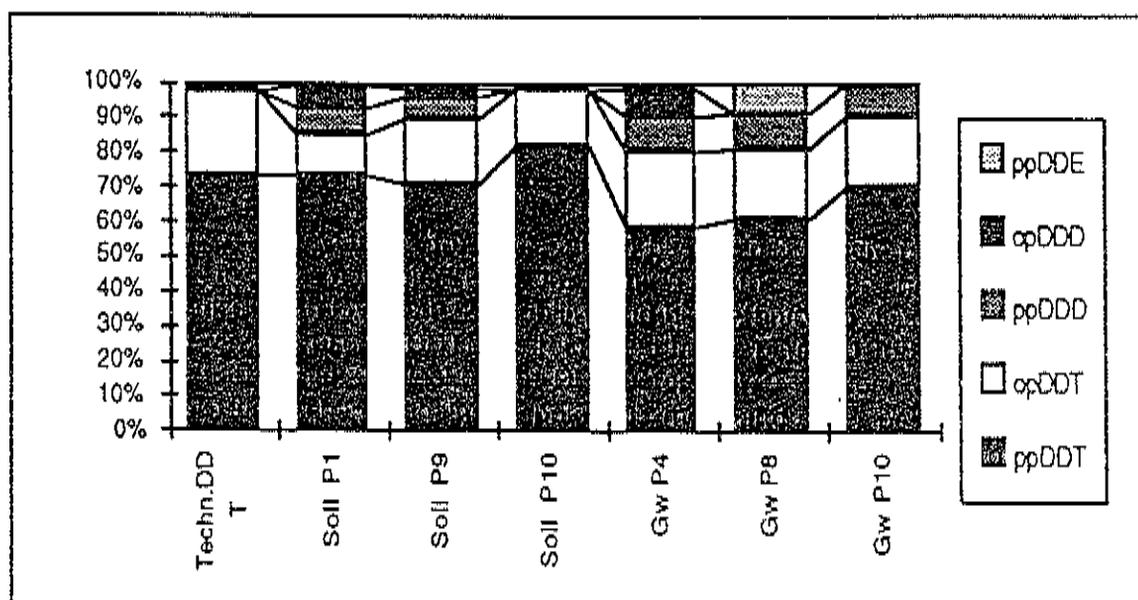
Figure 6 Composition of DDT samples.

The hydrogeological situation at the site is characterized by the groundwater levels given in Table 2, and the chemical composition in Tables 3 and 4. The values of the different chemical elements and ions are best described with confidence intervals. These are dependend on the frequency ditribution of the measurements; and the distributions will generally depend on the number of observations, especially when there are few observations. Piezometer P4 was significantly different from the others with high values of several chemical components.

It is not possible to point out which one of the specific characterisitcs in the composition of the groundwater in P4 is suitable to dissolve excess amounts of DDT. Indications point, however, to the facts that besides being a highly concentrated soil, with low hydraulic conductivity and high fluctuating groundwater levels, the groundwater was relatively high in TOC, Cl and HCO_3. P4 was also low in K and Mg, which could influence the capacity of the soil´s biological activity. This is however a less typical indication in this study, since P3 also was low in K and Mg, but had no DDT. The DDT-free water in P3 can however also be explained by the deep position of the filter relative to mean groundwater level. The ratios between DDT and DDE were low both in soil and water samples, indicating that microbiological activity is low or absent at the site.

6 ACKNOWKLEDMENTS

7 ABBREVIATIONS

Short name	Full name	Unit
S-DDT	Sum DDT and metabolic products	[mg/l (water)or mg/kg (soil)]
DDT	Dichloro-diphenyl-trichlorethane	do.
DDE	Dichloro-diphenyl-dichloroethylene	do.
DDD	Dichloro-diphenyl-dichloroethane	do.
DDA	Dichloro-diphenyl-acetic acid	
pp-DDT	1,1,1-trichloro-2,2-bis-(4-chlorophenyl) ethane	do.
op-DDT	1,1,1-trichloro-2-(4-chlorophenyl)ethane	do.
pp-DDE	1,1-dichloro-2,2-bis-(4-chlorophenyl)ethylene	do.
pp-DDD	1,1-dichloro-2,2-bis-(4-chlorophenyl)ethane	do.
GSD	Grain size distribution	[-]
EC	Electrical conductivity	[mS/m]
pH	log-H⁺-concentration	[-]
pF	log-(soil potential)	[-]
TOC	Total organic carbon	[mg/l or mg/kg]
CI	Confidence interval	[%]
Koc	Adsorption constant	[mg substance/gsoil % carb.]

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SIMULTANEOUS DETERMINATION OF PESTICIDES AND CORRESPONDING METABOLITES
By Robert Kreuzig

ABSTRACT

Plant protection products are considered part of the indispensible means of agricultural production. The common acceptance of extensive and frequent applications is based on chemical and microbial degradation of pesticides in the soil/plant system which counteracts accumulation in soil and exceeding of maximum residue limits (MRL). Besides metabolism studies in laboratory and lysimeter scale due to pesticide registration procedures, the fate of pesticides under field conditions is investigated extensively by the analytical determination of active compounds applied. But, in order to verify decreasing concentrations definetely as a result of degradation reactions and to distinguish between metabolism and the formation of non-extractable residues, it is urgently recommended to determine simultaneously parent compounds and corresponding metabolites.

1   INTRODUCTION

Due to large-scale industrial production and extensive applications of pesticides, adverse impacts on environmental compartments have to be considered. Contamination pathways are shown in Fig 1. Air pollution is caused in direct drift during spray application and in post applicative volatilization of pesticides from plant and soil surfaces. Besides photochemical degradation, these xenobiotics underly a long-range transport in the atmosphere. Then, dry and wet deposition lead to an ubiquitous distribution and to an impact on remote ecosystems.

Particular crop stands are the target site of plant protection measures and contaminated directly by pesticide application. During the delay time between last application and harvesting, degradation reactions counteract pesticide accumulation and exceeding of maximum residue limits.

Despite interception of the spray solution in established crop stands, wash off as well as soil contamination by drift and specific application forms constitute an impact on soil quality. The fate of pesticides in soil is dependent on physico-chemical properties of the soil and the pesticide itself. So, the solubility of the active compound in the soil solution is the decisive parameter for adsorption, desorption as well as leaching processes. This fact decides about the extent of bioavailability and plant uptake as well as about leaching and ground water contamination. Further, polluted drainage water and, after strong precipitation events, surface run off can lead to surface water pollution and pesticide accumulation in aquatic sediments.

Despite possible adverse effects, the acceptance of frequent pesticide applications is mainly based on the chemical and microbial degradation of active compounds applied. Besides total mineralization, degradation products are formed in complex reaction schemes. Depending on persistence of compounds and bioactivity of soil, metabolites contribute to soil pollution. Modified physico-chemical properties of degradation products lead to increasing leaching tendencies and bioavailability. Possibly maintained biocide efficacy emphasizes the importance of metabolites, too.
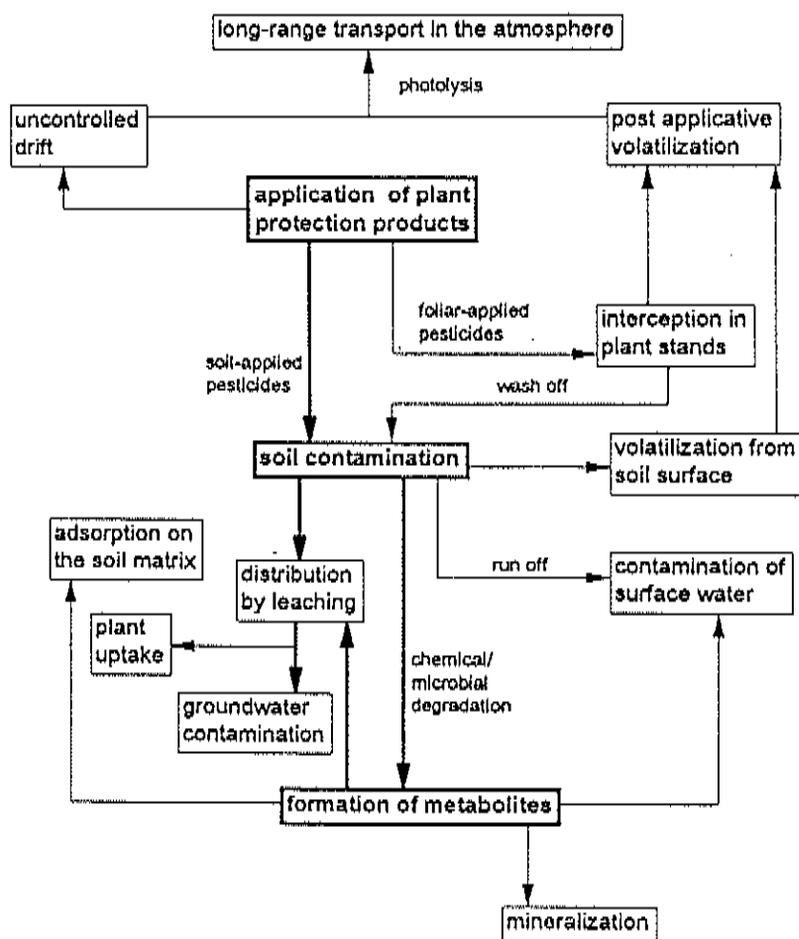
Figure 1   Fate of pesticides in agro-ecosystems

2   PESTICIDE DEGRADATION IN SOIL

Due to the development of less persistent pesticides, degradation processes are investigated extensively in laboratory and field experiments. In laboratory batch experiments as well as in outdoor lysimeter studies, ^{14}C-labelled active substances are applied to determine mass ballances and to identify metabolic pathways. But, not every pesticide is purchasable as a ^{14}C-labelled tracer and not every analytical laboratory is able to perform metabolism studies by applying radiotracer techniques. Further, due to different water and matter dynamics, laboratory scale studies only yield tendencies without sufficient transferability to all agricultural production sites. The fate of pesticides under field conditions, therefore, is investigated extensively by the determination of parent compounds.

In modern agricultural practice, pesticides with high efficacy and little half-life are applied. In Fig. 2 the residue situation of the morpholine fungicide fenpropimorph is shown after splitted application of 1.3 kg/ha to a winter wheat stand.
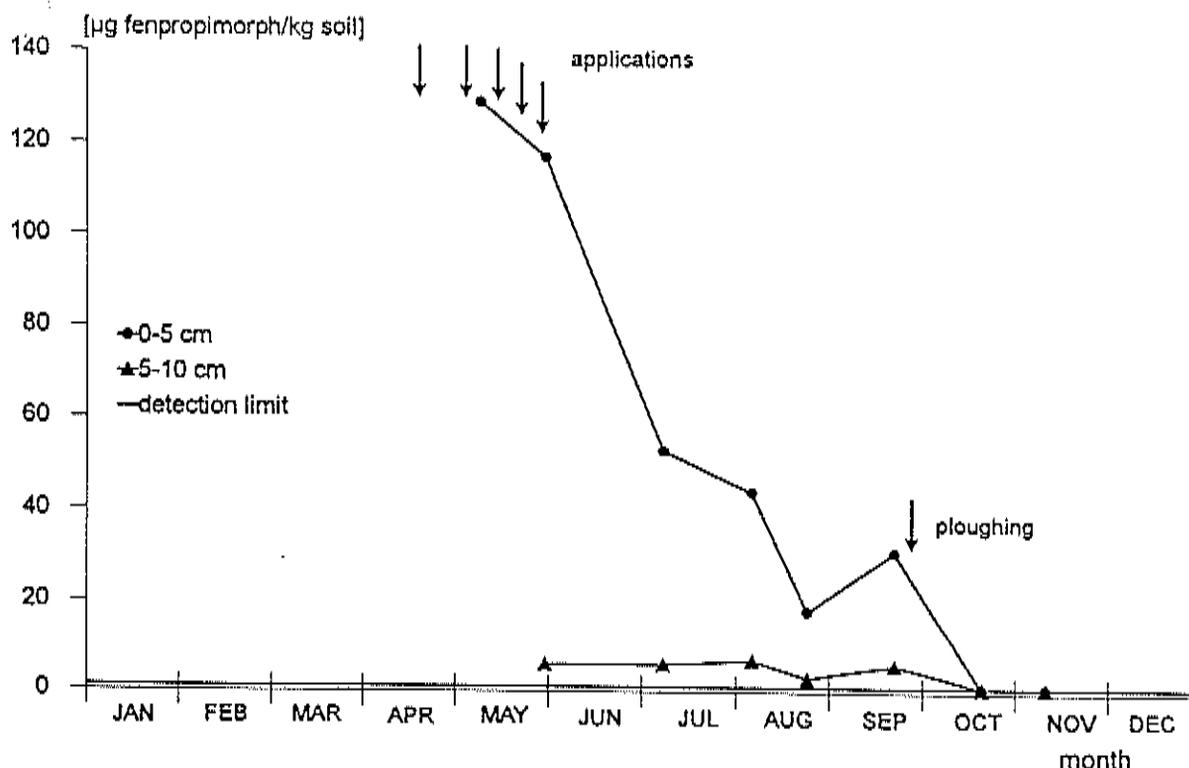
Figure 2 Concentrations of fenpropimorph in topsoil during a vegetation period

Highest concentrations up to 130 μg fenpropimorph/kg soil were determined in the 0-5 cm soil layer directly after plant protection measures (Gottesbüren et al., 1992). During the vegetation period, fenpropimorph concentrations decreased in topsoil and, after ploughing, no residues were detectable above the detection limit of 5 μg/kg soil. In numerous investigations, decreasing concentrations of parent compounds applied are explained exclusively with degradation processes in soil. Performing metabolite analysis, it is possible to verify the degradation of fenpropimorph to the main metabolite fenpropimorphic acid (Stockmaier, 1992). But, due to significant differences between the concentration levels of parent compound and corresponding metabolite, other substance losses also have to be considered So, in a lysimeter experiment, ¹⁴C-labelled fenpropimorph formulation was applied to a winter wheat stand and the formation of a morpholine ring cleavage product as a further metabolite was confirmed (Fig. 3). But, 2,6-(cis)-dimethylmorpholine, which is also expected as a metabolite, was not detectable in the open lysimeter system due to its high volatility (Ebing et al., 1994). That is why the significance of volatile degradation products inclusive ¹⁴CO₂, which is formed by mineralization, has to be investigated in closed cultivation chambers to set up detailed mass balances.
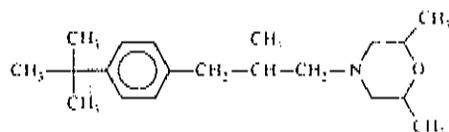
4-[3-4-(1,1-dimethylethylphenyl)-2-methyl]-propyl-2,6-(cis)-dimethylmorpholine
fenpropimorph
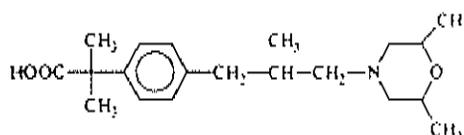
4-[3-[4-(2-carboxypropyl)-phenyl]-2-methyl]-propyl-2,6-(cis)-dimethylmorpholine
fenpropimorphic acid
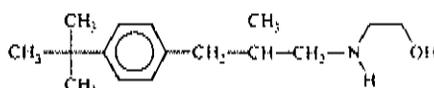
1-(N-hydroxyethylamino)-2-methyl-3-(4-tertiary-butylphenyl)-propane
morpholine ring cleavage product
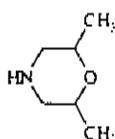
2,6-(cis)-dimethylmorpholine

Figure 3 Structures of fenpropimorph and corresponding metabolites

Further, the irreversible adsorption of pesticides on the soil matrix has to be considered. So, applying a sequential extraction scheme combined with final combustion, $^{14}CO_2$ sampling and liquid scintillation counting (Fig. 4), non-extractable residues were determined in the lysimeter monolith and predominated the extractable ones down to subsoil.

Such investigations show clearly that the fate of pesticides in soil is characterized insufficiently by the determination of parent compounds. It is necessary, therefore, to gather substance and soil dependent parameters by performing radiotracer experiments in laboratory scale which have to be validated by investigations under field conditions. But, in order to describe such complex processes, sophisticated analytical methods have to be developed and adapted, respectively, including modern techniques like supercritical fluid extraction and chromatography.
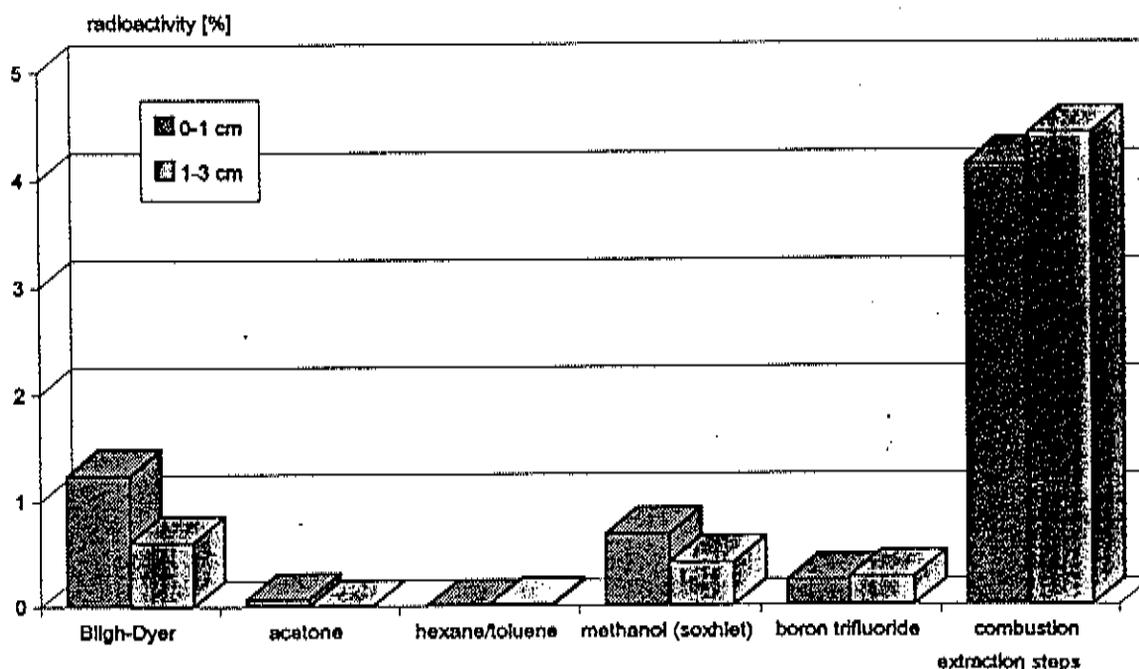
Figure 4   Sequential extraction scheme of soil samples for quantitative deter-
mination of ^{14}C-fenpropimorph residues

3   LEACHING BEHAVIOUR

In soil, fenpropimorph is metabolized rapidly to fenpropimorphic acid by oxidation
of the tertiary butyl group. So, due to higher polarity and lower adsorption coeffi-
cients (K_D-values) of the degradation product, increasing leaching tendency is
expected. But, already in the lysimeter experiment, the total residues decreased
with increasing soil depth (Fig. 5).
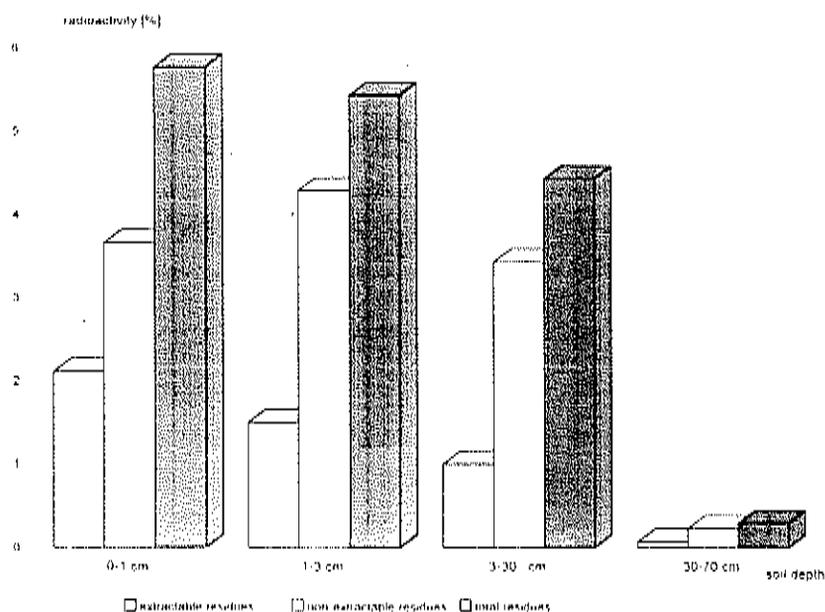
Figure 5   Distribution of extractable and non-extractable residues in soil
layers of the lysimeter monoltih

Field studies at 2 investigation sites also yield similar results (Fig. 6). In clayay silt as well as in silty sand the metabolite was detectable only in the 0-5 cm layer while, directly depending on the adsorption capacity of soil, fenpropimorph was determined in little concentrations down to the 5-10 and 20-30 cm layer, respectively. On one hand, this special residue situation is caused in the dryness of summer 1992. On the other hand, complex reaction schemes of degradation processes in soil only yield degradation products in ultra low concentrations. Despite methylation of fenpropimorphic acid, which is absolutely required for sensitive GC/NPD or GC/MS determination, the detection limit is only 10 μg/kg soil while the parent compound is detectable down to 5 μg/kg soil (Dieckmann et al., 1993).
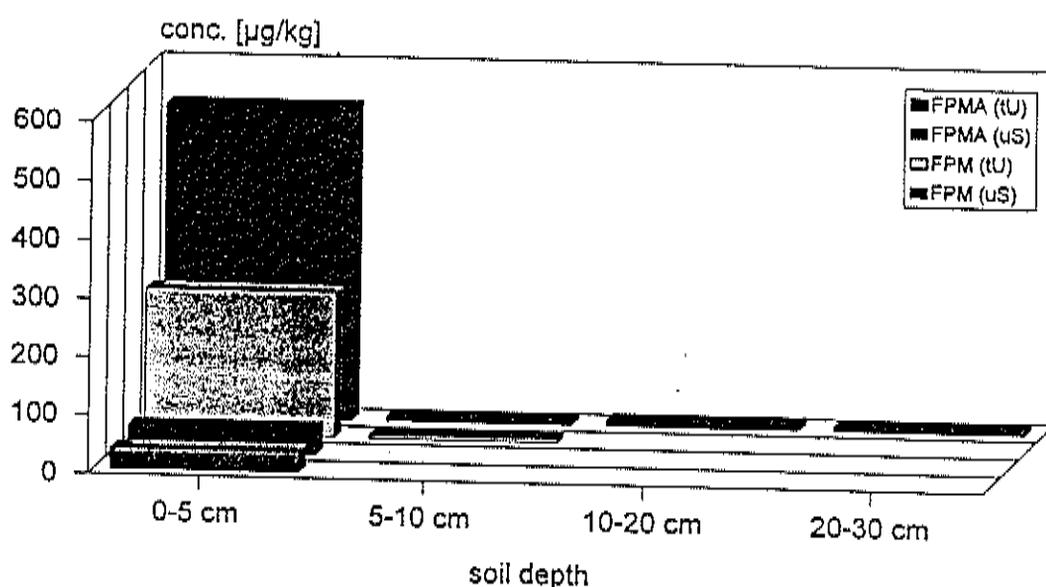
Figure 6   Leaching behaviour of fenpropimorph (FPM) and fenpropimorphic acid (FPMS) in clayay silt (tU) and silty sand (uS)

Incorporating first results into mathematical simulation models shows that leaching tendency of the main metabolite is directly dependent on water content of soil. Due to precipitation events during the investigation period of 70 days, a decrease of fenpropimorphic acid in the 0-5 cm layer is reflected by increasing concentrations in the 5-10 cm layer (Fig 7). But, this hint cannot be validated in a concentration range of 1-10 μg/kg by the detection of the fenpropimorphic acid methyl ester. That is why selective clean up procedures and more sensitive derivatization steps like the pentafluorobenzylation are in the centre of analytical efforts to improve detection limits down to 1 μg metabolite/kg soil. But, for further methodical development in order to establish metabolite analysis in pesticide science as well as in waste analysis, it is necessary to improve the availability of metabolites as reference chemicals because, until today, these standards were supplied only by a few industrial producers of plant protection products or these substances have to be synthesized often without exact knowledge of the reaction instructions.
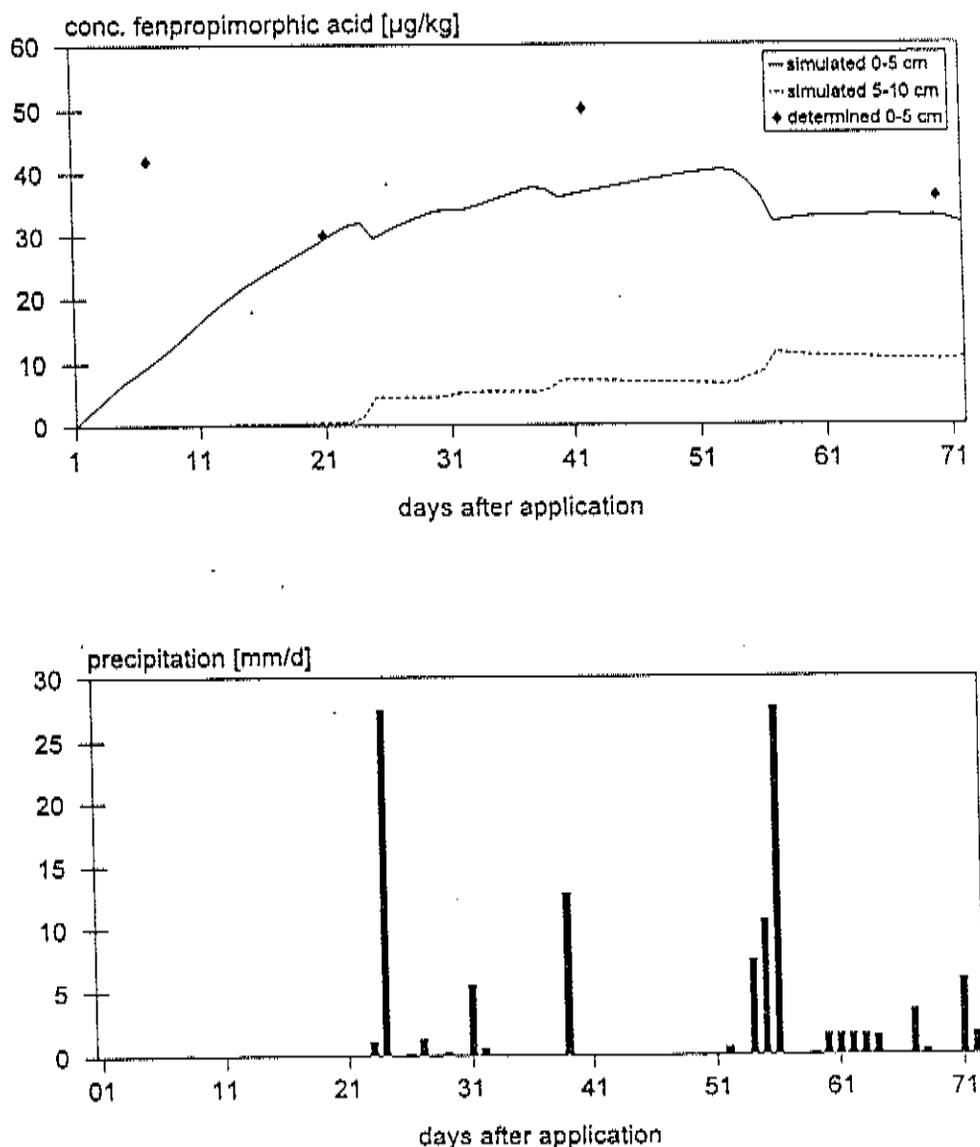
Figure 7   Simulation of leaching behaviour of fenpropimorph depending on precipitation events

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EVALUATION OF HEXACHLOROCYCLOHEXANE RESIDUES IN DIFFERENT LOCALITIES OF THE SLOVAK REPUBLIC

By Juliana Schlosserova

ABSTRACT

This contribution presents the levels of HCH in soils of the Slovak Republic. The fate of HCH residues was studied in soils, mainly in arable lands provenanced to different parts of the country. Consequently agricultural products were analysed in order to study the transport of HCH from soils into plants . These tests were provided under real field conditions. The HCH study started in 1984 and has been gradually enlarged up to 1711 tested samples altogether. The results indicated a strong degradation during some years up to ug/kg and lower contamination levels which can no more cause a HCH cumulation in agricultural products.

1   INTRODUCTION

The soil contamination by hexachlorocyclohexane and consequently the HCH cumulation in agricultural products were of great interest due to their long persistance in our ecosystem.

In the Slovak Republic hexachlorocyclohexane was synthetised in the former CHZJD factory in Bratislava. During the years 1956-1966 there was produced more than 1300 tonnes of gamma-HCH. Some additional raw HCH was imported from the former Yugoslavia. After isolation of the gamma isomer it was formulated into different pesticides in the same factory. Naturally, the produced pesticides were intended partly for domestic utilisation. A very rough estimate of annual consumption of Lindane containing pesticides in the Slovak Republic was about 1 tonne per year. This amount has been gradually decreased. The variety utilised Lindane based formulations has been as well descended: e.g. in the List of Permitted Pesticides for 1972 were listed 11 pesticides on the basis of Lindane. These were insecticides into the most important crops (potatoes, beet roots, rapeseeds, hops), staining agents for treating seeds of cereals, maize, legumes , sugar beet, cucumber, cotton, hemp, rapeseed, water melon, soil des insectants for growing beet roots, sugar beet, cereals, maize, tobacco, hops, young fruit trees and vines, and fumigant, as it is stated in Table 1.

The application of all these pesticides was possible only with some restrictive precautions. The wide and systematic utilisation of Lindane containing insecticides was banned in 1974. In 1981 there were permitted only 4 seed staining agents which are given in Table 2. The year 1992 was the last one when Lindane seed treating agents were permitted as formulations Lindane WP 80 for rapeseed and Lindane 50/35 WP for flax and hemp seeds (Table 2). In the List of Permitted Pesticides for 1993 was given a new Lindane containing pesticide. Emdenit was intended for controlling pine insects but only for a two years period.

Table 1 Lindane containing pesticides permitted in 1972

1972	11 permitted pesticides	

DYMOGAN	16% Lindane	CS
	ornemental plants, room (not feeds, foods)	
AEROSOL DL	2.5% Lindane, 1% DDT	CS
	potatoes 6 l/ha, only 1 application	
GAMACID	0.95% Lindane	CS
	hops 180-200 kg/ha	
	beets 20 kg/ha	
	(not water sourcesm not root veg. follow.year)	
GAMADYNE	0.5% Lindane, 3% DDT	CS
	rapeseeds, potatoes 20 kg/ha, 1 application	
LIDYKOL	4% Lindane, 46% DDT	CS
	rapeseeds, potatoes 1-2 kg/ha	
HERMAL L50	50% Lindane, 35% Thiram	CS
	corn, maize, legumes 3-4 kg/t	
	sugar beet, feed beet 10-12 kg/t	
	flax, hemp, cucumber, meloon 5-8 kg/t	
	(not apply near water sources)	
HERMAL L50M	50% Lindane, 35% Thiram	CS
	maize 3 kg/t	
	(not apply near water sources)	
HEXANAL 90	90% Lindane	CS
	rapeseed 4 kg/t	
	(not apply near water sources)	
LINDAN susp.80	80% Lindane	A
	rapeseed 50 kg/t	
	hops, young trees, tobacco 0.01-0.5%	
SANIGRAN spec.	8% Lindane,	F
	corn 5 kg/t (not near water sources)	
LINDENAL	7,9% Lindane	CS
	corn, sugar and feed beet, maize, tobacco,	
	ornamentals, young fruit trees and vine, hops,	
	30-40 kg/ha soil desinsection	
	(not water sources, not root veg.follow.year)	

Table 2 Lindane containing pesticides permitted in 1981 and 1992

1981	4 permitted pesticides	

HERMAL L50	50% Lindane, 35% Thiram	CS
	corn 4 kg /t	
	maize, leguminous 3 kg/t	
	suger beet, feed beet 10-12 kg/t	
	flax, hemp, cucumber, meloon 5-8 kg/t	
	(not apply near water sources)	
HERMAL L50M	50% Lindane, 35% Thiram	CS
	maize 3 kg/t	
	(not apply near water sources)	
LINDAN WP80	80% Lindane	A
	rapeseed 50 kg/t	
	hops, young trees and vine, tobacco	
	0.01-0.5%	
SANIGRAN spec.	8% Lindane,	F
	corn 5 kg/t (not near water sources	

1992	2 permitted pesticides	
LINDAN WP80	80% Lindane rapeseed 600 kg/t	A
LINDRAM 50/35 WP	50% Lindan, 35% Thiram flax, hemp 8 kg/t	CS
for both:	not apply near water sources no potatoe and root vegetable in foll. year	

Due to the longlasting systematic application of the above mentioned pesticides the persistant hexachlorocyclohexane had slowly spread in the environment. It became a serious environmental organic compound and consequently one of the target pollutants. The HCH residues survived in soils for some tenths of years. The determination of HCH cumulation levels in soils and consequently in agricultural products has still remained highly actual due to its chemical and biological stability.

The goal of this study was to gain an informative view on Lindane appearance in samples representing different parts of the Slovak Republic. The fact that the hexachlorocyclohexane residues are highly resistant to decomposition led the Central Agricultural Controlling and Testing Institute in Bratislava to carry out a study on HCH occurence in the soil environment followed by analyses of agricultural products: feeds and row materials of plant origin from different parts of the country.

Lindane was one of the most widely utilised insecticide on worldwide scale. Its insecticidal properties were discovered in the early 1940s by ICI Ltd. Lindane excellently acts for controlling a wide range of sucking and chewing insects attacking foliage and roots. It also gives a control of insects of grains in storage as well as those found in household and livestock. Lindane is a chlorinated hydrocarbon with stomach, contact and fumigant actions with a relatively long residual activity. Lindane is the commercial name for the gamma isomer of hexachlorocyclohexane . Even this stereoisomer performs the greatest insecticidal activity.The reaction product of the HCH synthesis contains five stereoisomers of hexachlorocyclohexane. The chlorination reaction of benzene in order to gain HCH was at first carried out by M.Faraday in 1825. The isolation method for the active gamma isomer from the reaction product was discovered by van Linden in 1912.

2   EXPERIMENTAL

A trace analytical method characteristic for lipophilic compounds was used to gain the residual level of hexachlorocyclohexane in the samples.
The physically treated samples of soils and agricultural products were extracted by non-polar organic solvent in presence of a small amount of activated siloxid. After moisture removal the combinated n-hexane extracts were evaporated on a rotary vacuum evaporator. In order to remove the not desirable coextractes a low cost clean-up method was performed: liquid-liquid extraction with concentrated sulphuric acid. After allowing to separate the two phases the supernate was dried by passing through a layer of water-free natrium sulphate and consequently evaporated just to dryness.

After dissolving the evaporated in a proper volume of iso-octane or n-hexane the HCH content was determined by means of ECD - GC (Unicam made, type PU 4550). The separation was provided either on packed column (OV-17 + QF) under isothermal conditions or on capillary column (SPB 5) under temperature programm. For determination of the HCH levels in more recent samples there was used the Automass 150 GC/MS system a product of ATI Unicam.

3   RESULTS AND DISCUSSION

The repeated and longlasting application of Lindane containing pesticides by farmers became a good reason to start carrying out a study on HCH occurence. The search started in 1984 (Table 3). with feed analyses followed by soil analyses of 695 samples in 1986-1989. A part of the samples was provenanced to the field trials of the Field Testing Stations throughout the country.

Tabel 3 Survey of samples analysed on Lindane appearance

Year	Samples	Commodity	Country
1984	27	feed components	India
	35	feeds	Slovak Republic
1985	47	foods + components	India, Hungary
	22	foods	Slovak Republic
1986-89	695	soil	Slovak Republic
1991-92	152	soil	Slovak Republic
1987-89	337	agric. products	Slovak Republic
1992-93	396	soil	Slovak Republic
Total	1711		

During the years 1987-89 the study was enlarged by 337 agricultural products. The number of analysed samples has been gradually extended up 1243 soil samples. Altogether there were tested 1711 samples of soils and agricultural products.

The determined HCH levels were evaluated according to limit values given in Table 4. The working limit 0.05 mg gamma-HCH/kg of air-dried soil was lower than the A-level in the former Holland liste (0.1 mg/kg).

Table 4. Limit values for Lindane

Commodity	Lindane mg/kg	Notes
Soil	0.05	working limit
Agric. products:		
domestic: feed dry	0.200	Hygienic Standard
feed fresh	0.100	Hygienic Standard
vegetable	0.100	Hygienic Standard
rapeseed	.	not given
imported: feed dry	0.500	Hygienic Standard

3.1. Gamma - hexachlorocyclohexane

3.1.1 Soils

The studied soil samples, mainly agricultural soils, were provenanced from different localities of the Slovak Republic and covered nearly the whole country with a greater stress on the intensive agricultural regions. The soil study started in years 1986-89 when 695 soil samples were analysed on residues of chlorinated insecticides, see Table 5. The geographic position of the sampling localities are illustrated in the map of the Slovak Republic in Fig.1. There were 424 soil samples originated in some agricultural farms from South and East Slovakia (localities 3, 4, 6, 10, and partly from 7 and 23) including strips of fields intended for baby production. The rest of the soil samples in number of 271 samples represented 180 strips of fields in 22 Field Testing Stations throughout the country (localities 1, 2, 5, 8, 9, 11 - 22, 24 - 26 and partly 7 and 23).

The results of Lindane cumulation levels showed a quite high positive Lindane accurence (Table 5). Only in 6.3 per cent of samples was not detected HCH at all. Naturally, this result was a consequence of the longlasting and systematic utilization of chlorinated pesticides. The level of Lindane residues differed from one field strip to the other in the same locality, e.g. strips of fields A-VII and A-VIII at the locality Velke Ripnany (Table 14). This findings could be a result of the different rates and numbers of applications at different strips of fields.

Table 5 Lindane contamination levels in soils, 1986-89

Locality		samples	Mean Lindane content, mg/kg	Findings % Negat.	Overlim
1	Bratislava	13	0.014	7.7	0
2	Bahon	18	0.010	16.6	0
3	Nitra	39	0.012	20.5	12.8
4	Dun.Streda	16	0.019	25.0	0
5	Calovo	15	0.026	0	20.0
6	Galanta	39	0.044	0	58.9
7	Nove Zamky	110	0.025	5.4	16.3
8	Zeliezovce	10	0.022	20.0	10.0
9	Senica	8	0.018	0	0
10	Lucenec	100	0.024	2.0	19.0
11	V.Ripnany	31	0.049	3.2	37.7
12	D.Plachtince	8	0.016	12.5	0
13	Viglas	5	0.019	0	0
14	Detva	6	0.035	16.6	33.3
15	Beluse	11	0.022	9.0	0
16	Bodorova	17	0.013	0	0
17	Trestena	8	0.023	0	0
18	Spis.Bela	7	0.032	0	14.2
19	Spis.Vlachy	8	0.014	37.5	12.5
20	Haniska	12	0.025	0	16.6
21	Zborov	12	0.041	16.6	41.7
22	Trebisov	9	0.047	22.2	44.4
23	Michalovce	161	0.034	3.1	29.8
24	Jakubovany	13	0.049	0	61.5
25	Vranov	10	0.017	20.0	0
26	Rim.Sobota	9	0.023	0	0
Total		695	0.025	6.3	21.8

According to the given limit value in 21.8 per cent of samples the determined Lindane level exceeded it. It means that 289 samples were overlimitely contaminated. Namely in locality (21) Zborov was found the highest contamination level : 0.11 mg/kg. The highest appearance of samples with over limited contamination (28.6 per cent) and as well the highest mean content (0.031 mg/kg what was 1.55 higher than in West-Slovakia) was found in soils referring to East-Slovak agricultural regions (Table 6). The highest number of Lindane free samples were found in soil samples from West-Slovakia.

Table 6. Mean levels of Lindane content and percentage of negative and overlimited findings of Lindane in soils, 1986-1989

Localities	Samples	Mean levels mg/kg	Findings Negat.	/per cent/ Overlim.
West	268	0.021	8.9	18.6
Middle	186	0.025	3.2	17.7
East	241	0.031	5.8	28.6
Total	695	0.026	6.3	21.8

Among the soil samples there were analysed soil samples from gardens situated in the vicinity of the former HCH factory. The level of Lindane residues fell into the range 0.0109 - 0.0168 mg/kg (locality 1 in Table 5. and Fig 1). This level represented a third of the limit value. There were not found spots with limit exceeding content. The Lindane occurance in groundwaters from the same sites were not higher than 0.02 ug/l . The limit value was much more higher , 3 ug per litre. After a two years interruption the soil contamination study continued by searching after Lindane residues in localities referring to numbers 27 - 34 in Table 7. and Fig.2. The localities 27 - 32 were studied within the Complex Target Monitoring of Pollutants in the environment of the Slovak Republic. The reasons for the selection of these samples were positive findings of Lindane residues in feeds or foods provenanced from this localities.

Table 7. Lindane contamination levels in soils, 1991-92

Locality	Samples	Mean Lindane content,mg/kg	Findings % Negat.	Overlim.
27.Lubisa	29	0.0019	0	0
28.Rosina	22	0.0002	5	0
29.Trnove	6	0.0002	33.3	0
30.Strecno	6	0.0007	16.6	0
31.Turie	20	0.0003	0	0
32.Chor.Grob	17	0.0008	0	0
33.Smolenice	12	0.0013	0	0
34.S-West region	40	0.0011	2.6	0
Total	152	0.0009	3.3	0
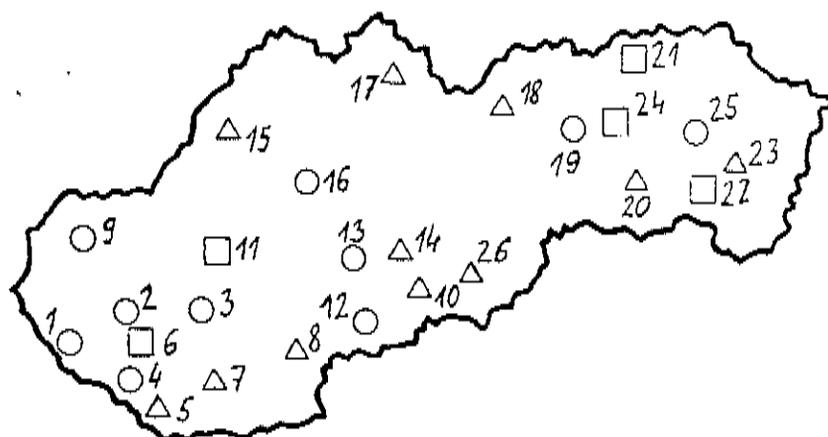
Figure 1.
Mean values of Lindane levels in soils analysed in 1986-1989 from different localities of the Slovak Republic. The symbols represent the following concentration ranges:
up to 0.02 mg/kg ○, 0.02 - 0.04 mg/kg △
0.04 - 0.05 mg/kg □, above 0.05 mg/kg ●
The names of the localities referring to the numbers on the map are listed in Table 5.
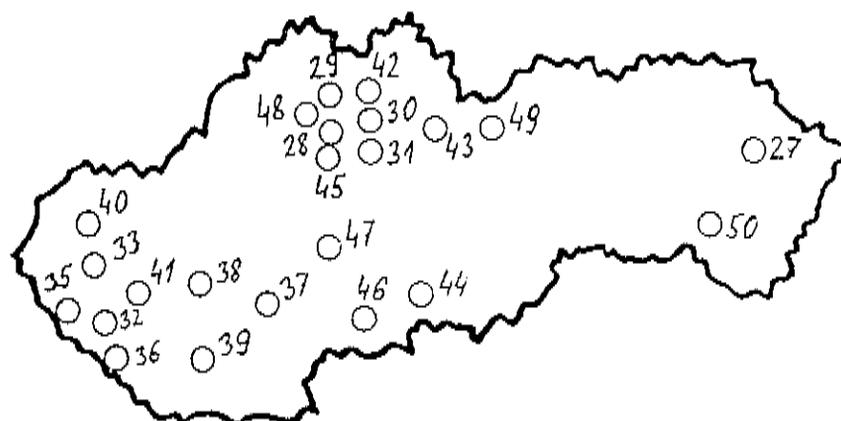
Figure 2.
Mean values of Lindane levels in soils analysed in 1991 - 1992 and 1992 - 1993. The symbols represent the following concentration ranges:
up to 0.02 mg/kg ○, 0.02 - 0.04 mg/kg △
0.04 - 0.05 mg/kg □, above 0.05 mg/kg ●
The names of the localities referring to the numbers on the map are listed in Table 7 and 8.

The south - west region 34 is an intensive agricultural region of the Slovak Republic. The Lindane appearance in the 40 samples was deeply below the limit value. The mean Lindane content was 0.0011 mg/kg.

The locality 33 represented a paint factory site. The tested soils were sampled from a profile up to the depth of 6 meters at 5 sampling sites. The greater depth the higher HCH content. It had not exceeded the level of 0.008 mg/kg.
The results of 152 soil samples showed a quite low contamination level: about 2 per cent of the limit value for the soils. The mean Lindane content in samples tested in this period was 0.0009 mg/kg. This value had decreased about thirthy times in comparison to the samples studied in years 1986 - 89 :

1986-89	695 samples	0.0250 mg/kg mean Lindane content
1991-92	152 samples	0.0009 mg/kg mean Lindane content
1992-93	396 samples	0.0009 mg/kg mean Lindane content

The more recently analysed soil samples were contaminated by Lindane in very low concentrations. It confirms the fact, the longer elapsed time after Lindane application, the lower determined levels in soils. The group of 396 samples tested in 1992-93 were provenanced to strips of fields in 16 bioproduction regions. Their geographical positions with numbering 35 - 50 are depicted in Fig 2 The samples were contaminated in ug and less than ug /kg levels. The highest finding was 0.0070 mg/kg at a strip of field in the Middle-Slovak locality of 47 Zvolen, see Table 8.

Table 8. Lindane contamination levels in soils intended for bioproduction, 1992-93

Region	Samples	Mean	Maximum Lindane,mg/kg
35.Bratislava	44	0.0009	0.0040
36.D. Streda	30	0.0012	0.0040
37.Levice	47	0.0009	0.0030
38.Nitra	31	0.0009	0.0010
39.N.Zamky	4	0.0008	0.0010
40.Senica	11	0.0005	0.0010
41.Trnava	68	0.0009	0.0060
42.D.Kubin	28	0.0009	0.0010
43.Lipt.Mikulas	18	0.0006	0.0010
44.Lucenec	5	0.0010	0.0010
45.Martin	15	0.0005	0.0010
46.V.Krtis	13	0.0005	0.0010
47.Zvolen	19	0.0013	0.0070
48.Zilina	15	0.0008	0.0010
49.Poprad	31	0.0025	0.0020
50.Trebisov	17	0.0006	0.0010
Total	396	0.0009	

The conclusion of the soil contamination study on appearance of gamma-hexachlorocyclohexane which was represented by 1243 samples tested during the years 1986-1993 from different parts of the Slovak Republic is the following: the Lindane appearance in soils performed a remarcable decreasing tendency up to concentrations on the detection level of the utilised analytical determination method in the more recent soil samples.

3.1.2 Agricultural products

To gain a more detailed view of the fate of gamma-hexachlorocyclohexane in the environment of the Slovak Republic there was studied a great variety of agricultural products of plant origin: different sorts of feeds and feed mixtures, row materials and samples of vegetables.

During the years 1984 - 85 and 1987 - 89 there were studied altohether samples in number of 468 (Table 3). None of the feeds and feed components imported from Hungary /maize seeds/and India/ groundnut, soybean and cotton residues with oil content up to 3 per cent / exceeded the limit value for gamma-HCH given by Hygienic Standard (Table 4). The highest cumulation level was found in maize seeds from Hungary (Table 9).

Table 9 Lindane levels in imported feed components and feeds
         from years 1984-85.

Commodity	Samples	Mean Lindane content,mg/kg	Findings % Negat.	Overlim.
groundnut res.	46	0.026	60.0	0
soybean res.	19	0.016	63.1	0
cotton res.	5	0.006	0	0
maize seeds	5	0.087	0	0
total	74	0.026	52.7	0

In four samples of domestic origin Lindane exceeded the limit value for domestic feeds which is 2.5 stronger than that for the imported feeds (Table 4). The mean gamma-hexachlorocyclohexane content in the tested 57 samples was 0.054 mg/kg (Table 10). Five samples were Lindane free.

Table 10. Lindane levels in domestic feeds, 1984-85

Commodity	Samples	Mean Lindane content,mg/kg	Findings, % Negat.	Overlim.
dry feed mixture	4	0.012	0	25.0
dairy cow feed	7	0.069	14.3	14.3
lucerne green	5	0.021	20.0	0
clover	1	0.038	0	0
meadow hay	19	0.063	5.2	10.5
pasture	6	0.033	16.7	0
wheat grit	2	0.018	0	0
maize green	2	0.011	50.0	0
maize silage	4	0.013	0	0
wheat straw	4	0.025	0	0
barley chaff	1	0.016	0	0
beet chips	1	0.023	0	0
draff	1	0.032	0	0
total	57	0.054	8.7	7.0

The 337 samples of agricultural products from different regions of the Slovak Republic represented 24 different commodities (Table 11). It was notable that in 63 samples Lindane was not cumulated at all. Namely: the majority of winter wheats and maizes grown in South - West, and samples of lucernes and clovers grown in the mountainous Middle Slovakia. From the 274 Lindane positive samples only 8 samples exceeded the hygienic limit value. This samples represented 7 commodities, listed in Table 12.

Table 11 Percentage of negative and overlimited findings of Lindane in agricultural products analysed in years 1987 - 1989.

Commodity	Samples	Findings Nogat.	/per cent/ Ovorlim.
rape seed	76	0	?
winter wheat	24	66.7	0
beetroot bulb	8	0	12.5
leaves	11	0	9.1
maize leaves	9	11.1	11.1
lucerne	76	51.3	0
clover	11	36.4	0
pasture	6	0	0
meadow hay	69	1.4	2.8
wheat straw	6	0	16.7
diary cow food	7	0	14.3
others [a]	34	8.8	2.9
total	337	18.7	3.0 [b]

[a] cabbage, pea seeds, spring barley, beet chips, maize seeds, maize silage, diary cow food, rye straw, pea straw, chopped straw, wheat grit, barley chaff, dry feed mixture. The samples were analyzed in numbers less than 6.

[b] the percentage was calculated without taking into account the number of rapeseed samples

Table 12. Agricultural crops with exceeding Lindane levels analyzed in years 1987-89

Crop	Lindane mg/kg	Provenance
hay of meadow	0.208	Ziar n/Hronom,Middle Slovakia
feed for diary cow	0.204	Humenne, East Slovakia
mixture of dry feeds	0.230	Sladkovicovo, West Slovakia
straw of winter wheat	0.205	Galanta, West Slovakia
maize leaves	0.106	Galanta, West Slovakia
beetroot bulb	0.109	Galanta, West Slovakia
leaves	0.139	Galanta, West Slovakia

Among the tested 24 commodities of agricultural products the highest Lindane cumulation level was determined in samples of rapeseeds with mean concentration 0.038 mg/kg. The rapeseeds were grown at the following localities:

8 Zeliezovce, 11 Velke Ripnany, 12 Dolne Plachtince, 14 Detva, 15 Belusa, 23 Michalovce and 26 Rimavska Sobota. The geographic positions of the localities are shown in Fig.2.

3.1.3 Soil - plant pairs

The 232 soil-plant sample pairs were analyzed in order to study the transport of Lindane from soil to plant under real field conditions . The tests were provided on soils contaminated up to 91.8 per cent (Table 13). The results show that there was found a cumulation of Lindane in plants: in 73.7 per cent of plant samples was Lindane positively detected. The process of HCH up-take by plants was studied from the point of following factors: the type of agricultural plant , the soil contamination level and the growing period of biomass.

Table 13 Percentage of negative and overlimited findings of Lindane in 232 soil-plant sample pairs

Commodity	Findings Negat.	/ per cent/ Overlim.
soil	8.2	16.8
plant	26.3	1.7

As it is shown in Table 14, at the strip of field A-VII in locality (11) Ripnany in the soil contaminated near the limit value (in soil profile 0 - 60 cm) the grown winter wheat was not contaminated at all in 1988 and slighly contaminated in 1989. There was found a transport of Lindane into the rapeseeds grown on the same strip of field.The cumulation level of gamma-HCH in the 8 tested varietes of rape seeds fell into the range from 0.021 mg/kg / variety Darmor/ to 0.095 mg/kg / for variety OP-08/. The mean Lindane cumulation level was 0.0405 mg/kg.
In the A-VIII strip of field from the same locality the soil was contaminated up to 50 per cent of the limit value in the 0-30 cm profile and overlimitely contaminated in the 30- 60 cm profile. The winter wheat and the spring barley grown there were free of Lindane content.

Table 14. Lindane levels in soil - plant sample pairs

Locality	Commodity	Lindane, mg/kg
15.BelusaVI.	soil 0-60cm/1988/	0.040
	winter wheat/1988/	0.002
	spring barley /1989/	neg.
	rapeseed/1989/:Jet Neuf	0.016
	Silesia	0.058
	Belinda	0.063
	Solida	0.027
	Ceres	0.025
	Darmor	0.023
	Rubin	0.030
	SL 506	0.029
	SL 509	0.031
	OP 08	0.024
	OP 014	0.022
	Arabela	0.023

Table 14. Lindane levels in soil - plant sample pairs (continued)

Locality	Commodity	Lindane, mg/kg
11.V.RipnanyA-VII	soil 0-60cm/1988/	0.046
	0-30cm/1988/	0.049
	30-60cm/1988/	0.032
	winter wheat/1988/	neg.
	/1989/	0.009
	rapeseed/1989/:Darmor	0.021
	Rubin	0.032
	Ceres	0.037
	Arabela	0.025
	SL 506	0.027
	SL 509	0.057
	OP 08	0.095
	OP 014	0.030
11.V.RipnanyA-VIII	soil 0-30cm/1988/	0.026
	0-60cm/1988/	0.080
	winter wheat/1988/	neg.
	spring barley/1989/	neg.

In the Belusa (15) locality the soil was higherly contaminated by Lindane, but below the limit value. The winter wheat produced in 1988 was slightly cumulated by Lindane and the spring barley grown one year later was not contaminated at all. In the same year there were grown 12 varietes of rapeseeds. They confirmed a transport from soil: the mean cumulation level was 0.030 mg Lindane per kg of seeds of tested rapeseeds. The Lindane levels were from 0.016 mg/kg (Jet Neuf) to 0.063 mg/kg (Belinda).

The transport of the HCH was studied for a wide range of different plants, such as: cabbage, corn, maize, sugar beet, rape-seed, pastorage, etc. In some cases the particular plant parts were analyzed separately in order to learn more about the process. This process was not observed in most of agricultural plants. E.g. winter wheat and spring barley despite of the fact that they were grown in contaminated soils remained Lindane free. There was not found a strong relationship between the level of Lindane concentration in soils and plants for different types of searched plants. The only higher Lindane levels were determined in rape seeds. They were in average 3-times higher contaminated than the other tested plants. This finding can be explained by the cumulation of the lipophilic Lindane in productive parts of the plant. The cumulation level in rapeseeds was slightly influenced by the level of soil contamination:
e.g. in V.Ripnany 0.046 mg/kg soil 0.040 mg/kg rape seeds
in Belusa 0.040 mg/kg soil 0.030 mg/kg rape seeds.

There was not found a remarcable influence of the rapeseed varietes on the Lindane take-up by plants and its cumulation in them.
The study of repeated mowings of lucerne showed an influence of the growing period of biomass on the contamination level of the chloroorganic insecticide Lindane (Tab 15).

Table 15. Influence of growing period of biomass on Lindane levels

Locality	Commodity	Lindane, mg/kg
23.MichalovceIV.P	soil 0-60cm/1989/	0.144
	lucerne/1989/Istmowing	0.082
	2nd mowing	0.043
	3rd mowing	0.039
	4th mowing	0.030
15.BalusaX.	soil 0-60cm/1989/	0.021
	lucerne/1989/ 2nd mowing	0.010
	3rd mowing	0.009
	4th mowing	0.008

3.2 OTHER HEXACHLOROCYCLOHEXANE ISOMERS

Beside the gamma-hexachlorocyclohexane there were detected alpha, beta and delta isomers of HCH in the tested samples. The results showed a much more lower appearance of these stereoisomers in comparison to the gamma - HCH either in soils or agricultural crops. From Table 16. it can be seen the ratio of determined isomers in soils from West Bahon, Middle / Bodorova/ and East / Haniska / Slovak intensive agricultural regions. In the case of agricultural crops there was found a quite similar situation (Table 17).

Table 16. Contamination levels of HCH isomers in soils

Locality		Hexachlorocyclohexane, mg/kg		
		alpha	beta	gamma
2.Bahon	I.	0.004	0.007	0.012
	II.	0.003	0.003	0.001
	IV.	0.002	0.004	0.009
	V.	0.001	neg.	0.003
	IX.	0.005	0.002	0.014
	III.agro	0.002	0.004	0.016
	IV.agro	0.003	neg.	0.015
	VI.agro	neg.	0.002	0.002
16.Bodorova	II.	neg.	neg.	0.007
	III.	0.002	0.002	0.008
	III-V.B	0.002	0.003	0.010
	V. + VI.	0.005	0.006	0.014
20.Haniska	I.	0.006	0.002	0.035
	III.	0.002	0.002	0.022
	V.	0.001	0.001	0.024
	VI.	0.001	0.001	0.039
	VIII.	0.009	neg.	0.054

Table 17. Levels of HCH isomers in hay from East-Slovak region Michalovce

Locality					Hexachlorocyclohexane, mg/kg	
		alpha	beta	gamma	delta	
IV.P	2nd mowing	0.003	0.006	0.082	0.001	
	3rd mowing	0.001	neg.	0.043	neg.	
	4th mowing	0.001	neg.	0.039	neg.	
	5th mowing	0.001	neg.	0.030	neg.	
VI.P	2nd mowing	0.001	0.003	0.045	0.001	
	3rd mowing	neg.	0.004	0.038	0.003	
	4th mowing	0.001	0.002	0.033	neg.	
VII.Z	2nd mowing	0.001	0.003	0.034	0.003	
	3rd mowing	neg.	0.003	0.031	0.002	
	4th mowing	neg.	0.002	0.005	0.002	
	5th mowing	neg.	0.002	0.004	0.002	

6 Technical Solutions for the Remediation of Halogenated Pesticides

HCH CONTAMINATED SOIL: OCCURRENCE AND OPTIONS FOR REMEDIATION
By Richard P.J. Swannell

1   INTRODUCTION

Hexachlorocyclohexane (HCH) was first prepared by Michael Faraday in 1825 by the simple exothermic reaction of benzene and chlorine in the presence of sunlight. It was subsequently found to be a mixture of several isomers, some of which had insecticidal properties. This discovery, coupled with the low mammalian toxicity of the compound, led to the large scale production of HCH throughout the industrialised world, and the formulation of the compound into a wide range of products. However, one consequence of HCH manufacture may have been the inadvertent contamination of the environment.

It is the aim of this paper to discuss specifically the contamination of soil. Firstly, the practices which could lead to HCH contamination of soil are discussed, with reference primarily to the situation in the UK. Secondly the persistence of HCH isomers in soil is considered, and finally the paper concludes with a discussion of which treatment methods may be most suitable for treating HCH contamination.

2   THE POTENTIAL FOR HCH CONTAMINATION OF SOIL IN THE UK

There are two types of HCH which may be involved in soil contamination: technical grade HCH, which consists of 65-70 % a-HCH, 7-10 % ß-HCH, 14-15 % y-HCH, <7 % δ-HCH, and lindane which consists of more than 99 % y-HCH (WHO, 1992b). Both products have been used as broad spectrum insecticides. However, y-HCH is the most insecticidally active compound, making lindane the preferred pesticide (WHO, 1992b). The use of technical grade HCH was prohibited in the EC in 1979.

Production of HCH ceased in the UK in 1983. It is currently produced in Austria, France, Spain, China, India, Turkey and regions within the Confederation of Independent States (CIS). Industry in the UK imports HCH and formulates it into a range of products particularly wood preservatives, agrochemicals, pharmaceutical and veterinary products. A large percentage of these materials is subsequently exported. This trade has decreased over the last four years from 885 t of y-HCH in 1988 to 362 t in 1991 (DTI, 1992). Competition from other pesticides, particularly pyrethroids, may be responsible.

Lindane and technical grade HCH are also adventitiously imported into the UK on fleeces and hides (estimated as 0.7 t in 1988 [CES, 1989]). Concentrations are particularly high (approximately 160 mg HCH/kg) on material imported from South America (CES, 1989). The HCH isomers are liberated during washing and scouring of wool and find their way in relatively high concentrations (approximately 400 mg/l in wool scouring effluents) into the aqueous effluents from these processes (CES, 1989). HCH is also released during animal skin processing at tanneries and the production of wool grease (CES, 1989).

The proper use of y-HCH as an insecticide either for wood treatment or crop protection is unlikely to lead to soil contamination (CES, 1989; WHO, 1992b). This is because y-HCH is fairly biodegradable at low concentrations (WHO, 1992b). Uses of land which could give rise to contamination of soil with HCH in the UK are summarised in Table 1.

Table 1. Potential Sources of HCH Contaminated Soil

Industry	Relevant Isomers of HCH	Possible Sources of Contamination
Formulators of Agrochemicals, Wood Preservatives, Veterinary and Pharmaceutical Plants	γ-HCH	Spillage of HCH-contaminated liquid or sludge onto soil. Potential for mixed contamination (i.e. HCH mixed with other products). Inadequate disposal of sludge.
Wood Treatment Plants	γ-HCH	Spillage of HCH-contaminated liquid or sludge onto soil. Drying timber. Inadequate disposal of sludge. Potential for mixed contamination.
Fleece Washing, Wool Scouring, Grease Processing	α-HCH, ß-HCH γ-HCH, δ-HCH	Spillage of HCH-contaminated effluent or sludge onto soil. Inadequate disposal of sludge.
Tanneries	α-HCH, ß-HCH γ-HCH, δ-HCH	Spillage of HCH-contaminated effluent or sludge onto soil. Drying hides. Inadequate disposal of sludge.
Disused Manufacturing Plants*	α-HCH, ß-HCH, δ-HCH	Spillage of HCH-contaminated liquid or sludge onto soil. Potential for mixed contamination. Inadequate disposal of sludge.
Disposal Sites and those Which Treat HCH contaminated waste	α-HCH, ß-HCH, δ-HCH, γ-HCH	Spillage of HCH-contaminated liquid or sludge onto soil. Potential for mixed contamination. Inadequate disposal of solid waste.
Treatment of Tree Saplings	γ-HCH	Spillage of HCH-contaminated liquid. Inadequate disposal methods for spent containers.
Pesticide Storage Facilities	γ-HCH	Spillage of HCH-contaminated liquid. Inadequate disposal methods for spent containers.

Any contamination at disused manufacturing plants is likely to give rise to only low concentrations of γ-HCH in the soil because this isomer was the most valuable economically.

Soil contamination may arise after the spillage of HCH containing liquid or solid onto soil (CES, 1989; WHO, 1992 a & b). This could occur at any of the sites identified in Table 1. It is impossible to quantify how often such accidents might occur, but repeated spills could result in an accumulation of HCH. A second contaminative pathway may be aqueous runoff after water has been used to douse a fire (Petit et al., 1994). Moreover, soil contamination may also result from the inappropriate disposal of sludge either at an industrial plant or at a waste disposal site. A waste sludge is produced from wood preservation plants which may well contain contaminants (Table 1). Similar sludges may well arise from formulators, tanneries, wool scourers and grease processors. HCH contamination may be dispersed from the original manufacturing site by improper waste disposal practices and the inadvertent selling of contaminated material. For example, around one disused plant in the Netherlands, the HCH contamination was spread to another 30 sites locally (Grinwis, this volume), apparently by these methods.

Organic solvent preservatives such as those containing γ-HCH have been applied using brushing, spraying and immersion methods. Brushing and spraying are used to treat construction timbers in situ and γ-HCH was used in the 1970's and early 1980's for this purpose. However, the use of the γ-isomer for remedial wood treatment has almost ceased in the UK. Furthermore, routine remedial wood treatment is unlikely to have resulted in soil contamination.

Drying of HCH-treated material may also lead to run off which could enter soil. For example, treated timbers were often dried in the open in the past, and at tanneries, hides may have been dried outdoors. Nonetheless, industrial practice at sites using pesticides has improved in the UK in recent years (CES, 1989). For example in the timber preservation industry in the 1980's, UK legislation has encouraged careful bunding of the area around treatment facilities in order to contain spillage. However, before modifications were made soil could have become contaminated and former sites could contain residues of HCH and other compounds. Even at well-managed sites, accidental spills may well occur.

Historically, the Forestry Commission in the UK used γ-HCH to treat saplings prior to planting to restrict the infestation by the pine weevil (Swannell, 1993). The use of HCH was phased out 5 years ago and replaced with pyrethroid insecticides. Again, some soil contamination may have occurred through spillage or as a result of inappropriate disposal methods. However, it is likely that only small amounts of lindane may have leaked to the environment, except if washings and waste pesticide were deliberately discharged to soil, or if containers holding residues of lindane were buried as a method of disposal.

If HCH contamination of soil has occurred, it may well be in association with other toxic compounds. For example at wood treatment sites a range of pesticide-based and heavy-metal based preservatives has been used (e.g. dieldrin, pentachlorophenol, naphthenates, quinolates, creosote, borate, Cu, Cr, As and tributyl tin oxide [Wilkinson, 1979]). At disused industrial plants the contamination may well be mixed in with other compounds used on site (for example, HCH contamination has been found with mercury (pers. comm. Ms A. Grinwis, November 1992) and mixed with a range of chlorobenzenes, chlorophenols and dioxins [Jürgens & Roth, 1989]). Thus, any treatment of the soil may well have to deal with heavy metals and toxic organic compounds other than HCH.

3   ABIOTIC FATE OF HCH

Once contamination of soil has occurred, HCH it is likely to sorb to organic matter and can persist in the soil (Rijnaarts et al., 1990; WHO, 1992a & b). Thus, in organic soils it is unlikely to move through the soil profile, but HCH may be mobile in soils which contain little organic matter (WHO, 1992a & b). When the soil is low in organic matter and highly permeable to water, there will be a risk of HCH isomers reaching the groundwater. Further, where groundwater levels are near to the soil surface, HCH may desorb into the aquifer. However, HCH isomers are poorly soluble in water (Table 2) and in some soils HCH has been found to be deposited as solid particles.

Table 2   Physical and Chemical properties of selected HCH isomers
(WHO, 1992a & b)

HCH isomers	Water Solubility (mg/l)	Relative density (20°C) (g/ml)	Vapour Pressure (20°C) (Pa)	Octanol/ Water Parti- tion Coefficient (log P_{ow})
a-HCH	2.0 (28°C)	1.87	2.67	3.82
ß-HCH	1.5 (20°C)	1.89	0.67	3.80
y-HCH	10.0 (20°C)	1.85	$4.3 * 10^{-3}$	3.2-3.7

In model soils, y-HCH has been found to evaporate with water, but in dry material no evaporation was noted (WHO, 1992b). This process suggests y-HCH may be transported in water vapour and deposited away from the initial site of contamination. The vapour pressure of a-HCH is three orders of magnitude higher than y-HCH and that for ß-HCH is two orders of magnitude higher, suggesting that evaporation is more significant for these isomers.

HCH tends to be fairly stable when exposed to daylight, but susceptible to UV radiation (WHO, 1992a & b). The products formed from such irradiation tend to be pentachlorocyclohexenes (PCCHs) and tetrachlorocyclohexenes (TCCHs). y-HCH can also be degraded hydrolytically, although the rate of hydrolysis is significantly effected by pH. At pH 9 the half-life is 48 h, at pH 7 it is 100 h but at pH 5 there is no measurable degradation (WHO, 1992b).

4   POTENTIAL METHODS FOR TREATING HCH-CONTAMINATED SOIL

Before consideration of remedial methods for HCH contamination of soil, a detailed site survey should be carried out (DoE, 1987; BSI, 1988; Ferguson, 1992). The survey should not only detail the extent of the contamination but, it must also assess the risk to groundwater and the wider environment. The chosen remedial technology should reflect the extent and concentration of HCH and any co-contaminants.

4.1   Cover and Containment

One approach to the discovery of contaminated land is to cover and contain the contamination within barriers of low permeability (Armishaw *et al.* 1992). The object of containment is to isolate the contaminated material, any associated leachate and gaseous products from the environment. There are a number of methods which may be used to treat soil:

* cover systems
* liners
* vertical in-ground barriers
* horizontal in-ground barriers
* macroencapsulation

Initially, cover systems were used primarily, but recently they have been used in conjunction with vertical and horizontal in-ground barriers to isolate the site either partially or totally. On the positive side these methods can be relatively cheap in comparison to other methods, but they do not reduce or remove the contamination. There is little doubt that cover and containment systems could restrict the mobility of HCH contamination. However, it is the continuity and integrity of the barrier in the long term which is the main cause of concern. Containment encloses the contamination until an unspecified later date when a complete remediation can be done. Such an approach was carried out in the Netherlands recently (Grinwis, this volume). Thirty HCH- contaminated sites were cleaned by removing the contaminated fraction to a contained site. The cleaned sites were covered with fresh top soil. At the moment, the contaminated soil is awaiting transport to a treatment facility for cleaning.

A variant on the containment system has been employed in continental Europe. The contaminated soil is sealed in drums and placed in deep salt mines, largely in Germany. This is a relatively expensive option (pers. comm. Mrs M. Louvrier, ANRED, Angers, France, November 1992). The cost of packing, transporting and storing the HCH-contaminated soil was approximately £250 per tonne.

4.2 Disposal to Landfill

Contractors can transport the contaminated soil from the site to a controlled landfill. There is little doubt that soil contaminated with HCH could be treated in this way and in the UK this is still a relatively cheap option. However, this is not a treatment process, it is more of a containment option (Armishaw *et al.,* 1992). Biodegradation of the contaminants may occur in the long term. However, landfills are not designed to optimise biodegradation processes hence the extent of degradation of HCH within a landfill is difficult to predict.

4.3 Physical Methods

Physical methods can be employed to separate contaminated fractions of soil from the bulk of material (Armishaw *et al.,* 1992). Separation can be carried out by exploiting differences in soil fraction characteristics (Pearl, 1992) for example:

* grain size
* settling velocity
* particle density
* surface chemical properties (exploited by froth floatation)
* magnetic susceptibility

In order to use these methods the soil needs to be in the appropriate form. Depending on the type of soil some pretreatment may be required such as:

* crushing
* washing and disaggregation
* screening
* "scrubbing" to dislodge contaminant coatings (e.g. oils)
* homogenization

Recent research conducted in the laboratory has studied the potential of physical methods for concentrating contaminants from a number of contaminated soil types (Pearl, 1992). Some success has been found by fractionation, magnetic separation for metals and froth flotation for organic compounds (Table 3). For example, fractionating by grain size is quite effective for the removal of lead (2-10 mm fraction of a gas works soil contained 99.7% of lead) although the remaining soil still contained sizeable amounts of arsenic, copper and zinc (Pearl, 1992). Magnetic separation was successful for iron and also concentrated lead, copper, zinc and nickel to a significant extent as the non-magnetic base metals were associated with the iron. These latter methods may be of value if HCH contamination is associated with metals. However, perhaps the most relevant strategy for HCH contaminated soil is the use of froth flotation to concentrate hydrophobic contaminants (mineral oil and polynuclear aromatic hydrocarbons (PAHs)) in soils obtained from a gas works (Table 3). By combining the fractions, removed by flotation of material of <3 mm particle size, 96% of the mineral oil and 80% of the PAHs could be concentrated in 31% of the weight of the original soil. Once a concentrated fraction has been obtained then this may be treated by other techniques e.g. chemical or biological. However, these methods will disrupt soil structure completely.

An alternative physical method for treating HCH contamination may be irradiation with spent nuclear fuel. Doses of 50 kGrays of gamma radiation reduced substantially the concentration of γ-HCH (Mincher et al., 1991). γ-HCH dissolved in ethanol decomposed from 0.25 g/l to 0.03 g/l after irradiation in a fuel storage pool for 7.5 h. No breakdown products were identified but the sample was not made radioactive by the treatment. This method has not been used to treat other isomers of HCH, nor has it been used to treat contaminated soil. But, this treatment maybe a valuable way to treat concentrated solutions of HCH obtained by chemical extraction. Whether it is a cost effective alternative to thermal decomposition remains to be determined.

Table 3 Contaminant Distribution of a Gas Works soil fractionated using Froth Flotation (from Pearl, 1992)

Fraction[a]	Weight (%)	Mineral Oils		PAHs	
		Assay g.kg⁻¹	Distribution (%)	Assay mg.kg⁻¹	Distribution (%)
Concentrate 1 Concentrate 2	28.2	75	91.4	419.2	73.1
Non-Floats	3.7	28	4.5	313.4	7.2
	68.1	1	4.1	46.7	19.7

[a] Two concentrated fractions were removed during froth floatation. The soil remaining in the aqueous phase that did not rise in the froth was termed the "non-floats".

4.4   Chemical Methods

Chemical methods can be used to extract and chemically decompose contaminants obtained from soils. However, soil type, particle size concentration of contaminant and the presence of other contaminants all effect the success of chemical treatment. Moreover, the majority of chemical methods involve treating the soil in a slurry or treating the contaminants once they have been mobilised into a liquid phase. Therefore, chemical methods are likely to be conducted on site or *ex situ* but probably not *in situ*. As HCH binds tightly to soil, simple washing of the soil is unlikely to remove HCH, but the following methods may be applicable to soil of different types contaminated with HCH (Armishaw *et al.*, 1992):

*   solvent extraction. A range of chemical compounds can be used to encourage dissolution of HCH from the soil into the aqueous phase e.g. Triton X-100 (not suitable for clays), Surco 233 or triethylamine. These methods can be effective in removing organic contamination but not inorganic compounds. However, the extraction process will disrupt soil structure, and reduce the soil microbial and invertebrate populations.

*   supercritical fluid extraction. This is the mixing of the soil with a cold pressurised liquid solvent e.g. CO_2, propane and butane. The advantages of the system are that the solvents have a low viscosity, that even hydrophobic contaminants are readily dissolved and that the pollutant can be readily extracted from the solvent and concentrated. This method is unlikely to be so disruptive to soil structure but will reduce the invertebrate and microbial population of the soil.

*   chemical dechlorination. This process uses reducants to remove chlorine atoms from organic molecules. There are at least two methods which may be used to treat HCH:

   1.   Treatment with alkali polyethylene glycols (APEGs). The reduction occurs in the aqueous phase so solvent extraction may be a necessary first step. However, in some instances the solvent may be added directly to the soil depending on soil type. Adding APEGs directly to soil is likely to disrupt soil structure and to impact soil microbes and invertebrates. The products are polyethylene glycol ethers and HCl (Lopez & King, 1989). The former are thought to be non-toxic, but further work is required to confirm their fate particularly as the ether will contain a partially dechlorinated HCH moiety.

   2.   Basic Catalytic Decomposition (BCD process). This involves heating the HCH with sodium hydroxide at 160°C in the presence of a catalyst. The HCH is converted to trichlorobenzene (TCB, largely the 1,2,4 isomer) according to the following equation:

$$HCH + 3\ NaOH \rightarrow TCB + 3NaCl + H_2O$$
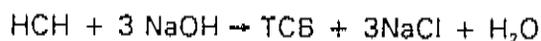
This method has been used in the laboratory to treat pure HCH (Azkona this volume) and work is beginning at pilot scale. The researchers are hoping to sell the trichlorobenzene produced. It is not known whether this method could be used to treat HCH contaminated soil.

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None of these processes completely decompose the target compound, or will necessarily remove any inorganic compounds in the soil. Only chemical dechlorination even chemically alters the compound. Chemical extraction methods could be sufficiently broad spectrum to remove a range of toxic organic compounds from soil. These methods could be used on site but require specific equipment to be conducted successfully. Moreover, each method should be tested initially at laboratory scale to determine which is the most successful extractant for the contaminated soil type. Once in the aqueous phase, chemical oxidation (UV or ozone treatment), chemical dechlorination, thermal destruction or even biological methods could be used to decompose the HCH. However, γ-HCH does seem to be relatively resistant to oxidation by potassium permanganate (Leigh, 1969).

Chemical methods do have a potential for treating HCH contaminated soil but most of the methods described require more research before they can be applied at a large scale to soil. Further, the extraction methods are likely to have a detrimental effect on soil quality.

4.5 Biological Methods

The four important HCH isomers are known to be biodegradable but at markedly different rates. γ-HCH is the most rapidly biodegraded isomer followed by α-HCH. ß-HCH and δ-HCH are rather resistant to biodegradation and are metabolised only very slowly (Bachmann et al., 1988a & b; Straube, 1991). However, these latter isomers are less toxic then γ-HCH (Straube, 1991).

γ-HCH Decomposition

γ-HCH is biodegraded by a range of micro-organisms both aerobically and anaerobically (WHO, 1992b). Its degradation under anaerobic conditions is more rapid, but it is thought that it is only completely mineralized to CO_2 aerobically (WHO, 1992b). Anaerobically, the degradation products have been found to be γ-3,4,5,6-tetrachlorocyclohexene (TCCH) primarily, α-HCH, 1,2,4-trichlorobenzene, and 1,4-dichlorobenzene (Figure 1). Generally, γ-HCH is steadily dechlorinated to volatile products and chloride ions (WHO, 1992b). A pathway for the degradation has been proposed for the fermentative bacteria such as *Clostridia, Citrobacter freundi* (Heritage & MacRae, 1977; Jagnow et al., 1977; Ohisa et al., 1980, 1982) and for *Pseudomonas* (WHO, 1992b). The latter is a facultative anaerobe and was found to convert γ-HCH to γ-pentachlorocyclohexene (γ-PCCH; the product of aerobic degradation), tetrachlorobenzene and α-HCH.

Aerobically, micro-organisms decompose γ-HCH to γ-PCCH and then to chlorobenzenes (particularly 1,2,4 trichlorobenzene), to 2,5 dichlorophenol and to mineral products (Ludwig et al., 1992; WHO, 1992b). Recently the mechanism of aerobic degradation of γ-HCH has been studied in detail in *Pseudomonas* (Johri et al., 1991; Imai et al., 1991; Nagasawa et al., 1993). A degradation pathway for *Pseudomonas paucimobilis* UT26 (also referred to as *Sphingomonas paucimobilis* (Nishiyama et al., 1992)) has been proposed (Nagasawa et al., 1993; Figure 2). This suggests that γ-HCH is cleaved to γ-PCCH, which is then stereoselectively cleaved to 1,3,4,6-tetrachloro-1,4-cyclohexadiene (TCDN). This unstable intermediate is then thought to spontaneously decompose to 1,2,4-trichlorobenzene (TCB).

The conversion of γ-HCH to TCB is apparently carried out by a single protein, HCH dechlorinase (Imai *et al.*, 1991). This enzyme appears to be novel both in terms of its ability to degrade HCH, and in its composition, as it contains sequences of amino acids not found in other enzymes of a similar type. The reason why the enzyme decomposes both γ-HCH and γ-PCCH is thought to be because both compounds have a similar stereochemistry (i.e. a *trans* and *diaxial* pair of hydrogen and chlorine atoms). ß-HCH does not have the same stereochemistry and is not decomposed by the isolated dechlorinase (Nagasawa *et al.*, 1993). Interestingly γ-PCCH is also a competitive inhibitor of γ-HCH decomposition by HCH dechlorinase, a finding which is consistent with the notion that both γ-HCH and γ-PCCH are degraded by the same enzyme. Therefore, when both substrates are present they compete for space in the enzyme's active site.

The unstable intermediate (TCDN) is converted to 2 products by *Pseudomonas paucimobilis* UT26; TCB spontaneously and 2,5 dichlorophenol via a dechlorinative hydroxylation. This latter step is thought to be enzyme-catalysed, but the protein has yet to be isolated (Nagasawa *et al.*, 1993).

The genetics of aerobic breakdown of γ-HCH is steadily being clarified (Imai *et al.*, 1991; Johri *et al.*, 1991). The gene for HCH-dechlorinase (known as *lin* A) has been identified and its nucleotide sequence determined. The gene was transferred into *E.coli*, which produced the HCH dechlorinase in high quantities (Imai *et al.*, 1991). The aerobic degradation pathway for γ-HCH in *P. ovalis* was found to be encoded for on extrachromosal DNA (plasmids). These genetic data could be conveyed to and expressed in other Pseudomonads which do not have the ability to degrade HCH (Johri *et al.*, 1991). In contrast, the evidence from *P. tralucida* suggests that HCH-degrading activity may be on a transposon (a genetic sequence which can transfer itself between chromosomal material and plasmids intracellularly).

The rate of degradation of γ-HCH in soils varies considerably, presumably depending on temperature, soil type, pH, redox conditions, starting concentration of γ-HCH and concentrations of inhibitory substances (Straube, 1991; WHO, 1992b). In field studies, half-lives varied from 12-174 days under largely aerobic conditions and 1.5-30 days under anaerobic conditions (WHO, 1992b). However, repeated additions of the pesticide can result in more rapid turnover rates as a competent microbial population develops (Senoo *et al.*, 1989). When soil is submerged completely in water allowing anaerobic conditions to develop, rapid dechlorination can occur resulting in half-lives of 24-334 h. These experiments were conducted at tropical temperatures of 28-30°C and with application rates of γ-HCH suitable for controlling pests (WHO, 1992b). However, these data suggest strongly that γ-HCH applied for agricultural purposes is unlikely to accumulate in soil.

The concentrations of HCH found in soil after contamination by the processes listed above, may be higher than those found in agriculture. Little research has studied the fate of γ-HCH in highly contaminated soil (>10 mg/kg), although a number of soil bacteria have been found to be able to decomposes this isomer rapidly (Senoo *et al.*, 1989; Sahu *et al.*, 1990; Straube, 1991). γ-HCH has also been found to be degradable in activated sludge, but again the concentrations used are relatively low (Nyholm *et al.*, 1992).

Adding organic compounds which easily decompose (e.g. glucose, acetate and peptone) has been found to encourage γ-HCH biodegradation (Straube, 1991). This may be either due to encouraging the co-metabolism of HCH (biodegradation by micro-organisms which does not yield any metabolic energy), or by encouraging the formation of anaerobic zones within the soil. Furthermore, it is noteworthy that little is known of the effect of the presence of other toxic organic and inorganic compounds on the biodegradation of γ-HCH.

α-HCH Decomposition

α-HCH is also biodegraded aerobically and anaerobically (WHO, 1992a) but largely at a slower rate than γ-HCH. Rapid anaerobic dechlorination to δ-TCCH was noted with *Clostridium sphenoides* in the laboratory (WHO, 1992a), but under field conditions more rapid rates of degradation were found aerobically (Bachmann *et al.*, 1988a; Doelman *et al.*, 1988a & b). Adding glucose and acetate apparently did not improve α-HCH decomposition (Bachmann *et al.*, 1988b). Degradation rates of α-HCH have been determined in contaminated soil and the rates are summarised in Table 4. It is noteworthy that the field experiments carried out by Doelman *et al.*, (1988b, 1990) showed a slower rate than the previous experiments which were carried out in the laboratory.

The degradation pathway under aerobic conditions is thought to be similar to γ-HCH, that is via α-PCCH and TCB, thence to chlorobenzenes and chlorophenols (Hühnerfuss *et al.*, 1992; Nagasawa *et al.*, 1993). For example, HCH dechlorinase degrades both α- and γ-HCH by apparently the same mechanism (Nagasawa *et al.*, 1993). The chlorobenzenes that have been isolated include 1,3 dichlorobenzene, 1,2,4 trichlorobenzene, di and tri chlorophenols and monochlorophenol (Hühnerfuss *et al.*, 1992).

ß- and δ- HCH Decomposition

The ß- and δ-isomers of HCH have been found to be more recalcitrant than α- and γ-HCH (Straube, 1991; WHO 1992a). There is some evidence that ß-HCH is biodegradable both aerobically and anaerobically, but the rate is fairly slow. The rate of ß-HCH decay in soils has been found to be variable. There is evidence for a half-life of 91 days in some soils, but in others, little decomposition was noted (WHO, 1992a). In the laboratory however, a strain of *Pseudomonas sp.* was isolated from the rhizosphere of HCH-treated sugar cane plants, which was capable of biodegrading α, γ, ß, δ isomers aerobically (Sahu *et al.*, 1990, 1992). The organism could degrade fairly high concentrations of both isomers quite rapidly (2 mg ß-HCH/l in 3 days and 10.5 mg δ-HCH/l in 8 days). The pathway for δ-HCH was thought to be similar to γ-HCH as δ-PCCH was identified as an intermediate. However, the bacterium could not grow on ß- or δ-HCH as the sole source of carbon and energy (Sahu *et al.*, 1993). Thus, the degradation was thought to be cometabolic. Imai *et al.* (1989) also showed that δ-HCH was biodegradable by *Pseudomonas paucimobilis* UT26, but in this case the organism could not decompose ß-HCH.

In summary, the data from the scientific literature suggest that all the isomers of HCH are biodegradable. Competent micro-organisms have, by and large, been isolated from agricultural land with a long history of HCH addition. The pathways of biodegradation of α and γ-HCH are fairly well understood. This is not the case for ß- and δ-HCH although there is at least an indication from the decomposition of δ-HCH suggesting that the degradative mechanism is similar to that found for γ-HCH. As yet, no bacteria have been isolated which can grow on ß- or δ-HCH alone, these isomers are cometabolized.

Biological Treatment Strategies for HCH

The data from the scientific literature suggest the use of biological methods to treat HCH contaminated soil may be possible although the clean up will be time consuming. The success of the treatment will depend on the following factors:

* the concentration of HCH in the soil and its physical state (i.e present as a solid or sorbed to surfaces)
* which isomers are present
* the presence of other toxic organic and inorganic substances which may inhibit degradation
* the presence of competent micro-organisms capable of degrading HCH
* optimal nutrient status, temperature and pH

For any particular contaminated site, laboratory tests need to be conducted with the contaminated soil to determine whether the soil contains a population of micro-organisms capable of degrading HCH. If so the optimal conditions need to be established. For example, anaerobic treatment is likely to be the most effective for treating γ-HCH, but aerobic treatment is required for the other isomers. The addition of competent micro-organisms capable of biodegrading the ß- and δ-HCH needs to be considered.

If biological treatment is feasible as a result of a site survey and preliminary laboratory work, then there are two principle strategies which could be used to encourage HCH decomposition: encouragement of HCH biodegradation in soil, and decomposition of HCH which has been extracted from soil.

Table 4. Rates of α-HCH Contamination in Highly Contaminated Soil

Initial Concentration (mg/ kg soil)	α-HCH degradation Rate	Reference	Comments (lab work unless otherwise stated)
400	23 mg/kg/day	Bachmann *et al.* (1988a)	aerobic degradation
	13 mg/kg/day		methanogenic degradation
5334	14 mg/kg/day	Doelman *et al.* (1985)	aerobic degradation
	10 mg/kg/day	Doelman *et al.* (1988b)	anaerobic degradation
420	2 mg/kg/day	Doelman *et al.* (1990)	aerobic degradation, small field experiment
367	reduced to 107 mg/kg in 23 wk in moist soil and to 62 mg/kg in soil slurry.		aerobic degradation. Field experiment using 6m³ soil. ß-HCH not degraded. α-HCH not degraded anaerobically.

HCH Decomposition in Soil

HCH biodegradation has been encouraged in soil in field experiments (Table 4) and in the laboratory (Urlings *et al.*, this volume) by attempting to optimise the conditions for the proliferation of indigenous HCH degraders. However, α- and γ-HCH, primarily, have been removed by this process. Recent laboratory trials have been conducted by adding an HCH-degrading Pseudomonad to clean soils (alluvial and sandy loam) contaminated with α-, ß- and γ-HCH (Sahu *et al.*, 1993). The soil was incubated at 30°C either flooded or nonflooded. Each soil received 5 mg of each HCH isomer/kg. The degradation of α- and γ-HCH was rapid in both the inoculated soils and complete removal of both isomers was seen within 2-10 days in the nonflooded soils.

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A slower degradation was seen in the flooded (predominantly anaerobic) soils. However, inoculation did not encourage the biodegradation of ß-HCH despite the micro-organism being able to decompose the insecticide under laboratory conditions. The authors proposed this may be because the decomposition of ß-HCH is cometabolic and hence growth substrates may need to be provided.

γ-HCH was not biodegraded in volcanic ash soils which had not previously been treated with the compound. However, addition of *P. paucimobilis* resulted in γ-HCH being rapidly biodegraded (Senoo *et al.*, 1992). The micro-organism was found to reside in the pores between soil aggregates and persisted until γ-HCH was exhausted. Their numbers then rapidly decreased and died out completely unless more γ-HCH was added (Nishiyama *et al.*, 1992). In contrast, in soils where γ-HCH had been applied regularly over many years the organisms persisted on or in the soil aggregates larger than 0.025 mm. When γ-HCH was added, the organisms multiplied in the inter-aggregate pores presumably because that was where the pesticide accumulated. After all the γ-HCH was decomposed, the inter-aggregate population rapidly declined. Thus, in soils deficient in HCH-degrading ability the addition of competent degraders may stimulate the degradation of the pesticide, but the degraders are unlikely to persist once the substrate is exhausted.

Decomposition of Extracted HCH

An alternative strategy is to remove the pesticide from the soil by chemical means (see Rulkens, and Urlings in this volume and Section 4.2 above) or by using specific HCH biosurfactants (Anu Appaiah & Karanth, 1991), and then treating the pesticide-contaminated effluent. There are a number of different ways that this may be achieved. An aqueous bioreactor could be built so that it supplies the optimal conditions for HCH biodegradation (aerobic, anaerobic or perhaps a biofilm reactor which contains aerobic and anaerobic zones) and it may be inoculated with a mixture of competent HCH degraders. The matrix used for the biodegradation of HCH could be an aqueous bioreactor or activated sludge, or activated carbon. The latter has the advantage of combining adsorption with biodegradation (Tsezos & Wang, 1991; Dalmacija *et al.*, 1992). This approach is certainly feasible given our current level of scientific understanding. Alternatively, a bacterium could be engineered to have a high rate of production of HCH-degrading enzymes. This has to some extent already been achieved with γ- and α-HCH degradation (Imai *et al.*, 1991) but little is yet known about the mechanism of cometabolic biodegradation of the ß- and δ-isomers. Nonetheless, this approach may well have considerable potential, once the engineered organism is obtained. Aqueous solutions of HCH (perhaps using surfactants to increase HCH solubility) could be rapidly decomposed, cost-effectively under defined conditions.

One further strategy of considerable promise is the chemical dehalogenation of HCH using biochemicals (Marks *et al.*, 1989; Marks & Maule, 1992). Alkali modified cobalamin immobilized onto QAE-Sephadex could dehalogenate a solution of 10 ppm γ-HCH by over 99% within 5 min. A column with heamatoporphyrin bonded to AH-Sepharose 4B was found to dehalogenate >99% of 10 ppm lindane when used continuously for 76 days with the same fluid residence time. This equates to a removal rate of 0.12 g/h/litre of bed volume. The product is tetrachlorocyclohexene which is then degraded to chlorobenzene (Marks *et al.*, 1989). This product could be further degraded biologically or purified and sold as a chemical intermediate. This method has yet to be tried with the other isomers of HCH and is still being operated at laboratory scale, but the technology does warrant further investigation.

Restoration of Soil Structure

There seems to be some potential to use biological methods to decompose HCH once it has been extracted into the aqueous phase. However, the extraction process is likely to disrupt soil structure and may not remove sufficient pesticide to comply with standards. Hence a polishing step which restores soil quality may be helpful. One novel approach may be to blend the extracted soil with a suitable quantity of animal and vegetable waste (such as composted municipal refuse) and add earthworms. Recent research has shown that earthworms added to soil containing 10 ppm technical grade HCH had developed a modified gut microbial flora consisting of 26-28 % HCH-degraders (Ramteke & Hans, 1992). The micro-organisms could degrade the α, ß and γ-isomers of HCH. Hence earthworms, used at sufficient density, could act as mobile soil cleaners by incubating contaminated soil particles with competent micro-organisms in their guts. They would also help improve soil structure, eventually returning the soil to a usable state. Whether this approach could be used on highly contaminated sites is doubtful owing to the toxicity of HCH or other co-contaminants (see Section 2 above), but at lower concentrations where rapid clean up is not required, such a simple approach may be efficient and cost-effective. However, more research is required to evaluate these ideas further.

In summary, biological treatment can be a relatively economic process particularly if it can be done *in situ*. However, the *in situ* treatment is difficult to control carefully, is slow, and its effectiveness will depend on environmental parameters beyond the operators control e.g. rainfall (or the lack of it) and temperature (particularly important if the treatment is to be carried out in the North of Britain). Also, *in situ* microbial methods certainly will be unable to deal with any inorganic contamination found with the HCH (although the use of hyperaccumulating plants may be an additional *in situ* possibility [Baker & Brooks, 1989; Baker *et al.*, 1991]). An *ex situ* treatment may be more effective and quicker but it will effect soil quality. In both cases the contamination can be converted to relatively non-toxic mineral products like H_2O and CO_2. But additional competent micro-organisms may need to be added to encourage the degradation of the recalcitrant isomers ß- and δ-HCH.

Biological methods can also be used to decontaminate effluent produced during chemical treatment either by biodegradation or by adsorption. MacRae (1985) showed that by attaching *Rhodopseudomonas sphaeroides* to magnetite and using a 4 stage process, 90 % of γ-HCH was removed (γ-HCH range = 0.1-1.7 mg/l). The mechanism appears to be abiotic and relies on the hydrophobic nature of the bacterium. This process, however, merely concentrates the γ-HCH either for recycling or for further treatment.

4.6   Thermal Methods

Thermal treatment could be used to deal with HCH contaminated soil by heating the soil to temperatures above 800°C. The type of thermal treatment method used depends on the soil type and the type of contamination. Different soil types present a range of materials handling problems; for example clays clog conveyors and form clods in thermal systems (Armishaw *et al.* 1992). Thermal methods can be most effective with organic compounds, but if mixed with metals, the metals will concentrate in the ash and will need to be disposed of carefully.

Thermal methods fall in two broad categories:

1. volatilisation and pyrolysis followed by combustion of the gaseous phase.
2. direct incineration of the soil matrix.

A secondary combustion phase can be included to oxidise any organic material volatilised in the first steps. Bag filters or electrostatic precipitators can remove fine particulate material and acid gases (e.g. HCl in the case of HCH) can be removed by scrubbing. As there are a range of thermal processes which could be used to treat soil contaminated with HCH it is sensible to confirm that complete oxidation of HCH is obtained by conducting pilot scale trials. The gas leaving the thermal treatment plant and the ash should be analyzed for toxic breakdown products from the combustion (e.g. dioxins). One method has been suggested (Urlings, 1992) which volatilises the HCH without generating dioxins. This approach heats the soil in a hydrogen-rich reducing atmosphere in the absence of oxygen. The trapped HCH then has to be further treated.

An alternative thermal treatment process was mentioned by Jürgens & Roth (1989). In this case the HCH isomers were thermally converted into useful products which were then sold (e.g. 1,2,4 trichlorobenzene, 2,5 dichlorophenol and 2,4,5 trichlorophenoxyacetic acid). Whether this process could be used to treat soils remains to be determined, but this method may be an alternative treatment for material extracted from soil by chemical methods.

Thermal processes, like chemical and physical methods, have the disadvantage of destroying soil structure during the treatment. Thermal processes are also an expensive option but if HCH is found as part of a mixture of other toxic organic compounds at high concentrations, thermal processes may be the most cost-effective option.

5   CONCLUSIONS

In this paper, a number of industrial practices have been identified which could have led to soil contamination with HCH, including for example: manufacture and formulation of pesticides, production of wood preservatives and veterinary compounds, wool scouring, leather manufacture, and waste disposal sites. The specific isomers of HCH detected in the soil will depend on the origin of the contamination. For example, manufacturers of HCH would have sold γ-HCH and disposed of the other unwanted isomers. In contrast, formulators of wood preservative and veterinary products would have only used the γ-HCH, suggesting that only this isomer will be found in their contaminated soil.

HCH contamination is unlikely to be found in isolation, but may well be mixed with other organic and inorganic compounds whose nature will depend on the use of the site. For example, at a wood treatment yard, γ-HCH may be found with other preservatives such as pentachlorophenol, creosote, dieldrin, copper, chrome and arsenic.

Once in soil the isomers are likely to adsorb onto particles and persist. There is some evidence that α- and ß-isomers may evaporate from the soil to be deposited elsewhere, or that the contamination may be dispersed aerially on dust and soil particles. There is also a suggestion that in the aqueous phase of strongly alkaline environments ($> pH\ 9$) γ-HCH may be hydrolysed.

Once HCH has been detected in soil, a detailed site investigation should be conducted to assess the extent of the contamination and the existence of co-contaminants. Based on this information a short list of the appropriate technologies can be assembled from the available physical, chemical, biological and thermal methods. However, as many of these methods are still being developed, testing of the selected techniques at laboratory scale is strongly re-commended. Only cover and containment methods have been used extensively for treating HCH contamination in the field, most of which are temporary measures until an effective treatment can be found. One innovative approach may be to cover and contain the site and then use *in situ* methods to treat the contamina-tion. Such an approach may allow the redevelopment of the site while it is still being treated.

The precise choice of method will depend on HCH concentration, the presence of other toxic compounds and their concentration, the soil type, where the site is located, the depth of the contamination and the time and resources available for the treatment. Moreover, treatment methods should not be considered in isolation but can be combined into an integrated and cost effective strategy for dealing with the contaminated soil. However, the treatment of the site is not the only objective. Restoration of soil quality should be considered particularly if the site is to be redeveloped for domestic, amenity, horticultural and agricultural purposes.

In conclusion, it is hoped that this paper has clearly defined the origins of HCH contamination of soil, and has suggested methods of dealing with such contamination. There is a need now to study these technologies further and to begin the task of remediating HCH-contaminated land.

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ALTERNATIVES AND PERSPECTIVES OF TECHNICAL SOLUTIONS
By Wim Rulkens

1 INTRODUCTION

During the technical production of the organochlorine pesticide γ-hexachlorocyclohexane (γ-HCH or lindane), several stereo-isomers are formed of which α-HCH, ß-HCH, γ-HCH and δ-HCH predominate. From these isomers, γ-HCH, the only effective insecticide among these isomers, can be extracted. In the past the remaining isomers were concentrated and finally dumped on or in the soil. Also the complete mixture of α, ß, γ, and δ-HCH was sometimes used as insecticide. It is also possible that part of the γ-HCH has converted into one of the other isomers. The result is a serious soil pollution problem in several countries.

Remedial actions are necessary. However, the question is what type of remedial actions are possible, what type of remedial actions are already applied in practice, what the future needs are with respect to remediation techniques, and what type of (cooperative) research is necessary. In discussing the various alternatives and perspectives for remedial actions suitable for removal of α, ß, γ-HCH from soil, the following three factors are of major relevance:

1. <u>The way the soil has been polluted:</u>
    *   By dumping the waste of the production process, mainly as a solid waste (HCH-isomers together with lime).
    *   By the use of the non-separated mixture of isomers.
    *   By chemical or microbiological transformation of γ-HCH into one of its isomers.
    *   By leaching of HCH from the top soil or from a dump site to the sub soil layers.

2. <u>The type of the soil:</u>
    *   Sandy soils
    *   Clay-like soils
    *   Humic substances containing soils

3. <u>The properties</u> of the α, ß and γ isomers. Relevant properties may be:
    *   The solubility in water, in aqueous solutions or organic solvents
    *   The adsorption and absorption characteristics with respect to:
      - sand;
      - clay;
      - humic substances
      - plants (and plant roots)
    *   The specific chemical/physical properties with respect to the ability to form physical/chemical bonds with other chemicals.
    *   The chemical stability. Hexachlorocyclohexanes are rather stable. However, it is known that under influence of light (UV), isomerisation can occur. Chemical removal of chlorine atoms is possible by a solution of sodium or potassium hydroxide in ethylene glycol.
    *   The thermal stability. At elevated temperatures such as obtained in thermal treatment processes or in wet air oxidation or hydrolysing processes, HCH is not stable.
    *   The volatility. At low temperature, HCH has a low volatility.

- The microbiological degradability by means of bacteria and fungi. Here we are dealing with several aspects:
  - The conditions for microbiological conversion (aerobic, anaerobic or combination of aerobic and anaerobic).
  - The products of the microbiological conversion. These can be:
    - H_2O, inorganic chloride and CO_2, (complete microbiological mineralisation)
    - Interconversion of the isomers
    - Biological degradation to intermediates which are less toxic or more easily biodegradable than the original compounds, or which can easily be removed by physical/chemical methods.

2 TREATMENT OPTIONS

In the discussion about possible treatment techniques (in general "treatment principles", because not every principle has already been developed to a technique that can be applied in practice), it is wishful to distinguish between the various possibilities in which contaminants can be present in the soil:

2.1 Hot spots

Hot spots are areas in which the soil is very strongly contaminated due to the dumping of HCH-containing waste material. In fact, these sites are hazardous waste sites. Treatment techniques that may be considered for <u>excavated soils</u> are:

- <u>Thermal</u> treatment. This method has been developed to full scale and can be applied in practice. Special attention has to be paid to the prevention of the emission of dioxines. The conditions of the treatment process have to be chosen very carefully. Destruction of dioxines in the waste gases requires specific process conditions, such as high temperature, surplus of oxygen, a minimal residence time of a few seconds and an appropriate mixing in the afterburner.

- Treatment by <u>extraction and classification using aqueous extracting agents.</u> Suitable for sandy soils containing not too many clay particles. This method has already been developed to full scale application in practice as well. For sandy soil classification techniques, based on hydrocyclones and fluidized bed columns can be used in combination with the use of detergents or other surface active compounds. In case large amounts of clay particles are present in the soil, it has been pointed out that flotation processes are very suitable for the selective removal of clay particles containing HCH.

In case large amounts of lime are present in the soil, a pretreatment step aimed at dissolving the lime has to be used. Problems arise if the contaminated soil consists mainly of clay particles or of waste material (including large amounts of lime).

- Treatment by <u>extraction using organic solvents</u> with high solubility with respect to the HCH-isomers. This treatment principle may be of interest in treating clay-like soils. Several organic solvents are possible. Acetone and alcohols can be mentioned here. The use of organic solvents means that apart from the extraction step for the soil, a treatment process for the organic solvent is also required in order to make reuse of this solvent possible. Attention also needs to be paid to the removal of remaining organic solvents from the treated soil.

The presence of lime requires a special pretreatment step. Extraction with organic solvents is still in the development stage.

- Treatment by extraction using supercritical CO_2. This method is in fact comparable with solvent extraction using organic solvents. A special pretreatment step is probably necessary in case of the presence of lime in the contaminated soil. The extraction with supercritical CO_2 is still in the development stage as well.

- Chemical detoxification of excavated soil. One of the possibilities is detoxification with NaPEG and KPEG reagents. These types of reagents are based on alkali metal and polyethylene glycol compounds. They can dehalogenate all types of halogenated organic pollutants such as HCH. Their potential application for the clean-up of contaminated soil has been demonstrated. However, the rate of dehalogenation and also the efficiency of the process are adversely influenced by the water content of the soil. This means that the soil has to be dried before treatment. At this moment, the process is still in the laboratory stage.

- Chemical detoxification of excavated soil contaminated with HCH's is also possible using wet air oxidation processes. No practical experience with contaminated soils is available.

In situ treatment of hot spots is unlikely.

In general, the treatment of "hot spots" is very expensive. According to Dutch experience with treating HCH containing soils, the treatment costs amount to about 100 - 150 US $.

2.2 Strongly polluted sites

These are also large areas where a relatively high concentration of HCH is observed. However, the presence of HCH is not concentrated and localized on hot spots, but is more diffuse and spread over the entire area. Treatment of such areas with a focus on cleaning the soil is technically possible with the techniques mentioned for the "hot spots". However, besides these relatively expensive techniques, cheaper treatment options are probably possible.

For excavated soil the following can be mentioned:

- Biological treatment techniques. Here, three modifications are possible.
  - Slurry reactor (bioreactors) in which the soil is intensively mixed in order to stimulate the microbiological conversion process. Because process control is easy, optimal conditions can be applied resulting in high conversion rates and high removal efficiencies. To a certain extent, this treatment system is comparable with the activated sludge system for waste water treatment. Aerobic and anaerobic conditions can be applied in slurry reactor systems.
  - Composting systems. These systems are comparable with composting systems used for treatment of organic solid wastes. In comparison with slurry reactors, substantially lower reaction rates are expected.
  - Landfarming system. In landfarming, the polluted soil is spread out in a thin layer on top of a specially constructed impermeable layer provided with a drainage system. Aerobic biological degradation of the pollutants in this layer is stimulated by regularly cultivating the layer.

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- Extensive microbiological treatment (or posttreatment) of soil placed on heaps in controlled soil disposal sites. This treatment system can be applied to non-pretreated soil or to soil already pretreated in a bio-reactor, in a composting system, or in a landfarm. Extensive treatment of soil placed on heaps may also be an interesting option for soils that are not fully cleaned after an extractive treatment process.

  From the above mentioned microbiological treatment systems, only land-farming has been developed for large scale practical application. However, at this moment this technique is only used for removal of easily biodegra-dable organic compounds from the soil. The technique has not been deve-loped yet for removal of HCH. The other systems are still in the development stage. A general bottleneck of all biological treatment tech-niques is the low bioavailability of the pollutants at low concentrations. This means that a complete clean-up of the soil is rarely achieved.

- **Physical/chemical treatment** techniques based on extraction and classification. In contrast to the physical treatment techniques already mentioned for the remediation of "hot spots", relatively simple chemical steps and classification and extraction steps are intended here. The following options are possible:
  - Simplified extraction of sandy soils using an aqueous extracting agent (for example aqueous solutions of detergents or sodiumhydroxide).
  - Separation of soil particles contaminated with HCH from clean soil particles using fluidised bed systems or hydrocyclones. The separated polluted fraction may be treated according to one of the more intensive treatments for hot spots.
  - Photochemical interconversion of hexachlorocyclohexane into easily biode-gradable isomers. This treatment step has to be fol-lowed by a microbiological treatment.
  - Chemical interconversion of hexachlorocyclohexane into easily biodegra-dable isomer. This treatment step has to be followed by a microbiological treatment step.

With exception of the thermal treatment techniques and the extrac-tion/classification techniques already mentioned for treatment of "hot spots", the other techniques are still in the research phase.

For **in situ treatment** the following techniques can be mentioned:

- In situ extraction with an aqueous extraction agent containing detergents, calciumchloride or sodiumchloride, or sodiumhydroxides. This treatment pro-cess basically consists of a percolation of the aqueous extracting agent into the contaminated site, followed by the removal and treatment of the percolate.

- **In situ biological treatment (biorestoration)**. This technique is focused on the improvement of process conditions for microbiological degradation in polluted sites by adding electron acceptors or donors, nutrients, co-substrates, surfac-tants and if necessary, also micro-organisms. These additions are achieved by infiltration of a water phase.

- Treatment by electroreclamation. Electroreclamation is a clean-up method based on electrokinetical processes, occurring when an electric current is generated between a cathode and an anode. In general, transport of pollutants is possible in three ways:
    - As charges ionic particles;
    - As charges colloidal particles;
    - As neutral colloidal particles present in the pore water between the soil particles.

As far as known, at this moment, these potential in situ treatment techniques are still in the research phase.

3 LESS POLLUTED AREAS

Large numbers of the areas polluted with hexachlorocyclohexane are only slightly contaminated with this pollutant. However, the pollution very often extends over a very large area. Besides, the pollution is often limited to the top layer of the soil. For large areas, excavation of the soil or intensive in situ treatment are not applicable. Potential treatment methods for these areas are:

- The use of green plants that can accumulate the pollutants. After harvesting, these plants have to be treated in order to concentrate or to destruct the pollutants.
- The use of plants with such a root structure that a controlled removal of the plant roots and the soil between these roots becomes possible. The removed layer, containing the plant tissues and the contaminated soil has to be treated in order to concentrate or destruct the pollutants.
- The use of small amounts of chemicals that may promote microbiological degradation or isomerisation.
- Cultivating the top layer in such a way that natural photochemical isomerisation and biological degradation is stimulated.

As far as known, there is no practical experience with the above mentioned treatment technique for slightly polluted soils at this stage.

4 CONCLUSION

Summarizing the different options for remediation of soils contaminated with HCH, the following can be concluded:

a. The type of contaminated site strongly governs the potential applicability of a remediation technique.
b. At this moment only two practical treatment techniques are available: Thermal treatment of excavated soil and treatment of excavated soil by extraction and classification. These techniques are rather expensive.
c. There is a strong need for alternative, cheap treatment techniques suitable for treating large areas that are only slightly polluted. Removal principles are known, however, a lot of research has to be done to evaluate these principles and to develop the most promising principles for practical application.

REMEDIATION TECHNIQUES FOR HCH STATE OF THE ART, DEVELOPMENTS AND PERSPECTIVES RELATED TO THE DUTCH SITUATION

By Leon Urlings, Geert Cuperus and Marc Leijendeckers

1 INTRODUCTION

In the Netherlands the production of hexachlorocyclohexane (HCH) took place at several sites. A location in Hengelo is renowned for its HCH production, which took place from 1948 to 1952 [1]. After chlorination of benzene, the produced mixture of α-, ß-, γ-, δ- and ε-HCH was ground with lime. Only the γ-isomer (lindane) is relevant for use as a pesticide, so after the separation of γ-HCH the remaining 85% of the production was stored on site. Other sites where production took place are e.g. Dagra in Bunschoten and the Handelskade in Deventer.

In 1977 the first soil contamination appeared at the Hengelo site. A large area in the vicinity of this and other former production plants has appeared to be contaminated. All isomers of HCH are present at the various sites. ß-HCH is most abundant as other isomers are shown to be more readily biodegradable. HCH is present in the soil adsorbed to the soil matrix but in Hengelo separate white particles also appear as a free product or associated with lime. This last phenomenon creates the bottleneck for many potential remedial techniques. The HCH here is also partially mixed with mercury which stems from another production plant in the area.

This article gives a summary of available and emerging treatment techniques which have been investigated for soil contaminated with HCH. Firstly, full scale and proven methods are presented, followed by several research initiatives in this field. Most of the work presented is related to the Dutch situation. In the Netherlands, the requirements for HCH remediation are 0.01 mg/kg (HCH total). Most of the proven technologies presented in chapter 2 are able to meet this requirement or will soon be able to do so. Much of the research work presented in chapter 3 aims at a relativity low cost treatment for the removal of a large part of the (readily available) HCH. Although meeting the requirements may take (much) longer, the most hazardous part of the contamination is tackled in this way. This document aims to give a state of the art and perspectives for future HCH treatment.

2 STATE OF THE ART

Various (almost) full scale processes have been developed and investigated particularly with regard to HCH. This involves both ex situ treatment and in situ remediation. The techniques can be divided into the following categories:-

1. Extraction techniques;
2. Thermal techniques;
3. Biological techniques;
4. Chemical techniques.

An overview of HCH treatment per technique is given below.

2.1 Extraction techniques

A series of three pilot remediations with soil from the Hengelo site was carried out by three contractors (Heymans Milieutechniek, Heidemij Reststoffendienst and Jaartsveld Groen en Milieu) on behalf of the Province of Overijssel. The three tests represent the possibilities of extraction very well.

2.1.1 Heymans Milieutechniek

In the Heymans' equipment the soil was first sieved (1.5 mm). Next the soil was mixed with extracting agents in a slurry phase. In a scrubber the slurry was thoroughly mixed to obtain a good shear. A hydrocyclone was used to separate the sludge from the sand. The sand fraction was treated a second time in the installation. Twenty samples were taken from the treated soil.

Three batches (each approx. 160 ton) were treated in this way. Table 1 summarizes the results of these tests. The removal efficiency of this process was very high (>97%). However, two of the batches showed large concentrations of HCH in one of the twenty samples taken from the treated soil. Possibly the presence of an HCH or HCH/lime particle interfered with the analysis. Re-analysis of the samples produced results which were in line with the other samples.

Table 1: Test results of Heymans Milieutechniek - all concentrations in mg/kg

Batch	HCH		Largest HCH	Hg	
	Prior to treatment	After treatment	concentration	Prior to treatment	After treatment
1	9.0	0.2	1.4	2.4	0.6
2	18.7	0.5	5.1	0.5	0.2
3	1.0	0.1	0.1	2.2	0.4

2.1.2 Jaartsveld Groen en Milieu

In this equipment the soil was first sieved (1 mm). Subsequently, flotation agents were added to the soil and the soil was treated in flotation cells. The foam, which contained the main part of the sludge fraction, was skimmed off. The sand fraction was fed to a hydrocyclone where the remaining fine particles were separated. This process was repeated with the remaining sand fraction, using optimal doses of the flotation agents (second treatment).

In table 2 the results of three batches (125 to 180 ton) are summarized. Once again a high efficiency has been achieved but in some individual soil samples high HCH concentrations were found.

Table 2: Test results of Jaartsveld Groen en Milieu - all concentrations in mg/kg

Batch	HCH			Largest HCH	Hg		
	Prior to treatment	1ˢᵗ treatment	2ⁿᵈ treatment	concentration 1ˢᵗ treatment	Prior to treatment	1ˢᵗ treatment	2ⁿᵈ treatment
1	9.0	0.8	0.1	2.4	2.4	1.0	<0.1
2	18.7	0.9	<0.1	1.2	0.5	<0.1	<0.1
3	1.0	0.4	<0.1	0.8	2.2	0.3	<0.1

2.1.3 Heidemij Reststoffendienst

In this process the soil was sieved first (1 mm). Hereafter the soil was fed to a hydrocyclone, where sludge (<40 μm) was removed. The sand fraction was mixed with flotation agents and treated in flotation cells. In the last step, the soil was washed to remove the HCH still present in the process water.

In table 3 the results of two test runs (approx. 150 ton) are summarized. Again the overall efficiency is fairly high, however, one individual soil sample out of 20 had a large concentration of HCH.

Table 3: Test results of Heidemij Reststoffendienst - all concentrations in mg/kg

Batch	HCH Prior to treatment	After treatment	Largest HCH concentration	Hg Prior to treatment	After treatment
1	9.0	0.2	1.9	2.4	<0.1
2	1.0	0.1	0.3	2.2	0.3

2.2 Thermal techniques

2.2.1 Central incineration

Incineration is a well known remedial technique for contaminated soil. In some incineration plants the remediation of soil contaminated with HCH soil has proven to be a success. Initial contents of approx. 70 mg/kg decreased to <0.1 mg/kg at temperatures of >600°C (e.g. at Ecotechniek B.V. and NBM Bodemsanering B.V.). Flue gas analysis has taken place and the results will be released shortly. Air pollution limits are very rigid. For dioxines e.g. the requirement is 0.1 ng TEQ/-m³. Several contractors are currently modifying their equipment. In afterburners (>1100°C), the formation of toxic compounds should be prevented.

2.2.2 Mourik Groot-Ammers

Mourik Groot-Ammers developed a mobile thermal system, operating at low temperatures. The system was tested on a semi-technical scale (approx. 100 kg). It appears to show large removal rates after roughly 100 hours of operation, see table 4. More than 99% of mercury was removed from an initial concentration of 4 mg/kg.

Table 4: Results Mourik Groot-Ammers - Low thermal system

HCH (μg/kg)	Reactor 1 Start	End	Reactor 2 Start	End
Alpha	400	<10	250	<10
Beta	4000	35	2500	<10
Gamma	<100	<10	<100	<10
Delta	<100	<10	<100	<10
Epsilon	250	<10	150	<10
Total HCH	4650	35	2900	<det. limit

2.3   Biological methods

Biological degradation of HCH has been studied by many researchers. Most of the experimental data are related to small scale degradation tests; to the best of our knowledge large scale applications did not take place yet.

Biodegradation of HCH in soil can take place aerobically or anaerobically. In the latter case temperatures > 20 °C are required for sufficient decomposition rates [5]. In the soil slow biodegradation also takes place anaerobically. Metabolites such as 1, 2, 3, 4, 5 pentachlorocyclohexane (PCCH) and mono-, di-and trichlorobenzenes (MCB, DCB and TCB respectively) are produced here.

The isomers, α- and γ-HCH have the highest conversion rates, ε- and δ-HCH have intermediate conversion rates and ß-HCH is reported to be highly persistent.

Conversion rates found by various authors cannot simply be compared. The difference in relevant parameters (of which organic content is an important one) is often great, and in many cases the research was not primarily aimed at optimum conversion rates. The kind of process used will also greatly influence conversion rates. Bachmann et al (Bachmann, 1988) showed that mass transfer limitation can significantly affect the degradation.

Table 5 presents two experiments in which mainly α- and γ-HCH have been studied. This overview represents typical results for this type of experiment.

Table 5: Summary of two biodegradation experiments

Reference	HCH isomer	Equipment	Conditions	Initial HCH concentration	Degradation %	Period weeks	Remarks
Mathur	γ	Stand in dark	Aerobe	32.7	84	8	No mineralization; conversion to mainly γ-PCCH (37%) and DCB (32%)
Bachmann[1]	α	Slurry shaken	Aerobe	370	97	4	Mineralization.
	α	Slurry shaken	Methanogenic	370	97	14	65% conversion to MCB, 20% to DCP/ TCP
	α	Slurry shaken	Sulphate reducing	320	28	14	
	α	Slurry shaken	Denitrifying	350	0	14	

[1] ß-HCH was not biodegraded in these four tests

2.4   Chemical techniques - the KPEG process

The research on chemical processes for HCH treatment is limited. The so-called KPEG process (see Taylor et al, 1990) was not specifically developed for HCH but for chlorinated wastes in general.

The process uses potassium hydroxide and polyethylene glycol (PEG-400) which react to give the reagent KPEG. The reagent is mixed with soil and heated to approx. 150 °C, whilst being stirred for one to four hours. The reagent KPEG (an alkoxide) replaces a Cl atom for an OH group.

The KPEG process has been demonstrated, both on pilot scale and on full scale, primarily for soil contaminated with PCB. It shows good removal efficiencies of up to 99% for soils contaminated with PCB in concentrations of up to thousands mg/kg. Costs are estimatyed at US$ 200-500/ton. Another technique is the Base Catalyzed Detoxification (see Azkona).

2.5   Groundwater treatment

In those cases where soil contaminated with HCH was excavated, groundwater treatment consisted mainly of filtration over a sand filter followed by an activated carbon filter. This method has shown to be effective in treating contaminated groundwater, at least when concentrations of benzene and chlorobenzenes are low.

Biological treatment has also been studied [10]. In a Rotating Disc Biological Contactor (RBC) a good removal of a- and γ-HCH was achieved. In this way a substantial saving on activated carbon costs was achieved. The overall cost reduction was about 30% compared with that of activated carbon treatment.

2.6   Remediation Techniques for HCH-related Compounds

There are proven full scale techniques for HCH-related compounds which may be used for the treatment of HCH contaminated sites. A recent literature search [14] showed that compounds like PCB's and pesticides have been studied in more detail than HCH. Several technologies have been successfully used to treat these kinds of contaminants [15]. Low thermal treatment gave good results within treatment costs of approximately US$ 125-225 per ton. A thermal Gas Phase Reduction Process operating at 850 °C immediately converts PCB's into smaller hydrocarbons. Extraction techniques can move contaminants from the solid into the liquid phase. These methods mainly use surfactants or organic solvents. The BEST technology can remove PCB's and pesticides using amines; costs range from US$ 90-280 per ton, depending on the scale. CF Systems uses liquefied propane which gave 98% PCB removal from sediment; costs are estimated at US$ 150-450 per ton. However, the contaminated liquid phase must then be treated.

3   EMERGING TECHNOLOGIES

3.1   Introduction

In the preceding text, full scale available techniques were reviewed. In this chapter, further research will be highlighted. Much of this work is aimed at treating readily available (and thus hazardous) HCH at relatively low costs.

As TAUW is closely involved in the problems of HCH it has used its R & D facilities to investigate and develop alternative routes for remediation. Research is aimed at both in situ and ex situ treatment. Thermal, extractive and biological techniques have been taken into account. On occasions co-operation took place with third parties.

3.2   Extractive techniques

Most of the research aims at finding an optimum extracting agent to be used for on site treatment or, perhaps, in situ treatment. Several organic acids and surfactants were used as an extracting agent. The organic acids are chosen for their potential ability to extract HCH and for their low toxicity in soils. Several tests have been carried out in batches to determine the extraction efficiency.

The efficiency is expressed as the influence on the partitioning of HCH between solid and liquid phase, the so-called K_d:

$$K_d = \frac{\text{solid concentration (g/kg)}}{\text{liquid concentration (g/l)}} (l/kg)$$

The K_d value is determined for water and subsequently for different extraction media, dissolved in the water.

Figure 1 depicts the results concerning extraction using salicylic acid and using a mixture of non-ionic surfactants (Emulan EL and Tamol NN 9104, 1:1). Both salicylic acid and the surfactants gave good results. The lower K_d value for water resulted from different concentration ranges which were used in the individual tests. ß-HCH seems particularly prone to extraction.
A second test has been carried out using only organic acids in water, see table 6. Here, the results have been influenced by an unfavourable speciation of HCH, probably present in a separate phase. The K_d values determined in this test were not significantly lower than those determined for water.
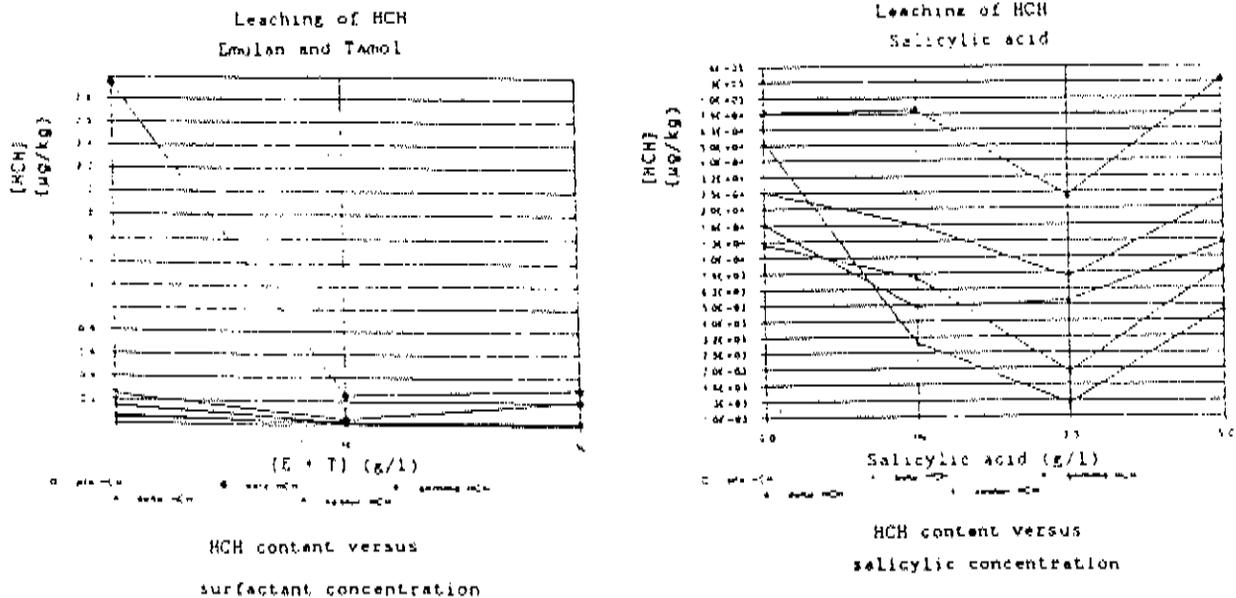

Figure 1:   Extraction of HCH using salicylic acid and surfactants - source: TAUW 1990

Table 6: Extraction of HCH using organic acids · source: TAUW 1991

Concentration (g/l)	Salicylic acid		Adipic acid		Ascorbic acid	
	1	2	1	5	1	5
HCH				K_d	(l/kg)	
Alpha	800	270	150	150	90	120
Beta	<280	2200	2400	2000	960	2000
Gamma	200	400	340	170	70	250
Delta	120	120	150	120	60	90
Epsilon	<2000	<170	<150	<150	<120	<150

A third test has been carried out using only surfactants. Emulan EL and Tamol NN 9104 were both added to a slurry of HCH soil in water (1:3), at 22 g/l. The soil used was previously treated in a biological slurry reactor for 16 weeks (see section 3.3). Table 7 presents the K_d value prior to and after biological treatment. Surprisingly enough, the K_d values are much lower after biological treatment, whereas an increase in the K_d value, after the removal of readily available contaminants, has been reported in other cases (see [11]). The initial HCH concentration was approx. 5 mg/kg.

Table 7: Extraction of HCH using surfactants after biological treatment · source: TAUW, 1991

HCH isomer	K_d (l/kg) in water prior to biological treatment	K_d (l/kg) in water after biological treatment	K_d (l/kg) for Emulan/Tamol both 22 g/l
Alpha	3515	464	2.4
Beta	74	13	2.7
Gamma	390	251	>3.4
Delta	120	111	>4.7
Epsilon	20	<84·	<2.0

Based on the results obtained from the tests mentioned and on the consideration that extrapolated remediation costs would rise beyond the cost of traditional methods, it was decided to start a more fundamental research into the speciation of HCH in the soil. The aim of this research is to explain the results of the tests so far and to determine the exact mechanism for the removal of HCH, in order to adjust the remedial technique to this mechanism.

This research is still going on. The speciation of HCH is determined by sequential extraction using agents dissolved in water, each one affecting a special type of binding of HCH to the soil. The K_d is determined at each extraction step - in order of strength of the extracting agent - see table 8.

Table 8: Speciation of HCH (all K_d values in l/kg) · source: TAUW, 1992

Extraction agent Type of binding affected	Water Free HCH	Sodium Acetate Carbonate	Hydroxyl amine Fe and Mn	Caustic Soda Humic acids
HCH isomer				
Alpha	154	311	77	240
Beta	358	554	114	309
Gamma	364	588	94	450
Delta	139	167	48	406
Epsilon	104	138	32	180

Based on the lowered K_d value it is concluded that a substantial extraction is achieved in the extraction step focused on iron- and manganese binding of HCH. Additional tests are being conducted to verify this hypothesis and to further optimize the extraction.

Another method for enhanced extraction has been studied by Appelo [12]. From batch tests it was concluded that the addition of sufficient NaCl (approx. 12.5 mmol/l) could enhance desorption by a factor 2. It is presumed that Na^+ causes clay to peptize, thus increasing the contact area of HCH with the water. Successive field tests, including an increase in temperature, are planned to assess the possibilities of an in situ treatment.

3.3   Biological techniques

Microbial degradation was studied at TAUW in two systems. The first test was conducted by treating contaminated soil in a slurry system. The slurry was stirred and no additional supply of oxygen took place. The system remained aerobic throughout the entire period. Table 9 presents the results of this test.

Table 9: Biodegradation of HCH in a slurry system - source: TAUW, 1991

Period (weeks)	Alpha HCH (µg/kg d.w.)	Beta HCH (µg/kg d.w.)	Gamma HCH (µg/kg d.w.)	Delta HCH (µg/kg d.w.)	Epsilon HCH (µg/kg d.w.)	HCB[1] (µg/kg d.w.)
0	50,000	25,000	20,000	10,000	6,500	<100
1	45,000	40,000	6,000	15,000	2,500	45
2	15,000	20,000	3,500	5,500	3,000	<100
3	3,000	6,000	850	950	600	<100
4	2,500	2,500	400	400	200	<100
6	2,000	8,500	550	1,000	550	<100
8	600	15,000	400	250	550	<10
12	1,500	15,000	850	1,000	850	<100
16	<2,000	9,000	<2,000	<2,500	<2,000	<100

1) HCB = hexachlorobenzene

The sampling of the soil for analysis on ß- and δ-HCH seems to be strongly influenced by inhomogeneous distribution. No accumulation of intermediate products took place. Later the soil was extracted using surfactants, see section 3.2.

The second test investigated the ability of the white rot fungus "Phanerochaete Chrysosporium" to biodegrade HCH. This fungus was applied to a parallel test for the biodegradation of Polycyclic Aromatic Hydrocarbons (PAH).

Again a slurry system was used under aerobic conditions, the initial concentration was approx. 1 mg/kg. However, this indicative test showed that no degradation of HCH had taken place after eight weeks. Further investigations were not pursued.

3.4   In situ remediation

In order to assess the perspectives of in situ treatment, a test, using surfactants, was conducted on laboratory scale and a field test has recently been started. In this field test in situ biorestoration is being explored.

On laboratory scale a soil column (0.7 kg) was flushed with a surfactant solution of 20 g/l (Emulan EL and Tamol NN 9104 1:1). The up flow was 1 l/day. After four weeks the upper and under layer of the column were sampled and analyzed, see table 10.

Table 10: HCH removal with surfactants in a soil column - source: TAUW, 1990

HCH	Initial Concentration	(mg/kg) Upper Layer Treated soil	Under Layer
Alpha	250	900	550
Beta	2,950	650	900
Gamma	45	30	35
Delta	73	40	50
Epsilon	150	60	70
Total	3,468	1,680	1,605

In accordance with section 3.2 ß-HCH was the most easily extracted. Extrapolated to field conditions the remediation costs for such a system are estimated though to be in excess of f 1,000.00/ton.

Good results are obtained when only sodium hydroxide (0.01-1N) was used as a reagent and solvent for extraction. Batch experiments with HCH-contaminated soil showed very high removal efficiencies of the *alpha-*, *beta-* and *gamma*-isomers (Table 11). This high efficiency may be due to partial chemical decomposition of all HCH-isomers by sodium hydroxide. Intermediates of HCH breakdown, such as chlorobenzenes, were isolated in the soil.

Table 11 HCH-removal in loamy sand (L/S = 10) using sodium hydroxide.

	180 µg HCH/Kg DS Total removal (%)			11.9 g HCH/Kg DS Total removal (%)
	0.01N	0.1N	1N	1N
alpha-HCH	83	98	98	44
beta-HCH	87	74	93	81
gamma-HCH	85	91	91	5
delta-HCH	87	93	93	-3
epsilon-HCH	90	96	96	51

The decomposition of HCH may be a result of hydrolysis at a high pH. *Gamma*-HCH was reported to hydrolyse at pH 9 with a half-life of 48 hours and 100 hours at pH 7 [18]. Another study reported base hydrolysis of *alpha-* and *gamma*-isomers at various pH and temperatures [19].

An in-situ biorestoration of a HCH-soil in the Netherlands has been executed in combination with groundwater treatment [14]. Biological decomposition was stimulated by lowering the groundwater level and thereby increasing the unsaturated zone. Soil vapour extraction was conducted to increase the oxygen supply and the soil vapour was lead through an activated coal filter. The groundwater was treated with a biological fixed film reactor (Biopur®) and an activated coal filter. The results did not indicate a significant biological removal after about 1 year of operation mainly due to unfavourable local circumstances of the soil layer and the presence of debris and foundation rests. The experiment has therefore been discontinued.

Lab-scale column experiments were performed to accompany the in-situ remediation. In this case, no HCH-reduction was noticed contradicting previous work. The reasons behind the lack of result are yet unknown but may be related to conditions already mentioned in 3.4 (see *alpha*-HCH). A recent study [20] stressed the effect of intra-particle mass-transfer and desorption on aerobic biodegradation of HCH.

3.5 Thermal techniques

Concerning thermal techniques, the low thermal process of Mourik Groot-Ammers is currently in development. Up-scaling to on site scale is soon to take place. High thermal processes are well defined. In general, the bottleneck in thermal treatment is the possible formation of by-products such as dioxins. Research is currently aimed at optimizing or developing flue gas treatment techniques.

A new development is the Thermal Hydrodechlorination (THD) process [13]. Here gasses are fed to a fixed catalyst bed consisting of activated carbon. A reductive dechlorination takes place in this bed. Processes like these are very promising in combination with thermal treatment of soil contaminated with HCH.

4   EVALUATION AND PERSPECTIVES

The preceding text has given a broad overview on the state of the art concerning the treatment of HCH contaminated soil, with the emphasis being placed on the Dutch situation. All the classical techniques used for soil remediation have been investigated. Practical experience on a large scale is very restricted, as much of the contaminated soil is stored. Research into various processes or optimizations are still taking place.

Extraction techniques appear to give good results, but the specific distribution of HCH in the soil gives rise to local hot spots, even in the treated soil. Optimization here would mean separating the HCH or HCH/lime aggregates from the soil.

Thermal treatment has shown to effectively remove HCH. Some large scale incinerators are currently being modified (flue gas treatment in afterburners) to treat chlorinated soils. A low thermal technique has been developed which will be scaled up to on site applications. Here, the problem of dioxins may have to be investigated beforehand.

Biological treatment per definition is a low cost technique and is therefore popular. Research so far has shown that α- and γ-HCH are sensitive to this treatment. On the other hand, ß-HCH has shown very low conversion rates and is, in some cases, reported to be persistent. Another drawback is the presence of HCH/lime aggregates which are hardly affected by biological activity.

In situ treatment has this same drawback as biological treatment. Extractive techniques will take a very long time, not to mention the expected high costs for really effective extracting agents. In situ biorestoration is confined to areas where the HCH/lime particles are absent.

To summarize, it can be stated that some techniques are available which require a well defined modification. These are:

- Incineration : Existing plants are currently being modified (flue gas) for the treatment of chlorinated wastes;
- Low thermal
  treatment   : Up-scaling to on site application has to take place.

Investigation into the production of dioxins is required for thermal treatment in general.

Other techniques require further research, ideas have already been postulated:

- Extraction : Speciation research is essential. If the particles consist mainly of
  HCH/lime, than a pre-treatment with acid may give good results;
- Biological : Optimum conditions for biodegrada-tion, particularly for ß-HCH,
  and field testing require further research;
- In situ
  treatment : Application is confined to areas which do not contain any aggre-
  gates. For extraction more specific and effective agents have to
  be looked for or regeneration of the agents has to be considered.

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CONCEPTS OF PESTICIDE WASTE DISPOSAL
By Jozef Polkowski and Andrzej Silowezki

The continuous increase in population involves the necessity of food production development. One of the ways available is to minimize the losses caused by plant diseases, pests and weeds. Pesticides are used for that purpose. The necessity of using pesticides now as well as in the future is obvious. In order to achieve the desired protection efficiency and to minimize at the same time the by-effects of pesticide use, the following conditions are to be met:

- the possibilities of plant diseases and pest invasion should be forecast as precisely as possible;
- the pesticide producer should act flexibly, including a proper evaluation of the market demand for the given product; he should produce the required amount of it within the required period of time;
- the distributor of pesticides should immediately react to market demand;
- the protective measures should be taken by specialized, competent enterprises.

Moreover, an effective cooperation of these units has to be ensured.
Unfortunately, in Poland none of the mentioned conditions has been met sufficiently for many years and the mutual cooperation has not been effective either. The very complicated organization of the production process, the import, storage and distribution of pesticides caused perturbations in such a cooperation.
Further difficulties involved weather anomalia, causing plant diseases and pest invasions that entailed the necessity of purchasing pesticides abroad.

Furthermore, the transport of pesticides by rail has generated some perturbations, together with atomized trade work and unqualified personnel. All the various methods of it have been developed. Especially in the USA, much research was done on the decomposition of pesticides. The findings of that research served as a basis for the design and construction of a laboratory plant at the Sosnicowice Department of the Institute of Plants Protection. The method of decomposting pesticides by incineration is assumed to be the only one sensibly motivated in Poland; however, the technical difficulties met have led to a delay in its implementation.

One should assume that without any technical aid from industrialized countries, this problem will not be solved in Poland in the near future. An additional problem are the environmental protection regulations dealing with the emission of toxic compounds to the atmosphere and the storage of ashes from pesticide waste incinerators.

The mentioned "Main lines..." stipulate the necessity of waste pesticides storage registration, so as to facilitate waste incineration in the future.
These regulations shall force the local civil authorities, social organiza-tions and pesticide distributors to build suitable storage buildings, to keep records of wastes and to prepare reports. This information must then be sent to the organizations and units responsible for waste disposal.

Polish organizations and authorities supervising these problems are:
- Department of Plants Production of the Ministry of Agriculture;
- Chief Sanitary Inspectorate of State Sanitary Supervision;
- State Labour Inspection;
- Control Department of State Environmental Protection Inspectorate.

The "Main lines..." also describe the way pesticide packages are to be disposed of. The used packages containing residues of pesticides of Ia, Ib, II and III toxicity classes should be recorded and stored in the same way as pesticides. The pesticide packages of the IVth toxicity class should be disposed as municipal waste. Disposal of pesticide packages in ways that are not in accordance with the environmental protection requirements is forbidden (for example combusting in bonfires, boilers, also burying and storage in burial grounds).

Other pesticide wastes (plants, parts of plants and animals) should be composted in suitable places. The method of it was elaborated by the Sosnicowice Department of the Institute of Plants Protection.

Further and more detailed presentation of the "Main lines..." in author's incorrectnesses caused the forming of pesticides stocks, which has resulted in the pesticides becoming overdue.

The largest stocks of overdue pesticides have been accumulated in the decade 1970-1980, when apart from the reasons mentioned above, the use of DDT and other chlorinated hydrocarbons was forbidden, followed by their withdrawal from the market.

The largest amounts of unused pesticides are stored in the following voivodships: Koszalin, Szczecin, Bydgoszcz, Suwalki, Torún, Gorzów. In the voivodships Kielce, Kalisz, Chelm, Radom, Elblag and Opole, large amounts of pesticides are dumped as well.

Overdue pesticides are stored in so-called "mogilniki", i.e. burial grounds. According to data supplied by PIOS (State Environmental Protection Inspectorate), there are officially 178 burial grounds in Poland containing approx. 6000 tons of pesticides but these data are significantly lowered. In the evaluations done independently by PIOS and PIS (State Sanitary Supervision), one can observe the uniformity of views that according to environmental protection regulations, the burial grounds (mogilniki) cannot be considered as the final form of pesticide disposal. From an ecological point of view, such a disposal is harmful because sooner or later damage to the burial bunker construction will cause penetration of stored toxic substances into the environment, which will be especially hazardous for waters.

Several cases of self-ignition of buried pesticides have been observed in the past as well as some cases of substances penetration followed by contamination of soil and groundwater.

To date, the existing rules with regard to the disposal of overdue and withdrawn pesticides were issued in the Law on the Environmental Protection and Achitecture, dated 31 January 1980. The mentioned law includes the interdiction (under penalty) of storage, dumping and removal of any waste on dumping grounds. This interdiction refers also to the unlawful (i.e. not authorized by competent authorities) disposal of raw materials, products, by-products and other materials considered to be unuseful for economical purposes (Art. 106, point 5).

Incineration of wastes on the surface of the ground is also prohibited, except for cases defined by local voivodship authorities.

In consideration of the general regulations enclosed in the mentioned act and in view of the necessity of a detailed and precise determination of ways to dispose of hazardous wastes including pesticides, the main lines of such a waste disposal were to be determined.

The elaborated "Main lines of disposal of withdrawn and unuseful pesticides, pesticides packages and other wastes containing pesticides and sewage from spraying machinery washing" will come into force as a common Law issed by the Ministry of Environmental Protection, Natural Resources and Forestry and by the Ministry of Agriculture.

Similar regulations will consider the disposal of:
- pesticides unuseful for agricultural purposes;
- unidentified substances;
- pesticides not being specified in the present list of pesticides admitted for trade and use (regulations of Ministry of Agriculture);
- pesticide packages;
- wastewater, soil, plants, parts of plants and animals excessively contaminated with pesticides.

According to the mentioned "Main lines...", the withdrawn pesticides have to be collected in storage buildings equipped according to the requirements issued by the sanitary and environmental protection supervisors. The design of such store buildings can be offered by the Institute of Plants Protection in Poznan.

Until suitable storage buildings will be constructed, the pesticide wastes can be stored in substitute stores that should be authorized by the local Department of Environmental Protection of the Voivodship Office.
Other ways of disposing of waste stored in this way depend on the chosen method.
One of the methods available is the so-called "final storage", an example being the chemical waste storage at Bonfold, Switzerland. During 12 years, about 120 thousand tons of hazardous wastes from Switzerland and neighbouring regions in Germany and France have been buried there. The "graveyard" has been organized in a trough with tight subsoil, after the necessary geological research has been done there. The hazards presented by toxic matter getting into the groundwater is minimized. The exploited graveyard has been closed with layers of clay and soil and the whole area is forested. The adjoining environment is still being monitored for possible pollutants.

The second method for disposing of pesticides is incineration. In practice, incineration is the method applied more frequently. In Europe, there are numerous incineration plants for hazardous wastes. Once the "Main lines..." will be in force, the interested authorities will be forced to rationalize the methods used for the disposal of pesticide wastes. Moreover, activities will be developed focusing on getting a plant for the safe decomposition of such wastes operational.

Finally, it should be noticed that while Poland's pesticide application index is one of the lowest (approx. 1 kg/ha), the amounts of pesticide wastes produced are among the largest - which leads to significant hazards for the environment.

7. Remediation Cases

TEN YEARS OF SOIL CLEAN UP IN THE HCH-PROJECT IN TWENTE, THE NETHERLANDS

By Annemarieke Grinwis and Gabe de Jong

1 INTRODUCTION

In this abstract an overview will be given about the way the soil pollution with HCH in Twente is handled by province Overijssel. First there will be some attention for history. Then the following subjects will be discussed:
- making an inventory of the sites;
- investigation methods
- soil remediation:
  - remove and temporary storage or
  - isolation, control and management;
- clean up criteria;
- finally some subjects will be given on which new challenges are open.

2 HISTORY

In the seventies, it was known by the authorities that on the territory of the earlier company Stork & Co. chemical industries there was an open storage of HCH waste. In the period between 1948-1952 the company produced HCH for the use of insecticide. The first two years the whole mixture of isomers was used. In 1950 the company started to separate the mixture because the gamma-isomer was the most effective insecticide. In the seventies the legal successor was asked by the authorities to remove the waste. A part of it was packed in drums and removed to a salt mine, but it was not known that contaminated soil, building material and parts of the waste had followed another route. In 1977 a contamination outside the company territory was discovered for the first time. In the following years lots of sites contaminated with HCH were discovered. Most of them can be found in the southern part of Hengelo and to the south-west of Enschede, very near the factory. However, contaminated sites are also found to the north of Hengelo, in Borne and Oldenzaal, some 10-20 km away from the source.

3 INTERIM ACT ON SOIL CLEAN-UP

Of course, the HCH-problem in Twente was not the only soil contamination in the Netherlands. So in 1983, the Interim Act on Soil Clean up came into force.
The act and the companion guide give directions for a systematic approach of solving contamination problems in the soil. The act and guide consider three major subjects:
- the legal responsibilities;
- the financing system;
- the technical undertaking.

The following aspects are important:
- the province is responsible for enforcement of the act;
- there is a yearly budget, but major projects (costs over 10 million guilders) are directly financed by the government;
- the principle of the polluter pays. In the project a legal procedure is going on against the originator.

4   INVENTORY OF THE SITES

The investigations about the HCH-problem in Twente have been systematically undertaken.

The following routes were used:
- an appeal was made in the local press, asking for people who had knowledge of transport and disposal of waste or soil from the company in the area;
- the archives of the present and former owners of the company territory were investigated. Also archives on environmental licences.
- drivers of transport companies which had dealt with AKZO, reacted to the appeal in the press and were interviewed.
- air photography, first trying to spot soil contamination. Secondly looking for sites with deviations in the soil profile, such as filled-up sand or clay winnings, digging activities etc.
- a rough field check and chemical analysis of two mixed samples per hectare.
- Quality control of cow's milk (a lot of sites were used as pasture).

In total 132 sites were suspected, of which 57 heavily. 70 sites were investigated further. The other 62 proved to be clean after the rough field check and chemical analysis. After further investigation another 28 sites proved to be clean or just slightly contaminated. This means that now 42 sites are cleaned up or under investigation.

5   METHODS OF INVESTIGATION

First known contaminated sites were checked for the type of contamination.
In addition to HCH there was found:
- mercury, from chloric alkali process;
- lead, from the use of conduit pipes;
- sometimes HCB.
In the groundwater the following degradation-products of HCH were found:
- chlorobenzenes;
- chlorophenols;
- benzene.

The extent of the contamination on a site was first investigated in a extremely systematical pattern. After the first clean-ups we learned the following aspects:
- mostly the depth of contaminated soil was the same as the disturbed profile;
- the cause of contamination was important for recognizing a pattern;
- four main causes were recognized:
    1. levelling with polluted soil after subsidence;
    2. owners of site who had sold good sand (1-2 m) and filled up with contaminated soil;
    3. the site was used as a sand and/or clay winning and filled up with waste afterwards;
    4. top soil was polluted by spreading through the air.

6   INVESTIGATION OF REMEDIATION POSSIBILITIES

The systematic investigation about extent was followed by an investigation about possibilities for remediation. Removal and clean-up of the soil was preferred. However when talking about sites with more than about 30.000 m3 of contaminated soil or former multipurpose landfills a specific investigation about removal or isolation is necessary.

The first assessment about the quantity of removable soil said 150.000 m3. Purpose is to remove the soil, clean up to below detection limit and make reuse for all purposes possible.

At the moment the decision about the remediation variant was taken, clean-up of the soil was not possible. A method was expected within some years. So a temporary storage place had to be found. At first the search was directed towards existing storage depots. These appeared either too small or not suitable or not willing to accept the HCH soil. After some time it became obvious that this project required its own temporary storage depot.

The following conditions were made:
- it had to be large enough for at least storage of the soil from urgent sites (150.000 m3);
- no migration of contaminants from the stored soil should be tolerated;
- the storage depot should be near the contaminated sites;
- necessary licences had to be obtainable.

A former landfill at Beckum, also illegally used for dumping HCH-waste, appeared suitable. The only disadvantage: it is in a rural area. The landfill was isolated with bentonite-cement-foil walls before it was used as a storage depot. The walls were placed on the base of the first aquifer. The soil in storage is topped with a HDPE foil (1 mm), on this some 40 cm top soil and grass for the sake of appearance. A yearly monitoring programm is carried out in order to check on the condition that migration of the contaminants is not occuring. The contaminated soil was separated into three parts because of expectations about remediation techniques.
A = organic (HCH)
B = inorganic (Hg)
C = organic + inorganic (HCH + Hg)

At the moment, it is questionable whether this distinction is important. With the most experiments about soil treatment techniques the presence of a small amount of Hg together with HCH is not the important difficulty.

7 CLEANING PLANT

In the mean time a cleaning technique is developed for cleaning this soil. Considering the large amount of soil it pays off and saves the environment to build the cleaning installation in the vicinity of the polluted locations. It appears that by the end of 1994 the first amount of soil wil be cleaned in a plant with a nominal capacity of 120,000 tons of soil per year on the commercial grounds of Hengelo.

Realisation can produce an important contribution to the solution of the HCH problem in the region Twente. Especially for the polluted locations in the direct vicinity of the installation, cleaning up the soil in this installation saves on transport costs. Realising a soil-cleaning installation in the region Twente corresponds with the wish of the ministry and the Service Center Soilcleaning (SCS) to promote the countrywide spreading of cleaning capacity in the Netherlands. Thus avoiding unnecessary transport over long distances.

The SCS wants to work up the temporary stored HCH polluted soil, on short terms (within five years). In a study of the SCS it will be able to realise this with a process based on mineral-separating techniques.

The intended cleaning installation will have a multi-functional character. The installation will be able to process polluted soil with a large diversity of polluting materials. For example pollutions of HCH, cyanide, heavy metals and carburetted hydrogen.

8 CLEAN-UP CRITERIA

In the guide to the interim act on soil clean-up the following A-, B- and C-values are valid:

	A	B	C
soil (mg/kg d.m.)	0.0002 *)	0,5	5
groundwater (ug/l)	0.02	0,2	1

*) when organic matter < 2%.

The A-value is at this moment below the detection limit. Then the A-value is replaced by the detection limit, which is 0.01 mg/kg d.m.

In the project lots of discussions attended risk assessment. It led to the following conditions for clean-up.
- Above C-value remediation of a site is needed.
- Soil is excavated when the total of HCH-isomers rises above 1 mg/kg d.m. or ß HCH rises above 0,5 mg/kg d.m.
- In the root zone (= 1 m) the mean concentration of ß HCH on a site has to stay below 0.005 mg/kg d.m. when the site is used for food production or housing.

At the moment 17 sites have been excavated and 1 site has been isolated. In total 136.000 m3 soil has been stored. In October 1992 the first 8.000 m3 soil was transported from the depot to an extraction plant for clean-up.

9 CHALLENGES FOR THE NEAR FUTURE

1. Treatment of the soil in order to attain a clean (A-value) and reusable product for all purposes. Realizing a treatment plant at a small distance from the storage depot.

2. Reduction of the volume of groundwater and time needed for the clean-up of the contaminated groundwater.

3. Finding a usable solution for isolation, management and control of the vast and mostly deep waste disposals in which HCH is one of the pollutants.

"DEVENTER HANDELSKADE" PROJECT
TECHNICAL INTERPRETATION OF THE CHOICE OF A GEOHYDROLOGICAL ISO-
LATION OPTION WITH SUPPLEMENTARY MEASURES TO FACILITATE BUILDING
DEVELOPMENT.
By Annemarieke Grinwis

1   DESCRIPTION OF THE PROBLEM

Nature

Between 1946 and mid-1962 there was a pesticide factory in Deventer. In particu-
lar, HCH was processed. The soil was first analysed in 1985. The various soil
analyses revealed that the site is polluted with HCH, and the ground water with
HCH and its decomposition products, primarily monochlorobenzene. The ground
water is also polluted to a lesser extent with aromatic compounds, chlorophenols
and di- and trichlorobenzenes. Secondary contamination with mercury, such as
that found in connection with the HCH problem in Twente in the province of Over-
ijssel, was not encountered.

Cause of soil pollution

During production, the waste product of gamma-HCH (the other isomers) was
temporarily stored in factory buildings and/or outdoors on the factory site. It is
possible that some of the waste material (the liquid proportion) was buried or
dumped on the outdoor part of the factory site. In view of the fact that the munici-
pal sewer was blocked as a result of the company's discharge activities in the
fifties, it can also be assumed that waste was disposed of through this sewer. It is
also probable that emissions from stacks and/or dispersal by the wind caused
some surface contamination with HCH.

Extent of the contamination

Geohydrological data
The table below shows the local soil structure and ground water flow.

SOIL STRUCTURE			GROUND WATER FLOW	
			Direction	Rate
Covering layer	1-2 m - gs 2-6 m - gs	sand loamy sand clayey loam	mainly vertical	
1st water- bearing group	6-25 m - gs	medium-coarse sand	horizontal in south-westerly direction to the IJssel	60-70 m/a
Separating layer	25-65 m - gs	clay		0 m/a
Water table: 5 m above New Amsterdam Datum (3 m below ground surface)				

Soil

The pollution situation in the soil is as follows:
- a core of pollution on the northern part of the factory site;
- a second core around the municipal sewer with a depth varying from 8-12 metres below the ground surface (m - gs);
- slight contamination of the surface owing to emissions from stacks and/or wind dispersal.

Ground water

- The ground water at the factory site and the sewer is strongly polluted down to a depth of 30 m - gs.
- From this source the pollution spreads in a plume towards the IJssel river.

The table below shows the surface areas of the contaminated soil and the volumes of polluted water. The degree of pollution is also given.

	Contaminated		Maximum concentration	
	area m2	volume m3	HCH	MCB
soil	20.000	68.000	4.225	- mg/kg
groundwater . site	20.000	60.000	2.500	52 ug/l
. tail	270.000	± 6.000.000	380	3000 ug/l

Risks to public health and the environment

The risk analysis of this contaminated site indicates that in the present situation there is a public health risk associated with the execution of excavation work.
In addition, under hot, calm weather conditions there could again be odour nuisance, and it cannot be excluded that there would be some risk due to the evaporation of pollutants. The spread of pollutants via ground water also poses an environmental risk.

Clean-up options

In order to eliminate these risks a total of six clean-up options were drafted and each of these options was subdivided into another six sub-options.
1. Restoration of the multifunctionality of the soil. (Option I)
2. Isolation option. This option includes elaborations of the sub-options involving isolation by geohydrological and civil engineering techniques. The site is covered by a layer of asphalt. (Option IV)
3. Optimization option(s). These options involve geohydrological isolation of the contamination in the vertical plane; the various sub-options provide for the removal of an increasing volume of contaminated soil in the horizontal plane, so that an increasing number of uses are made possible over a growing surface of the contaminated site. (Options VIa - VId)

The following table shows a comparison of the technical, environmental and financial aspects of the various options.

Options Aspects	restoratio multifunc- tionality	isolation geohydrolo-gical	optimization
technical	.	+	+
environmental	++	+	+ -> ++
financial	f 79 mio	f 26.6 mio	f 28 -> 35 mio

Choice of options

The province of Overijssel selected the optimization option, sub-option VIc. The Ministry of Public Housing, Planning and the Environment refused to approve this choice because, from the point of view of soil clean-up, it is not the most inexpensive or efficient solution. In the context of the interim law on soil clean-up the Ministry has chosen the geohydrological isolation option. However, in view of the importance of this matter in the context of town and country planning, the Ministry did approve the drafting of supplementary measures that will allow the site to be used for a building development (a college). These supplementary measures will be financed by the state (from town and country planning funds), the province and the municipality.

2 GEOHYDROLOGICAL ISOLATION OPTION WITH SUPPLEMENTARY MEASURES TO MAKE BUILDING DEVELOPMENT POSSIBLE

Underpinning the planned measures by means of risk analysis

A study was carried out to determine what measures are needed to control the risks of building on the contaminated site. This involved carrying out exposure calculations with the help of the C-soil model developed by the National Institute for Public Health and the Environment. This model takes account of the following exposure paths:

1. Ingestion and inhalation of soil particles.
2. Dermal contact with the soil.
3. Inhalation from the air.
4. Ingestion from drinking water.
5. Inhalation from steam during showering (drinking water as carrier).
6. Plant cultivation.

The risks are controlled by:

1. Covering contaminated areas on which no building is to be carried out by a layer of asphalt (10 cm).
2. Spreading a 1 - 1.25 m thick layer of clean soil for the cable and pipeline trench. Measures must be taken to ensure that no dermal contact occurs during the necessary excavation work and that drinking water does not become contaminated.
3. Laying the sewer in clean soil.
4. Prohibiting plant cultivation and green spaces on contaminated soil.

Specific attention was paid to controlling the exposure path "inhalation from the air", because this sensitive path cannot be controlled by simple means after the site has been developed. In this situation the path is especially sensitive because considerable concentrations of HCH and mono-, di- and trichlorobenzenes are present in the ground water (up to 1500 µg/l).

Calculation of the risk associated with evaporation to the air inside the building

A calculation was performed to determine the residual risks associated with evaporation into the crawl space of the building after a clean layer of soil has been spread over the contaminated soil under the buildings.
Two different mathematical models were used: a simple diffusion model based on Fick's 1st law, and the C-soil model (National Institute for Public Health and the Environment). In principle there are 4 processes by means of which vertical transport can occur in the soil:
- soil air diffusion;
- pore water diffusion;
- convective transport with evaporating water;
- convective transport with air.

Diffusion via the water phase is a factor of 1000 less than via the soil air phase and is therefore negligible. Convective transport with water occurs if water is carried to the boundary between soil and crawl space by capillary rise and evaporates there. Convective transport with air occurs if air or gas is produced in the soil and is transported to the boundary layer. This latter transport path is regarded as negligible in the context of this project.

The diffusion model takes account of soil air diffusion as a transport path. The C-soil model assumes the occurrence of soil air diffusion and convective transport with evaporating water. However, at this site the ground water level is 3 m below the ground surface and the soil is sandy, so that capillary rise to the boundary between the soil and the crawl space is not to be expected.
Model calculations were carried out for beta and gamma HCH, on account of the differences in their physical properties, and for monochlorobenzene, on account of its higher volatility in comparison with the other chlorobenzenes. The evaporation varies as a function of concentration, depth, height of crawl space and air changes.

The concentration in the air inside the building was measured and compared to the acceptable concentration in air (ACA) and ACA/100. These test values are defined as the maximum acceptable risk level and the negligible risk level, respectively. On this basis it was concluded that it would be possible to build, provided the requirements listed below are fulfilled.

Conclusions with regard to control of the risks by determining the limitations on the use of the site

The partially cleaned-up part of the site is suitable for office buildings, provided:
- the following basic requirements are fulfilled: 1 m crawl space above 1 m clean soil (< A-value). If there is residual contamination below the clean soil and this residual contamination exceeds the risk threshold value of 1.8 mg/kg of total HCH, an additional impermeable layer must be provided;
- the number of air changes in the crawl space is at least 1.25/hour;
- no additional earth moving is carried out;
- the pile driving technique used does not cause contamination of the clean surface layer;
- the air inside the building is monitored;
- additional measures are taken if the risk threshold value in the air in the crawl space or the ACA value in the air inside the building is exceeded.

The asphalt-covered site is suitable for a limited number of uses (parking space for cars, cycles), provided:
- account is taken of future maintenance;
- the sealed isolation layer is not damaged or broken open.

Cables and pipelines (domestic connections) must only be laid in the layer of clean soil of the partially cleaned-up part of the site.

Unpurified ground water must not be used.

Before the building is taken into use, the monochlorobenzene concentration in the ground water must be reduced to 600 µg/l (equilibrium concentration with 0.15 mg/kg of dry substance in ground).

Costs and benefits of making the site suitable for use

The excess costs with regard to soil clean-up at the site of the building are estimated at $3,5.10^6$ NLG. The qualitative benefits are:
- better ways of using the site than simply as a parking site;
- limitation of car travel and the associated environmental pollution by using a site in the direct vicinity of the railway station for a building intended for a large number of visitors.

Maintenance system

The effectiveness of the isolation and control measures must be perpetually monitored and corrective action must be taken if necessary. For this reason a maintenance system must be developed that will include provision for technical as well as organisational aspects. For example:
- overview of those involved and their responsibilities;
- measures for monitoring the systems for controlling ground water and air:
    - ground water level and concentrations; functioning of the extraction system, including purification;
    - concentrations in the crawl space air and air changes; functioning of the ventilation system.
- servicing and reinvestment measures;
- restrictions in the use of the site;
- emergency response plan;
- provision of information to those involved.

3   CONCLUSIONS

1. The risks to which people are exposed in connection with HCH-contaminated soil are mainly associated with exposure to food (of both animal and vegetable origin) that has been produced on the contaminated soil. However, even when an HCH-contaminated site has been used for a building development, the exposure route from the soil to the interior air is not by definition negligible. In particular, consideration must be given to volatile decomposition products of HCH, such as monochlorobenzene.

2. The C-soil model must be treated with caution with regard to the "inhalation air" exposure path, because the model assumes diffusion + convective transport with evaporating water. However, convective transport is only applicable if the capillary rise extends from the ground water to the boundary of the soil with the air.

3. An air change rate of 1.25/h is more technically demanding in the case of large buildings than in that of houses, because the standard Dutch regulations for house building are such that this air change rate is more likely to be achieved by natural ventilation.

4. Isolation combined with a better quality of use of a site requires a lot of thought to be given to maintenance. It is important to gain a better insight into the organisational, budgeting and preservation aspects of maintenance systems.

8. Concluding Remarks

CONCLUSIONS AND STATEMENTS OF 1ST AND 2ND FORUM

On the basis of the two HCH forums held, some conclusions were drawn. In this chapter these conclusions will be briefly reflected.

- Soil contamination due to HCH is not an individual problem of some European countries, but a worldwide problem. Production plants have existed in Germany, Turkey, The Netherlands, Spain, Slowakia, Austria, Brazil, China, Commonwealth of Independent States (CIS), India, Italy, Japan, Mexico, Rumania, Ukrania, U.S.A.

- A first approach of the extend of remediation showed figures of 10 to 50 billion German Marks within the European Community and worldwide of 100-500 billion German Marks. Roughly 1000 to 5000 contaminated sites are expected worldwide.

- The problems were classified in different categories such as diffuse problems (with low concentrations measured in Norway and Slowakia), scattered problems (with a large numbers of underground storage tombs all over the country in Poland) and strongly polluted sites. The last category of sites was subdivided into production sites (e.g. Magdeburg, Deventer and Bilbao), hot spots and dump sites (Heideweg in the Netherlands, Quarry Antonie in Saxony Anhalt and dumps around the airport of Bilbao in Basque Country). Many of the problems occur in various combinations of a.m. categories.

  For the different contaminated sites it was stated that different remediation approaches in relation tot the various future uses are needed.

- In order to set priorities and to support decision making the instrument of risk assessment should be applied. Therefore investigations and analytical data are required. New problems and new chemical analyses were presented (toxaphene and metabolites).
  Further use of analytical data in combination with production data and historical activities seems necessary. An important issue how to use the acquired data was raised. In order to assure a proper use of data a comparison of the different risk assessment systems, accessible and understandable for people involved is recommended.

- The results of the risk assessment are necessary to evaluate the feasibility of the various solutions (technical and forthcoming financial and environmental aspects)

- Possible approaches are:

  • monitoring to reveal more data and follow e.g. deposition rates (Norway, Slowakia, Umweltdatenbank in Germany)
  • restrictive land use in combination with biological or other in situ remediation techniques (use of plants)
  • (permanent)disposal of soil under isolated and controlled conditions
  • (partial) remediation of soil (extraction, low thermal volatilization and biodegradation)
  • hazardous waste treatment
    The following methods were presented:
    catalytic thermal hydrogenation
    base catalyzed detoxification (BCD)
    dechlorination with sodiumhydroxide and sodiumcarboxide
    high energy beam radiation (only for water)

- Emphasis at the next Forums will be put on the remedial actions and strategies

Working groups are installed to work on the items of risk assessment, remedial technologies and support.