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Overview of contaminated site remediation methods

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Target

Examples of different methods used for remediation of suspected contaminated site

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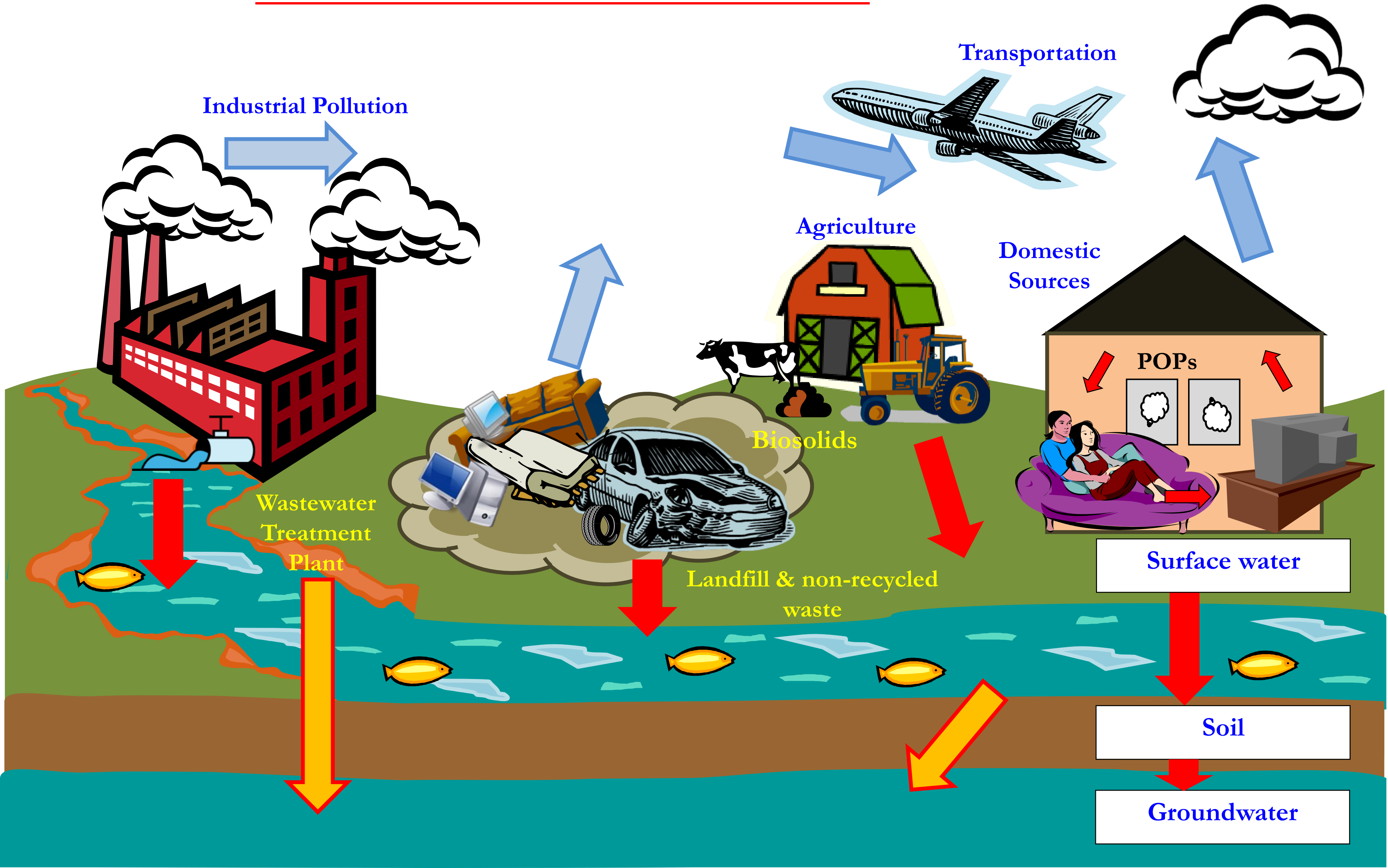
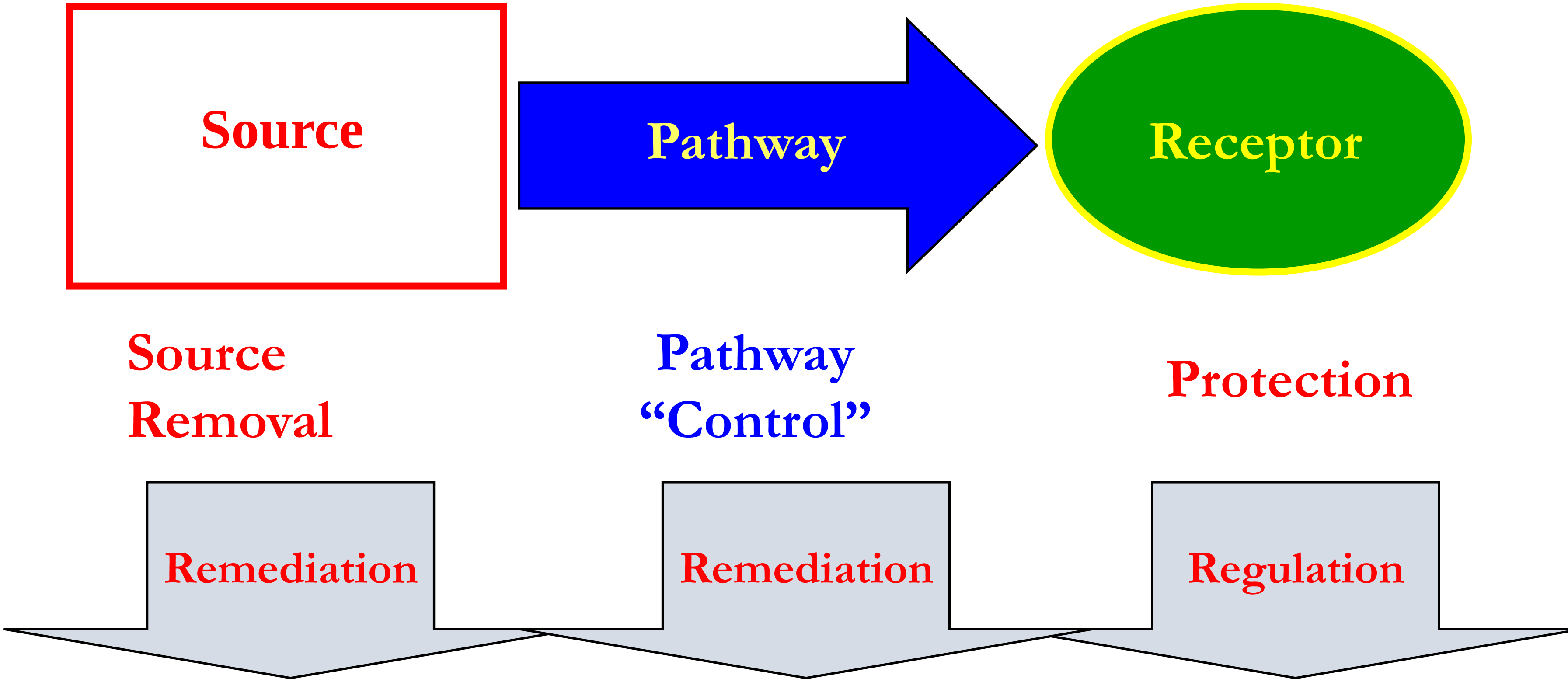
Contaminated sites

Routes of POPs contamination



Contaminated land management



- ✓ Destruction
- ✓ Extraction

- ✓ Stabilization
- ✓ Immobilization

- ✓ Land use limitations

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Breaking the Chain

- **Source removal** includes technologies aiming towards treatment of the source of pollution

- **Breaking the pathway** includes technologies hindering leakage and further spreading of pollutants

- **Hindering a contaminant** to reach a receptor could mean changing the land-use by regulation.

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Remediation

a treatment that

"permanently and significantly reduces the volume, toxicity or mobility of hazardous substances, pollutants and contaminants as a principal element"

(U.S. EPA)

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Classification of remediation

- **Stabilization:** where a contaminant remains *in situ* but is rendered less mobile and or less toxic by some combination of biological, chemical or physical processes. For most practical site remediation some combination of these outcomes is achieved (treatment trains).

- **Containment:** where the contaminated matrix is contained in a way which prevents exposure of the surrounding environment.

- **Immobilisation:** where contaminants are changed into less available constituents by some transportation process or by adding immobilizing agents.

(need of long term performance assessment)

Classification of remediation

- **Destruction** as a result of a complete biological and/or physico-chemical degradation of contaminants (e.g. at elevated temperatures by thermal treatments);

- **Removal** of contaminants by

  (a) some process of phase transfer/ mobilisation and recapture (e.g. leaching and sorption);

  (b) some process of concentration and recovery / harvesting (e.g. by physical separation), or

  (c) a combination (e.g. via hyper-accumulator plants);

- **Recycling** might be the "ultimate" form of removal;

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Classification of remediation

Ranking in order of preference (environmental benefit of permanently removing a contamination problem):

Recycling > destruction > removal > stabilization > immobilization > containment

Wider environmental effects, costs and other benefits must also be considered.

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Remediation technologies

- **In-situ**
  no escavation

- **Ex-situ**
  on site ***off site***
  escavation escavation + transportation

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Remediation technologies

Established

Established treatment technologies are those which have been widely applied in full-scale interventions.

Efficiency, process parameters and costs are well known.

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Remediation technologies

Innovative

Innovative treatment technologies

can achieve the same results as established technologies at a lower cost, or they can be more effective than established technologies at the same costs.

Efficiency, process parameters and costs

must be further assessed.

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Remediation technologies

- Innovative treatment technologies are newly developed technologies

- Innovative treatment technologies may be new technologies or technologies already in use for industrial applications

- Technologies other than incineration, solidification/stablization, or conventional pump and treat

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Remediation technologies

- Biological
- Physical, Chemical, Physico-chemical
- Thermal
- *Combinations (treatment trains)*

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Biodegradation or bioremediation

- Metabolic activity is key to biodegradation

- Accomplish complete mineralization or partial degradation in both aerobic and anaerobic environments

- Stimulate indigenous microbes to enhance biodegradation

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Remediation technologies

- Biopiles (*ex*)
- Slurry-phase bioremediation - Bioslurry (*ex*)
- Bioventing (*in*)
- Composting (*ex*)
- Enhanced bioremediation (*in*)
- Solid-phase bioremediation - Landfarming (*ex*)
- Monitored natural attenuation - Intrinsic bioremediation *(in)*
- Phytoremediation (*in*)

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Bioremediation technologies

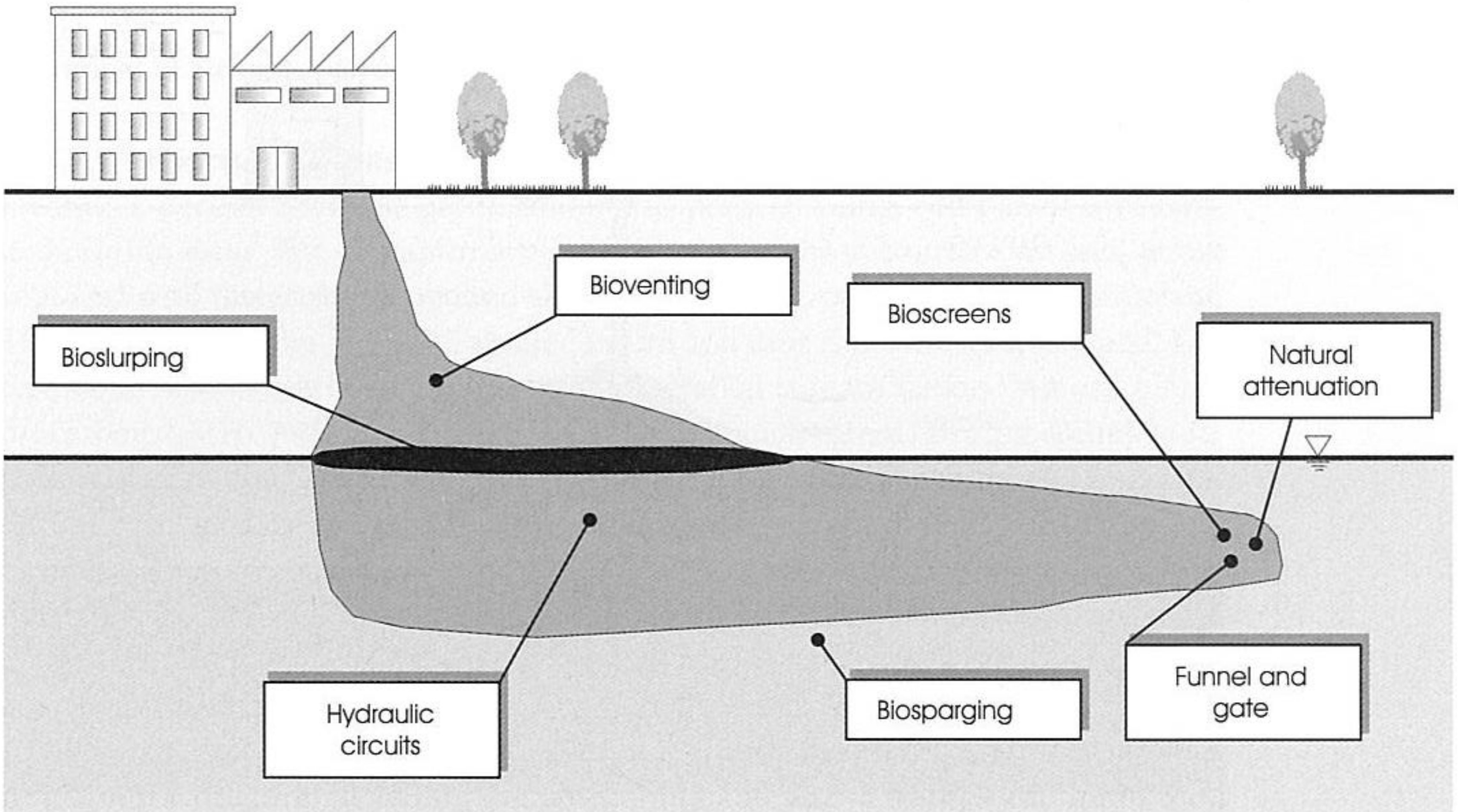

Fig. 12.4 Localization of different microbial in situ technologies.

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Remediation technologies - advantages

- May result in complete degradation of organic compounds to nontoxic byproducts.
- There are minimum mechanical equipment requirements
- It can be implemented as in-situ or ex-situ process. In-situ bioremediation is safer since it does not require excavation of contaminated soils. Also, it does not disturb the natural surroundings of the site.
- Low cost (esp. energy) compared to other remediation technologies.
- Composting also enriches the treated soil, providing nutrients for revegetation.

Remediation technologies - disadvantages

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- There is a potential for partial degradation to metabolites that are still toxic and/or potentially more highly mobile in the environment.
- The process is highly sensitive to toxins and environmental conditions. The physical form, amount, location, and distribution of contaminants have major impacts on the degree to which contaminants are degraded
- Extensive monitoring is required to determine biodegradation rates.
- Soil and contaminant characteristics affect bioavailability. Bioavailability of contaminants in soil can decrease with time, as the contaminants "age" and become more strongly sorbed to soil particles.
- It may be difficult to control volatile organic compounds during ex-situ bioremediation process.
- Generally requires longer treatment time as compared to other remediation technologies

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Physical processes

- Physical properties of the contaminants or of the contaminated medium are used.
- By means of a physical mechanism the phase transfer of contaminants is induced.
- No modification of the chemical structure of contaminants occurs.

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Physical processes - advantages

- Fast treatment
- Treats variety of contaminants
- Applicable to all media
- Less site characterization required
- Lower relative cost

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Physical processes - limitations

- Often do not treat but only transfer the contaminant
- Residuals require treatment
- Limited by site characteristics

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Chemical processes

The chemical structure (and then the behaviour) of the pollutant is changed by means of chemical reactions

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Chemical processes - advantages

- Fast treatment
- Treat variety of contaminants
- Applicable to all media

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Chemical processes - limitations

- Require extensive site characterization
- Limited by site characteristics
- Residuals require treatment

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Physical and chemical technologies

- Landfill cap systems *(in or ex)*
- Chemical dehalogenation *(ex)*
- Electrokinetic *(in)*
- Soil vapour extraction (SVE) *(in or ex)*
- Soil flushing (in)
- Soil washing (ex)
- Supercritical water oxidation *(ex)*
- Solvent extraction *(ex)*
- Solvated electron *(ex)*
- Solar detoxification *(ex)*
- Solidification/stabilization *(in or ex)*

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Physical and chemical technologies

Technology	Main Target Contaminants
✓ Landfill cap systems *(in or ex)*	all kind of contaminants
✓ Chemical Dehalogenation *(ex)*	X-VOCs, X-SVOCs, PCBs, Diox/Fur.
✓ Electrokinetic *(in)*	Heavy Metals
✓ Soil vapour extraction (SVE) *(in or ex)*	X- (VOCs, SVOCs)
✓ Soil Flushing *(in)*	X- (VOCs, SVOCs), PAHs, H.M.
✓ Soil Washing *(ex)*	X- (VOCs, SVOCs), PAHs, H.M., PCBs, Pest.
✓ Supercritical water oxidation *(ex)*	X- (VOCs, SVOCs), PCBs, Pest.
✓ Solvent extraction *(ex)*	X- (VOCs, SVOCs), PAHs, H.M., PCBs, Pest., Diox/Fur.
✓ Solvated electron *(ex)*	X-VOCs, X-SVOCs, PCBs, Diox/Fur., Pest.
✓ Solar detoxification *(ex)*	X- (VOCs, SVOCs), PAHs, H.M., PCBs, Pest., Diox/Fur.
✓ Solidification/stabilization *(in or ex)*	Heavy metals, PAHs, PCBs, Inorg.

Main limitations available physical-chemical technologies

	Landfill /Cap Systems	Solidification/Stabilization	Vapor 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 (Chiarenzelli, 1998). Potential leaking of hazardous compounds.	Precautions must be taken to minimize components leaching from stabilized 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.

Main limitations available physical-chemical technologies

	Base catalyzed dechlorination (BCD)	Electrochemical oxidation	Solvent extraction Chemical dehalog. Radiolytic degradation
Technical/ Economical	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	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 pretreatment 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.

Main limitations available physical-chemical technologies

	Solvated electron	Supercritical water oxidation	Solar detoxification - Photochemical degradation
Technical/ Economical	May require a pretreatment 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 200μm. 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	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 specialized control equipment, reactor materials and safety practices.	Low environmental impact due to limited use of chemicals and low off-gas generation rates.

Main limitations available physical-chemical technologies

	Gas phase chemical reduction	Catalytic hydrogenation
Technical/ Economical	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	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 specialized 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.

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Thermal processes

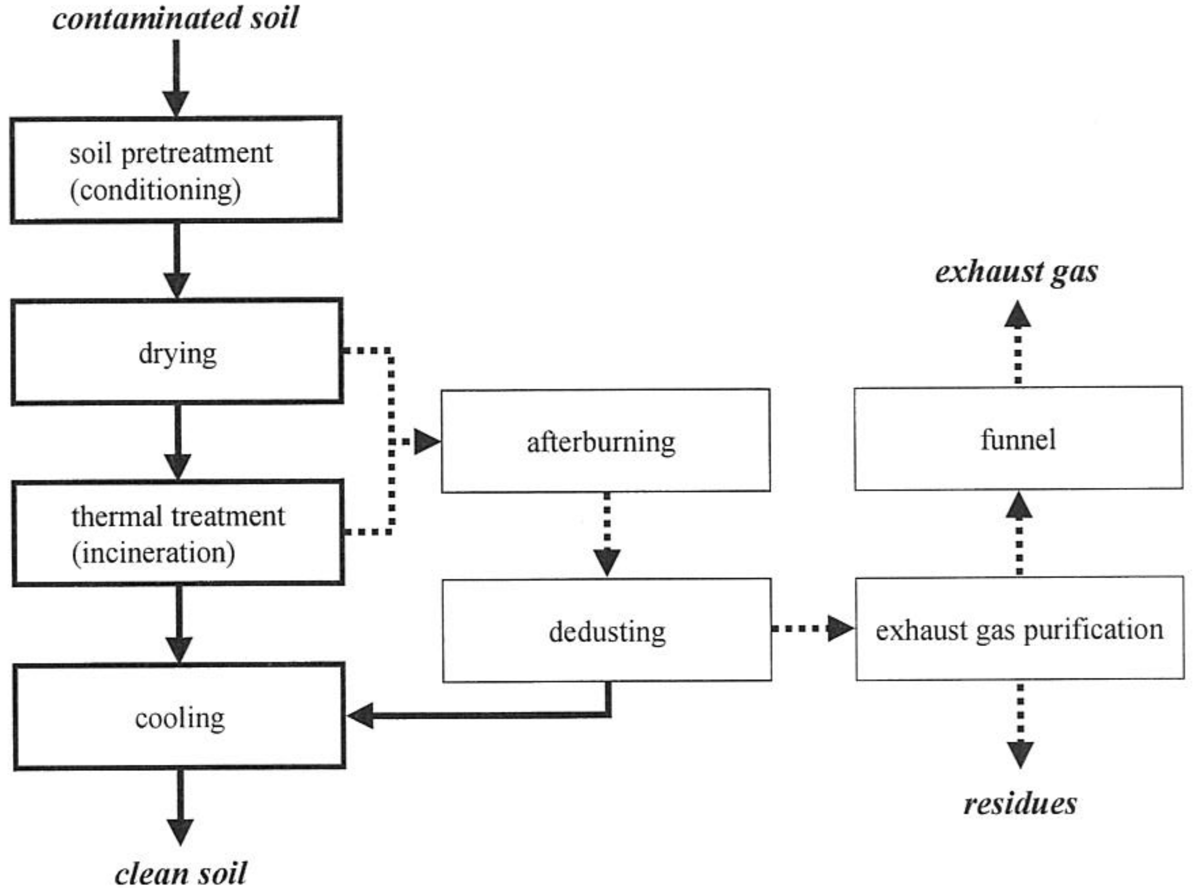

Fig. 9.1 The thermal ex situ treatment process.

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Thermal processes - advantages

- Fast treatment
- Applicable to organics
- Applicable to solid media
- Significant reduction in volume

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Thermal processes - limitations

- Not applicable to inorganics
- Not applicable to liquid or gaseous media
- Residuals require treatment
- Efficiency controlled by contaminant
- Higher relative cost

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Thermal technologies

- Combustion systems (ex)
- Thermal desorption systems (in or ex)
- Pyrolysis (ex)
- Plasma Arc Systems (ex)
- Vitrification (in or ex)

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Thermal technologies

Technology	Main Target Contaminants
✓ Combustion systems (ex)	X- (VOCs, X-SVOCs), PAHs, PCBs, Pest., Diox/Fur.
✓ Thermal desorption systems (in or ex)	VOCs, SVOCs, PAHs, PCBs, Pest., Diox/Fur.
✓ Pyrolysis (ex)	X- (VOCs, SVOCs), PAHs, PCBs, Pest., Diox/Fur.
✓ Plasma Arc Systems (ex)	PCBs, Pest., Diox/Fur.
✓ Vitrification (in or ex)	X- (VOCs, SVOCs), PAHs, H.M., PCBs, Pest., Diox/Fur., Inorg.

Thermal hazardous waste site remediation

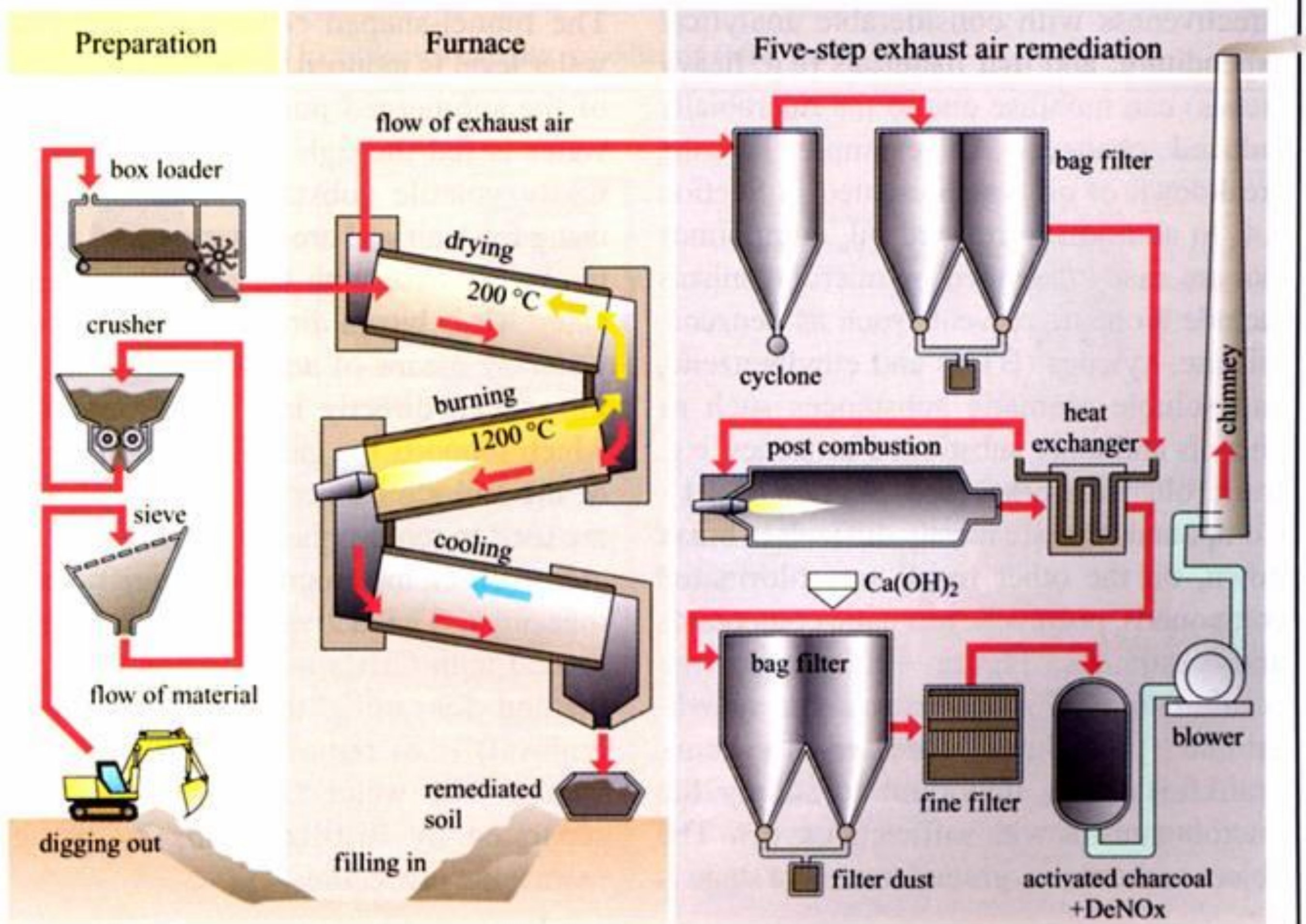

Figure 4.5.4 Thermal hazardous waste site remediation (after Bank 1994)

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Thermal desorption

- It is not a typical oxidation or decomposition of the contaminant
- Leaked contaminants can be processed, reused or disposed of
- Emission cleaning devices are needed
- There are three types of thermal desorption processes

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Thermal desorption - applications

- Usable for VOCs, SVOCs, pesticides and PCBs
- Not applicable for metals (except mercury), plastics, tar
- Usable for different ranges of contaminants
- Used in combination with stabilization or dechlorination
- Usable for soils ranging from sands to highly impermeable clays (if these are previously mixed with sand)
- The boiling point of the contaminant is a key factor in determining applicability

Main limitations of available termic technologies

	Combustion Systems	Thermal Desorption	Pyrolysis
Technical Economical	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	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.

Main limitations of available termic technologies

	Thermal desorption integrated technologies	Plasma Arc Systems	Vitrification
Technical/ Economical	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	Combustion of off-gases requires control and emissions treatment. Process conditions must be selected and controlled in order to minimize 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 vaporized organics. The vitrified nature of the formed matrix greatly reduces any potential leaching of metals or other residual pollutants.

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Solvent extraction processes

- **VOCs**
- **SVOCs**
- **X- VOCs**
- **X- SVOCs**
- **PAHs**
- **Heavy Metals**
- **PCBs**
- **Pesticides**
- **Dioxines/Furanes**

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Solvent extraction processes

- Combination or stand alone technology

- Separates contaminants from wastes, soils, sediments, sludges, or water

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Solvent extraction processes

- Contaminated material excavated and enter into feed preparation system
- Feed transferred to extraction vessel(s), and mixed with solvents
- Important solvent characteristics

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Solvent extraction processes

- Feed and solvent streams can enter a continuous contact system in parallel flow or counterflow configurations
- Decontaminated solids separated from extraction solvents
- Extraction solvent is transferred to solvent recovery system

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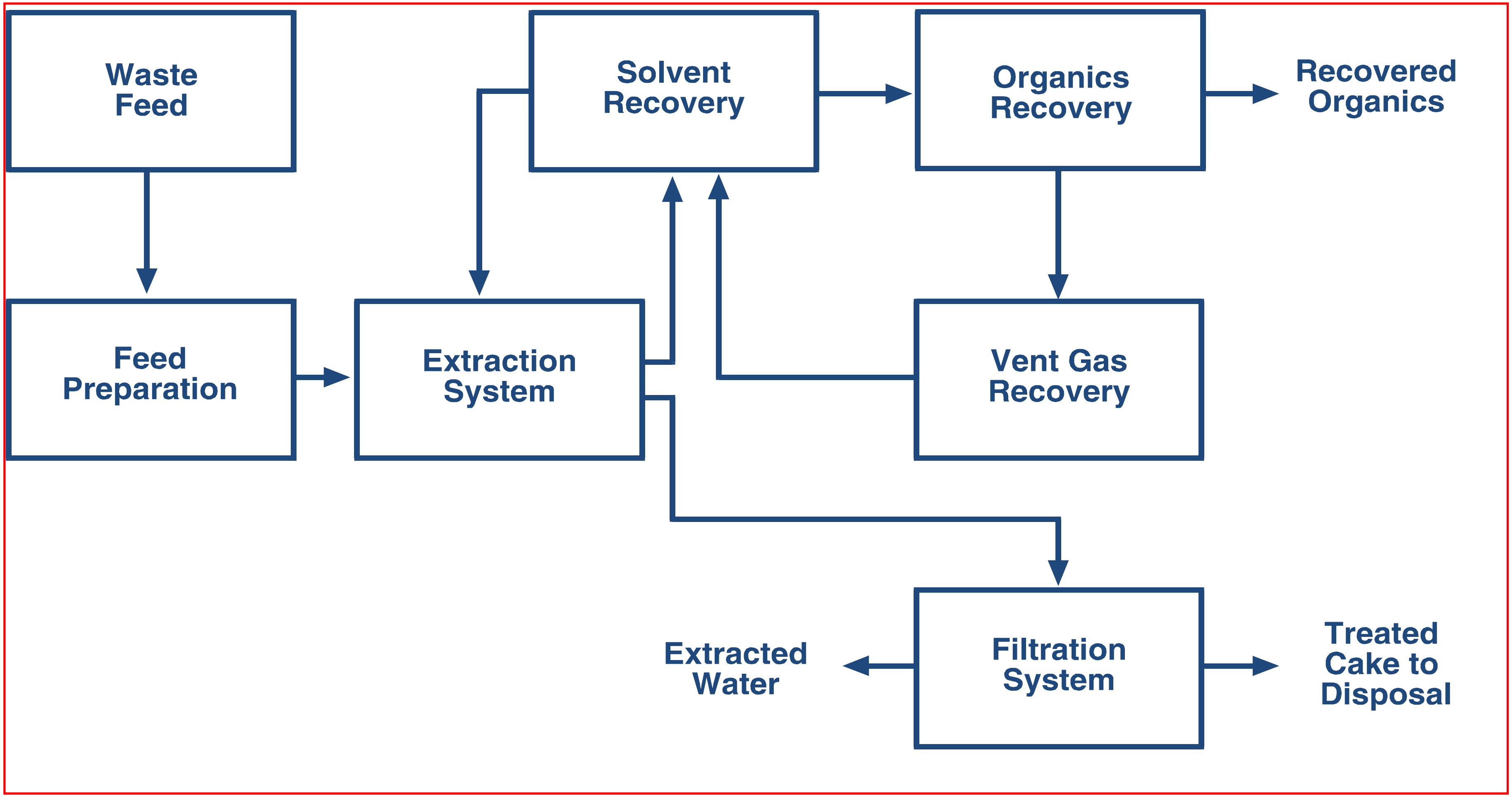
Solvent extraction process



Solvent extraction process

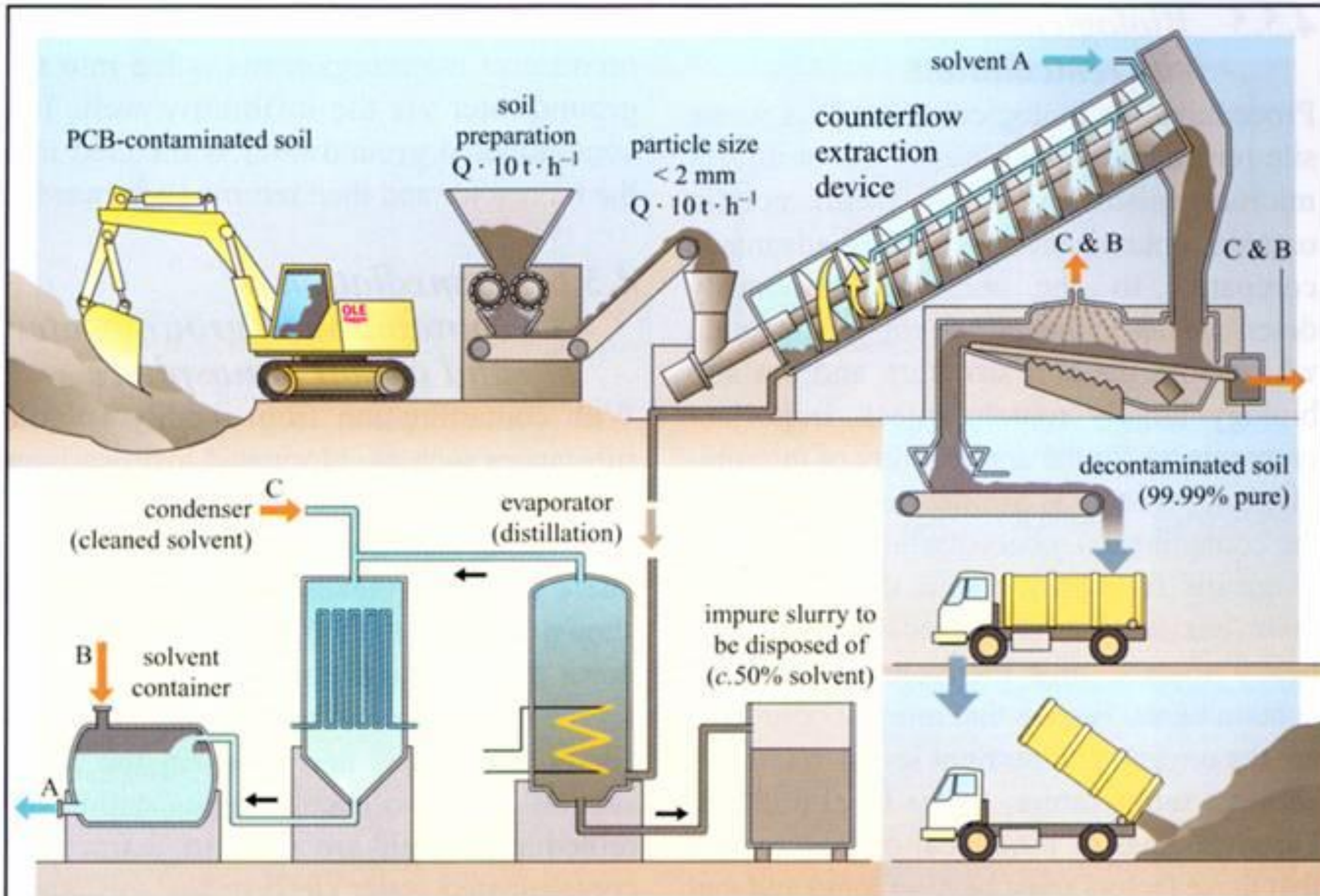


Figure 4.5.3 Counterflow extraction with solvents (after Bank, 1994)

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Solvent extraction processes - applications

- **Media treated: sediments, sludges and soils**
- **Contaminants treated**
- **Treats refinery wastes**
- **Generally NOT used to treat soils with inorganic compounds**

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Solvent extraction processes - advantages

- Reduces volume of hazardous waste to be treated
- Effective in treating:
  - Wood treating wastes
  - Slop oil emulsion solids
  - Separator sludge
  - Tank bottoms
- Media can be returned to site after meeting required standards

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Solvent extraction processes - limitations

- Organically bound metals restrict handling
- Presence of detergents can be unfavorable
- Traces of solvents may remain in solids
- Not effective on very high molecular weight organics
- Moisture content levels affect performance

Remediation technology assessment

Many technologies available

Many ratable and non ratable parameters must be considered

Assessment of remediation technology is a difficult process

Process to asses remediation technology

Collect information

Define criteria to assess information

Screen and evaluate information

Create data bases

Identify common parameters between different technologies

Define criteria to compare common parameters between different technologies

Define ranking criteria for each common parameter

Give a ranking to each technology for each parameter

Some elements of asses remediation technology

- Applicability (target contaminants)
- Minimum achievable concentration
- Clean-up time required
- Reliability and maintenance
- Decontaminated soil quality
- Residuals produced (by-products post treatment needed)
- Site data needed
- Overall cost
- Public acceptability
- Safety
- Development status
- Environmental impacts
- Performance dependency on site characteristics . . .

Process to select remediation technology

Select specific common parameters between different technologies

Selected parameters become criteria for technology comparison

Weight each criteria

Rank technologies on the basis of their performance in each weighted criteria

Choose the best ranked technology

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Case study: Spolana Neratovice, CR

History of the site

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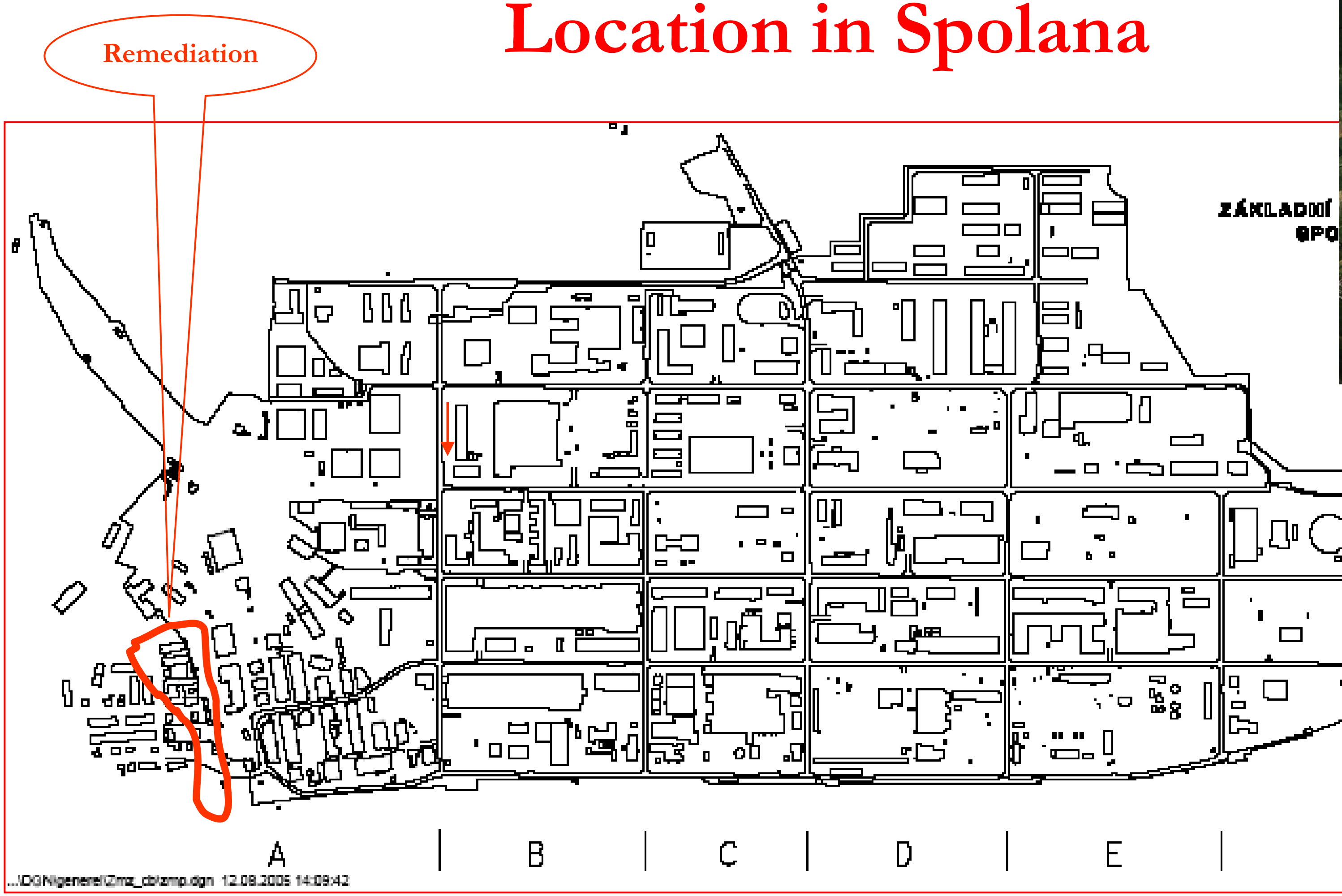
POPs problems in Spolana - Ghost of the past

The Spolana Neratovice chemical site is a large chemical complex based on chlorine chemistry.

During the 1960s, the production unit called PCP (pentachlorophenol) produced insecticides and herbicides.

- 1961 – production of HCHs (13% γ) → pesticides + production of TrCBz → production of TeCBz and HCB
- HCB → pentachlorophenolate Na → PeCP
- TeCBz → trichlorophenolate Na → 245-T → Agent Orange
- High contents of PCDDs/Fs

Location in Spolana



Floods 2002

In 2001, the activities concerning to the decontamination and decommission production building operations contaminated with dioxins and mercury.

In August 2002, during the catastrophic floods affecting the lower basin of the Vltava and Elbe Spolana site was inundated by overflowing Labe.

Mercury problem in Spolana Neratovice

History

- Industrial area – Spolana Neratovice – 1898
- Amalgam electrolysis - 1948

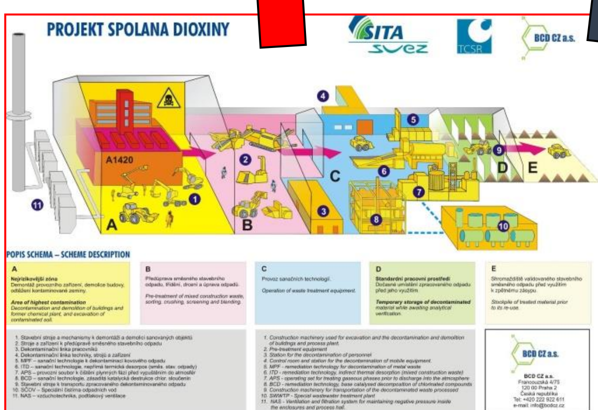
Sixties

- Production of OCPs – component of Agent Orange
- Chlorine production

Results

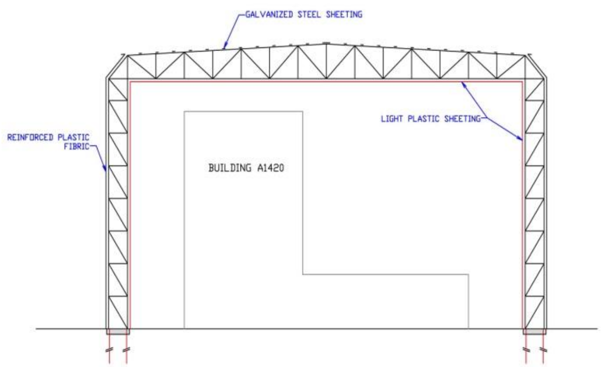
- Serious ills of employees
- Site contamination (POPs, Hg, Cl compounds..)

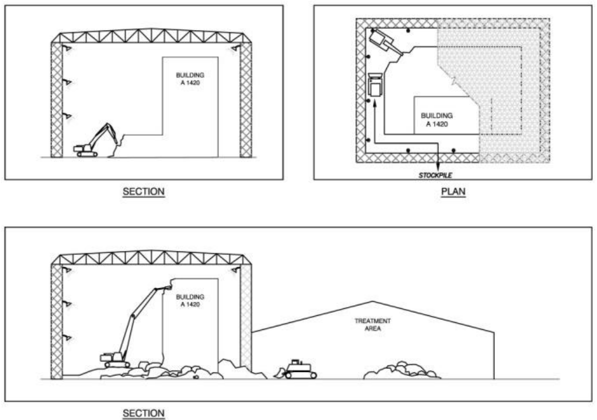
Spolana Neratovice



Spolana Neratovice – example of non-combustion technology application

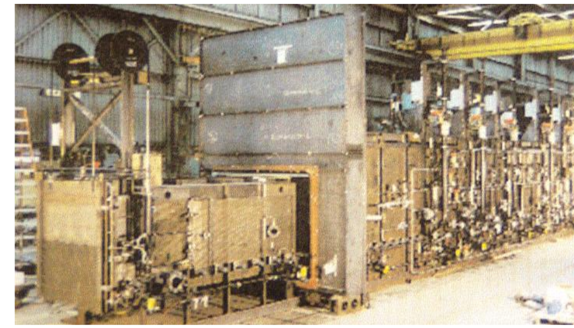
Decontamination/demolition





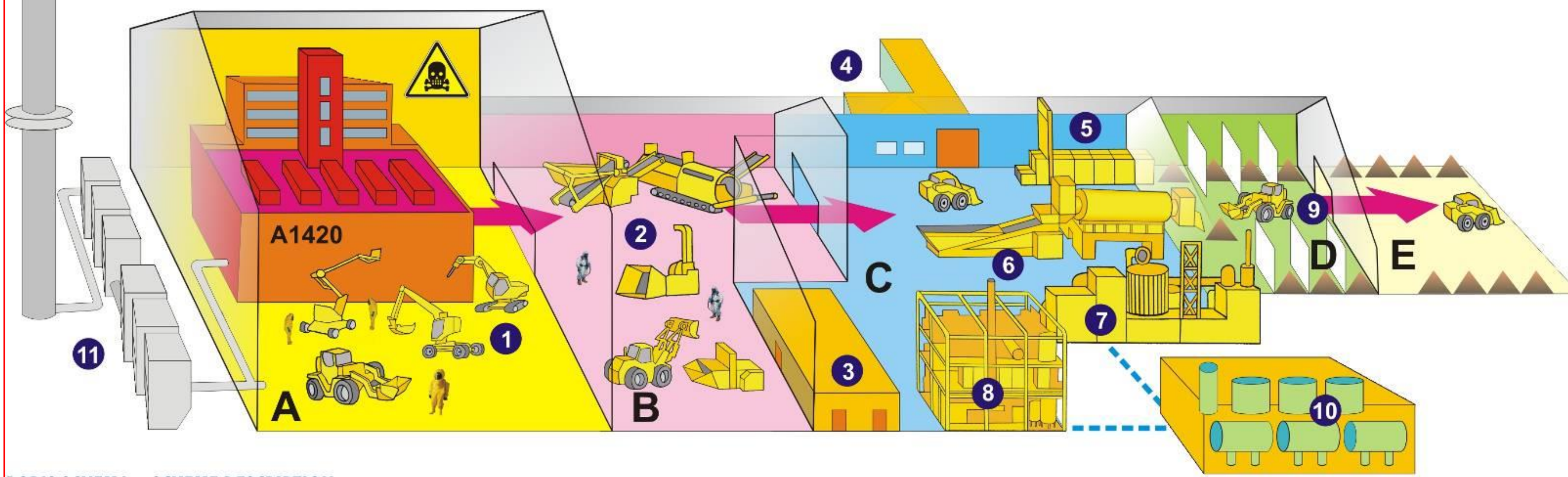
Indirect thermal desorption

Metal part furnace



Project Spolana Neratovice

PROJEKT SPOLANA DIOXINY



POPIS SCHEMA – SCHEME DESCRIPTION

A

Nejrizikovější zóna
Demontáž provozního zařízení, demolice budovy, odtěžení kontaminované zeminy.

Area of highest contamination
Decontamination and demolition of buildings and former chemical plant, and excavation of contaminated soil.

B

Předúprava směsného stavebního odpadu, třídění, drcení a úprava odpadů.

Pre-treatment of mixed construction waste, sorting, crushing, screening and blending.

C

Provoz sanačních technologií.

Operation of waste treatment equipment.

D

Standardní pracovní prostředí
Dočasné umístění zpracovaného odpadu před jeho využitím.

Temporary storage of decontaminated *material while awaiting analytical verification.*

E

Shromaždiště validovaného stavebního směsného odpadu před využitím k zpětnému zásypu.

Stockpile of treated material prior to its re-use.

1. Stavební stroje a mechanismy k demontáži a demolici sanovaných objektů
2. Stroje a zařízení k předúpravě směsného stavebního odpadu
3. Dekontaminační linka pracovníků
4. Dekontaminační linka techniky, strojů a zařízení
5. MPF – sanační technologie k dekontaminaci kovového odpadu
6. ITD – sanační technologie, nepřímá termická desorpce (směs. stav. odpady)
7. APS – provozní soubor k čištění plynných fází před vypuštěním do atmosfér
8. BCD – sanační technologie, zásaditá katalycká destrukce chlor. sloučenin
9. Stavební stroje k transportu zpracovaného dekontaminovaného odpadu
10. SČOV – Speciální čistírna odpadních vod
11. NAS – vzduchotechnika, podtlakový ventilace

1. *Construction machinery used for excavation and the decontamination and demolition of buildings and process plant.*
2. *Pre-treatment equipment*
3. *Station for the decontamination of personnel*
4. *Control room and station for the decontamination of mobile equipment.*
5. *MPF - remediation technology for decontamination of metal waste*
6. *ITD - remediation technology, indirect thermal desorption (mixed construction waste)*
7. *APS - operating set for treating gaseous phases prior to discharge into the atmosphere*
8. *BCD - remediation technology, base catalysed decomposition of chlorinated compounds*
9. *Construction machinery for transportation of the decontaminated waste processed*
10. *SWWTP - Special wastewater treatment plant*
11. *NAS - Ventilation and filtration system for maintaining negative pressure inside the enclosures and process hall.*

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Base Catalyzed Dechlorination (BCD) Unit

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TEŞEKKÜR EDERİM…

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MINISTRY OF ENVIRONMENT,
URBANIZATION AND CLIMATE CHANGE

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