Economic and ecologically favourable destruction of polyhalogenated pollutants using the DMCR* - technology

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

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Introduction

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

Description of the DCMR technology

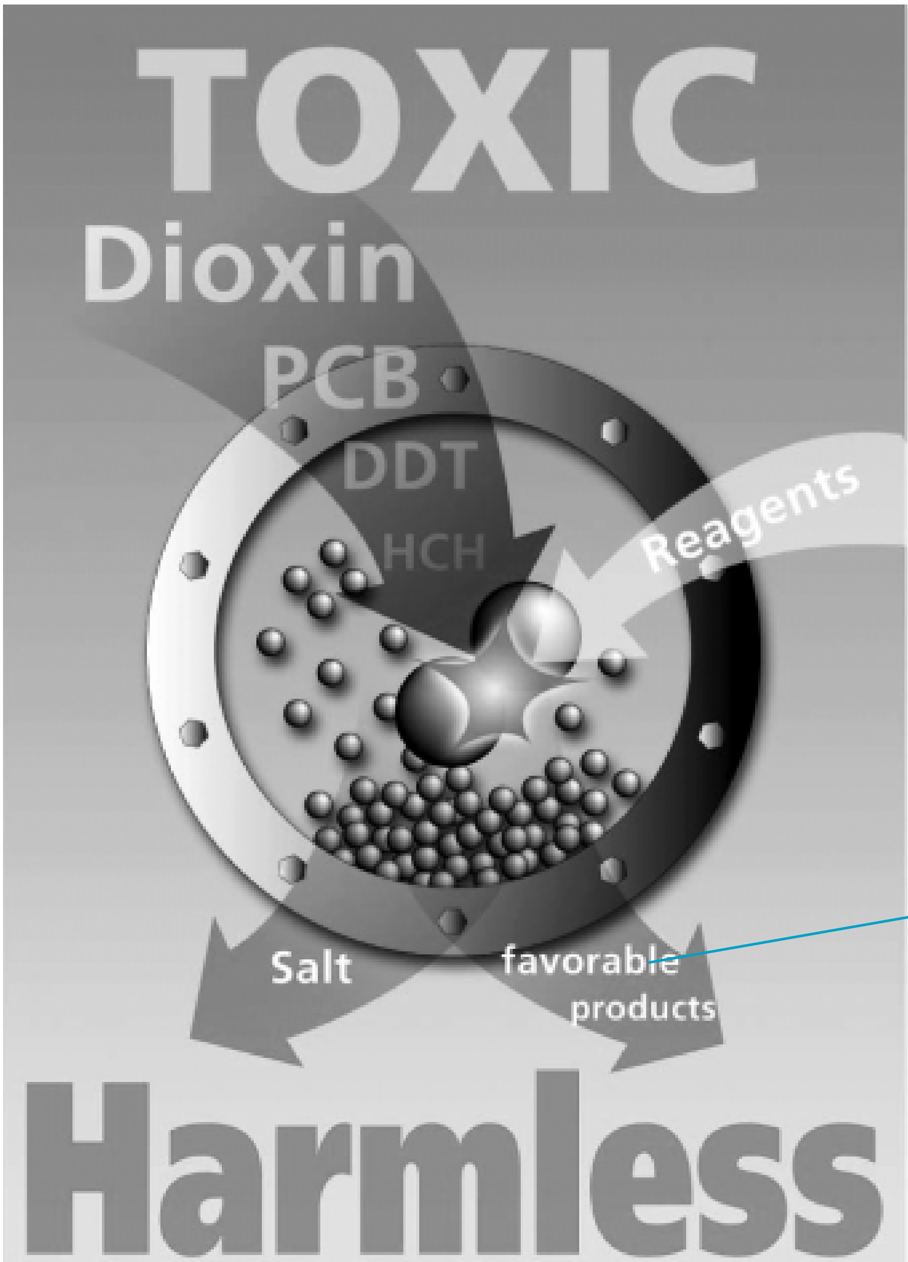

Figure 1. The fundamental and innovative principle of the DMCR technology at a glance.

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 manage-ment and recycling or reuse of particular contaminated materials worldwide.

By utilising base metals like magnesium or sodium as dehalogenation reagents in a specific combination with applying mechanochemical conditions using ball mills, these toxic substances are very quickly and efficiently eliminated inside a contaminated complex material at room temperature. The process works virtually regardless how complex the structure of contaminated materials may be. No matter how strongly the contaminants may be bound to particular compounds (e.g. clay fractions or humic acids in soil), the process works.

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. The organic bound halogen, as the source of the high toxicity of polyhalogenated hydrocarbons, is removed from the molecule entirely and transformed into a harmless inorganic chloride.

The technology has been applied successfully for the detoxification of contaminated soils and contaminated oils in co-operation with European companies during feasibility/treatability studies and small pilot scale projects implemented over the last years. A one-time investment gives benefits with an immediate solution for a broad spectrum of contamination problems and expected low operational and maintenance costs.

R-*Cl*	+	Mg	+	*"H"*	⇒	R-*H*	+	MgCl_2
(PCB)		*Base Metal (Magnesium)*		*Hydrogen-Donor*		*Biphenyl*		*Salt*
		TOXIC			⇒	HARMLESS		

Figure 2 and 3. Overview of the DMCR process characterisation: One example outlined (simple scheme) for dehalogenation using DMCR: PCBs are dehalogenated by magnesium metal in the presence of an appropriate hydrogen donor (alcohols, polyethers and so forth) yielding harmless biphenyl and magnesium chloride.

Process characterisation

Treatment of contaminated materials or pure toxic compounds in vibratory mills takes place in one single operation step. These mills function, simultaneously as highly effective mixing devices and reactors. At the same time, organic bound chlorine is stripped off by the added base metal, which serves as the actual dehalogenation reagent, and released as a harmless inorganic chloride. It is exchanged by hydrogen stemming from the added hydrogen donor to be shown in Figure 3.

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

The main idea behind this technology is the use of the multifunctional capabilities of vibratory mills. They serve not only as mixing devices (due to their outstanding mechanical capabilities), but also as highly effective chemical reactors for the destruction of 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. The milling process creates optimal conditions for a permanent and intimate contact between contaminants and reagents by simultaneously:

- breaking down particular structures down to the molecular level and
- extremely efficient mixing with the added dehalogenating agents.

Additionally, 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 characterised 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. Pure HCH production residues (e.g. to be found at "Grube Antonie", Bitterfeld, Germany, total amount approx. 100,000 tonnes) can be converted to trichlorobenzene or cyclohexane being 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, aluminium, 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 utilised shaped like coarse granules, small lumps etcetera 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 completely, 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 tonnes 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 pre-processing

By comparison with other detoxification technologies particular preprocessing like extracting or washing of a contaminated solid matrix is not necessary if this technology is used right from the start.

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 small pilot scale projects covering PCB, HCH and DDT degradation in soils, PCB degradation in transformer oils and destruction of PCBs and polyhalogenated pollutants in used lubricating oils. Some results of the treatment of PCB contaminated soils are shown in Figure 4. Concerning specific projects, scaling-up is currently under way. Pertaining to particular areas of application potential co-operation partners are still searched worldwide.

Wide range of areas of application

Petrochemical industry, refineries (e.g. used lubricating oils containing polyhalogenated pollutants), electrical industry (recycling of transformers, condensers, trash from disassembling electronic devices), energy and electricity supply companies (contaminated materials coming from production plants or from leakages or contaminated soil around those facilities), industrial wastes (waste from production of hexachlorocyclohexane; other HCH-isomers than gamma-HCH, lindane), residential areas, municipal buildings (PCBs as softeners for concrete adhesives), recycling plants, scrap metal recycling plants (interesting opportunity: to combine usefully two problems with eachother 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), waste incineration plants, hazardous waste incineration facilities (ashes and filter dusts contaminated by dioxins and related toxic compounds), wood and timber industry (pentachlorophenol), 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).

Rentability

On the base of data obtained so far, the technology is expected to be considerable cheaper 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. availability/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.

Summary

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 pre-processing.
- Economic/ecological benefits: Low energy costs, toxic compounds can be converted to usable products, re-use 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. Search for competent partners. URL:www.tribochem.com

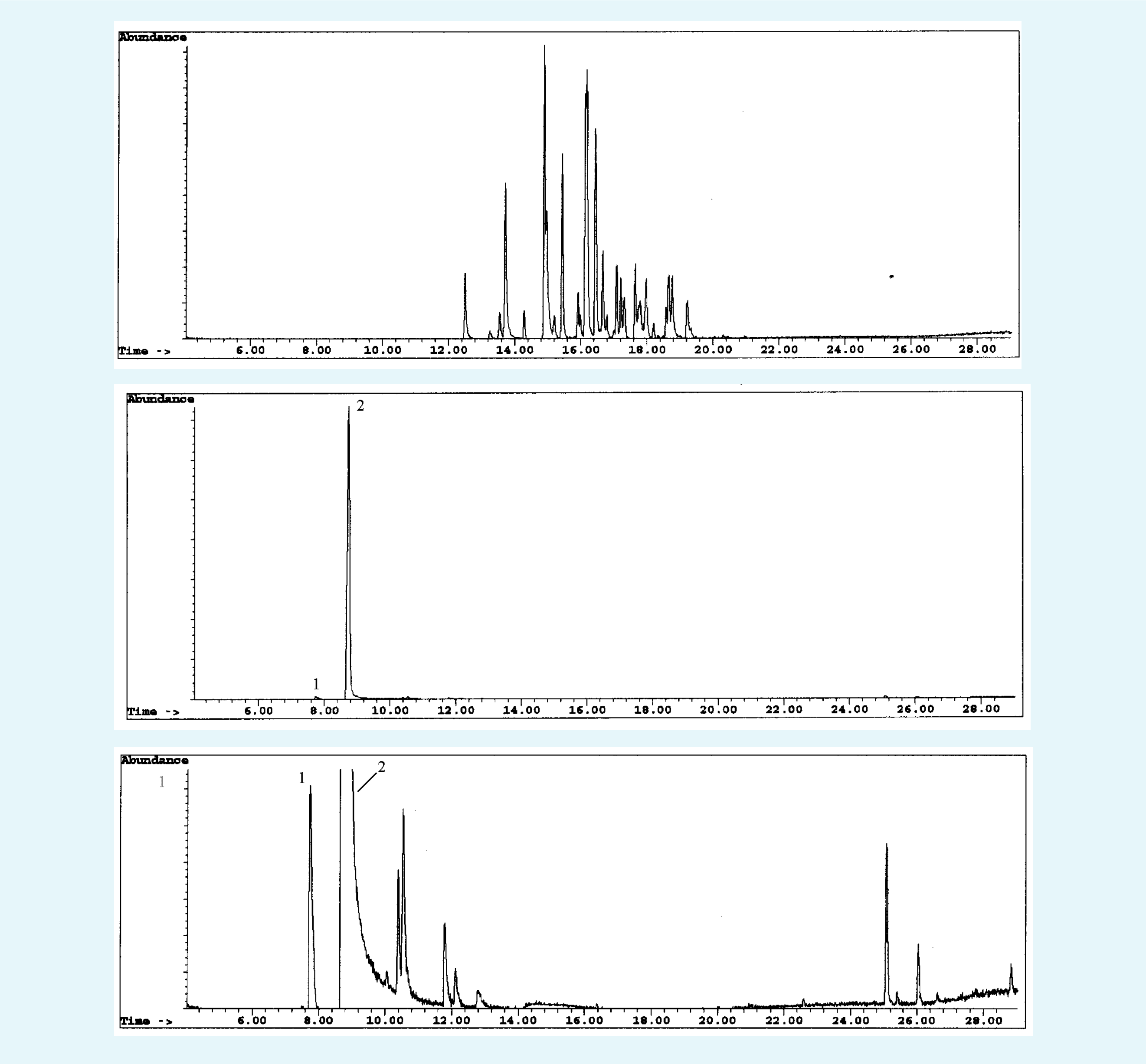

Figure 4. Complete dehalogenation of 5,000 ppm PCB (Chlophen A 30) in soil by magnesium at room temperature. MSD-GC prior to (first image at the top) and after milling (second image at the middle = normal resolution, third image at the bottom = high resolution of second image).

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

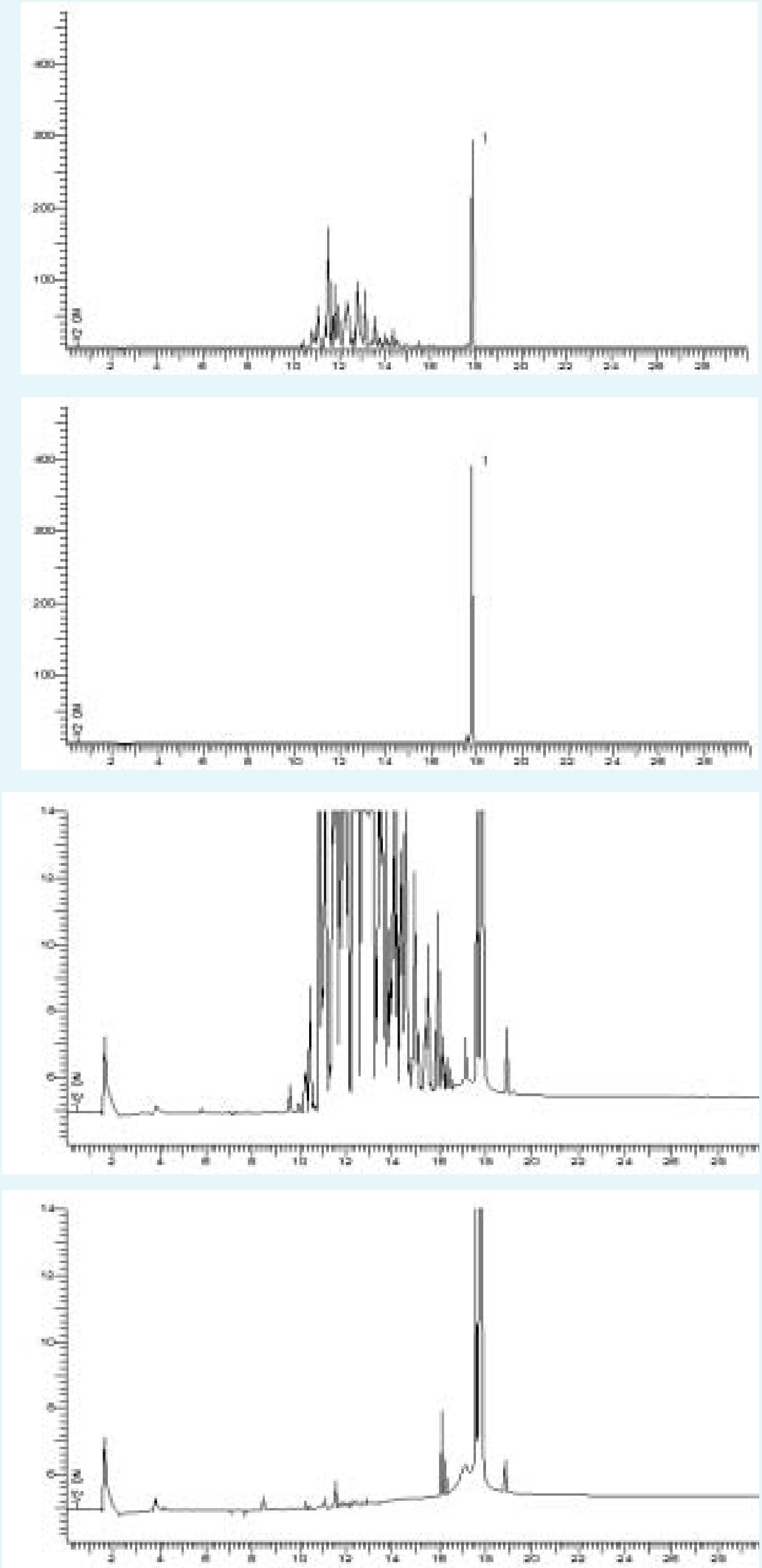

Figure 5. Gaschromatograms (detector: ECD) of a PCB contaminated soil (app. 250 ppm PCB) *prior* to (at the top) and after PCB dechlorination (> 99.9 %, second image) directly inside the soil utilising a vibratory mill and appropriate reagents at room temperature. High resolutions of these GCs displayed by third and fourth image, resp.

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