

Thermal desorption of HCH

Temperature and time effects

M. M. Araújo¹ · S. G. Ignatius¹ · A. O. Oliveira¹ · S. S. Oliveira¹ ·
F. L. Fertonani² · I. A. Paste²

Received: 11 January 2015 / Accepted: 26 May 2015 / Published online: 24 June 2015
© Akadémiai Kiadó, Budapest, Hungary 2015

Abstract To evaluate the effectiveness of the thermal remediation of soil decontamination, samples containing organochlorine insecticide hexachlorocyclohexane (HCH) were subjected to different temperatures depending on the exposure time. For this study, reference material and technical grade HCH were heated separately at $\beta = 1$ and $10\text{ }^{\circ}\text{C min}^{-1}$ in a thermogravimetric analyzer and contaminated soil samples were heated in an oven at different temperatures and heating time. To determine gaseous emissions generated during the heating of HCH isomers, HCH technical grade samples were heated in a closed system (reactor) and sample gases/vapors were collected for qualitative analysis. The results indicate that the contaminants are removed from soil to temperatures considerably lower than the respective boiling point. The thermogravimetric curves have shown that heating to $400\text{ }^{\circ}\text{C}$ HCH results in fusion processes followed by evaporation, and investigating in the oven, the reduction in HCH concentration present in the contaminated soil depends on the temperature and length of heating. Gaseous

emissions detected were from isomers of HCH, chlorine derivatives and benzene compounds. The laboratory tests show that parameters such as temperature, heating time and air flow can influence the thermal decontamination process of the subsoil.

Keywords Pollution · Soils · Hexachlorocyclohexane · Thermal analysis · Thermal decontamination

Introduction

The thermal processes have been used in the last years as an effective alternative to organic soil decontamination and, in some cases, the most economical solution for this purpose [1]. The thermal desorption is a process to thermal remediation of soils and groundwater which physically separates soil contaminants by heating it for a period of time sufficient to volatilize the contaminants for later collection and treatment. It is suitable for remediation of contaminated soil and groundwater with chlorinated solvents [2]. This process differs from incineration, vitrification and pyrolysis, as a physical process, endothermic, which uses lower temperatures (typically up to $600\text{ }^{\circ}\text{C}$). Depending on the temperature, the heating can reduce the viscosity of the contaminant, decrease the surface tension and increase solubility and volatility.

Studies of the thermal analysis in laboratory provide important features to help in the selection of strategies for the remediation of soils by thermal desorption, such as temperature required for operation of the technique, the heating rate of the medium, treatment time, flow rate of gas environment, soil heating behavior, properties of the contaminant and removal rate of the thermal reactions products [3–5].

✉ F. L. Fertonani
fertonan@ibilce.unesp.br

I. A. Paste
pastre@ibilce.unesp.br

¹ Institute for Technological Research of the State of São Paulo - IPT, 532 Professor Almeida Prado Avenue, São Paulo, SP, Brazil

² Department of Chemistry and Environmental Sciences, Institute of Biosciences, Letters and Exact Sciences, IBILCE-Unesp, 2265 Cristóvão Colombo Street, São José do Rio Preto, SP, Brazil

Thermogravimetric analyzers (TG) can be used to evaluate the physical and chemical processes involved in the mass change of a soil sample, which allows determining and controlling the temperature of loss or mass gain, with high sensitivity and can exclude the need for chemical analysis at first approach [5–7].

This paper aims to present thermogravimetric data, which involves HCH volatilization and its HCH derivatives from reference sample materials (RM) and from anthropogenic contaminated soil samples. To access the decontamination process in a large scale, experiments were realized in a closed system (reactor) using different heating temperatures and heating times, and the gases emanated from the soil sample were collected and analyzed by gas chromatography.

This insecticide (HCH technical degree) and, despite being banned in many countries, its isomers, alpha(α)-, beta(β)-, gamma(γ)- and delta(δ)-HCH have been found through investigations in soil and groundwater because they are persistent in the environment. In Brazil, there are several lands contaminated with HCH, e.g., the case of “Cidade dos Meninos (Rio de Janeiro/Brazil)”, where wastes, part of the production of a technical grade HCH, were abandoned before the factory be disabled in 1955 [8, 9].

Experimental

Materials

Reference material (designated as RM) of the isomers alpha (97.5 % purity), beta (97.5 % purity), gamma (98.6 % purity), delta-HCH (98.5 % purity), technical grade HCH and anthropogenic contaminated soils from the contaminated land with HCH localized in Santo André, São Paulo State, Brazil, was used in laboratory tests.

Quantitative analysis by GC (Table 1) of the technical grade HCH (t-g HCH) showed that, in accordance with the literature [4, 8], the content of the HCH isomers in t-g HCH was only about 7 % by mass of the composition, and the rest of the composition is formed by benzene and chlorobenzene.

Qualitative analysis of the t-g HCH was performed by X-ray diffractometry—XRD (Phillips mark, PW2404 model), indicating the presence of talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$], quartz (SiO_2), illite [$(\text{K}, \text{H}_3\text{O}) \text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$], kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] and goethite [$\text{Fe}(\text{OH})$], and fluorescence X-ray spectroscopy (Panalytical mark, X'Pert PRO MPD model) detected Si, Al, along with Mg, Cl, K, Fe, Ti and traces of the Ba, Mn, Zr, Na, S, Ca, P, Cu, Rb, Y and Ni. Some of the elements like H, He, Li, Be, B, C, N and O could not be detected in fluorescence X-ray spectroscopy analysis. The remaining, that is, 93 % by mass, consists of clay minerals identified by testing the X-ray

diffraction. A particle size analysis by sedimentation [10] of the technical grade HCH revealed that the product is rated granulometrically as “silt”.

The contaminated soil from the land located in Santo André, São Paulo, Brazil, containing the isomers α -, β -, γ - and δ -HCH, with initial concentrations and characteristics is given in Table 1. The grain size of the contaminated soil samples tested showed to be sand silt clay with boulders.

Chromatographic analyses

The gas chromatography (GC) experiments were performed on a Shimadzu GC-2010 Plus coupled with an electron capture detector (ECD). A methyl 5 % phenyl polysiloxane capillary column (30 m \times 0.53 mm i.d. \times 1.50 μm film thickness) was used. The injector port was maintained at 320 °C and with a split ratio of 1:5. The column temperature is 150 °C and then increased at a rate of 5 °C min^{-1} to 300 °C. Nitrogen was used as carrier gas with a flow rate of 5.23 mL min^{-1} and a linear velocity of about 0.35 m s^{-1} . Operating temperature of the ECD was 330 °C. Quantification was accomplished by the calibration factor for each component of interest, relative to the internal standard. All values represent the average of duplicate samples.

Thermogravimetric analysis

Thermogravimetric analyzes were carried in two steps: (1a) RM samples were subjected to TG/DTG and DSC analysis in the Chemical Processes and Particle Technology Laboratory of the Institute for Technological Research, IPT, São Paulo-Brazil, using a METTLER operated under a carrier gas flow of nitrogen of 50 mL min^{-1} and a heating rate of $\beta = 1$ °C min^{-1} , initial temperature of 20 °C and final temperature of 340 °C. The initial sample mass of about (6.0 \pm 1.2) mg were placed in an alumina crucible, approximately hemispherical; (1b) TG and DSC curves α -, β -, γ -, δ -HCH isomers (RM) and t-g HCH were obtained from the Fundamental Chemistry Department of Chemistry Institute of the University of São Paulo, USP, São Paulo-SP, Brazil, using a Netzsch STA 409 PC/PG coupled to a mass spectrometer (QMS 403C AEOLOS) operated under a carrier gas flow of nitrogen (t-g HCH) and synthetic air (RM) of 50 mL min^{-1} and a heating rate of $\beta = 10$ °C min^{-1} , initial temperature of 30 °C and final temperature of 550 °C. The initial samples of about (10 \pm 5) mg were placed in alumina crucibles, approximately hemispherical.

Treatability tests bench scale

Treatability tests bench scale were devised to determine the temperature and time required for removal of contaminants

Table 1 Characteristics of the materials used in the tests

Initial contamination level	Contaminated soil (HCH/ $\mu\text{g g}^{-1}$)					Technical grade (HCH/ mg g^{-1})					Soil support utilized in batch thermal reactor
	α	β	γ	δ	Σ HCH	α	β	γ	δ	Σ HCH	
	65.73	25.50	0.96	4.20	96.40	26	15	16	14	71	
Minerals	Mass (% of the dry mineral fraction)										
Clay/<2 μm	23					6					–
Silt/2–53 μm	17					86					–
Sand fine/53–250 μm	17					7.5					–
Sand media/250–500 μm	16					0.4					–
Sand coarse/500 μm –2 mm	12					0.1					–
Boulders/>2 mm	15					0					–
Water content/%	18.11					3					18.53
Dry soil mass/g	2.667					–					15.34
Mass of water/g	4.830					–					28.41
Volume of the compressed soil/ m^3	0.01					–					982.37
Apparent dry specific weight/ kN m^{-3}	2.442					–					1.562

Performed according to the Brazilian Association of Technical Standards NBR 7181 [10]

from soil samples from prospective remediation sites and t-g HCH. Several kinds of tests were considered, including a heating/convection test with flow through of air or water vapor; however, a simple heating test with the soil sample in a ceramic crucible has proven adequate for design of field projects [4].

Crucibles of porcelain and ceramic containing samples (about 10 g) of contaminated soil were inserted into oven and stove and subjected to different temperature values (120, 200, 250, 300 and 350 °C) and different heating times (0.1; 0.5; 1; 2; 6; 24; 48; 96; 192; 480 h).

The treatability tests were carried out by placing soil samples in uncovered crucibles and heating them in a muffle oven at different temperatures from 120 to 350 °C. The treatment temperatures were chosen based on the boiling points of HCH isomers. The temperatures were increased over a period of several time and then held constant at the desired treatment temperature from 360 to 480 h.

A system of vapor extraction was coupled in the oven. The gaseous emissions generated during heating in a muffle oven and during this test were held in a vapor treatment system installed in equipment used for heating before gaseous emission being released into the atmosphere. This system was composed of scrubber with NaOH (10 mol m^{-3}) and activated carbon (300 g); the organic content fixed in these materials was analyzed by GC after treatability tests.

Pre- and post-treatment analyses were performed to determine the initial and final concentrations of contaminants after treatability test bench scale by GC technique.

Batch thermal reactor

The thermal reactor system (Fig. 1) was designed as a research tool in intermediate conditions between the bench tests and the technical application of thermal subsurface decontamination technique in scale field. This equipment was used to evaluate the heating time in soil on a larger scale and influence of the gas extraction system (so it was used as support and contaminated soil).

The support soil has similarity to the granulometric characteristics of contaminated soil: sandy clay silt with boulders. The support soil was collected on the campus of IPT on the surface without interference of the contaminant HCH.

Batch thermal reactor consists of a concrete reactor to accommodate the contaminated compacted soil; electrical resistance; rock wool on the surface; temperature controllers; controlling power; vacuum pump; condenser; scrubber; zeolite and activated carbon filters; and system for data acquisition.

The reactor is a cylinder (internal diameter 1.20 m and internal height 0.95 m) made of concrete ring, in which the support soil samples were initially placed. Compaction of support soil layers in the batch thermal reactor was performed as follows: The support soil was then compressed to 92 % of the maximum dry density (ρd_{max}) and moisture content of 18 % (rounding the optimum moisture content obtained 17.83 %). Such parameters were defined based on the results of mini compression tests.

Compression was performed in 10 layers of 0.085 m of support soil. Therefore, the water mass (m_w) to be added for each layer considering final moisture (w) to obtain

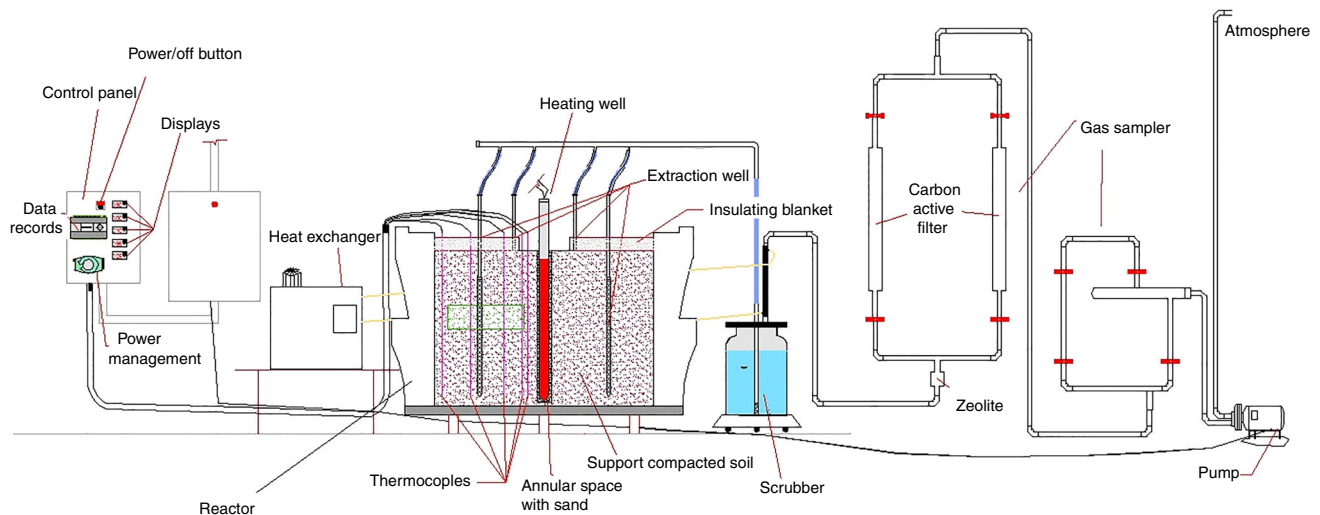


Fig. 1 Batch thermal reactor

$w = 19\%$ has been calculated, resulting $m_w = 29,155.00$ g. Compression of the layers would be made simultaneously to the homogenization, to avoid loss of moisture during compression.

During the homogenization process of the layers, a control moisture removing layer of three capsules of each sample with part 1/6 (30,434.00 g of support soil) was made, totaling 10 samples per layer. The results are summarized in Table 1.

For the test with contaminated soil, a portion of this contaminated soil was inserted in the batch thermal reactor. The insertion occurred after excavation of the support soil (Fig. 2). The excavation was made to a depth of 0.43 m from the top and 0.20×0.42 m of area.

To compress the contaminated soil portion (28,000 g) inserted into the batch thermal reactor in the hygroscopic moisture (5%, estimated value), 3500 g of water was added, which therefore leads to contaminated soil mass to the total amount of 31,500 g with content of approximately 18% moisture. Table 1 shows the amount of materials used compacting contaminated soil.

The heating well consists of a heating electrical resistance with 4500 W of power and 220 V in a casing consisting of stainless steel with a diameter of 0.0508 m and total length and usable length (heated section) 1 and 0.6 m, respectively. The heating well is installed in the center of the reactor with the support soil and subsequently with a portion of contaminated soil compacted.

The hole to install the heating well of the compacted soil in the concrete ring was handmade with an auger 0.0762 m diameter. The annular space between the heating well and the hole was filled with sand (dry).

The thermal insulator was placed on the surface of the compacted soil to minimize heat loss to the external environment. This insulator was made with blanket of rock

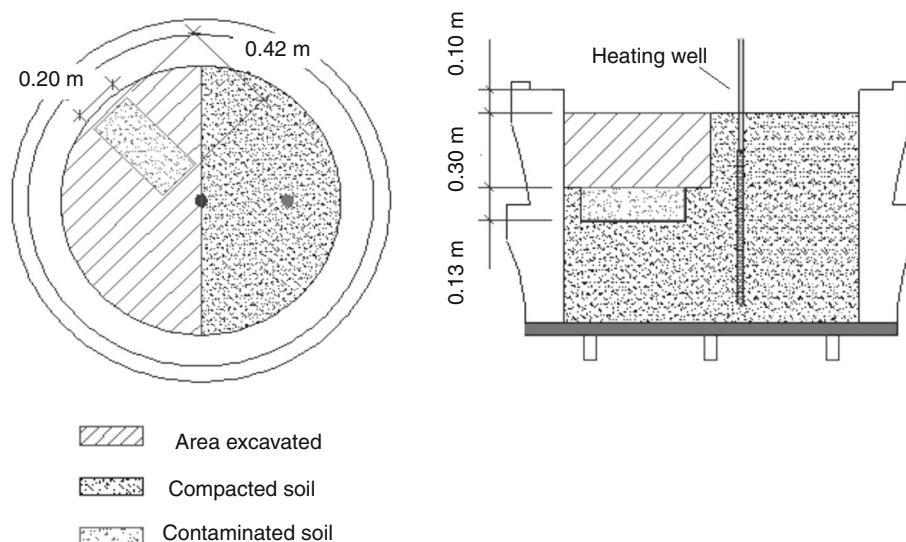
wool aluminized thickness 0.05 m, density 0.032 g cm^{-3} to be able to tolerate, without damage, and temperatures between 700 and 800 °C.

For the temperatures recording, were used type K thermocouples that connected to a data logger, whose function was to indicate the temperatures at each point of the end of the thermocouple rod, for temperature control in the reactor. The K-type thermocouple works in the temperature range from -200 to 1250 °C and has a rod 0.7 m long with a compensating cable that connects the shaft to the controller. The rod thermocouple was made of stainless steel with a diameter of 0.004 m, wall thickness of 0.001 m and length of 1 m. The five thermocouples were arranged in the experiments in the reactor according to the distance of thermocouple heating well.

A system for the extraction and treatment of emissions was used to filter the gaseous emissions produced during the thermal desorption process and prevent them from being released directly into the atmosphere. The system contained a radial compressor (model CRE-03, built in cast aluminum, driven by an electric motor 2.68 mW TEFC) that promoted the vacuum required for the extraction. The gas was inserted straight into the condenser, and after passing through a scrubber (0.25 mol m^{-3} of NaOH), a zeolite filter and an activated carbon filter were dispensed into the atmosphere.

The extraction gas/vapor wells were also manufactured with stainless steel tubes with length of 1 m, with slotted tube length of 0.60 m, made pre-filter with a particle size between 0.0015 and 0.003 m and stainless steel screen. The extraction well was installed in holes made with auger diameter slightly larger than the wells. Due to the larger diameter of the hole, the wells had a small gap after installation, filled with fine sand and bentonite along the slotted tube length to the top of the contaminated soil compacted.

Fig. 2 Insertion of contaminated soil sample. **a** Batch thermal reactor *top view* showing the excavated area for contaminated soil insertion, **b** profile side of the batch thermal reactor



Emissions analysis

A system for collection of vapors (Fig. 3) was used in laboratory testing with sample of t-g HCH to assess exhaust emissions generated during heating. The apparatus on a laboratory scale consisted of a cylindrical stainless steel reactor (autoclave), useful volume of 1 m³.

One sample 100 g of t-g HCH was placed in the central compartment of the reactor (see Figs. 1, 2) and subjected to gradual heating. One thermocouple measures the temperature directly within sample. A carrier gas (air) passed through the autoclave with a flow 100 mL min⁻¹ was controlled by a flowmeter. The sample was heated at 20 °C from room temperature to 500 °C at 101.325 kPa. The gas outlet was located at the top of the autoclave. Pollutants, carried by airflow, were trapped in heat exchange followed by a gas scrubber with NaOH solution (1×10^3 mol m⁻³) before being released into the atmosphere. Most of the effluent was condensed in the traps.

The result of the chromatographic analysis of volatile organic compounds and semi-volatile compounds present in the technical HCH before heating showed the presence of benzene and chlorobenzene, besides HCH isomers. Benzene is used in the production of HCH with chlorine, and its presence in the sample can reveal that not all of the benzene used in the production of technical grade HCH is consumed. The benzene in the presence of chlorobenzene can produce chlorine gas, which may explain the presence of chlorobenzene in the sample before heating.

The gases and vapors were collected, after different times and heating temperatures of the t-g HCH sample, in appropriate plastic bags sampling (“bags”), numbered from 1 to 9, as shown in Table 4.

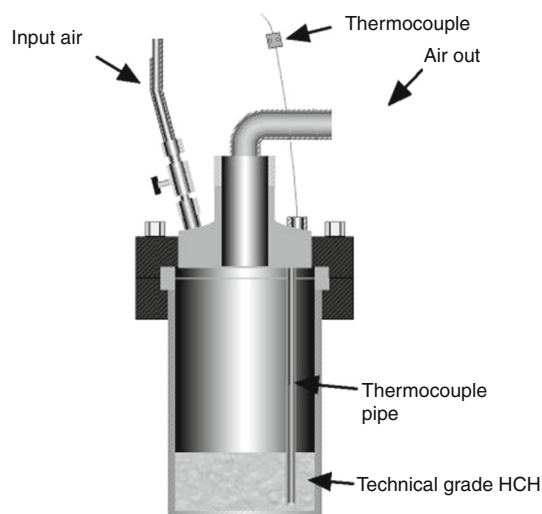


Fig. 3 Reactor used in the experimental to evaluated emissions gas/vapors

Quantitative analysis of gaseous compounds generated in the reactors analysis was performed by gas chromatography coupled to mass spectrometry (GC).

The remaining solid material (residue) derived from tests on reactor was just extracted and then analyzed qualitatively by GC technic. Gaseous emissions generated during heating in these tests were retained in a treatment system, as above described, before being released into the atmosphere.

Results

Thermogravimetric analysis

Figure 4a, b, respectively, represents TG and DSC curves of the reference material (RM) isomers of HCH (Fig. 5)

obtained for the temperature interval of ($25 \leq T \leq 350$) °C, nitrogen flow of 50 mL min^{-1} and a heating rate of $\beta = 1 \text{ °C min}^{-1}$. TG curves show mass loss of approximately 94 % in mass in a single-step process and were ascribed to the evaporation of HCH isomers, after melting them, as shown in Table 2. Residual mass was observed close to 6 %.

The initial temperature ($T_{i\text{-onset}}$) removal of isomers follows the order: $T_{i\alpha} = T_{i\delta} < T_{i\gamma} < T_{i\beta}$ and the ΔT ($T_i - T_f$): $\beta < \alpha < \gamma < \delta$; considering the mass difference between the isomers samples, β -isomer presents the minor mass as δ -isomer, the major values of T_i and T_f and the minor ΔT value. These characteristics were ascribed to a difference in the molecular structure existing between the isomers.

DSC curves (Fig. 4b) show different profiles for the α - to δ -isomers. The β -isomer profile presents only an endothermic peak at $T_{\text{peak}} = 200 \text{ °C}$ ascribed to a slow sublimation process, since the peak fusion is absent. All other isomers present a sharp fusion peak and a second endothermic peak ascribed to evaporation of the liquid phase (Table 2). The isomers α -, γ - and δ -HCH present different values of ΔT observed for the separation of the peaks of fusion and evaporation: $\Delta T_{\text{peak}}: \alpha < \delta < \gamma$ -isomer. The α -isomer shows a sharp peak followed by an immediate evaporation peak, different from the other HCH isomers.

Figure 6a shows TG/DTG and DSC curves and mass spectra results obtained for a sample of a reference α -HCH isomer. The TG/DTG curve shows only a step of mass loss of 99.9 % in mass from $T_i = 140$ up to $T_f = 230 \text{ °C}$ and the DTG curve with a $T_{\text{peak}} = 230 \text{ °C}$. The DSC curve reveals that two endothermic processes are occurring as pointed out former; there are a fusion peak at $T_{\text{peak}} = 120 \text{ °C}$ and an evaporation peak at $T_{\text{peak}} = 235 \text{ °C}$.

Simultaneously, the mass spectra obtained for isomer α -HCH collected at temperatures of:

- 32.1 °C do not permit identifying the presence of the component α -HCH isomer in the carrier gas;
- 180 °C permit identifying and confirming the evaporation of the α -HCH isomer after melting point (the same behavior was obtained for γ -, β - and δ -HCH isomers species); and
- 270 °C confirm the absence of carbonaceous materials, allowing suggesting that the HCH isomers do not decompose itself at elevated temperatures and the absence of oxidative process.

The same behavior was observed for the other isomers except for β -HCH. This isomer does not present melting point peak, but only evaporation peak; which is similar to sucrose DSC curves obtained for low heating rate

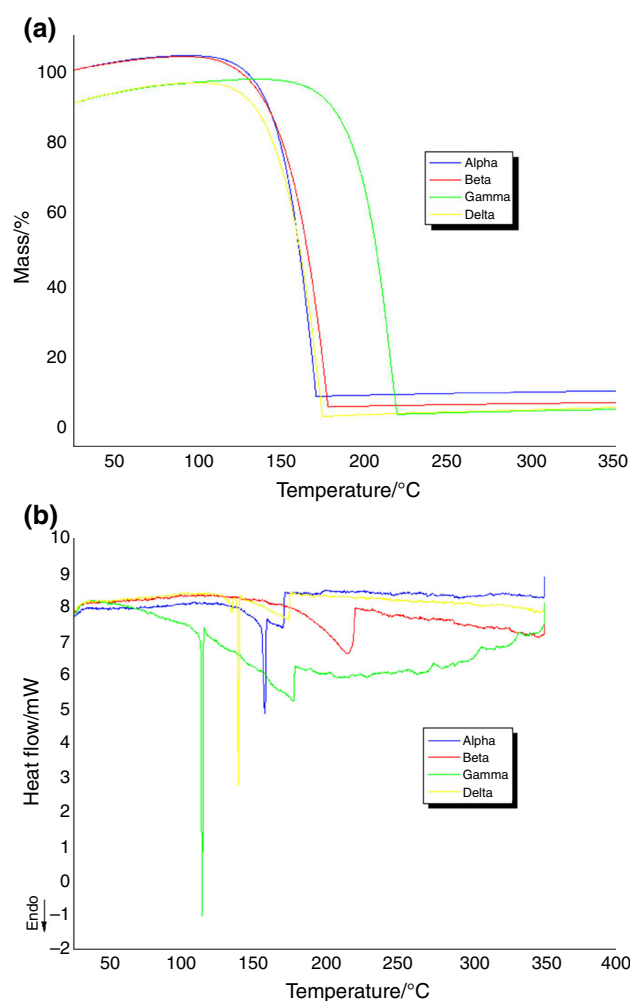
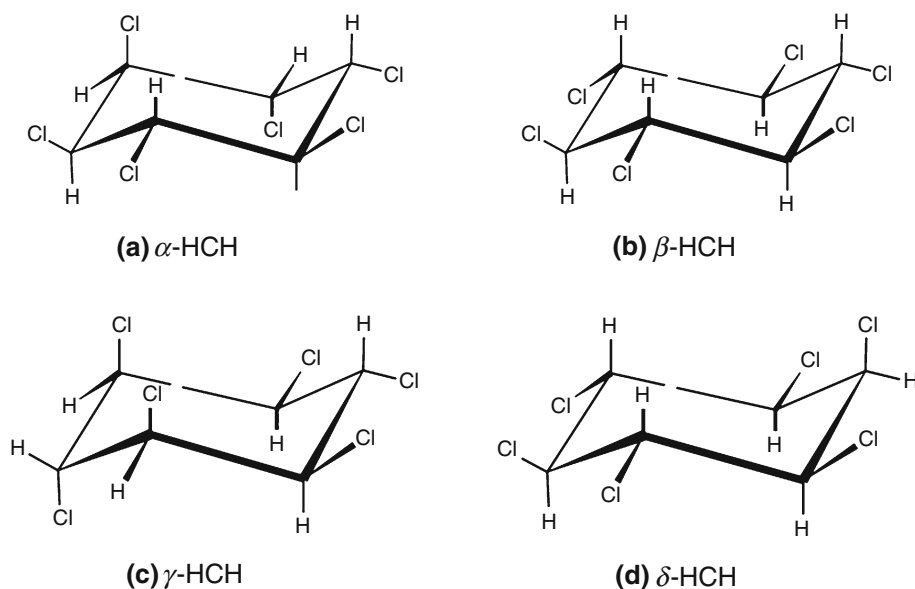


Fig. 4 TG (a) and DSC (b) curves of α -, β -, γ - and δ -HCH isomers; $\beta = 1 \text{ °C min}^{-1}$; ($25 \leq \Delta T \leq 350$) °C; flow of $\text{N}_2 = 50 \text{ mL min}^{-1}$

($\beta \leq 0.1 \text{ °C min}^{-1}$) [results not published—COPERSU-CAR seal off]. This phenomenon can be attributed to the original characteristic of the sample that absorbs the heat very slowly since the timescale of the heating process is very long (near 200 min); under these circumstance, the absorbed thermal energy is used to disrupt the crystal system preventing the observation of a sharp melting peak of the β -isomer of HCH. This system shows only a peak ascribed to a very slow kinetics evaporation process of HCH, β -isomer [12].

The TG/DTG and DSC curves, Fig. 6b, show the thermal effects on a sample of a synthetic t-g HCH-contaminated soil in a proportion of 1:10, t-g HCH: soil. From this figure, the temperature range necessary to remove the HCH contents can be identified. The temperature range to remove t-g HCH content was about 50 °C, starting from $T_i = 150$ up to $T_f = 200 \text{ °C}$, at which a significant $\sim 11 \%$ mass loss was observed.

Fig. 5 Isomers of hexachlorocyclohexane (HCH)**Table 2** Melting temperature of HCH isomers (DSC), % of mass loss (TG) and % residue (TG); $\beta = 1 \text{ }^\circ\text{C min}^{-1}$; ($25 \leq \Delta T \leq 350$) $^\circ\text{C}$; flow of N_2 : 50 mL min^{-1}

Isomer	$T_{\text{peak}}/^\circ\text{C}$	$M_{\text{loss}}/\%$	$R/\%$
α -HCH	156.09	90.97	9.04
β -HCH	–	90.53	9.47
γ -HCH	112.68	93.85	6.82
δ -HCH	137.70	91.13	8.88

T_{peak} peak temperature; M_{loss} mass loss; R residue

The DSC curve shows two endothermic peaks in the temperature range from 125 up to 225 $^\circ\text{C}$, with peaks at $T_{\text{peak}} = 150 \text{ }^\circ\text{C}$ and $T_{\text{peak}} = 180 \text{ }^\circ\text{C}$, ascribed to a fusion peak, as previously observed for the reference isomer materials (Fig. 6a), and elimination of the other HCH isomers. Despite the peak temperatures observed in Fig. 6a for the reference material of α -HCH isomer, the melting peak and evaporation peak, shown in the Fig. 6b, appeared wide, shifted to lower temperature values and attenuated. These peak temperature values appear attenuated and shifted because they are an intermediate value between the highest and lower melting point of α -HCH (156.09 $^\circ\text{C}$) and γ -HCH (112.98 $^\circ\text{C}$) isomers, respectively [12, 13].

Figure 7, specifically Fig. 7a ($T = 200 \text{ }^\circ\text{C}$ for 1 h), where are showed the relative mass loss (mg g^{-1}) of the α -HCH isomers in collected soil samples (anthropogenic contaminated soil) after thermal treatment, it can be noted that the mass loss is in agreement with TG data, occurring removal of closely HCH isomers in a single step. This step occurs after melting of the isomer α -HCH, present as the major constituent species, in no more than 30 min, as previously confirmed by the DSC curves.

For temperatures above 200 $^\circ\text{C}$, the removal time of HCH isomers is meaningfully reduced as depicted in Fig. 7c–e.

Treatability tests bench scale

The results of the experiments conducted in the oven in samples of contaminated soil for treatability tests bench scale are shown in Fig. 8.

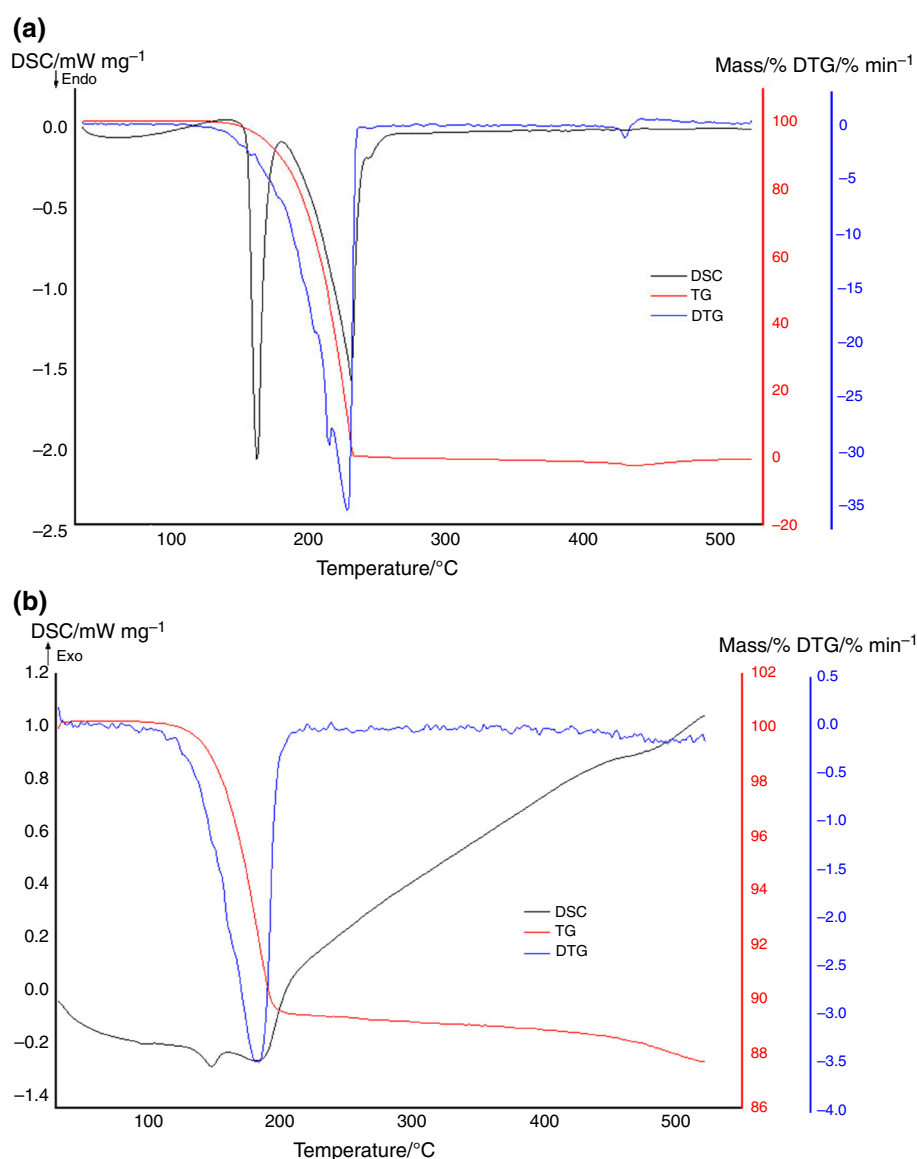
Environmental Agency of São Paulo state, Brazil (Cetesb), established prevention values for α -, β -, and γ -HCH to the soil considering industrial scenario: 0.04; 0.2; 0.2 $\mu\text{g g}^{-1}$, respectively [11]. These values were used for comparison with the concentrations of HCH isomers obtained in this work after thermal treatment of samples. These values are used because the sample of anthropogenic contaminated soil was collected in an industrial zone of São Paulo state.

The results of these tests showed that, for the most parts of the analyzed samples, for determination of the stabilization concentration of HCH and its reduction from the initial to a lower concentration, less than $10 \mu\text{g g}^{-1}$, the temperature and time required were 250 $^\circ\text{C}$ and 1 h, respectively (see Fig. 7c).

The results pointed out in Fig. 7a–e suggest that only γ -HCH isomer (lindane) showed a significant concentration reduction between the HCH isomers present in the anthropogenic contaminated soil.

The reduction in concentration from initial γ -HCH (Fig. 7c) isomer measured in accordance with guiding values accepted by Cetesb-São Paulo state, Brazil [11], was obtained for the parameters, heating temperatures and heating time of 200/30; 250/30 and 300/30 $^\circ\text{C min}^{-1}$.

Fig. 6 Simultaneous TG–DTA and DTG curves of HCH: **a** α -HCH (MR), in synthetic air; **b** γ -HCH; in N_2 flow of 50 mL min^{-1} ; $\beta = 10 \text{ }^\circ\text{C min}^{-1}$



Thus, considering these parameters, a significant reduction in the concentration was obtained about an average of $0.1 \mu\text{g g}^{-1}$. In further experiments using heating temperature of $350 \text{ }^\circ\text{C}$, the γ -HCH isomer reduction was significant in 0.1 h of heating.

For β -HCH isomer elimination, a significant content reduction occurred only at heating temperature of $350 \text{ }^\circ\text{C}$ after 96 h, maintaining the average $0.2 \mu\text{g g}^{-1}$ (99.1 % reduction in concentration) after 192 and 480 h of heating (Fig. 7e).

The results indicate that the contaminants were removed from soil at temperatures considerably below their boiling point [4, 6].

Batch thermal reactor

Figure 8 shows the evolution temperature as function of the experiment time and the thermocouple distance to the

heating well, used to remove the HCH isomers from the anthropogenic contaminated soil. The temperature was monitored during the realization of the tests, and data are collected and presented in Table 3.

The samples were collected in the batch thermal reactor, for chemical analysis, through a spiral auger about 0.05 m of diameter, at distances of 0.19 and 0.37 m from the heating well in which thermocouples indicate temperatures of 170 and $240 \text{ }^\circ\text{C}$, respectively. Samples were collected at 240 h after heating time, initial time of the temperature stabilization and 480 h after heating time. The pressure during the tests was maintained constant at 1961.33 kPa.

In connection with Fig. 8 and Table 3, it can be observed from Table 2 that the concentration of most of the isomers was, after thermal treating, below the assumed detection limit, which was $0.00006 \mu\text{g g}^{-1}$ [11]. An exception was obtained for the β -HCH isomer whose final concentration

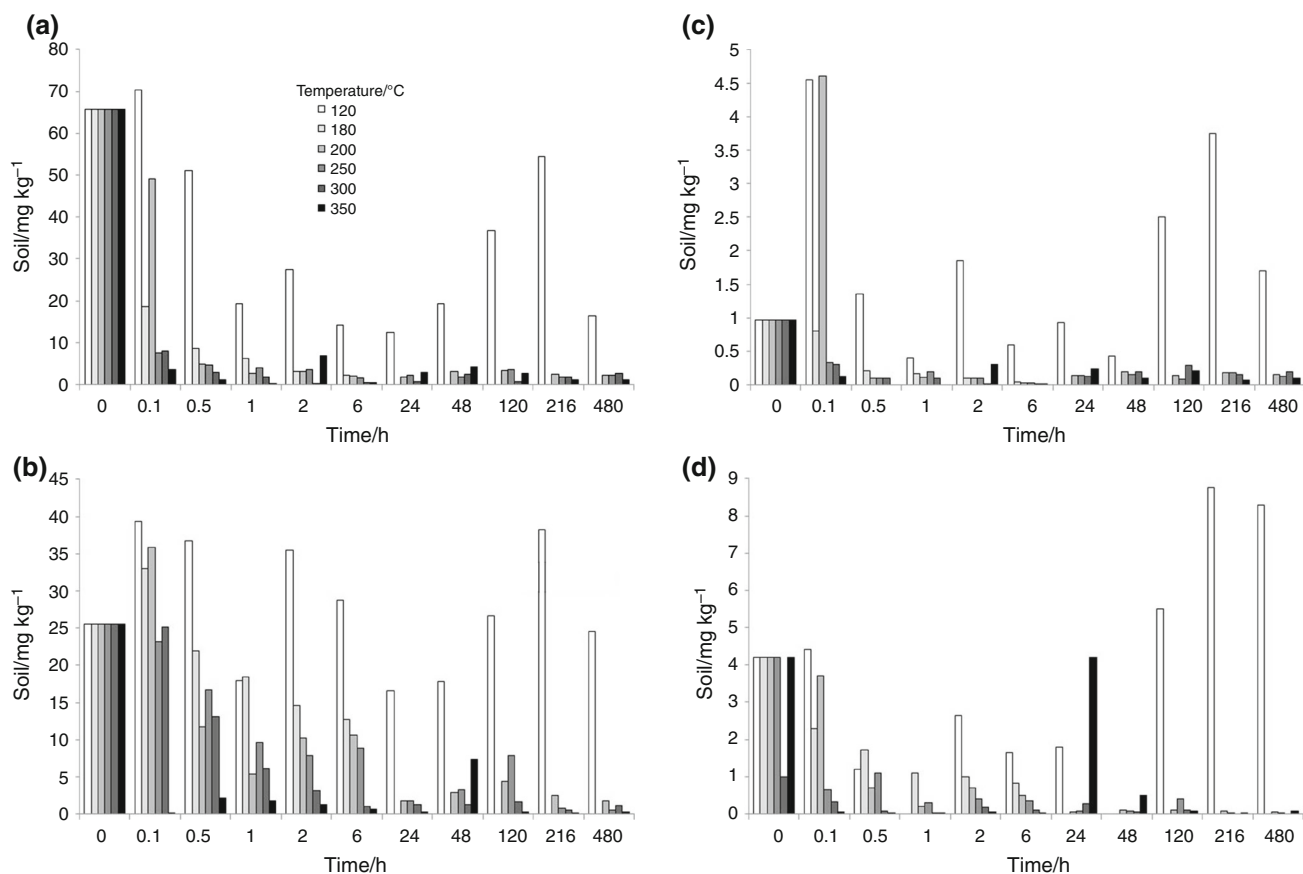
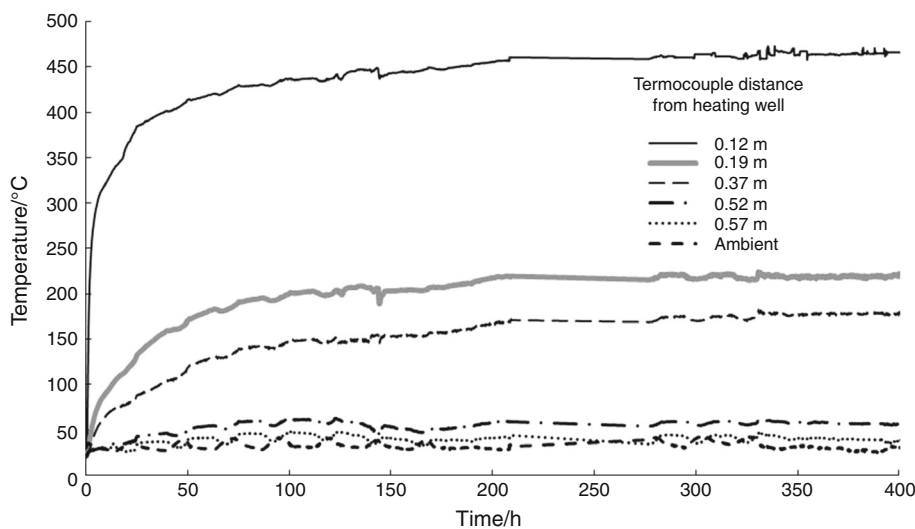


Fig. 7 HCH concentrations measured in collected soil samples after thermal treatment: **a** α -HCH; **b** β -HCH; **c** γ -HCH; **d** δ -HCH

Fig. 8 Temperature variations in the batch thermal reactor with time; for the installed sensors, the distance indicated the heating well



was $0.52 \mu\text{g g}^{-1}$, applying heating temperature of $170 \text{ }^\circ\text{C}$ by 240 h and producing a reduction of 99.8 % over the initial concentration of β -HCH isomer, a value that fits the industrial scenario to the guiding values [11].

In case of heating up to $240 \text{ }^\circ\text{C}$ for 240 h or to $170 \text{ }^\circ\text{C}$ for 480 h, results indicated that the concentration of all isomers was below the limit of detection adopted by Cetesb-São Paulo state, Brazil [11]. These results indicate

Table 3 Temperature at different depths in the batch thermal reactor

Depth/m	D_H /m				
	0.12	0.19	0.37	0.52	0.57
	T/°C				
0.45	456.0	219.0	165.5	56.0	39.0
0.35	401.5	204.0	140.5	53.0	37.5
0.25	336.5	175.0	122.5	49.5	37.5
0.15	234.0	126.0	93.5	44.5	35.5
0.05	106.0	57.0	54.0	34.5	29.5

D_H horizontal distance of the thermocouples to the heating well

Table 4 Collected samples of gases and vapors in the reactor

Bag	T/ °C	Time/ h	Main compounds detected
1	130	1	Chloromethane, benzene
2	180	2	Methylene chloride, ethyl chloride, benzene, Lindane
	250	6	Lindane, ethyl chloride
4	351	8	Dichloroethene, trichloroethylene, chlorobenzene
5	400	9	Chlorobenzene, lindane
6	450	15	Lindane
7	500	18	Pentachlorobenzene; α -, β -, γ -, δ -HCH; furan; polychlorinated biphenyls (PCB)
8	330	216	Benzene; tetrachloroethylene; chlorobenzene;
9	300		chlorophenol; dichlorobenzene; trichlorobenzene; benzene; toluene

that the HCH concentrations decreased by approximately 99.9999 % compared with initial concentration.

Emissions analysis

The result of the chromatographic analysis of volatile organic compounds and semi-volatile compounds present in the technical HCH before heating is shown in Table 4. The results showed the presence of benzene and chlorobenzene, besides HCH isomers.

Benzene is used in the production of HCH with chlorine, and its presence in the sample can reveal that not all of the benzene used in the production of technical HCH is consumed. The benzene in the presence of chlorobenzene can produce chlorine gas, which may explain the presence of chlorobenzene in the sample after heating as shown in Table 4.

Table 4 shows the major products detected in the gaseous materials found in the samples used in the experimental assays to evaluate gas/vapors emissions. It is

noticed that most of the compounds are chlorinated, although there are benzene molecules in the gas phase.

The presence of chlorinated compounds may be due to decomposition of chlorobenzene. Another possibility for the presence of benzene, under these conditions, is the volatilization of benzene present in the technical grade HCH sample as a contaminant.

The results of the gaseous emissions obtained in this experiment show part of the HCH isomers volatilized, showing that evaporation can really be an important process in thermal remediation systems [12–14].

Similar to results obtained above, the use of an alkaline solution of NaOH to assess the dechlorination of HCH showed that the NaOH solution was an environment useful to retain the isomers. Thus, the analysis by GC of the NaOH solution used in the experiments carried out to assess the compound species present in this alkaline solution detected presence of isomers β -HCH and γ -HCH, showing the efficiency of scrubber generated during heating of HCH [15].

The qualitative analysis of the activated carbon samples of extract revealed the presence of small proportions of higher aliphatic hydrocarbons, phthalate plasticizers and the isomers of α -, β -, and γ -HCH. The gas and vapors samples collected from output of the system revealed the absence of HCH isomers.

Conclusions

The TG/DTG and DSC data, as well as the reactors' data, appear to be similar in effect of temperature. There are only differences in mass of the sample, pressure effects and gas flow rate. Based on the thermal analysis carried out, it was found that up to 400 °C HCH isomers are completely volatilized.

Thermal analyses showed that with the heating of the samples occurs first the fusion of the HCH isomers and then volatilization. The isomer β -HCH was the unique isomer that did not present the endothermic peak of fusion. In all experiments, the contaminant (HCH) removal occurs mainly by evaporation, and the mass of the sample, gas flow rate and the level of contamination are considered as second-order parameters.

Thus, regarding the decontamination, the results of the thermal treatment show that for a reduction of the concentration of HCH isomers of nearly 100 %, of the original one, are required short periods of heating time and temperatures below the boiling point of the HCH isomers.

In particular, the reduction in concentration from initial γ -HCH isomer measured in accordance with guiding values accepted by *Cetesb* guiding values was obtained for heating temperatures and heating time of 200/30; 250/30;

300/30 and 350/6 °C min⁻¹, with a significant reduction in the concentration of γ -HCH about a value of 0.1 $\mu\text{g g}^{-1}$.

By the other side, the β -HCH isomer elimination occurred with a significant reduction in its initial concentration at heating temperature of 350 °C/96 h, maintaining an average of 0.2 $\mu\text{g g}^{-1}$ (99.8 % reduction in the initial concentration) even after 192 and 480 h on heating. This reduction over the initial concentration of β -HCH isomer is a value that fits the industrial scenario to the *Cetesb* guiding values.

In general way, the gaseous emissions evaluated in this work pointed out that nearly 100 % of the HCH isomers were volatilized. This situation showed that evaporation can really be an important and efficient process in the thermal remediation systems.

References

- Kingston JT, Dahlen PR, Johnson PC, Foote E, Williams S. Critical evaluation of state-of-the-art in situ thermal treatment technologies for DNAPL source zone treatment. 2010. <http://www.clu-in.org/download/techfocus/thermal/Thermal-ER-0314-FR.pdf>. Accessed 4 Jan 2010.
- United States Environmental Protection Agency. How to evaluate alternative cleanup technologies for underground storage tank sites: a guide for corrective action plan reviewers. Washington. DC: Usepa; 1995.
- Qi Z, Chen T, Bai S, Yan M, Lu S, Buekens A, Yan J, Bilmãu C, Li X. Effect of temperature and particle size on the thermal desorption of PCBs from contaminated soil. *Environ Sci Pollut Res*. 2014. doi:10.1007/s1135601323924.
- Stegemeier GL, Vinegar HJ. Thermal conduction heating for in situ thermal desorption of soils. In: Oh CH, editor. Hazardous and radioactive waste treatment technologies handbook. Boca Raton: CRC Press; 2001.
- Risoul V, Renault V, Trouvé G, Gilot P. A laboratory pilot study of thermal decontamination of soils polluted by PCBs. Comparison with thermogravimetric analysis. *Waste Manag*. 2002;22:61–72.
- Risoul V, Pichon C, Trouvé G, Peters WA, Gilot P, Prado G. Thermogravimetric study of thermal decontamination of soils polluted by hexachlorobenzene, 4-chlorobiphenyl, naphthalene, or n-decane. *J Hazard Mater*. 1999;64:295–311.
- Kucerík J, Siewert C. Practical application of thermogravimetric in soil science. Part 2. Modeling and prediction of soil respiration using thermal mass losses. *J Therm Anal Calorim*. 2014;116:563–70.
- Agency for Toxic Substances and Disease Registry. Toxicological profile for alpha, beta-, gamma-, and delta-hexachlorocyclohexane. Atlanta: ATSDR; 2005.
- Environmental Agency of the São Paulo State–Brazil. Toxicological Information Sheet: hexachlorocyclohexane. CETESB:2014. <http://www.cetesb.sp.gov.br/userfiles/file/laboratorios/fit/Hexaclorociclohexanos.pdf>. Accessed 01 Mar 2014.
- Brazilian Association of Technical Standards. NBR 7181: particle size analysis of soils. Rio de Janeiro: ABNT; 1984.
- Environmental Agency of the São Paulo State–Brazil. Decision of directors No. 045/2014/E/C/I, of 20 February: 2014. <http://www.cetesb.sp.gov.br/userfiles/file/solo/valores-orientadores-2014.pdf>. Accessed 28 Feb 2014.
- Rodant F, Vechio S, Catalani G, Guidotti M. Thermal analysis and non-isothermal kinetics study of some pesticides: part II—chlorinate derivatives. *J Therm Anal Calorim*. 2000;60:606–22.
- Huang YT, Hseu ZY, Hsi HC. Influences of thermal decontamination on Mercury removal, soil properties and repartitioning of coexisting heavy metals. *Chemosphere*. 2011;84:1244–9.
- Gilot P, Howard JB, Peters W. Evaporation phenomena during thermal decontamination of soils. *Environ Sci Technol*. 2007;37:461–6.
- Ukisu Y, Miyadera T. Dechlorination of hexachlorocyclohexanes with alkaline 2-propanol and palladium catalyst. *J Hazard Mater*. 2005;122:1–6.