Basel Convention Coordinating Centre
Stockholm Convention Regional Centre
URUGUAY

LATU

Ministerio de Vivienda
Ordenamiento Territorial
y Medio Ambiente
MVOTMA

Contaminated Sites

Regional Training in Hazardous Waste
September 30 – October 2, 2014
San José, Costa Rica

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo

NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Contaminated Sites

- **What are they and how are they generated?**
  - Contaminated sites are places where persistent toxic substances or waste in connection with industrial, commercial, agricultural and household (anthropogenic) activities, have been stored, buried and/or dumped.

  - At contaminated sites, these substances are concentrated, exceeding the safety levels recommended for a certain use (agricultural, residential, commercial, industrial).

  - Once in the environment, persistent toxic substances affect the quality of soil, water and air, and they can also cause health damages.

- Therefore, it is important to identify contaminated sites in order to prevent health risks arising from their inadequate use or environmental damages caused by transportation of these substances from the site to its surroundings.

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Soil Structure

- The soil is the thin upper layer of the earth's crust. It is a vulnerable system, subject to alterations that can jeopardize its natural balance.

- The average composition of the soil, in percentage by volume, is as follows:
  - 50% solid matter.
  - 20-30% aqueous dissolution.
  - 20-30% edaphic air.

Soil Structure

Aqueous Dissolution

- It acts as an intermediary between the lithosphere and living organisms, and it contains the necessary solutes for the development of the existing vegetation.

- The type and concentration of ions present basically depend on the type of soil and the time of the year. Mainly ions Cl^-, $SO_4^=$ and Ca^{+2}, to a lesser extent Mg^{+2}, $H_3SiO_4^-$, K^+, Na^+ and Mn^{+2} and, as a minority, Al^{+3}, Fe^{+3}, Zn^{+2}, $Cu2^{+2}$ and $H_2PO_4^-$ are present.

RED de CENTROS
Convenio de Basilea Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention Latin America & the Caribbean
Stockholm Convention

Soil Structure

Solid Phase

It represents nearly half of the total soil composition and is comprised of 45% inorganic fraction and 5% organic fraction.

- **Inorganic Fraction**

Consists of mineral particles of different sizes that, from the largest to the smallest, are named as follows: gravel (>2mm), sands (0.05-2mm), silts (2-50 mm) and clays (<2mm).

Soil Structure

- **Inorganic Fraction (Cont.)**

The size of the particles forming a certain soil determines the latter's texture and provides information on its porosity, where air circulates, and edaphic aqueous medium.

Pore size is also important as it determines soil permeability, that is, the rate at which air and water can move through it, from the most superficial to the deepest layers.

Soil Structure

- **Inorganic Fraction (Cont.)**

Composed of primary and secondary minerals.

- *Primary:* formed at high temperatures and deriving from igneous and metamorphic rocks such as quartz, feldspars, micas, etc.

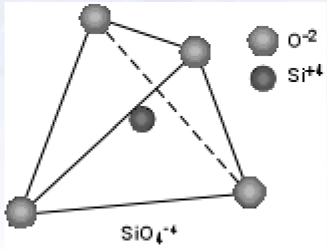
- *Secondary:* formed from low temperature reactions and deriving from sedimentary rocks or the weathering of primary minerals such as, for example, carbonates, some oxides, sulfur compounds, etc.

Soil Structure

- **Inorganic Fraction (Cont.)**

Although the chemical composition of the inorganic fractions of the soil is variable, most of them contain mineral silicate.

The structural unit is SiO_4.



RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Soil Structure

- **Organic Fraction**

It represents a very small weight percentage of the global soil composition. It is of vital relevance to determine its fertility as it is a food source for microorganisms, participates in various edaphic chemical processes and affects its physical properties.

It is mainly composed of plant residues in decomposition phase and, in a lesser proportion, of living organisms and organic matter resistant to biological and chemical degradation.

Soil Structure

- **Organic Fraction (Cont.)**

The soil also contains organic matter that is almost non-degradable, called humus fraction.

Humus mainly consists of humic and fulvic acids, which are a complex mix of macromolecules. The humus fraction is nitrogen-enriched in relation to the initial plant matter and a significant part thereof is insoluble in water, so it accumulates in the most superficial layers of the soil.

Soil Structure

• Organic Fraction (Cont.)

The beneficial effects of the soil's organic matter may be summarized in the following aspects:

- It allows plant growth by contributing an important proportion of essential bio-nutrients: nitrogen (almost all of it), phosphorus (between 50-60%) and sulfur (around 80%).
- It regulates the availability of many metal cations by absorbing them; these act as micronutrients or toxic elements, depending on the case.
- It exerts a buffering action by maintaining the soil's pH due to the presence of acid functions in its molecules.
- It regulates soil moisture, due to its moisture holding capacity, interacting in many cases with silicates.
- It improves the granular structure of the soil, benefiting permeability and aeration, by interacting with mineral particles and favoring particle aggregation.

Soil Structure

The soil presents a sequential structure. Different layers or horizons can be observed at different depths, which have different physical and chemical properties, depending on their formation process.

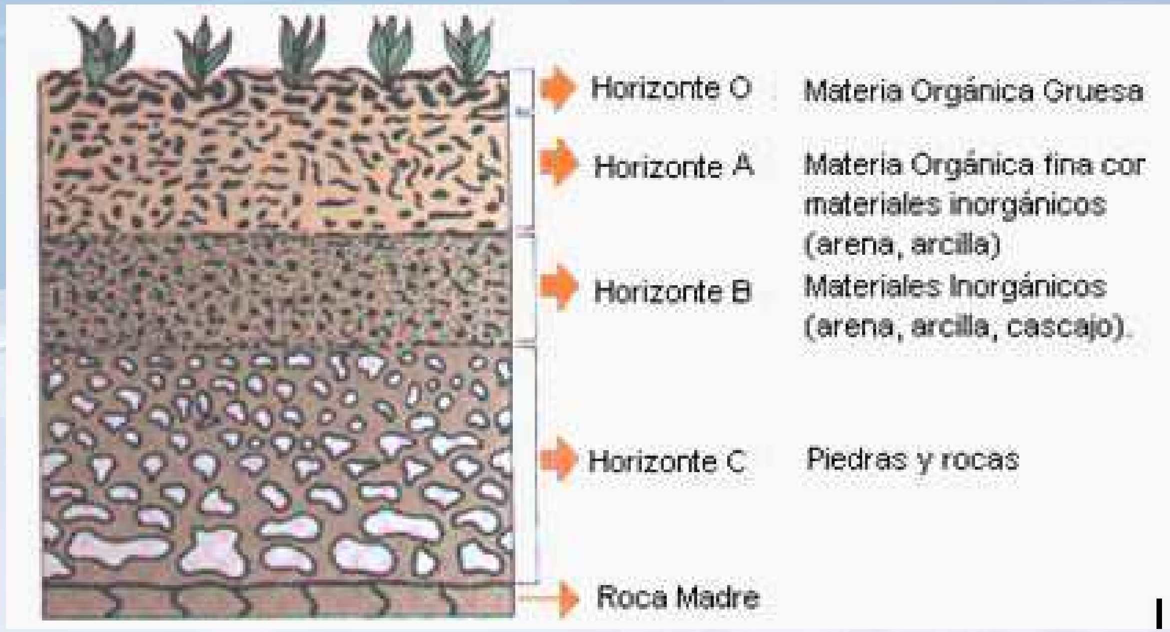
Basically, three layers can be distinguished:

• The outermost layer (A horizon), where great leaching of some of its components takes place, and which consists of mineral particles (mainly silicic materials) and organic matter from living organisms.

• Immediately below lies a layer (B horizon) where leaching compounds from the previous layer accumulate. Here oxidation of organic matter takes place and iron oxides (III) can be found.

• In the deepest layer (C horizon), hardly any leaching occurs and little particulate matter is present. As depth increases, less oxygen is present (due to its consumption in the oxidation processes of organic matter and to the formation of oxides) and a parallel increase in the amount of carbon dioxide is detected.

Soil Structure



Soil Structure

Soil pit

Soil Structure

Soil formation is influenced by the following factors:

- Time.
- Precipitation. Rains regulate edaphic moisture and air contents.
- Temperature. It has an influence on the speed of chemical reactions, the microbial activity and, therefore, on the composition of organic matter.
- Land topography. The existence of slopes or inclinations affects surface water retention and drainage, influencing soil formation rates.
- Vegetation. Vegetation retains moisture, so the leaching degree decreases. It also favors rock disaggregation.

Soil Structure

Soil formation is influenced by the following factors:

• Microorganisms. In natural soils there is a biomass, called edaphon, formed by microorganisms. It consists of bacteria, viruses, fungi, algae, lichens, protozoa and other higher species. These microorganisms enable the development of many biochemical processes associated with the aqueous phase of the soil and influence soil structure.

• Parent material. The original rock of the land determines the chemical composition of the soil as it is the base material from which it is formed. The types of rocks that can be soil parent material are: igneous, sedimentary and metamorphic rocks.

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Soil Structure

Igneous rocks are formed by the solidification of molten material that flows to the surface. Depending on the cooling rate of this material, coarse grained rocks (if it is slow) or fine grained rocks (when solidification is fast) will be formed.

Sedimentary rocks are formed as a result of the sedimentation of materials deposited by wind, water, ice or gravity. They can be composed of aluminium, silicon or iron salts, of calcium and magnesium carbonates or combinations of these compounds.

Metamorphic rocks are formed by the recrystallization of the two previous types of rocks when subject to high pressures and high temperatures. The most commonly known are marbles.

Main Physicochemical Processes

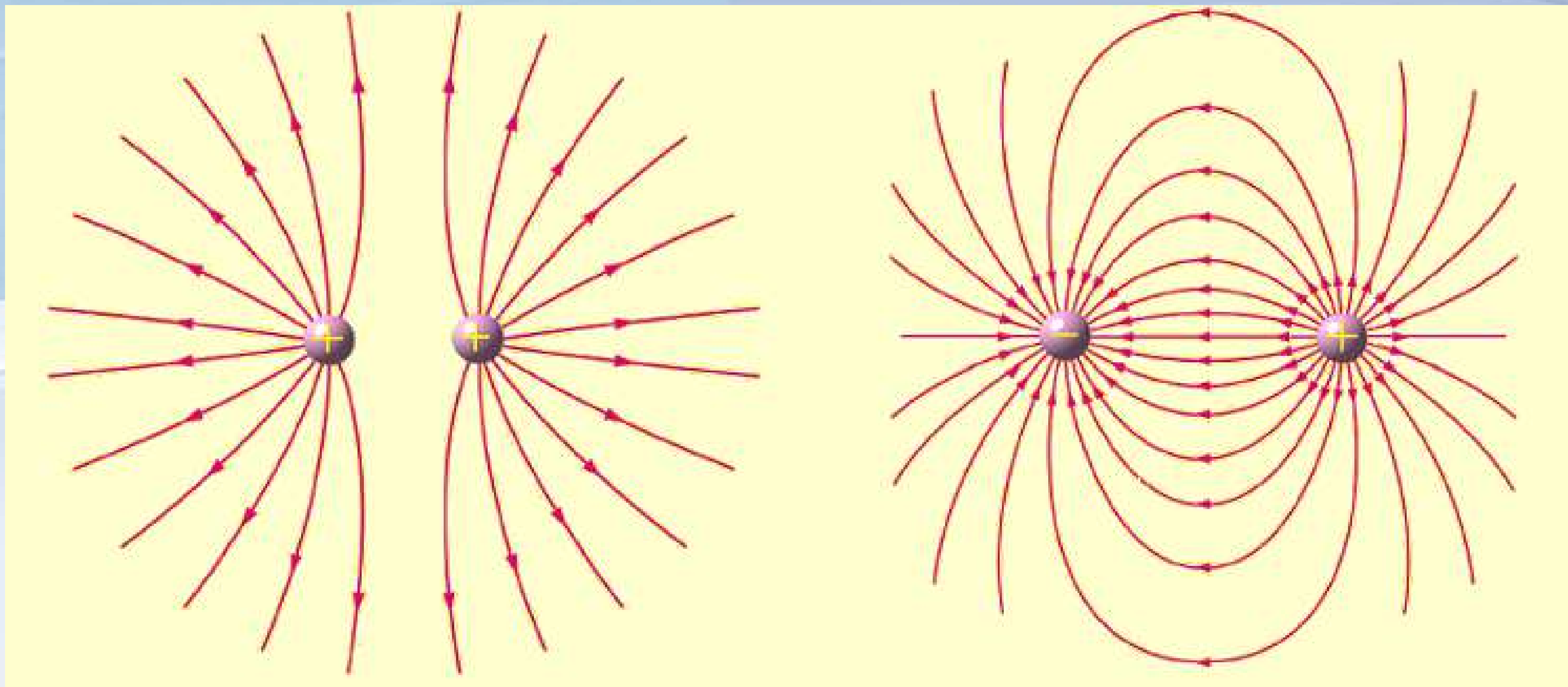
Adsorption Phenomena

• Adsorption and ion exchange phenomena are very important as they determine the capacity of the different soluble soil compounds to participate in different chemical reactions.

• Colloidal size particles (clays and humic substances) participate in these processes and, due to their small dimensions, present a high specific surface. This is the most influencing parameter in adsorption processes.

• Colloidal particles adsorb ions of the same sign on their surface and, consequently, electrostatic repulsions are exerted on them, thus allowing them to be suspended in the soil solution. To neutralize the surface charge of colloidal particles, a distribution of charges of the opposite sign is established in the solution.

Main Physicochemical Processes



RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Main Physicochemical Processes

Cation Exchange Phenomena

• The negative charge of the soil colloidal particles retains cations. This retention is of great importance to the soil since it reduces the loss of some ions due to leaching, while keeping them available to be taken up by vegetation. Usually adsorbed cations are mainly Ca^{+2}, Mg^{+2}, K^{+} and Na^{+}.

• Cations adsorbed by colloidal particles can be exchanged by other ions present in the soil solution. The process by which a cation is substituted by another one is known as cation exchange. The distribution of the main exchangeable cations in agricultural soils is $Ca^{+2} > Mg^{+2} > K^{+} = NH_4^{+} = Na^{+}$.

Main Physicochemical Processes

Anion Exchange Phenomena

• They occur in a much lower proportion than cation exchanges and in soils where the colloid changes its charge to positive and has the ability to retain anions: highly weathered soils containing high amounts of Al and Fe. A significant example is the adsorption of phosphate ions, which form insoluble compounds that are very difficult to assimilate by plants. Low pH soils.

Main Physicochemical Processes

Acid-Base Phenomena

• As the soil is transformed by weathering processes, it suffers changes in its pH value. This value mainly depends on the presence of certain cations in the soil, which may come from the atmosphere, plant residues, fertilizers, chemical reactions, percolating water, etc.

Main Physicochemical Processes

Acid-Base Phenomena

The optimum pH for most crops is between 6 and 7.5, but there are certain phenomena that can cause excessive acidification of the soil, such as:

- Acid precipitations.
- Acidification due to organic matter from plant residues that may release soluble acid compounds.
- Use of ammonia fertilizers that can suffer nitrification reactions.
- CO_2 dissolution.
- Cation adsorption by plants during growth, which are exchanged by H^+.
- Oxidation of iron sulfides in pyrolytic soils.

A side effect of acidification and salt solubility increase is salinization, which is considered an important pollution problem.

Main Physicochemical Processes

Oxidation Reduction Phenomena

Due to the presence of electron acceptor and donor species in the soil, redox reactions can take place, causing changes in the oxidation numbers of elements constituting the organic and inorganic species that participate in such reactions.

The medium pH influences these redox processes.

The main electron acceptor is the oxygen in the edaphic air that basically comes from the atmosphere, while the most abundant donor species is the soil's organic matter.

Contaminated Soils (Sites)

The environmental impact man is having on soil has caused soil contamination to be one of the environmental issues receiving the greatest attention. This is due to the direct risks that contaminated soils pose to human health, and to economic reasons arising from the limitation of its use.

Contaminated soil means a portion of land, either surface or subterranean, the quality of which has been altered.

Several alterations are produced and they can be originated by different causes: the result of industrial, agricultural or service activities, both current or past.

Contaminated Soils (Sites)

Pollutants can cause:

- Contamination of groundwater by leachate.
- Contamination of surface water by runoff.
- Air pollution due to combustion, evaporation, sublimation or wind drift.
- Poisoning by direct contact.
- Poisoning through the food chain.
- Fire and explosion.

Contaminated Soils (Sites)

Contamination is usually divided into two types:

• Endogenous contamination: Consisting of imbalances in soil constituents that cause variations in some species in concentrations harmful to living beings:

- Mobilization of metals caused by acidification processes.
- Increase in the percentage of Na^{+} in soil, causing salinization, which affects its production capacity.

• Exogenous contamination: Caused by different kinds of dumping or excess of agricultural products (metals, hydrocarbons, pesticides, fertilizers, etc.), components that are alien to the original soil composition.

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Main Pollutants

Heavy Metals

• They can be found in the structure of soil particles; however, they are hazardous when present in the soil solution and therefore act as micronutrients.

• Their main sources are industrial discharges, mining activities, waste, pesticides, traffic, etc.

• Metals dumped in largest amounts are Mn, Zn, Cu, Cr, Pb, Ni, Cd and Hg, many of which are highly toxic.

• Contamination by metals can occur in surface and groundwater by percolation.

Main Pollutants

Heavy Metals

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Main Pollutants

Heavy Metals

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Main Pollutants

Organic Compounds

- They are highly complex due to their diversity and high reactivity. The main pollutants are oil derivatives.

- The mobility of these compounds will depend on the type of soil (contents of organic matter, ion exchange capacity, etc.) and on the chemical properties of pollutants (solubility in aqueous medium, vapor pressure, etc.)

- Another important factor to consider is their degradation, as metabolites more toxic than the original product can be produced.

Main Pollutants

Organic Compounds

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo

NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Main Pollutants

Organic Compounds

Main Pollutants

Organic Compounds

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Main Pollutants

Organic Compounds

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Main Pollutants

Fertilizers

• The main problems are associated with nitrogen and the accumulation thereof in the form of nitrates (NO_3^-). Nitrates are in general hardly retained in the soil so they will leach, contaminating aquifers and surface waters. Excess of nitrates causes eutrophication and toxicity.

• Phosphorus present in fertilizers usually contributes to the presence of cadmium.

• Excess of organic manures can lead to soil salinization, rendering the soil useless.

Main Pollutants

Pesticides

• Synthetic compounds are hazardous due to their persistence and toxicity, as well as their potential bioaccumulation (in the same organism) and biomagnification (trophic chain).

• They may undergo chemical transformations forming more toxic metabolites. Their mobility will depend on their chemical characteristics.

• They mainly accumulate and are transformed in the organic matter of soils.

Main Pollutants

Pesticides

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo

NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Main Pollutants

Acidification

• It can be caused by industrial discharges, waste accumulation, acid rain and ammonia fertilizers, among others. The main problems are the dissolution of insoluble compounds and the release of (bioavailable) toxic metals. It also occurs due to changes in the aerobic and anaerobic conditions of the soil.

Main Pollutants

Salinization

• It is the accumulation of soluble or easily soluble salts in the soil, such as NaCl, Na_2SO_4, $CaCO_3$, $MgCO_3$, etc.

• It is a common phenomenon in arid regions, where groundwater contains high concentrations of these salts and the evaporation rate is high. When the phreatic level is high, there is an upward movement of saline water that evaporates when reaching the surface, leaving the salts on the soil horizons.

• Anthropogenic salinization can occur due to the discharge of industrial compounds, excessive use of fertilizers, use of irrigation waters with high saline contents, land characteristics or excessive soil use.

• Salinization causes several chemical and physical problems in the soil. Chemical problems include the reduced availability of iron, phosphorus, potassium and most micronutrients, since they form insoluble solid phases.

• Physical problems include the formation of crusts that block pores, reducing soil permeability (water and air).

• The soil not only becomes unusable for farming, but it is easily eroded, losing its different horizons and making recovery more difficult.

Treatment Technologies

In order to choose the most adequate treatment for contaminated soil, the soil must be perfectly characterized.

It is important to have detailed information on the pollutants, both organic or inorganic.

To proceed to the remediation stage, there are different systems that can be classified into two categories:

- **On-site techniques:** pollutants do not need to be removed from the site, treatment is carried out *in situ*.
- **Off-site techniques:** pollutants need to be removed from the soil and transported to the treatment facilities.

The main treatment techniques currently used are: thermal, physicochemical and biological technologies.

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Treatment Technologies

Thermal Technologies

• Off-site techniques that cause the destruction of pollutants by using high temperatures. The main thermal technologies are:

- Incineration: usually performed in rotary kilns, it is the controlled combustion of the soil in conditions of excess oxygen and at temperatures of around 870-1,200°C, in order to prevent the formation of other pollutants (dioxins and furans). It is used for organic pollutants (oils, petroleum derivatives, solvents, etc). It is highly efficient (elimination of over 99.99%). High temperatures also destroy the soil's natural organic matter, so the soil remains biologically inert.
- Thermal Desorption: it is similar to incineration but temperatures are not so high (150-600°C) to avoid polluting combustion, pollutants are desorbed from the soil through a flow of hot air. It is used for volatile or semi-volatile pollutants (e.g. solvents).
- Infrared thermal treatment: it is similar to the rotary kiln used for incineration, except that heating is produced in a unit heated by infrared radiation.

Treatment Technologies

Physicochemical Technologies

- **Soil washing:** it is the extraction of soil pollutants by using an aqueous liquid medium (acid, bases, chelating agents such as EDTA, etc.). The injection of an aqueous solvent increases the solubility of the pollutant, which is washed with it. It can be used on-site or off-site and both for organic and inorganic pollutants. It has low efficacy in soils with high clay contents.

- ***In situ* soil venting or vacuum extraction:** it is a technique to eliminate volatile compounds. A vacuum is applied to the soil by the use of pumps, thus causing the migration of volatile compounds to the surface of the soil and supplying clean air. Widely used for gas station soils. It may cause atmospheric pollution. Air injection only can also be used. The flow should be directed to carbon filters for pollutant retention.

Treatment Technologies

Physicochemical Technologies

Soil remediation by thermal conduction, St. Paul Island

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe
Convenio de Estocolmo
NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean
Stockholm Convention

Treatment Technologies

Physicochemical Technologies

Source: http://es.astecinc.com

Treatment Technologies

Physicochemical Technologies

• **Solidification/stabilization:** it can be done both on-site and off-site. It consists of applying a binding agent that reduces pollutant mobility. Binding materials usually include: cement, asphalts, silicates, organic polymers, etc. It is basically used for heavy metal contamination.

• **Vitrification:** it can be done on-site and off-site. It may be considered as a mixed system of immobilization and thermal treatment. The soil is melted (1,600-2,000°C) into a vitreous siliceous matrix with very high durability. Low effectiveness in moist soils.

• **Electromigration:** it is the application of an electric field to the soil; pollutants will migrate from cathode to anode. Used for heavy metals, it can be applied both on-site and off-site.

Treatment Technologies

Biological Technologies

Biodegradation techniques through microorganisms, applicable to organic compounds (pesticides, petroleum derivatives, oils). The main available techniques are:

- **Landfarming:** off-site technique that involves excavating contaminated soil and spreading it into open spaces so that it can be aerated by tilling. Leachate can be generated.

- **Composting:** contaminated soil is mixed with highly biodegradable material (straw, wood chips, etc.) and its aerobic biodegradation takes place in controlled conditions.

- ***In situ* Bioremediation:** it involves promoting the biodegradation of pollutants by stimulating microbial populations present in the soil (autochthonous) or external (allochthonous). This stimulation is achieved by injecting nutrients (nitrogen and phosphorus) and oxygen.

Treatment Technologies

When soil cleanup is not feasible, actions can be taken to limit risks from contact. The most usual practice is to cover the site's surface, which is called sealing with concrete, asphalt or clay. Sealing works as a barrier and pollutants are confined to the covered area.

Basel Convention Coordinating Centre
Stockholm Convention Regional Centre
URUGUAY

LATU

Ministerio de Vivienda
Ordenamiento Territorial
y Medio Ambiente
MVOTMA

Thank you!

Gabriela Medina

http://www.ccbasilea-crestocolmo.org.uy/es

RED de CENTROS
Convenio de Basilea
Latinoamérica & Caribe

Convenio de Estocolmo

NETWORK of CENTRES
Basel Convention
Latin America & the Caribbean

Stockholm Convention