# Economic and Ecologically Favorable
# Detoxification of Polyhalogenated Pollutants in Complex Matter
# Applying the DMCR-Technology

*(DMCR = **D**ehalogenation by **M**echano**c**hemical **R**eaction)*

## - Features and Highlights -

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# Introduction

Hazardous polyhalogenated pollutants, e.g. PCBs, dioxins, pesticides like DDT, hexachlorocyclohexane (HCH, lindane) or dieldrine, wood preservatives like pentachlorophenol (PCP), solvents like fluorinated chlorohydrocarbons (CFCs) or trichloroethylene (TCE), jeopardize the environment worldwide, e.g. soils and drinking water resources, and cause especially serious environmental and health problems mankind is faced with nearly all over the world at the beginning of the 21st century.

The recently developed DMCR technology has revealed both effectiveness and interesting economical features for the destruction of polyhalogenated pollutants in a wide range of contaminated materials without harming the environment. It opens up interesting novel strategies for hazardous waste management and recycling or re-use of particular contaminated materials worldwide.

By means of utilizing base metals like magnesium or sodium as dehalogenation reagents in a specific combination with applying mechanochemical conditions using vibratory mills, these toxic substances are eliminated directly inside a contaminated complex material at room temperature and in a short time very efficiently. The process works virtually regardless how complex the structure of a contaminated material may be and how strongly the contaminants may be bound adsorptively to particular compounds, e.g. clay fractions or humic acids regarding soils.

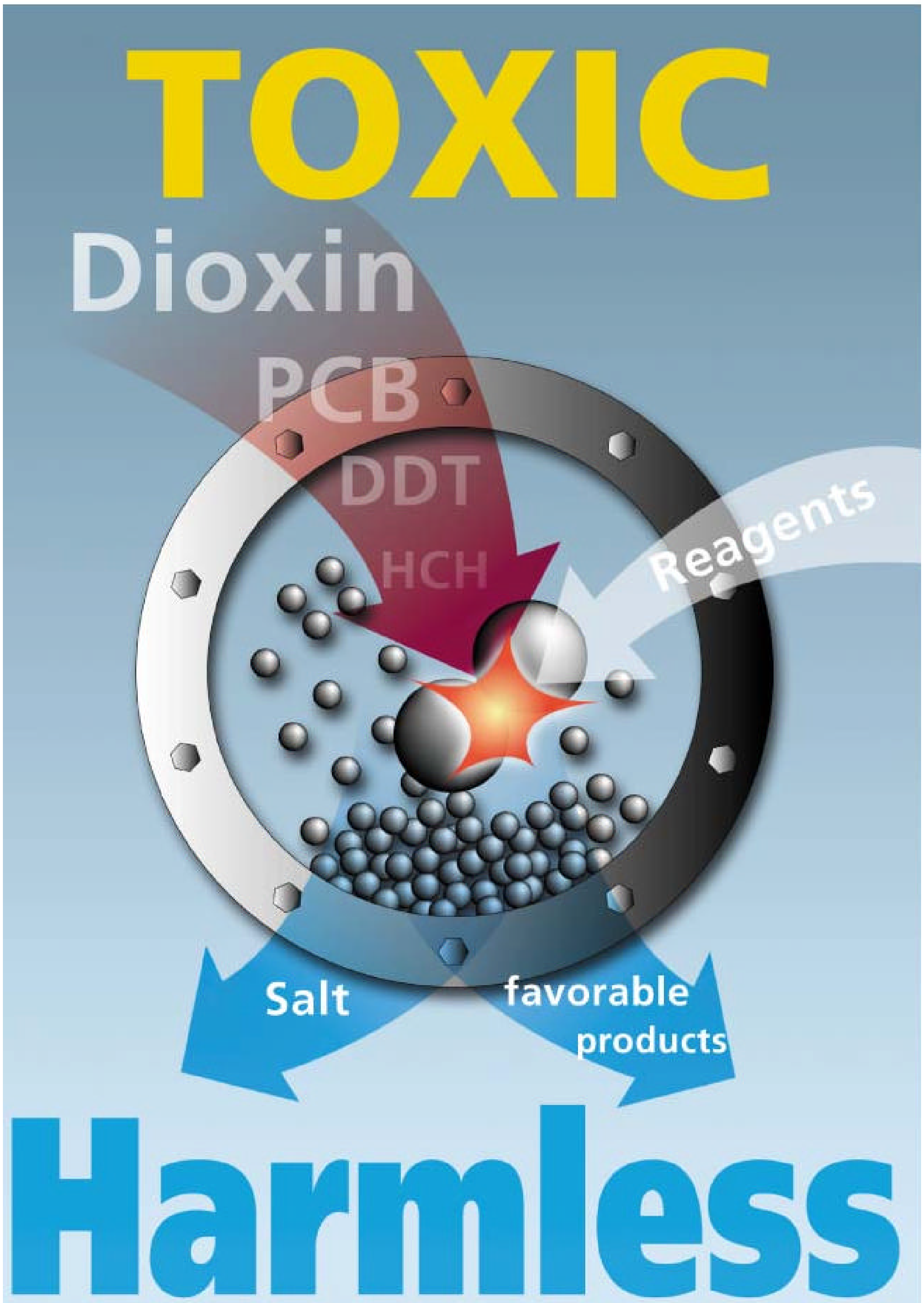
The toxicity of polyhalogenated compounds is due to the so-called "organic halogen" specifically bound to these compounds. Therefore, these substances can be detoxified by stripping off the "organic halogen" entirely via a chemical reaction. As the source of the high toxicity of polyhalogenated hydrocarbons, the organic bound halogen is removed from the molecule entirely, being transformed into a harmless inorganic chloride.

This technology benefits from pretty low operational and maintenance costs allowing immediate resolution of very different contamination problems with the use of a one time investment. It is designed for the requirements of the 21st century.

The technology has been applied successfully to the detoxification of contaminated soils and contaminated oils in co-operation with European companies during feasibility studies and small pilot scale projects implemented over the last years.

This document provides a compilation of features and highlights in order to give an overview of this innovative dehalogenation technology. In the appendix you will find a short summary, too.

The fundamental and innovative principle of the DMCR technology at a glance:



## Features and Highlights

**Process Characterization:** By treating contaminated materials or pure toxic compounds in vibratory mills applied as highly effective mixing devices and reactors at the same time and in one single operation step, organic bound chlorine is stripped off from the pollutant´s molecule by added base metals like sodium, magnesium, aluminum, iron or alloys, exchanged by hydrogen by means of added suitable hydrogen donors and released as a harmless inorganic chloride (e.g. magnesium chloride, when using magnesium metal).


| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $R\text{–}Cl$ | + | Mg | + | "*H*" | $\Rightarrow$ | $R\text{–}H$ | + | $MgCl_2$ |
| *(PCB)* | | *Base Metal (Magnesium)* | | *Hydrogen-Donor* | | *Biphenyl* | | *Salt* |
| **TOXIC** | | | | | $\Rightarrow$ | **HARMLESS** | | |

*One example (rough, simplified scheme, not stoichiometric) for dehalogenation using DMCR: PCBs are dehalogenated by Magnesium metal in the presence of an appropriate hydrogen donor yielding harmless biphenyl and magnesium chloride*

Thus, the process applies vibratory mills as the core units and degradation takes place by reductive dehalogenation.

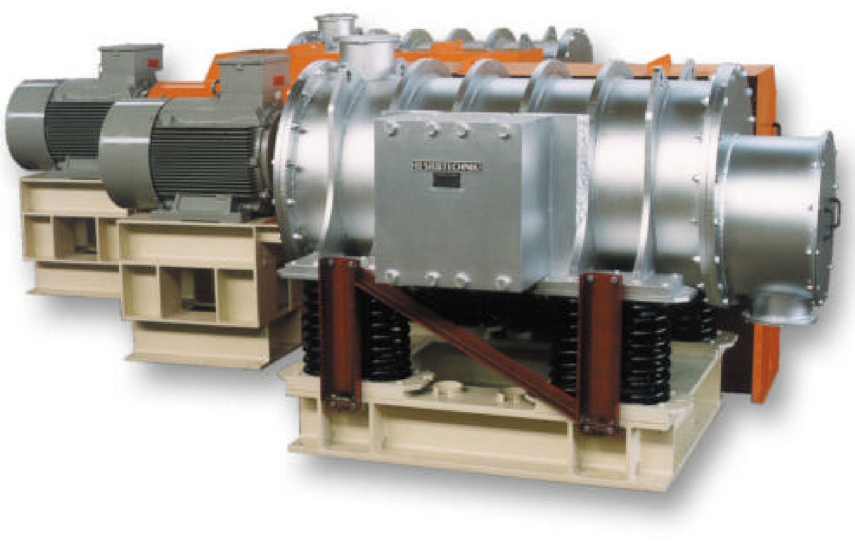
The main idea behind this technology is that vibratory mills cannot serve as unique mixing devices only due to their outstanding mechanical capabilities, but can be utilized as highly effective chemical reactors, too, in order to destroy polyhalogenated pollutants by adding appropriate degradation agents.

The process proves that inside a vibratory mill several required important operation steps like conditioning, mixing, dispersing of contaminated materials and added reagents and degrading the pollutants, can be perfectly and effectively combined in one single operation step only. Milling provides both optimal conditioning a contaminated material by breaking up agglomerations (furthermore, in addition, by effective breaking down particular structures down to the molecular level) and its thorough and extremly efficient mixing with the added dehalogenating agents at the same time, so that a permanently intimate contact between contaminants and reagents can be established. In addition, from the added base metal a highly reactive metal dispersion is produced, which is essential for the dehalogenation reaction.

Therefore, the whole process may be characterized as a reductive dehalogenation promoted under mechanochemical conditions.

Pollutants can be eliminated at room temperature and in a short time (within minutes up to one hour).

The process may be combined with or may be used in addition to other common remediation processes like soil washing or biological degradation. It may be combined with remediation processes for other contaminants, too, e.g. asbestos. Asbestos may be ground down to harmless non-crystalline matter and polyhalogenated pollutants may be dehalogenated in one single step simultaneously.



**Treatable Materials:** Solid, solid-liquid and liquid contaminated materials (like soils, filter dusts, sludges, transformer and capacitor or used lubricating oils) or pure contaminants or mixtures of them can be treated in general by the DMCR process.

Pure liquids like PCB transformer or capacitor oils are also treated successfully, because the added metal is finely ground and dispersed during milling and, therefore, highly activated for the PCB dehalogenation.

**Treatable Pollutants:** Every halogenated pollutant can be treated in general, e.g. PCBs, dioxins (PCDD), dibenzofuranes (PCDF), pentachlorophenol (PCP), insecticides like DDT, hexachlorocyclohexane (HCH), dieldrin (HEOD), fluorinated hydrocarbons, chlorinated solvents like trichloroethylene (TCE), halogenated chemical weapons like lost, lewisite, adamsite.

The process is likely to readily treat wastes consisting of a range of contaminants or mixtures reducing waste handling and the associated risk.

**Concentration Levels:** Successfully treatable concentration levels range from ppb to pure contaminants. Note that highly concentrated or pure contaminants cannot be treated efficiently by conventional methods like incineration or biological approaches. Using DMCR, for instance, pure PCB oils can be converted to biphenyl – a valuable chemical compound that can be sold. Hexachlorocyclohexane can be converted to trichlorobenzene or cyclohexane, which are valuable chemical compounds as well.

**Elimination Directly Inside Complex Matter:** Pollutants are eliminated directly inside a contaminated material, virtually regardless how complex its structure may be and how strongly the pollutants may be bound adsorptively to particular compounds (e.g. clays regarding soils).

**Room Temperature and Short Time:** The process operates at low temperatures, usually room temperature, and in a short time (within minutes up to one hour), reducing energy consumption and reducing the potential for the formation of dioxins.

**Simple and Readily Available Reagents:** The pollutants are attacked and converted by simple and readily available reagents like base metals, e.g. sodium, magnesium, aluminum, zinc, iron or alloys, and some additives (hydrogen donors). Selecting a specific metal and hydrogen donor for treatment can partly depend on the kind of the particular contaminated matrix and contaminant to be treated and/or, especially, on economic aspects.

**Re-use of Scrap Metals/Alloys:** Note that different scrap metals and alloys in various shapes (e.g. small lumps, filings, granules, coarse or fine powders) may be used in this process, because they are always ground down to very small particle sizes leading to a finely divided and, therefore, highly reactive dehalogenating agent. This opens up an interesting alternative to common recycling methods for those metals and alloys. Compared to conventional sodium approaches, sodium metal is not required to be applied as a fine dispersion, but may be utilized shaped like coarse granules, small lumps et cetera as well.

**Defined Degradation Products:** The method can be designed on principle such that only a few well-defined, harmless and/or easier disposable and/or even profitably usable degradation products occur through a well-defined reaction mechanism causing a total dehalogenation of the parent polyhalogenated contaminants.

**Recycling of Contaminated Matter:** Due to the very mild operational conditions, detoxified materials like oils are not destroyed, like when incinerated, so that they can be recycled or used again for other purposes.

**Simple Process Design:** The process uses ball milling as the one single, virtually universally applicable operational key step. Ball milling is a well established and readily available technology worldwide. Only one single step is required to destroy the hazardous compounds completly, there are no complicated steps for removing the reagents or degradation products. It is a major part in other, common chemical dehalogenation processes like the APEG or sodium processes.

**On Site and Off Site Operations:** The technology may be implemented in relatively small plants consisting of vibratory mills as the "core units" and reactors, using only low energy, equipment, personal and reagent costs. It can be set up as a mobile unit and, therefore, may be transported to and operated at the contaminated site directly.

**Scale/Throughput:** In principle, plants can be designed for treating 10 kilograms/hr to several tons of contaminated matter per hour. For high throughputs, off site treating is strongly recommended. Note that pilot scale devices are being available at the moment only, because full scale operating plants are still under development. Therefore, especially regarding upgrading for particular solutions, we are still looking for co-operation partners.

**No Particular Preprocessing:** By comparison with other detoxification technologies particular preprocessing like extracting or washing of a contaminated solid matrix are unnecessary from the start using this technology.

**Combination with Other Processes:** The DMCR process can be combined with or may be used in addition to other common remediation processes like soil washing or biological degradation. It may be combined with remediation processes for other contaminants, too, e.g. asbestos. Asbestos may be ground down to harmless non-crystalline matter and polyhalogenated pollutants may be dehalogenated in one single step simultaneously.

**Current Technology Status:** The features described before base upon feasibility and pilot scale projects covering PCB and DDT degradation in soils, PCB degradation in transformer oils and destruction of PCBs and polyhalogenated pollutants in used lubricating oils. Concerning specific projects, scaling-up is currently under way. Pertaining to particular areas of application we are still looking for co-operation partners worldwide.

We are working on several interesting problems, e.g.:

- Detoxification and recycling of PCB contaminated transformer oils
- Decontamination of used lubricating oils polluted by PCBs and other polyhalogenated matter
- Contaminated soils
- Filter dusts, slags and ashes contaminated by dioxins and PCB
- Construction materials contaminated by PCBs
- Decontamination of PCB contaminated electrical devices, dismantling and recycling of valuable compounds

**Rentability:** On the base of data obtained so far, the technology is expected to be much more affordable than conventional chemical methods for reductive dehalogenation, e.g. dehalogenation by sodium dispersion. Note that rentability will partly depend on the kind of the particular problem to be solved, the legislative conditions and constraints as well as the economic parameters (e.g. availibility/cost for reagents, energy) prevailing in the specific country/region of the world, where the problem has to be solved. DMCR can be competitive with other conventional remediation technologies, especially when contaminated materials can be recycled or highly concentrated contaminants can be converted to profitably usable products, e.g. PCB contaminated transformer or capacitor oils and pure HCH isomers, resp.

## Wide Range of Areas of Application

### Petrochemical Industry, Refineries

Used lubricating oils containing polyhalogenated pollutants can be detoxified at room temperature and can be recycled after the dehalogenation step. So far, most of them have been high-temperature incinerated causing an considerable increase of the carbon dioxide content of the atmosphere.

**Electrical Industry** (recycling of transformers, condensers, trash from disassembling electronic devices)

Decontamination and recycling of PCB transformer and condenser oils.

### Energy and Electricity Supply Companies

Contaminated materials coming out of production plants or of leakages or contaminated soil around those facilities, e.g. PCB contaminated transformer oils or PCB contaminated soils around transformer stations, can be treated successfully.

### Industrial Wastes

Waste from production of hexachlorocyclohexane (other HCH-isomers than γ-HCH, Lindane) can dehalogenated to the profitably usable solvent cyclohexane. Thus, in addition to the detoxification profit can be made.

Soils contaminated by HCH can be detoxified entirely using the same approach, which has to be modified slightly only.

### Residence Areas, Municipal Buildings

PCBs have been used in huge amounts as softeners for concrete adhesives worldwide and, therefore, jeopardize public health in many countries. Contaminated construction materials like concrete can be detoxified and recycled.

### Recycling Plants, Scrap Metal Recycling Plants

Because of the use of base metals as dehalogenating agents also scrap metals can be applied in the process. This opens up the interesting opportunity to combine usefully two problems to each other and solve them in one single, universal step: On one hand, very toxic and hazardous pollutants are destroyed and contaminated materials are detoxified, on the other hand scrap metals, which perform the dehalogenation, are re-used.

**Garbage Incineration Plants, Hazardous Waste Incineration Facilities**

Ashes and filter dusts contaminated by dioxins and related toxic compounds can be treated in order to destroy the contaminants.

**Wood and Timber Industry**

Wood preservatives consisting of or containing pentachlorphenol (PCP) or other polyhalogenated compounds or contaminated premises, e.g. soils, can be decontaminated.

**Agriculture**

Contaminated sludges and areas with pesticides or residues of pesticides may be decontaminated.

**Military**

Toxic chemical agents and combat gases containing halogen like lost, lewisite, adamsite etc. may be destroyed at room temperature prinicipally.

**Appendix #1:** Analytical results of treatment of PCB contaminated soils.

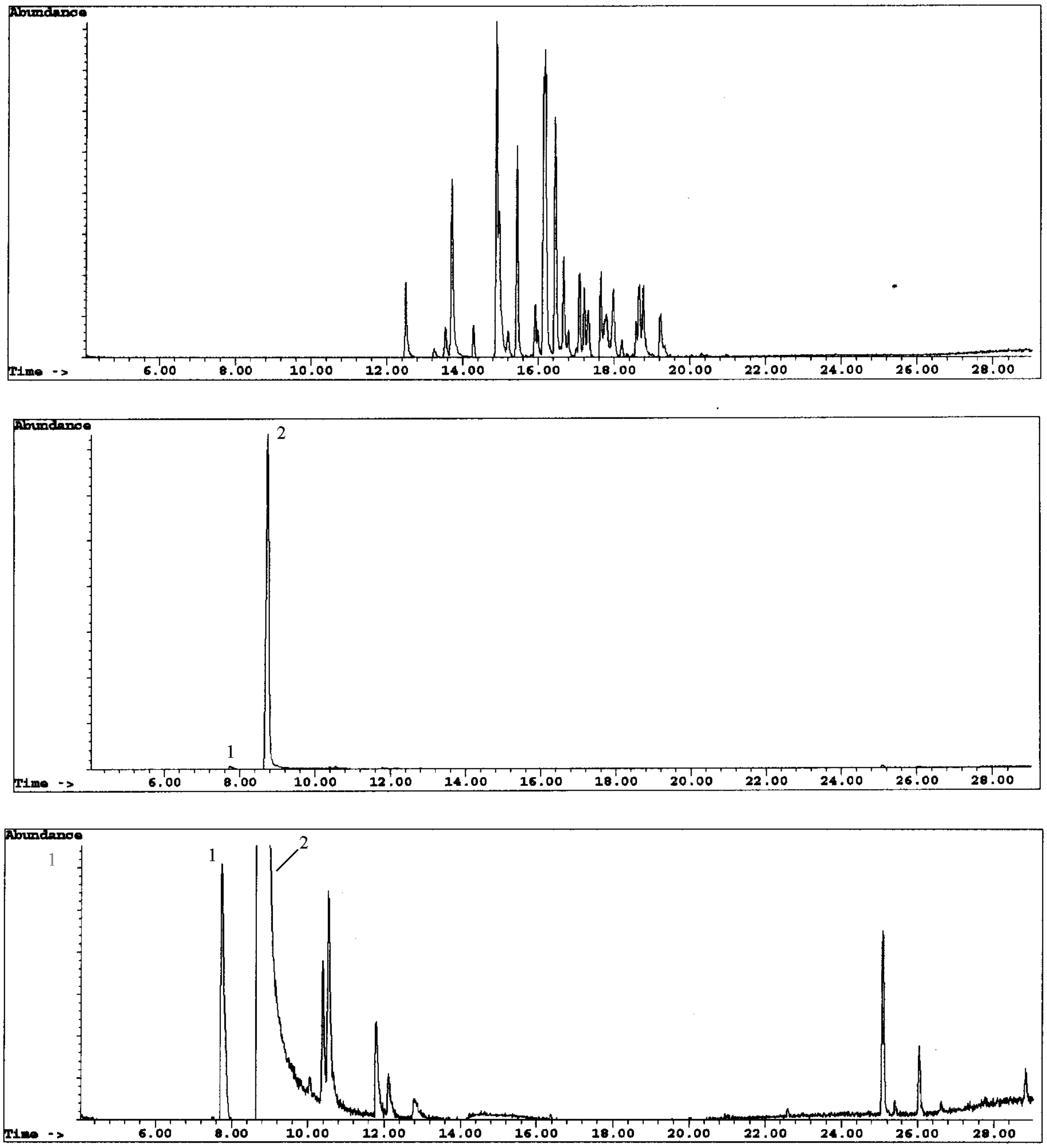



**Fig. 1.** Complete dehalogenation of 5000 ppm PCB (Chlophen A 30) in soil by magnesium at room temperature. MSD-GC prior to (first image at the top) and after milling (second image at the middle = normal resolution, third image at the bottom = high resolution of second image).

1 = phenylcyclohexane, 2 = biphenyl, minor peaks at higher retention times represent completly dehalogenated compounds. Method: external standard.

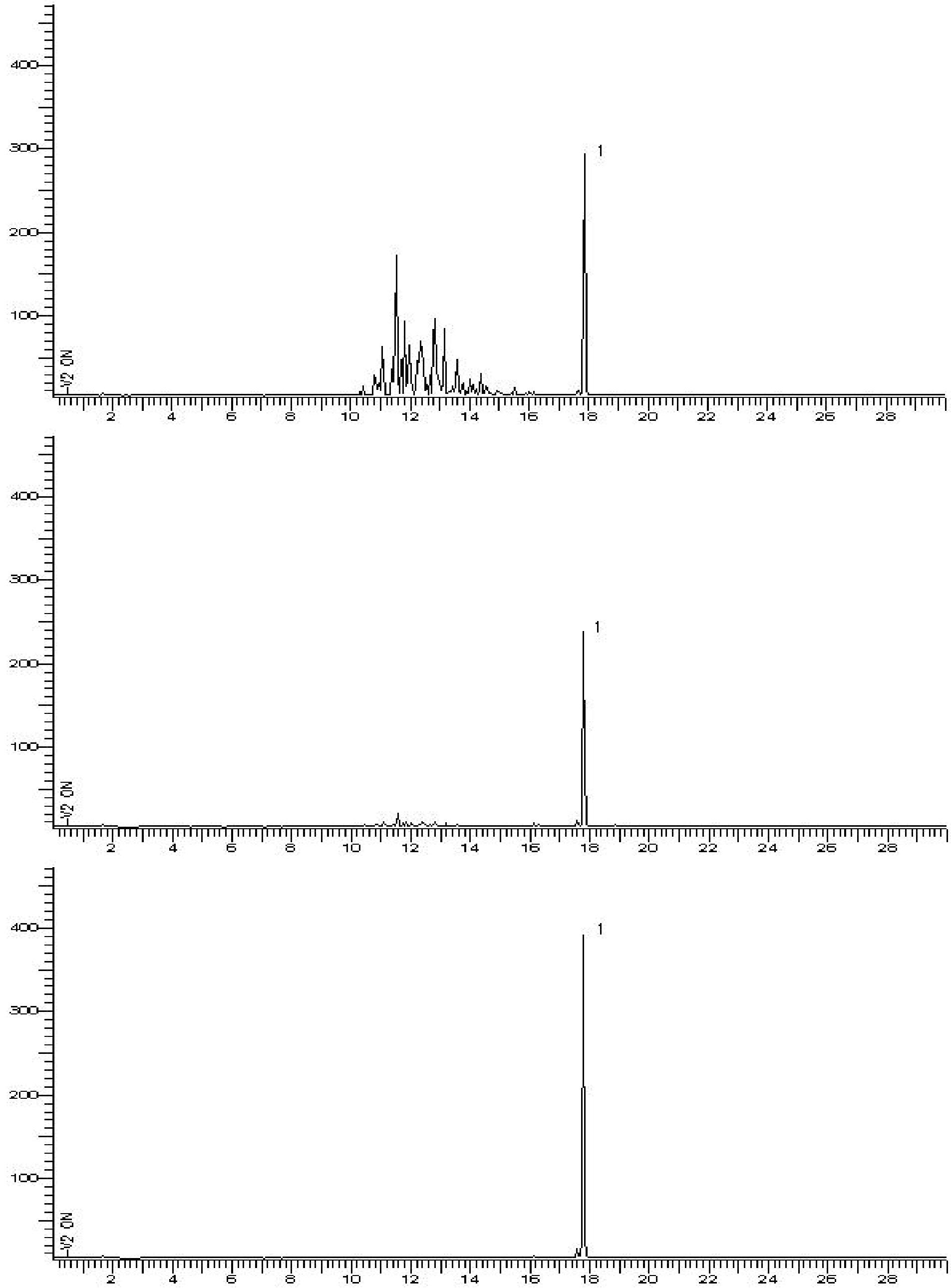



**Fig. 2.** ECD-GC of a PCB contaminated soil (250 ppm PCB) prior to dechlorination treatment applying sodium lumps at room temperature (at the top), after 92 % dechlorination (at the middle) and after more than 99.9 % dechlorination (at the bottom).

1 = decachlorobiphenyl (internal standard, contains 4 minor impurities).

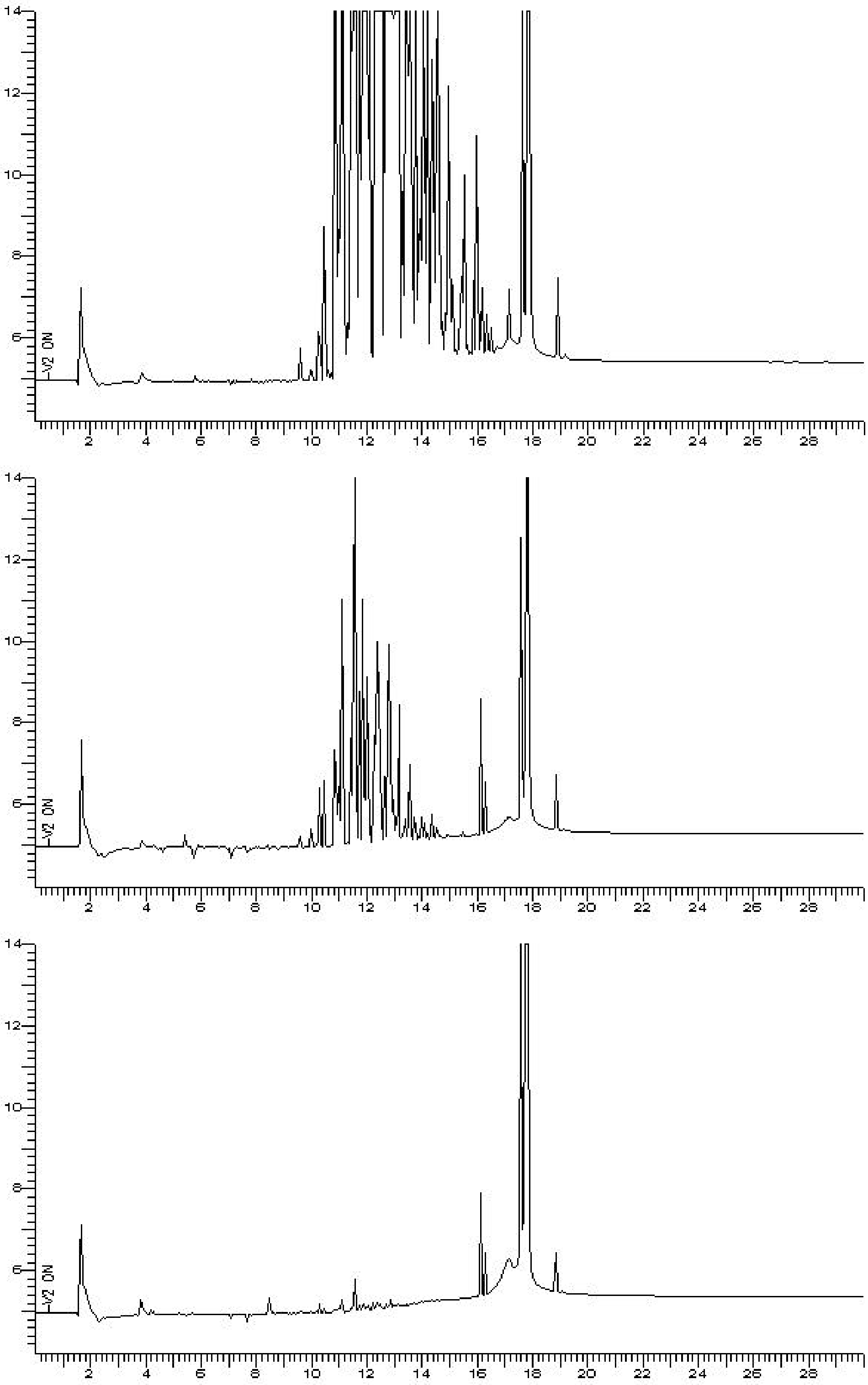
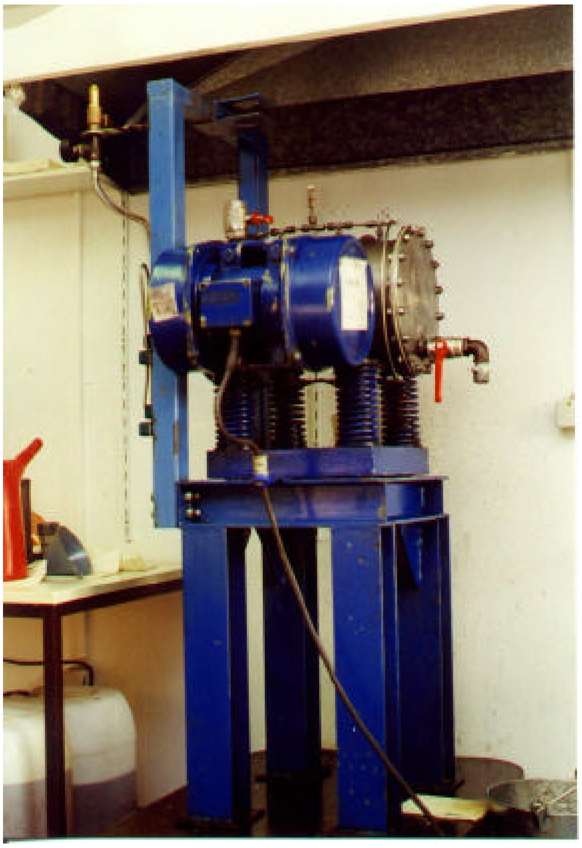
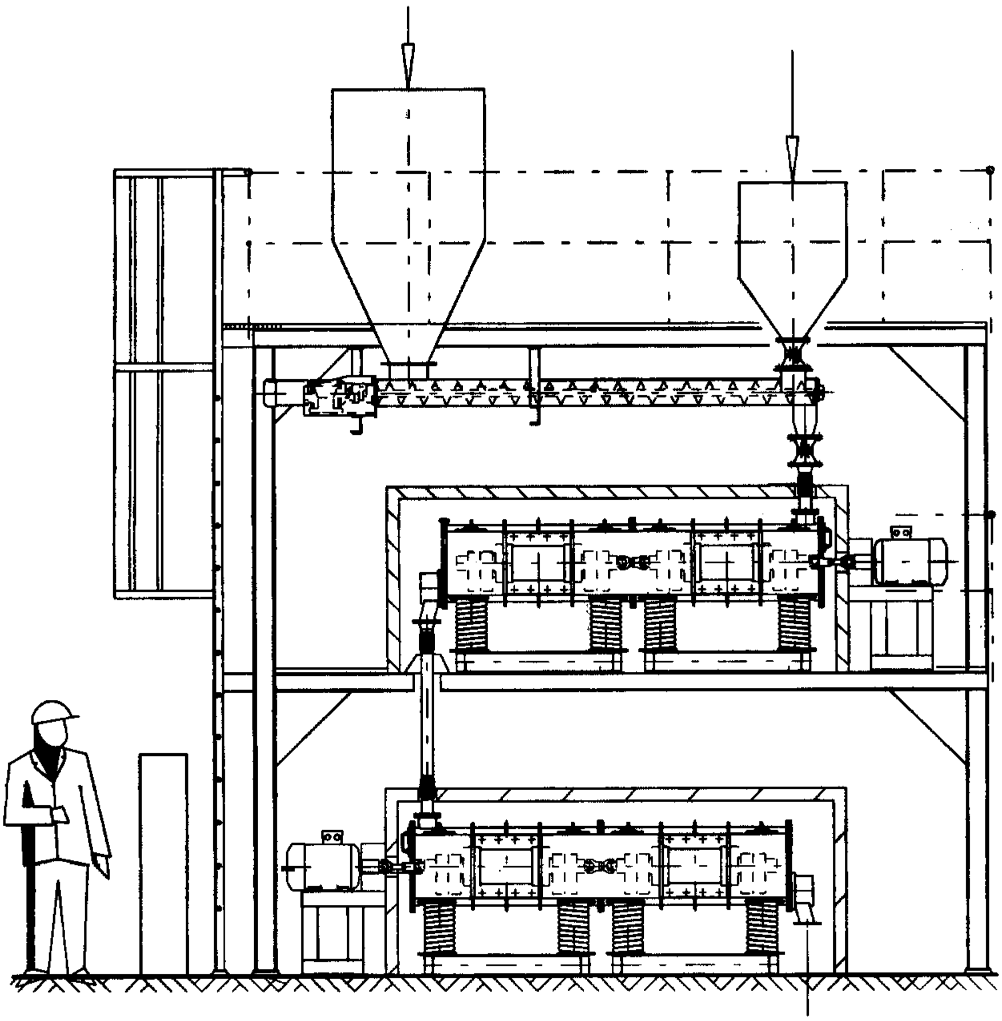



**Fig. 3.** High resolutions of GCs shown by Fig. 2.

**Appendix #2:** Photographs of a vibratory mill designed as a pilot device for the treatment of PCB contaminated transformer oils (batch process).



**Appendix #3:** Outline of an off site vibratory mill plant capable of treating solid materials principally (throughput appr. up to 1 ton per hour). Courtesy by Siebtechnik GmbH, Muelheim/Ruhr, Germany.



**Appendix #4:**

# Key Features of the *DMCR TECHNOLOGY*

**DESTRUCTION OF POLYHALOGENATED POLLUTANTS IN COMPLEX MATERIALS**

**INSIDE A VIBRATORY MILL**
**IN ONE SINGLE UNIVERSAL STEP BY:**

***CONDITIONING***
***+ MIXING***
***+ DISPERSING***
***+ REACTING (Dehalogenation)***

**AT ROOM TEMPERATURE AND IN A SHORT TIME**

**Dehalogenation Reaction Mechanism**
*(schematic, simplified, not stoichiometric;*
*PCBs are dehalogenated by magnesium as one example):*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $R{-}Cl$ | + | Mg | + | "$H$" | $\Rightarrow$ | $R{-}H$ | + | $MgCl_2$ |
| *(PCB)* | | *Base Metal (Magnesium)* | | *Hydrogen-Donor* | | *Biphenyl* | | *Salt* |
| **TOXIC** | | | | | $\Rightarrow$ | **HARMLESS** | | |

# Economic and Ecologically Favorable Destruction of Polyhalogenated Pollutants in Complex Materials Applying the DMCR-Technology

***(DMCR = Dehalogenation by Mechanochemical Reaction)***

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By applying ball milling to contaminated materials and adding reagents (base metal, hydrogen donor), polyhalogenated pollutants like HCH, DDT, PCB, dioxin, PCP are reductively dehalogenated directly inside the contaminated matrix – virtually regardless of their state. A ball mill is used as a highly effective mixing device and a mechanochemical reactor in one single operation step simultaneously: The contaminated material is conditioned optimally, it is effectively mixed with the dehalogenation reagents, and the metal is dispersed and therefore mechanically activated for the dehalogenation of the pollutants.

**Features and Highlights of DMCR:**

- **Complete degradation of the pollutants directly inside the contaminated matrix at room temperature, ambient pressure and in a short time by reductive dehalogenation applying base metals (e.g. Mg, Na) plus an appropriate hydrogen donor.**
- **Well-defined, harmless and/or easier disposable and/or even profitably usable degradation products (e.g. PCBs yield biphenyl).**
- **Destruction of polyhalogenated pollutants both in liquid and solid-liquid and solid contaminated materials (e.g. mineral oils, sludges, soils) and of virtually pure toxic compounds or mixtures of it. Therefore high number of areas of application.**
- **Implementation on site or off site.**
- **No particular preprocessing.**
- **Economic/ecological benefits: Low energy costs, toxic compounds can be converted to usable products, reuse of scrap metals, detoxified materials can be recycled (e.g. transformer oils), no harmful emissions to the environment.**
- **Status: Feasibility studies and pilot scale projects, currently scaling up.**

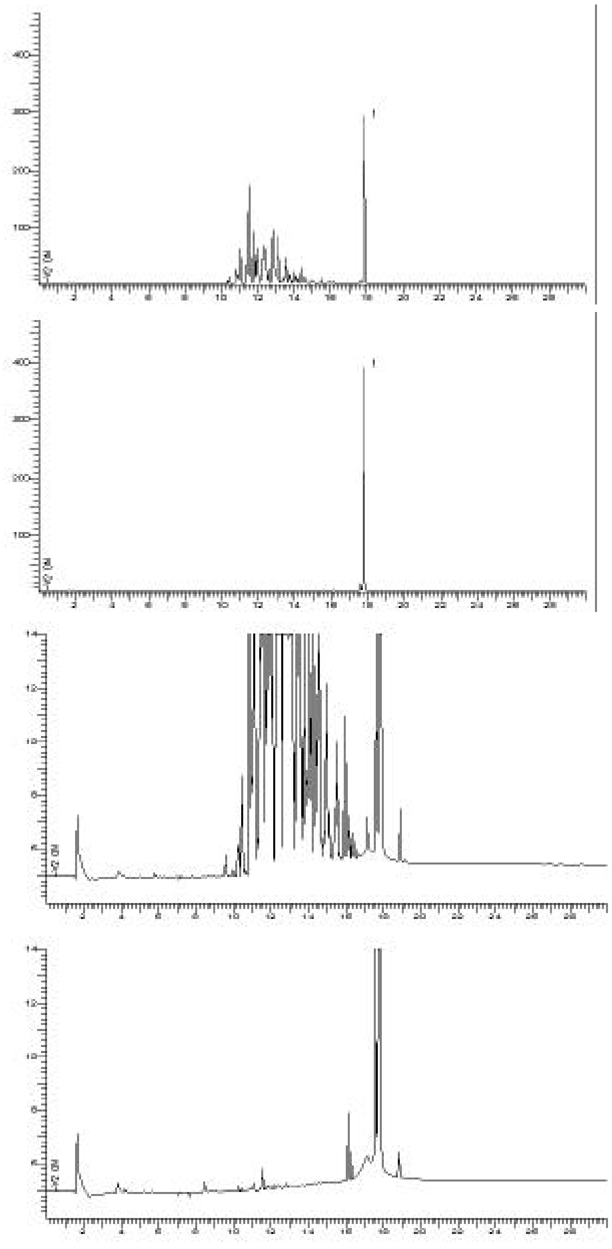

**Fig.** Gaschromatograms (detector: ECD) of a PCB contaminated soil (appr. 250 ppm PCB) ***prior*** to (at the top) and ***after*** PCB dechlorination (> 99.9 %, second image) directly inside the soil utilizing a vibratory mill and appropriate reagents at room temperature. High resolutions of these GCs displayed by third and fourth image, resp.

1 = decachlorobiphenyl (internal standard, contains 4 minor impurities).

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