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Arh Hig Rada Toksikol 2001;52:253-280

CONFERENCE PAPER

OVERVIEW OF REMEDIATION TECHNOLOGIES FOR PERSISTENT TOXIC SUBSTANCES

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Received October 2000

This paper gives a review of established and emerging technologies for the treatment of wastes and soils contaminated by Persistent Toxic Substances which include the Persistent Organic Pollutants. The technologies are classified as biological, physico-chemical, and thermal treatments, describing main unit operations and comparing technical, social and environmental limitations, including some potential risks and environmental impacts. Estimated overall costs, cleanup times, reliability, and maintenance levels are also presented in order to assess advantages and limitations of each technology.

Key words:
PCBs, pesticides, POPs, PTS, remediation, soil, treatment, waste

Remediation of polluted sites has become a crucial issue because of the increasing global awareness of pollution, overexploitation of natural resources, and adverse effects of unclean processes on environment and human health. This has increasingly led to the issuing of tighter norms and regulations related to storage, transportation, treatment, and disposal of liquid and solid waste, as well as remediation of contaminated sites. These measures are also significantly influencing the development and the use of hazardous compounds to comply with regulatory limits.

Presented at the ICS-UNIDO Workshop on Contamination of Food and Agroproducts, 28 September – 1 October 2000, Varaždin, Croatia

Stringent cleanup standards are being directed to protect soil, vegetative and ecological systems and to prevent contamination of groundwater.

The purpose of this paper is to review the existing technologies for the treatment of waste and PTS contaminated soils, presenting their limitations and some technical, environmental, social and economic criteria for the evaluation and the selection of a suitable technique. This paper, of which the first part overviews general properties of PTS, is mainly focused on remediation technologies addressing problems generated by already produced PTSs (e.g. pesticides and PCBs). Technologies to prevent PTS formation and effects (such as dioxins and furans) are not dealt with in this review.

Some key criteria for selecting an appropriate remediation approach are presented in the section about remediation technologies, including overall costs, cleanup time, reliability, and maintenance. The technologies discussed have been classified as »established« and »emerging/Innovative« in order to differentiate between those which have demonstrated their full-scale application and those which have proved their efficiency on a laboratory or pilot level only.

Each section is divided in physico-chemical, thermal, and biological techniques, although some technologies combine thermal and chemical or thermal and biological methods. Each technology is basically described in operational conditions and through unit operations. The main limitations of each technology are also presented and classified as technical/economical, social, and environmental (including environmental impacts and safety risks). The list of technologies discussed is not exhaustive since many are currently being developed and others are variations of the existing ones.

Finally, some recommendations and conclusions are presented in order to stress the importance of considering both ratable and non-ratable criteria during the selection of technologies and while assessing and performing PTS remediation projects.

SUMMARY OF PROPERTIES OF PTS

PTS is a group of substances with specific characteristics of persistence, bioaccumulation, and toxicity. The group of PTS is integrated by the POPs (Persistent Organic Pollutants) and some inorganic compounds (mercury, cadmium, lead, and compounds). Table 1 gives a list of PTSs. POPs are highly stable organic compounds used as pesticides, herbicides, fungicides, or in chemical industry. They are also generated as byproducts of combustion and industrial processes. They persist in the environment, accumulate in the fatty tissues of living organisms, and are toxic to humans and wildlife. POPs are typically semi-volatile; they travel long distances and condense over colder regions of the planet. They are classified through lipophilicity, persistence (resistance to photolytic, chemical, and biological degradation), and toxicity.

The Convention on Long-Range Transboundary Air Pollution (LRTAP) has defined criteria and procedures for adding substances to the Protocol on Persistent Organic Pollutants. A party proposing to add a substance to the list of POPs must provide the LRTAP Executive Body with a risk profile on that substance and information related to these four characteristics (1):

Table 1 *List of Persistent Toxic Substances*

Aldrin	Dieldrin	Hexachlorobenzene, HCB
Chlordane	Endrin	Mirex
Chlordecone	Heptachlor	Polychlorinated biphenyls (PCBs)
DDT	Hexabromobiphenyl	Toxaphene
Dioxins and furans	Polychlorinated napthalenes	Polycyclic aromatic hydrocarbons
Polychlorinated benzenes	Polychlorinated paraffins	Kepone (chlordecone)
Polychlorinated phenols	Polybrominated compounds	Lindane
Isodrin	Parathion	Malathion
Alkyl-lead	Mercury and compounds	Octachlorostyrene
Dinitropyrene	Cadmium and compounds	Benzopyrene

☐ the potential for long-range transboundary atmospheric transport; vapour pressure below 1,000 Pa and an atmospheric half-life greater than two days or monitoring data that evidence the substance is found in remote regions.
☐ persistence; a half-life in water greater than two months, soil and sediment half-lives greater than six months or, alternatively, evidence that the substance is otherwise sufficiently persistent to be of concern.
☐ bioaccumulation; evidence that the fish bioaccumulation factor is greater than 5,000 or the log Kow is greater than 5 or, if those values are not achieved, other factors that could make the substance of concern.
☐ toxicity; potential to affect human health and/or the environment.

After a technical review, the parties to the protocol meeting within the LRTAP Executive Body decide by consensus whether a substance is within the scope of the protocol and whether to adopt the proposal to to add that substance in the protocol.

REMEDIATION TECHNOLOGIES

Waste and soil remediation technologies can be classified according to their development status. »Established technologies« are those having demonstrated full-scale applications and removal efficiencies whereas »emerging/innovative technologies« refer to methods having few or no reported full-scale applications, but have a proven pilot- and laboratory-scale removal efficiency.

Tables 2 and 3 present some criteria that can be considered to select a remediation technology. The overall cost includes design, construction, operation, and maintenance of the remediation program, but it does not include transportation costs (if it is done off-site), previous assessments or post treatment costs, and manpower (since this cost considerably varies from country to country). The reliability and maintenance criteria refer to the level of process complexity and the ease to maintain it.

Other criteria should also be considered when selecting a remediation technology, such as the technique's ability to clean up to a desired level (minimum pollutant concentration achievable by the technology), community acceptability, applicability, post-treatment costs, soil quality required after the intervention (in case of soil pollution), environmental impacts, and risks of remediation activities/processes.

Table 2 *Some criteria to assess established remediation technologies*

Remediation technology	**Overall cost * (USD/ton)**	**Clean-up time**	**Reliability and maintenance (level)**
Physico-chemical			
Landfill cap system (in or ex)	N.A.	–	Varies
Vapour extraction (in)	S	M to L	Average
Vapour extraction (ex)	S	M to L	High r. and low m.
Solidification/Stabilization (ex or in)	S to M	S to M	High r. and low m.
Thermal technologies			
Combustion systems (ex)	M to L	S to M	Average
Thermal desorption (in or ex)	S to M	S to M	Average
Pyrolysis (ex)	M to L	S	Average
Biological technologies			
Bioventing (in)	M	M to L	Low r. and high m.
Composting (ex)	M	M to L	Average
Biopiles (ex)	S	S	Average
Land farming (ex)	S	M to L	High r. and low m.

Table 3 *Some criteria to assess innovative and emerging remediation technologies*

Remediation technology	**Overall cost * (USD/ton)**	**Clean-up time**	**Reliability and maintenance (level)**
Physico-chemical			
Base catalysed dechlorination (ex)	M to L	S	Average
Electrochemical oxidation (in)	M to L	S to M	Low r. and high m.
Solvent extraction (ex)	M to L	S to M	Average
Solvated electron (ex)	L	S	Average
Supercritical water oxidation (ex)	S to M	S	Average
Solar detoxification (ex)	N.A.	S to M	N.A.
Gas phase chemical reduction (ex)	L	S to M	High m.
Catalytic hydrogenation (ex)	N.A.	S	High r. and low m.
Thermal technologies			
T. D. – Catalysed dehalog. (ex)	M to L	S	Low r. and high m.
T. D. – Pyrolysis (ex)	L	S	Average
T. D. – Retort system (ex)	M to L	S to M	Average
Plasma ARC Systems (ex)	L	S	Average
Vitrification (in or ex)	M to L	S	High r. and low m.
Biological technologies			
Bioslurry (ex)	M	S to M	Average
Enhanced bioremediation (in)	S	L	Low r. and high m.
Phytoremediation (in)	S to M	L	Average

(in)=*in situ* (ex)=*ex situ*; S=short term <6 months, M=medium, 6 to 12 months, L=long, >12 months
*Cost (USD): S<$150, M=$150–$300, L>$300
r.=reliability; m.= maintenance; T.D.=thermal desorption; N.A.=not available

ESTABLISHED TECHNOLOGIES – PHYSICO-CHEMICAL TECHNIQUES

Table 4 shows the main limitations of physico-chemical techniques established so far.

Landfill cap system

Landfill capping is one of the most common forms of remediation technologies. It is used to cover buried waste materials in order to prevent contact with the environment and to effectively manage the human and ecological risks associated with a remediation site. The design of landfill caps is specific and depends on the intended functions of the system. The most critical components of a landfill cap are the barrier layer and the drainage layer. Landfill caps can range from a one-layer system of fertile soil to a complex multi-layer system of soils and geosynthetics. In general, less complex systems are required in dry climates and systems that are more complex are needed in wet climate; the system complexity also depends on the type of waste (phase,

Table 4 *Main limitations of established physico-chemical technologies*

Landfill /Cap Systems	**Solidification/Stabilization**	**Vapour extraction (SVE)**
Technical/Economic		
The toxicity is not reduced and pollutants are not destroyed with these methods	The solidified material may hinder future site use if carried out *in-situ*. The process is not effective in immobilizing organic waste.	Low permeabilities, high humidity content and soil heterogeneity limit the performance. The method is only suitable for medium to high volatile compounds.
Social		
In some cases this methods may attract public opposition.	In some cases this methods may attract public opposition.	Usually does not attract public opposition.
Environmental/Risk		
Precautions must be taken to ensure the cap is not damaged by land use activities. Several semivolatile pollutants may evaporate more rapidly with increased moisture in soils and sediments (2). Potential leaking of hazardous compounds.	Precautions must be taken to minimise components leaching from stabilised media. Environmental conditions may affect the long-term immobilization of contaminants. There is no reduction of pollutants toxicity.	Potential releases of hazardous compounds during excavation and materials handling. Exhaust air from SVE requires secondary treatment.

hazardous or not hazardous, etc.). The materials used in the construction of landfill caps include low- and high-permeability soils and low-permeability geosynthetic products. The low-permeability materials prevent water to pass into the waste. The high permeability materials drain and collect water that percolates into the cap.

Landfill caps may be temporary or permanent. Temporary caps can be installed before permanent closure to minimise generation of leachate until a better remedy is performed. These caps are usually used to minimise infiltration when the underlying waste mass is undergoing settling. A more stable base will thus be provided for the final cover, reducing the cost of the post-closure maintenance. Landfill caps can also be applied to waste masses too large for other treatments. Disposal in a landfill is not a proper method for liquid pesticides or highly mobile waste. Inorganic pesticides or liquid pesticide waste containing about 5 percent organic material should be solidified or stabilised prior to disposal in a landfill (3).

Solidification/Stabilisation

This method for treating hazardous waste or highly contaminated soils is based on solidification or reduction in mobility of contaminants that are mostly heavy metals. The aim is to prevent contaminated materials from affecting the surrounding environment. The contaminated soil is mixed (either *in-situ* or *ex-situ*) with binding materials such as cement, pozzolanas, thermoplastics, fly-ash, lime-kiln dusts, and low-cost silicate-containing by-products to produce a stabilised mass (solidification) or less solid material that binds liquids and reduces mobility of contaminants (stabilization). The solidified material may hinder future site use if carried out *in-situ*. Environmental conditions may affect the long-term immobilisation of contaminants. The process is not effective in immobilising organic contaminants (4).

Vapour extraction

Soil vapor extraction (SVE) is a well-established, economic and efficient technique for the removal of volatile organic compounds (VOCs) and some halogenated organics. The technology can be used for treating contaminants *in-situ* or *ex-situ*. *In-situ* SVE is performed by means of a vacuum system that uses extraction wells to create a concentration gradient that enhances gas phase volatiles removal from soil through the extraction wells. During *ex-situ* SVE the excavated soil is placed over a network of aboveground piping where vacuum is applied to encourage volatilization of organics. The soil piles may be sealed with geomembranes to avoid volatile emissions and soil saturation due to percolation. This technique has an advantage over *in-situ* method as a result of increased passageways able to collect leachate and a making possible a more uniform treatment (5).

THERMAL TECHNIQUES

COMBUSTION SYSTEMS

High temperature incineration

This has been one of the most applied remediation technologies for the treatment of a variety of contaminant sources including several POPs. It is a high temperature (870 °C to 1200 °C) destructive *ex-situ* treatment of polluted soil; the waste and/or contaminated soil are fed into the incinerator, under controlled conditions; the high temperatures in the presence of oxygen volatilise and combust the contaminants into innocuous substances. Though variety of designs are available most incinerator designs are fitted with rotary kilns, combustion chambers equipped with an afterburner, a quench tower and an air pollution control system. Removal efficiencies of more than 99.99% are feasible. For PCBs and dioxins the high temperature incinerators can achieve destruction and removal efficiencies up to 99.9999% (6).

Modern incinerators are commonly described as destroying pesticides, PCBs, and similar chemicals very efficiently. However, recent tests suggest that incinerators achieved destruction efficiencies that are lower than those achieved by certain non-combustion technologies. In addition, some incinerators burning POPs (e.g. pesticides and PCBs) and other waste are associated with the spread of undestroyed and newly formed POPs (e.g. dioxins and furans) into the surrounding environment, contaminating air, soil, vegetation, wildlife and human populations (7).

The USEPA has approved high efficiency incinerators to destroy PCBs with concentrations above 50 mg/kg. Incinerators destroying liquid PCBs must meet technical requirements, for instance, 2-sec residence time at 1200°C and 3% of excess oxygen, alternatively, 1.5-sec residence time at 1600 °C and 2% of excess oxygen in the stack gases. The destruction and removal efficiency (DRE) for non-liquid PCBs must be equivalent to 99.9999% (<1 mg/kg) (Table 5).

Table 5 *Main limitations of established thermal technologies*

Combustion Systems	**Thermal Desorption**	**Pyrolysis**
Technical/Economic		
Require cleaning systems for heavy metals. Need strict control to prevent dioxins formation. Older types of cement kilns are not suitable.	Require dewatering to achieve proper soil moisture levels. It must be linked to a post treatment.	Does not attack inorganic compounds. Performance depends on the soil moisture content, which has correlation with overall cost.
Social		
In many cases may attract public opposition.	If it is linked to combustion systems may present public opposition.	Usually does not attract public opposition.
Environmental/Risk		
Emission of combustion products. Potential release of toxic compounds (dioxins, furans, chlorinated compounds).	Potential of fugitive emissions. Emission of combustion gases and potential formation of dioxins (when linked to combustion systems).	Require controls and systems to prevent dioxins formation. Needs control of combustion gases.

Cement kilns

The main processes employed in making cement clinker can be classified as either »wet« or »dry« depending on the method used to prepare the kiln feed. In the wet process the feed material is slurried and fed directly into the kiln. In the dry process, the kiln exhaust gases are used to dry raw material while it is being milled.

At very high temperatures of the cement kiln, and with the available long residence times, very high destruction efficiency is possible for hazardous waste. The highly alkaline conditions in a cement kiln are ideal for decomposing chlorinated organic waste. Chlorinated liquids, chlorine and sulphur are transformed in chlorides and sulphates. The quantities of the inorganic and mineral elements added in treating chlorinated waste are limited (usually is a small fraction of the large feed requirements of a commercial kiln). No liquid or solid residues requiring post treatment and/or disposal are generated since all residues are bound within the product.

The most appropriate waste to be processed in cement kilns are those which provide additional energy value as a substitute fuel, or material value as a substitute for portions of the raw material feed (e.g. calcium, silica, sulphur, alumina, or iron). Liquid waste or low ash waste can be relatively easy burnt in cement kilns. The material is fed in dry or in slurry form (especially for the »wet« process), or as a fuel supplement into the burning zone of the kiln. In this zone, high destruction efficiencies are achievable at a temperature of 1450 °C, as the gas passes though the kiln.

For the typical counter current process configuration, polluted-soils and solid waste cannot be fed into the firing end of the kiln, since they would discharge in the clinker without adequate treatment; in addition, they cannot be fed into the cool end of the kiln, as the waste would volatilise and would not be adequately destroyed. There are two suitable options for feeding the waste. The first one consists of feeding solid material to the middle of the kiln through a specially designed hopper; the kiln temperature at feeding point is approximately 1100 °C and increases as the materials pass further down the kiln. This involves a major modification of the rotary kiln. Monitoring and verification that complete destruction of stable chlorinated compounds such as PCBs occurs with the desired efficiency is required (8).

The second option includes a pre-treatment of the solid waste (e.g. thermal desorption, as the approach taken in Catalysed Dehalogenation systems). After such treatment, the material can be utilised as a raw material substitute, and the condensate can be incorporated in the liquid feed stream.

When properly operated, destruction of chlorinated compounds in cement kilns can be >99.00% complete with no adverse effect on the quality of the exhaust gas (9). The contribution of waste materials to the exhaust gases are relatively minor given that the waste are only used as a minor supplement to the main energy or raw material stream.

Thermal desorption

Thermal desorption is an *ex-situ* process to remove volatile and semi-volatile contaminants that are sorbed on the waste, by heating to temperatures (between 170 to 550 °C) high enough to volatilise the contaminants. Thermal desorption is not a standalone technology, and must be followed by a subsequent system to treat the off-gas (which is normally captured by a carrier gas or vacuum system) in order to remove particulates and contaminants. Wet scrubbers or fabric filters are one of the best units to remove particulates while contaminants are removed through condensation followed by carbon adsorption, or through a secondary combustion chamber or a catalytic oxidiser such as an afterburner. Thermal desorption may use either direct/indirect heat exchange or air/inert gas to transfer vaporised contaminants from the contaminated medium.

Thermal desorption has been widely applied to treat tar-contaminated soils, refinery waste, wood-treating waste, creosote-contaminated soils, hydrocarbon-contaminated soils, nonhalogenated VOCs, SVOCs, PAHs, PCBs, pesticides, mixed (radioactive and hazardous) waste, synthetic rubber processing waste, and paint waste. The bed temperatures (from 170 to 550 °C) and residence times used by thermal desorption systems will volatilise selected contaminants and drive off water, but typically will not oxidise or degrade organic compounds. Thermal desorption followed by direct combustion (e.g. using an afterburner) can be compared to an incineration system, and it can potentially have acceptability problems with local communities if used to treat hazardous waste.

There are different thermal desorption units available, including, Direct Fired (e.g. natural gas) rotary units, Indirect Fired, Hot oil Rotary Screw units, Molten Metal (e.g. tin) bath units and Infra Red heated batch units. Although thermal desorption units are commonly available, some systems may not be appropriate for treating chlorinated waste streams (10).

Pyrolysis

Pyrolysis is an established *ex-situ* remediation technology. It is a technique of chemical decomposition where the hazardous organic compounds are transformed, under pressure and heat, into gaseous components such as methane, carbon monoxide, hydrogen and a residue of ash and carbon contents. The technology is useful in the treatment of pesticides contained in oily sludge, sediments and soils. This technology is usually linked to a pre treatment technology such as thermal desorption or soil vapour extraction. Further discussion regarding Pyrolysis is provided on Thermal Desorption Integrated Technologies section.

BIOLOGICAL TECHNIQUES (Table 6)

Table 6 *Main limitations of established biological technologies*

Bioventing	**Composting /Biopiles**	**Land farming**
Technical/Economic		
Soil heterogeneity and low permeability may reduce efficiency. Low moisture content can limit biodegradation.	Large space area is needed. Existence of metals may affect the clean up performance. The final volume increases due to amendment addition (for composting). Medium to long term time to reach clean up levels.	Chlorinated and nitrated compounds may affect pollutants degradability. Climatic conditions may increase time required to clean up. Not suitable for PCBs.
Social		
No public opposition.	No public opposition (with proper odours and emissions control).	No public opposition.
Environmental/Risk		
Potential fugitive emissions of by products or hazardous compounds. Requires off gases trapping systems.	The risk of fugitive emissions may limit the treatment of pesticides. Requires odour control and off gasses trapping systems.	Potential release of VOCs or hazardous compounds during tilling.

Biological techniques use microorganisms or enzymes to degrade chemical contaminants. The key factor for bioremediation is identify and/or develop the appropriate bacteria/fungi and the deep understanding of how they survive, reproduce and grow on optimal conditions. Parameters like temperature, humidity, pH, available oxygen, rH, substrate, soil/ waste properties and degradation metabolites, must be controlled and understood in order to obtain effective results.

EPA has chosen bioremediation as a primary reasonable remedy to treat organic contaminants (including some POPs) in soils, sludge, and sediments at wood-treating sites (11). Bioremediation technologies were selected as treatment techniques for 17 of 47 sites in the US Office of Technology Assessment Wood Site Remediation survey. Biological techniques have lately been encouraged because allow accomplishing soil sustainability needs, since the decontaminated soil can be reused or restored to its original use.

Bioventing

This method uses air supplied through injection wells and, in some cases, circulated through vacuum extraction. The airflow increases the volatilisation of organic contaminants while simultaneously creates a proper environment for the aerobic biodegradation of the less volatile organics. Although there are many variants of this technology, the basic principle is to deliver optimised airflow rates to provide enough oxygen to the zone of contamination and, if requested, to add nutrients to sustain and promote biological degradation of organic compounds by the naturally occurring soil microorganisms. The optimal flow rates maximise the biodegradation while vapours move slowly through biologically active soil and minimise volatilisation of contaminants (12). There are different methods used to supply oxygen to the subsurface, including vertical and horizontal bioventing wells; in some cases bioventing is combined with SVE (Soil Vapour Extraction) to increase the control of the flow of the injected air.

The method is applicable for the removal of organic compounds with moderate to low volatility such as petroleum hydrocarbons, oils and lubricants. *Marley and Hoag* (13) demonstrated 99% removal of gasoline using this technique. Bioventing is not appropriate for the treatment of metal and inorganic contaminants.

Land Farming

Land farming is a well-known remediation technology for the treatment of petroleum hydrocarbons contaminated soils. It is a technique designed to enhance the microbial degradation of contaminants through periodic tilling to induce aeration, controlled moisture content and addition of nutrients such as nitrogen and phosphorus. *Pope and Matthews* (14) proposed a relatively standard operational methodology for this technology. The contaminated soil is usually excavated onto a designed lined bed (to avoid leaching) and mixed with a controlled amount of nutrients and soil additives such as bulking agents. Bioaugmentation of microbial culture also can also be performed to enhance the degradation rate.

The treatment is appropriate for small quantities of pesticides that can be diluted and applied to land at controlled rates. Some pesticides are biodegradable, they decompose through the action of naturally occurring microorganisms in soil. Land treatment is appropriate for pesticides that are susceptible to biodegradation in a short period of time (less than 26 weeks), under either aerobic or anaerobic conditions. The soil microorganisms' activity can be enhanced through the addition of biologically active materials such as compost, sewage sludge, or night soil.

Composting

Composting is an *ex-situ* solid-phase remediation technology. Unlike land farming, this technique requires thermophilic (55 to 65 °C) conditions due to the increased biological activity in the degraded organic material. The contaminated soil is excavated and mixed with bulking agents and organic additives (such as wood chips and vegetative waste) to improve soil structure for aeration and drainage. Proper additive selection ensures adequate porosity and provides a balance of carbon, nitrogen and phosphorous to promote thermophilic microbial activity. The system is optimised by controlling (via irrigation) moisture content, pH, temperature and nutrients (15), as well as the optimal carbon-to-nitrogen ratio. At the end of the process, organic-rich compost remains; this material can then be placed back onto the contaminated site, providing a fertile soil for reforestation.

The composting process is applicable to soils contaminated with biodegradable organic compounds, heavy oils, PAHs, and munitions (explosives) waste such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). It was reported that on a field experiment using compost, TNT reductions were as high as 99.7% in 40 days while removal efficiencies for RDX and HMX were 99.8% and 96.8%, respectively (16).

Biopiles

Biopiles or »engineered biopiles« are a modification of land farming method for petroleum hydrocarbons decontamination which gives the advantage of a relatively small land-space needed, as well as of capturing and treating volatile organic compounds. It is a full-scale *ex-situ* bioremediation technology in which the polluted excavated soils are stockpiled into a heap within the treatment bed in order to prevent further contamination and includes a delivery aeration system. In addition, features an irrigation/nutrient supply system applied to the treatment heap and a leachate collection system used to recycle the collected fluid. Moisture, heat, nutrients, oxygen, and pH are controlled parameters to enhance biodegradation of the contaminants. This process normally reduces the contaminants to carbon dioxide and water within three to six months of operation.

For PCBs the process requires the anaerobic dechlorination in a first stage, where the chlorinated congeners are reduced to less than three chlorines per biphenyl molecule. After an aerobic stage is used to degrade PCB congeners that contain three or fewer chlorines per each biphenyl molecule (17). HCH removal has also been reported using combined anaerobic-aerobic processes.

EMERGING AND INNOVATIVE TECHNOLOGIES – PHYSICO-CHEMICAL TECHNIQUES (Table 7a)

Table 7a *Main limitations of emerging/innovative physico-chemical technologies*

Base catalysed dechlorination (BCD)	**Electrochemical oxidation**	**Solvent extraction** **Chemical dehalog.** **Radiolytic degradation**
Technical/Economic		
Not economical to treat large volumes of aqueous waste. The waste may require pre-dilution to achieve required destruction efficiencies. Overall efficiency is limited by thermal desorption efficiency. Energy costs to treat pesticides waste may be higher, due to the solvents distilled from the mixture.	Highly dependent on soil moisture content. Requires neutralization of treated soil.	Less effective when treating weight organic and hydrophilic compounds. Requires secondary treatment (including extracted metals). Soil types and moisture may impact efficiency.
Social		
Generally not regarded adversely by community.	No public opposition.	No public opposition.
Environmental/Risk		
Potential to form dioxins and furans is low, since the system operates under an inert atmosphere and the process should dechlorinate dioxins. Exclusion of air is required to prevent auto ignition of hot oil. Alkaline pre-treatment and solvent extraction imply fire and explosion risks.	Acids' handling implies spill risk.	Solvent extraction implies fire and explosion risks. Must be assured the proper handling, recycling and disposal of used solvents.

Base Catalysed Dechlorination (BCD)

The Base Catalysed Dechlorination (BCD) system was developed to treat halogenated organic compounds. It is claimed that BCD is applicable for treatment of waste that contains up to 100,000 mg/kg of halogenated aliphatic or aromatic organic compounds such as PCBs. The formation of salt within the treated mixture may limit the concentration of halogenated material able to be treated. *Rogers* (18) reports a reduction of chlorinated organics to less than 2 mg/kg. The BCD process can involve direct dehalogenation or can be linked to a pre-treatment method such as thermal desorption that yields a relatively small quantity of a condensed volatile phase for separate treatment by the BCD process.

The BCD technology involves the addition of an alkali or alkaline earth metal to the polluted material that contains one or more halogenated or non-halogenated organic contaminant compounds. The BCD patent states that the alkaline chemical can be added to the contaminated medium in an aqueous solution, or in a high boiling point solvent. When the solid chemical is added as a suspension in water, the water helps to distribute the metal compound homogeneously throughout the contaminated medium.

A compound able to provide hydrogen ions to react with the contaminants is added to the mixture when hydrogen ions are not already present in the contaminated material. The hydrogen donor compound may include the high boiling point solvent in which the alkali or alkaline earth metal compound is added, or it may include aliphatic alcohols or hydrocarbons, amines or other alike compounds. A source of carbon (such as sucrose) must be added to activate these compounds to produce hydrogen ions.

The mixture is heated and maintained enough time to totally dehydrate the medium. After the water is removed from the medium during the dehydration step, the alkali is concentrated to a reactive state. The medium is further heated at temperatures from 200 to 400 °C with enough time (from 0.5 to 2 hours) to produce a reductive decomposition of the pollutants.

The mixture is neutralised by the addition of an acid. Depending on the nature of the feed material, the added substances and the site use, it may be possible for the treated material to be returned to the site, although may exist land use limitations if the material is oily and/or has a high salt content. The BCD process can reduce PCB from 10,000 mg/kg to below detectable limits in approximately 2 hours (18).

The BCD process mainly involves chlorine stripping; when treating chlorinated aromatic hydrocarbons the removal of chlorine atoms causes an increased concentration of lower chlorinated species. This does not generally represent a problem for PCBs treatment, but with components such as dioxins, the lower congeners (e.g. TCDD) can be more toxic than the highly chlorinated congeners (e.g. OCDD); the process must be therefore well monitored to ensure that the reaction continues to completion.

The BCD system is not appropriate for treating large volumes of aqueous media (including wet sludge) because of the cost of evaporating water. The technology is applicable for low volatility organic liquids and high volatility organic liquids.

Electrochemical Oxidation

Electrochemical Oxidation was initially developed for the high-efficiency conversion of several radioactive organic wastes into environmentally acceptable waste streams. In tests with chemical warfare agents, this process, also called Mediated Electrochemical Oxidation (MEO), was successfully applied in destroying an organophosphorous nerve agent to non-detectable levels after one hour and an organochlorine agent (mustard) after two hours (10).

The system includes an electrochemical cell used to generate oxidizing compounds at the anode in an acid solution (typically nitric acid). These oxidisers and the acid attack any organic compounds, converting most of them to carbon dioxide, water and inorganic ions, at low temperature (<80 °C) and atmospheric pressure. The organic content of the feed, which may be soluble or insoluble organic liquids or solids, can vary from 5 to 100% without affecting the process. In the same manner, the water content of the waste can vary over a wide range. Some compounds destroyed by this process include aliphatic and aromatic hydrocarbons, phenols, organophosphorous and organosulphuric compounds, chlorinated aliphatic and aromatic compounds.

Electrokinetics

This technology is used to remove heavy metals from contaminated soil. However, it can also be used for the treatment of radionuclides and organic contaminants. The technique is based on ion and water migration in an electric field. The movement of water is called electro-osmosis, and ion movement electromigration. This technique is mainly applied to metallic contaminants in the soil matrix. It involves the application of DC potential across the contaminated zone using electrodes in the ground.

To solve the limitations of electrokinetics technology, Surfactant-enhanced electrokinetics works by injecting surfactant into the soil at one of the electrodes. This reduces the interfacial tension between the contaminant and soil matrix: the surfactant can then extract the organics from the soil surface and carry them towards the cathode. Control of the direction and rate allows maximum contact between the surfactant and soil particles, maximising movement of the organics. The performance of the technique is highly dependent on the soil moisture content and is also limited by soil heterogeneity.

Solvent Extraction – Chemical Dehalogenation – Radiolytic Degradation

This *ex-situ* physico-chemical process reduces the volume of the pollutant that needs to be destroyed. The technology uses an extracting chemical to dissolve target contaminants from soils in a final solution suitable for treatment with recovery of the solvent. This process produces relatively clean soil or sediment that can be returned to the original site or disposed on landfill. In some practices, prior to the solvent extraction, a physical separation technique may be used to screen the soils into coarse and fine fractions, in order to enhance the kinetics of the extraction process. This pretreatment technology is very useful in mitigating organic waste and heavy metals.

Solvent extraction technology can be applied to soils contaminated with volatile and semi-volatile organic compounds and other higher boiling point complex organics, such as polynuclear aromatic hydrocarbons (PAHs), petroleum hydrocarbons, pesticide/insecticide, polychlorinated biphenyls (PCBs), dioxins, and pentachlorophenol (PCP). Recent US EPA regulatory guidelines allow solvent extraction applications with nonharmful solvents for the removal of PCBs (19).

Solvent Extraction techniques are cost-effective methods to treat materials contaminated by PCBs and by other chlorinated compounds, but the main limitation is that the contaminants transferred into the solvent must be destroyed through a secondary method. Different approaches have been developed to combine solvent extraction with other techniques like chemical dehalogenation with immobilised reagents (CDP) and gamma-ray irradiation. Recent studies show that PCB concentration in transformer oil was reduced from 700 mg/kg to non-detectable levels in less than 5 minutes using chemical dehalogenation. While the results for radiolytic degradation showed that the PCB concentrations decreased with an increased g-ray dose, nearly 60 mega rads were needed to degrade PCBs from 300 mg/kg down to 1 mg/kg in solvent saturated soil (20).

Solvated Electron

This technology uses sodium metal dissolved in liquid anhydrous ammonia to produce a dark blue solution of solvated electrons; the solvated electrons act as dehalogenating agents. Solvated electron solutions are rapidly formed when alkali or alkaline earth metals are dissolved in ammonia or in some amines, forming solutions containing the metal cation and free electrons.

Halogens can be separate from organic halides to yield a fully substituted parent hydrocarbon and a metal halide. The treatment of waste with »solvent electron« is performed with low to medium temperatures and the conversion of the waste occurs in seconds. It has been stated that there is no need for pre-treatment, although some dewatering of sludge and/or sediments might be required.

The method is claimed to be applicable to treat halogenated hydrocarbons, pesticides, dioxins, PCBs, herbicides, CFCs, and chemical warfare agents. It is also stated that waste have been successfully treated in bulk pure material, soils, sludge, sediments, porous and non-porous surfaces, oils, contaminated vessels, hardware, and contaminated clothing. Some tests had confirmed that Solvated Electron process destroys the three chemical agents that comprise 85 percent of all US chemical weapons stockpiles (21).

The process design employs a cement mixer like reactor in which contaminated material and liquid ammonia are mixed. The ammonia completely disperses the soil, including the clays and washes the contaminant from the soil. After brief mixing, a reactive metal charge is added (commonly calcium). The electrons released from the calcium rapidly dehalogenate the contaminants. Ammonia is recovered for further use, and the soil is deodorised. The decontaminated soil is suitable for return to the site, suitable for agricultural use since is enriched in nitrogen from trace amounts of residual ammonia. The method is able to treat soils with up to 25% water content (Table 7b).

Supercritical water oxidation

Supercritical water oxidation (SCWO) is an *ex-situ*, high temperature and pressure technology that uses the properties of supercritical water to destroy organic compounds and toxic waste. Under supercritical conditions, carbon is converted to carbon dioxide and hydrogen to water; chlorine atoms derived from chlorinated organic compounds to chloride ions, nitro-compounds to nitrates, sulfur to sulfates, and phosphorus to phosphate.

The properties of super critical water are used to operate this process. Gases like oxygen and organic substances are completely soluble in super critical water, whereas inorganic salts present reduced solubility under supercritical conditions. Organic sub-

Table 7b *Main limitations of emerging/innovative physico-chemical technologies*

Solvated electron	**Supercritical water oxidation**	**Solar detoxification – Photochemical degradation**
Technical/Economic		
May require a pre-treatment for dewatering of sludge and/or sediments.	The end products (ash and brine) require proper disposal. Limited to treat liquid waste with solids sizing less than 200?m. Applicable to waste with organic content less than 20%.	The photolysis rates for pesticides are highly dependent on latitude, season and other meteorological conditions.
Social		
No public opposition known at this stage.	Not known public opposition at this stage.	No known public opposition.
Environmental/Risk		
Ammonia is a volatile liquid; toxic and fire risks. Calcium metal combined with hydrogen may form explosive mixtures.	Due to the high temperatures and pressures used in this technology, requires specialised control equipment, reactor materials and safety practices.	Low environmental impact due to limited use of chemicals and low off-gas generation rates.

stances dissolve in the super critical water, and oxygen and the organic substances are brought into intimate single phase contact at temperatures and molecular densities that allow the conventional oxidation reactions to carry out rapidly to completion.

Process residues are contained if the waste contains inorganic salts or organics with halogens, sulphur or phosphorous. The effluent gases contain no oxides of nitrogen or acid gases such as hydrogen chloride or sulphur oxide. The process does not generate particulates and less than 10 mg/kg carbon monoxide has been measured.

It has been stressed that this system must be constructed of materials capable of resisting corrosion caused by halogen ions. The precipitation of salts may cause plugging problems in the system (22). Destruction and Removal Efficiencies of greater than 99% have been reported for the treatment of numerous hazardous organic compounds. SCWO can be applied to aqueous waste streams, sludge and contaminated soils. It is also applicable to treat acrylonitrile wastewater, cyanide wastewater, pesticide wastewater, PCBs, halogenated aliphatics and aromatics, and organic nitrogen compounds.

Solar detoxification –Photochemical degradation

Sunlight energy can be used to degrade organic compounds of synthetic and natural origin. Short wavelengths (295–400 nm) of solar spectrum are greatly attenuated by the atmosphere, such radiation is able to generate direct and indirect photolytic processes that can degrade soil and surface waters polluted with POPs (mainly pesticides). Since the mentioned wavelengths are attenuated more strongly than longer visible wavelengths, the rate of photolysis of pesticides is highly dependent on latitude, season and other meteorological conditions; thus, in tropical regions photochemical processes are a key factor to assess pesticides fate and degradation (23).

Solar energy is used to degrade hazardous organic chemicals by direct thermal decomposition or by photochemical reaction. Some advantages include savings in fuel use, improved thermal destruction of contaminants, and a reduction in exhaust gas volumes, including PICs (products of incomplete combustion). These processes can use either thermal energy or a range of photochemical reactions.

In order to use efficiently solar energy is required to concentrate the solar radiation to achieve high temperatures to decompose or destroy the contaminants. Solar radiation is reflected by mirrors (heliostats) and absorbed by a receiver reaching temperatures of up to 2,300 K. No auxiliary fuel is required and it has been demonstrated to show an improvement in the destruction and removal efficiency (DRE) of organics, including pesticides, by a factor of 100 or more against conventional thermal technologies. High destruction efficiencies can be achieved at a temperature of 750 °C that is lower than the temperature required for thermal incineration.

The main photochemical processes that aid thermal treatment in solar detoxification include photocatalytic oxidation using titanium dioxide (TiO_2) as a catalyst. Ultraviolet radiation is used to promote an oxidation reaction in photocatalytic reactions using a catalyst such as TiO_2 in the presence of oxygen. The reactivity of singlet oxygen, irradiated with visible light in the presence of dissolved oxygen, is used in the dye-sensitiser processes. The reactive species produced can then react with contaminant molecules in the waste.

Oxidative degradation of pesticides, including lindane in contaminated water has been tested with direct sunlight in a solar furnace. Singlet oxygen was effective against some of the pesticides but reacted slowly or not at all with others. All pesticides were degraded by OH radical generating agents (such as methylene blue). Each system has different capabilities, that need to be taken into consideration when making comparisons.

Gas Phase Chemical Reduction

Gas Phase Chemical Reduction (also known as Eco Logic Process) has been developed as an alternative to incineration technologies. The technology is based on gas-phase thermo-chemical reaction of hydrogen with organic compounds. Hydrogen combines with organic compounds at 850 °C or higher, in a reductive reaction to form lighter hydrocarbons (mainly methane). For chlorinated organic compounds, such as PCBs, the products are methane and hydrogen chloride. The reaction is carried out with water that functions as a reducing agent and generates hydrogen. The technology is a hydrogenation process and adds hydrogen atoms to any incompletely hydrogenated organic molecule, dechlorinating molecules and breaking down aromatic rings, therefore is non selective in its treatment of organic substances.

The process can quantitatively convert PCBs, PAHs, chlorophenols, dioxins, chlorobenzenes, pesticides and herbicides, to methane. The yield will be determined by the concentration of organics in the waste. Approximately 40% of the methane produced can be further converted to hydrogen through the water shift reaction and non-reacted methane is converted to hydrogen in the catalytic steam reformer. Therefore, the process can operate with the hydrogen produced itself (10).

The gas phase reduction process is likely to be preceded by a thermal desorption unit when treating solid waste. There is potential for the removal of organic contaminants from the solid material to be improved in the chemical reduction process, as the thermal desorber will operate under a reducing hydrogen atmosphere, offering simultaneous destruction. The technology needs water in its operation and therefore can process waste with relatively high water content. This aspect provides an advantage over other thermally based processes that require treatment for sludge with high water content (Table 7c).

Table 7c *Main limitations of emerging/innovative physico-chemical technologies*

Gas phase chemical reduction	**Catalytic hydrogenation**
Technical/Economic	
Pollutants such as sulphur and arsenic may inhibit treatment. Sulphur in combination with iron may produce slimes that require additional centrifuge separation. The existence of irregular solids may also limit waste treatment due to materials handling. May need to be linked to special waste handling facilities in order to improve waste material handling.	Potential poisoning of catalysts may decrease or nullify process efficiency.
Social	
Generally not regarded adversely by community.	No public opposition.
Environmental/Risk	
Potential fugitive emissions of PCBs, pesticides or dioxins. The handle, use and storage of hydrogen within the process represent fire and explosion risks. The facilities must be subjected to an internal hazardous operations reviews and specialised process control to prevent release of waste materials during a process upset.	Gaseous products may generate safety and toxicity hazards. Combustion products may require scrubbing that would generate aqueous waste.

Catalytic Hydrogenation

The destruction of halogenated waste by hydrogenation in the presence of noble metal catalysts has been studied for many years. Noble metal catalysts are particularly susceptible to poisoning by a several substances found on waste, thus limiting the applicability of the technology. It has been developed a process for the regeneration of PCB contaminated transformer fluids using hydrogenation catalysts based on metal sulphides, which are extremely robust and tolerant to most catalyst poisons (24). The process is also claimed to destroy a wide range of chlorinated hydrocarbons, forming hydrogen chloride and light hydrocarbons as by-products.

In different trials relatively high concentrations of pure POPs compounds were treated in a hydrocarbon solvent and all were destructed to levels below the detection limit of analysis, presenting destruction efficiencies from 99.9996% (for hexachlorobenzene) to 99.99999% (for 1,2,3,4-TCDD). It is claimed that the variations in destruction efficiencies reflect the differences in the instrument detection limits rather than real differences in the extent of destruction (25). Most off-gases are recycled through the reactor, although purge gases are discharged through a catalytic combustion chamber.

Different surveys have shown that successful dechlorination of polychlorinated aromatic compounds by using Ni catalysts requires severe reaction conditions, high temperature and high hydrogen pressure. Pd, Ru catalysts that permit successful dechlorination of polychlorinated aromatic compounds under mild conditions are not developed for large-scale applications because of their high cost (26).

Recent surveys have shown the preparation of a selective catalyst to convert environmentally problematic compounds into useful products, allowing to perform liquid phase hydrodechlorination under mild conditions, using bimetallic catalysts consisting of nickel or copper associated with palladium, supported on a high-surface area carbon. The results show that such bimetallic systems permit to carry out liquid phase hydrodechlorination of hexachlorobenzene under mild conditions (P_{H2} 1 atm, t=50 °C), and that the method of catalysts preparation has a strong effect on their selectivity (27).

THERMAL TECHNIQUES

Thermal Desorption Integrated Technologies

This section includes the technologies involving thermal desorption as a pre-treatment-separation technique integrated with a post treatment-destruction technology (Table 8).

Thermal Desorption – Catalysed Dehalogenation

This system is composed by a thermal desorption system linked to the Base Catalysed Dechlorination (BCD). The system uses an indirectly heated thermal desorber to split organic compounds from contaminated media (28). The system is designed to achieve feed material temperatures of up to 510 °C allowing an effective treatment of soils and sludge polluted with a wide range of low and high boiling point compounds. The system is applicable for hydrocarbons, pesticides, herbicides, PCBs, coal by-products, wood treating compounds, dioxins, and furans. The gases produced during

Table 8 *Main limitations of emerging/innovative thermal technologies*

Thermal desorption integrated technologies	Plasma Arc Systems	Vitrification
Technical/Economic		
Overall efficiencies of methods are limited by thermal desorption efficiency, that depends on soil type and conditions.	The removal of volatile metals and particulates formed from inorganic components may require treatment; these additional steps may increase the cost. This process usually has a relatively high capital and operating cost. Some systems are limited to treat liquids and gases. Solids can only be treated after extraction or by forming slurry mixtures.	Vitrification is a destructive process and the soil can no longer be used for agricultural purposes. The vitrified matrix may hinder future use of the site if done *in-situ*.
Social		
In some cases may attract public opposition.	Generally not regarded adversely by community.	No known public opposition.
Environmental/Risk		
Combustion of off-gases requires control and emissions treatment. Process conditions must be selected and controlled in order to minimise the risk of dioxin and furan formation, and require pollution control equipment to treat these in the event that small quantities are formed.	The absence of combustion gases results on a gas emission smaller than for incineration systems. A surge tank is provided to contain any uncontrolled release of gases from the treatment chamber. The use of mechanical seals and operation of the unit at slight negative pressures should prevent any fugitive emissions.	Cautions must be taken to prevent fugitive emissions of vaporised organics. The vitrified nature of the formed matrix greatly reduces any potential leaching of metals or other residual pollutants.

the process are treated by a vapour recovery system that includes an oil venturi, an oil scrubber, water scrubber, condensing unit and vapour phase carbon adsorption unit.

Contaminants and moisture volatilised from the contaminated material are entrained in the off-gas and are condensed and recovered by the scrubbers/condensers. The condensed mixture is separated and the organic contaminant is collected for recycling via solvent recovery, fuel substitution or treatment using the BCD process. Separated water can be treated by liquid phase carbon adsorption and sand filtration. Most of the treated water can be recycled back to the process for use in the scrubbers and cooling conveyor.

Thermal Desorption – Pyrolysis

The PCS (*Product Control Soméus*) Technology is based on thermal desorption combined with flash pyrolysis technique, and followed by combustion. The main operational units of the system include indirectly heated rotary reactor, indirectly cooled solid material cooler, and multi venturi scrubber, pyrolysis gas combustion chamber, water treatment, auxiliary equipment and automatic operation with continuous monitoring.

The rotary reactor is the main component of the system. Waste is partially vaporised in a reductive environment under low vacuum conditions (0 to 50 Pa). The reactor is cylindrical in shape, arranged horizontally and rotates around its axis. The operating temperature in the reactor ranges from 450 to 800 °C. The waste may be introduced directly, or after drying in a desorber. If needed, the waste is ground in a mill in order to homogenise to a size less than 5 mm. The waste is decomposed into solid and vapour phases which include heavy metals in water insoluble form, high boiling point organics in the solid phase, and volatile organic compounds, volatile heavy metals and halogens in the vapour phase.

After the pyrolysis, the vapour phase is combusted and rapidly cooled; the gas stream is cleaned in a gas scrubber before emission. Although dioxin and furan gases are not generally formed in a reductive environment, it is possible that they could be formed following the combustion step. Therefore, after combustion the resulting gases must be treated by scrubbing. The scrubber process water is cleaned, neutralised, and water recirculated.

The process applications include the conversion to energy of waste such as solid hazardous waste, PCB contaminated soil, mercury contaminated soil, hospital waste, municipal solid waste, sewage sludge and coal. In addition, the technology can treat a full range of chlorinated hydrocarbons, organochlorine pesticides, organic and/or inorganic materials combined with contamination of organics, halogens and heavy metals. Although, this technology is not applicable for treatment of liquids (water, flammable liquids and solvents), explosives and/or materials with highly oxidizing nature under heat treatment and materials that cannot be decomposed by thermal treatment at 600 °C.

Thermal desorption – Retort System

This technology is adapted to treat contaminated soils containing volatile organic compounds (VOCs) or some semi-VOCs. The process has been configured for the treatment of pesticide contaminated soils, especially for dip sites.

The system involves an indirectly fired retort that is used to remove the volatile materials through an off gas-vent, leaving the treated soil for return to its original site. The retort operates on a continuous basis under negative pressure, and under neutral conditions (i.e. neither oxidizing, nor reducing) resulting in some leakage of air into the system. The treated soil leaves the retort via an overflow washer from where it is transferred to a stockpile.

The retort contents are indirectly heated. A combustion chamber surrounds the retort and the components are initially brought up to operating temperature by heating a batch charge of inert material. When this mass is at opening temperature, feed is started. Bed temperatures are monitored to ensure that conditions are maintained by varying either the feed rate or the firing rate; temperatures are set in the range of 400–700 °C depending on the residence time required, type of contaminant and soil properties. To treat organochloride pesticide contaminated soils, the retort usually operates with a bed temperature of 450 to 500 °C (10).

Within the retort the pollutants are volatilised and/or decomposed and separate as part of the off-gas. The off-gases are then drawn by a fan through a hot gas filtration system that removes particulate matter, allowing the cleaned gases to go to an afterburner for the residual organics destruction. The afterburner is designed to operate at 1,100 °C with a two-second-residence time. From the afterburner, the gases are quenched to minimise dioxin and/or furan formation.

The retort process is only able to treat solids and sludge, although liquids (e.g. pesticides formulations) could be treated by first producing a slurry. Treatment of low volatility compounds such as PCBs is not proposed on the current development status.

Plasma ARC Systems

This technology uses high temperatures (around 10,000 °C) for pyrolysis, which result from the discharge of a large electric current in an inert gas, to convert hazardous chemicals such as PCBs, pesticides, CFCs, halon gases into innocuous and safe-emitted end products. The destructive process is made possible by the conversion of the hazardous compound by the superheated cloud of gas or plasma into atomic elements and subsequent treatment converts the atomic forms into innocuous substances.

A thermal plasma field is created by directing an electric current through a low-pressure gas stream. Plasma arc ranges can reach 5,000 to 15,000 °C. There are different variations of plasma arc processes like PACT (Plasma Arc Centrifugal Treatment) (29), PLASCON (In-Flight Plasma Arc System) and STARTECH (Plasma-electric waste converter) (10).

Vitrification

The soil is treated with high temperature to cause melting and forming a glass when cooled. This technology can either be carried out *in-situ* or *ex-situ*; consists on inserting graphite electrodes into the contaminated encased area and energizing with a high electrical resistance heating (more than 1,700°C) to melt soil into a molten block. It is applicable for the treatment of organics (including pesticides and PCBs), inorganics and radionuclides. The organic contaminants will normally be destroyed while the inorganics will be trapped into the vitrified matrix. The Plasma Arc Centrifugal Treatment (PACT) mentioned above is a combination of Plasma Arc and Vitrification techniques (10).

BIOLOGICAL TECHNOLOGIES

Biological techniques are commonly carried out with indigenous microorganisms since these present superior performance due to the better survival rates compared to strains taken from geographically different locations (non-indigenous inoculants). However, some studies (30) have illustrated that the use of indigenous microorganisms for bioremediation and as hosts for developing genetically engineered organisms does not provide any advantage in dynamic and highly competitive environments. Thus, the survey recommends that the site must be engineered to provide temporal advantages for the non-indigenous microorganisms, or the known inoculant must be able to degrade a specific compound better than the native strain (Table 9).

Table 9 *Main limitations of emerging/innovative biological technologies*

Phytoremediation	**Bioslurry**	**Enhanced bioremediation**
Technical/Economic		
The process may take years to achieve regulatory limits. Few data exist yet as input to standardization and regulatory acceptance.	Dewatering soil fines after treatment can be expensive. It is required an acceptable method for disposing of non recycled wastewater.	Water-based solution circulation may move pollutants to underlying ground water. Clogging may occur. It is not suitable for low permeability soil. High metal and chlorinated organic concentrations may be toxic to the organisms. This technology is not effective at low temperatures.
Social		
Not regarded adversely by community.	Not regarded adversely by community.	Not regarded adversely by community.
Environmental/Risk		
Appropriate waste management and disposal is required to prevent contamination of the food chain.	Cautions and operational conditions must be set to prevent potential fugitive emissions of pesticides.	Some POPs may be formed under anaerobic conditions. The mobilization of contaminants may affect surrounding environment (air and groundwater).

Bioslurry

This is a technique for sites that require greater process control, more complete and faster degradation rates. The contaminated soils are mixed with water to form a slurry in order to allow contact between microorganisms and contaminants. The slurry is then fed into a bioreactor where a controlled amount of air is supplied for mixing and aerating; inoculation may be performed to enhance treatment. If conditions (temperature, nutrient concentration and proper aeration) are optimised, slurry processes are faster than other biological processes. The treated slurry is suitable for direct land application, similar to composted soils (17). The clean-up time is less than twelve months. Slurry-phase bioreactors are used to remediate soils and sludge contaminated with explosives, petroleum hydrocarbons, petrochemicals, solvents, pesticides and other organic chemicals. Bioslurry is favoured over *in-situ* biological techniques for heterogeneous soils, low permeability soils and areas where underlying groundwater is difficult to capture.

Enhanced bioremediation

Enhanced bioremediation, also called biostimulation or bioaugmentation, is a process to increase the biodegradation rate of contaminated soil by the addition of nutrients and oxygen. The activity of microflora and fauna may be stimulated by circulating water-based solutions through the contaminated soils and/or addition of indigenous/ inoculated microorganisms, engineered microbial species or seeding with pollutant degrading bacteria so as to enhance biological degradation of contaminants or immobilization of inorganic contaminants (17). Although it could be done in anaerobic conditions, it is more advantageous when oxygen is not limiting in order to prevent the formation of persistent by-products such as vinyl chloride resulting from the anaerobic degradation of trichloroethylene.

This technique can be used *in situ* to treat soils contaminated with different pollutants such as petroleum hydrocarbons, solvents, pesticides, wood preservatives and/or nitrotoluenes.

Phytoremediation

This is an emerging cost-effective technology for in-situ treatment of hazardous contaminants in soils and water. The technique makes use of specific plants and planting techniques to accelerate the rate of degradation, accumulation, removal, transformation, stabilisation and destruction of targeted soil, water and even airborne contaminants (31). Although it is most suitable for sites with shallow contamination of organics and metals, some practice now make use of deep rooted plants such as poplars and alfalfa to attack, mitigate and contain pollutants located many feet below the surface.

The degradation process stimulates micro-organisms through the release of carbon-containing nutrients from their roots. The zone closely associated with the plant root, the rhizosphere, has many more metabolically active micro-organisms, as a result of the naturally released nutrients that they use for energy and other biological activity. It is this symbiotic relationship between plants and microbes that is responsible for the degradation process. Other known mechanisms whereby plants are able to effect remediation process are hydraulic barrier/containment, phytovolatilisation, phytoaccumulation, and phytodegradation (32).

RECOMMENDATIONS AND CONCLUSIONS

The difference between technologies that only separate and/or concentrate a pollutant (e.g. solvent extraction and thermal desorption) and those which destroy the contaminant (e.g. pyrolysis, oxidation, reduction, and biodegradation) must be considered when setting site-remediation goals. Those technologies that only immobilise contaminants (e.g. landfill cap systems, stabilization, and vitrification) should also be clearly differentiated. Current soil sustainability trends have enhanced the use of non-destructive technologies making it possible to reuse the treated soil.

Several ratable and non-ratable criteria should be considered for the selection of the most suitable technology. Non-ratable, or relative criteria, include public acceptability and risk and environmental impacts (which depend on the specific geographic site location). Ratable criteria may include the applicability of the method (in accordance with its development status), overall costs, minimum achievable concentration, cleanup time, reliability, maintenance, post treatment costs, and ability to use soil after treatment. Social, environmental, technical, and economical criteria should be considered during the technology selection process; the more criteria are involved, the better performance is obtained. In case of choosing more than one technology to treat a specific waste or soil, limitations, impacts and risks related to the combined methods should be considered. Environmental impact and risk assessments must be carefully considered in order to avoid or control the emissions of PTS during the remediation process.

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Sažetak

PREGLED TEHNOLOGIJA REMEDIJACIJE PERZISTENTNIH OTROVNIH TVARI

Ovaj članak donosi pregled postojećih i novonastajućih tehnologija obrade otpada i tla onečišćenog perzistentnim otrovnim tvarima uključujući i perzistentna organska onečišćivala (engl. *persistent organic pollutants*). Autor dijeli tehnologije obrade na biološke, fizikalno-kemijske i termalne te opisuje rad osnovnih uređaja i uspoređuje tehnička, društvena i ekološka ograničenja, uključujući moguće rizike i učinke na okoliš. Èlanak također razmatra ukupne procijenjene troškove, vrijeme potrebno za čišćenje te razine odgovornosti i održavanja dajući na uvid prednosti i ograničenja svake tehnologije zasebno.

Ključne rijeèi:
otpad, PCBs, pesticidi, poliklorirani bifenili, POPs, tlo

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