CHS
Convention Project
Chemical Safety

User Guide

Environmentally Sound Management of PCB contaminated equipment and materials

Knock Out for PCBs - Sustainable Chemical Management for an Environmentally Sound World

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FOREWORD

The aim of this handbook is to support public and private organisations and enterprises in dealing with polychlorinated biphenyls (PCBs) contaminated equipment and material in an environmentally sound manner. The guide will also support the introduction of a management system for recording, monitoring and environment-friendly disposal of PCB-contaminated transformers and capacitors in Macedonia. The industry, i.e. normally the owners of the PCB-contaminated equipment, will be informed about the risks and dangers when dealing with the equipment and about recommended solutions for disposal of such equipment. This handbook is intended to be written for technicians and engineers who professionally handle equipment and products that containing or suspected to contain PCBs.

The Republic of Macedonia has ratified the Stockholm Convention in 2001 – an international convention on control, reduction and elimination of Persistent Organic Pollutants (POPs). One year later, with the fund from the Global Environmental Facility (GEF) and assistance from the United Nations Industrial Development Organization (UNIDO), the Ministry of Environment and Physical Planning (MoEPP) started preparing a preliminary POPs inventory, identifying national priorities and defining action plans. The final output was a strategic document - The National Implementation Plan on Reduction and Elimination of POPs, which is the basis for further activities on PCBs phase-out.

This User Guide is part of the overall campaign on environmentally sound management of PCBs containing electrical equipment for all stages of its life cycle and describes the processes related to identification, labelling, decommissioning, storage, transport and disposal of the equipment as well as safety and emergency measures in cases of accidents.

1 Background

Polychlorinated biphenyls (PCBs) have been manufactured worldwide in many industrialized countries and were mostly used as coolants and dielectric fluids in transformers and capacitors.

The Stockholm Convention on Persistent Organic Pollutants (POPs) counts PCBs as one of the twelve substances targeted for worldwide elimination. The existing PCBs and all equipment contaminated with PCBs have to be eliminated in an environmentally sound manner until 2025 without producing hazards for human and the environment. The challenge to actualize this is twofold:

Most of the existing PCB contaminated equipments are still in use in some developing countries. The financial burden for safe and environmentally sound replacement of the PCB contaminated equipment is very high, especially for developing countries. Therefore, alternative solutions were made by allowing decontamination of transformers and use of the equipment until the end of its technical life-time. The decontamination technology must comply with the highest safety and environmental standards and be capable of reducing the PCB contamination level of those pieces of equipment to the legally permitted value of less than 50 ppm[1] and assure that the PCBs level remains below that limit.

From a technical point of view, PCBs have quite advantageous characteristics and thus found a wide range of applications such as dielectric, cooling and hydraulic fluids as well as fluids for thermal transmission in transformers, capacitors, hydraulic machines etc. Later on, it was realized that PCBs have serious health and environmental impacts, including carcinogenicity, reproductive impairment, immune system changes and loss of biological diversity etc.

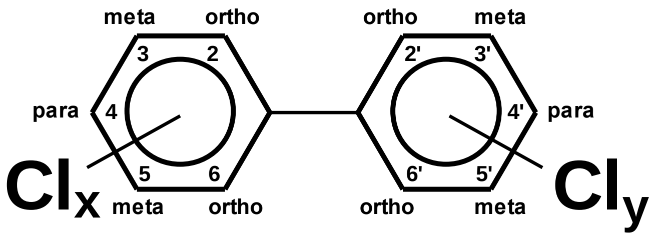
1.1 About PCBs

Polychlorinated biphenyls, commonly known as PCBs, are a group of chlorinated aromatic hydrocarbons characterized by the biphenyl structure (two phenyl rings $(C_6H_5)_2$) with at least one of any of its 10 hydrogen atoms have been substituted by chlorine. In theory there are 209 congeners and 130 of them have been found in commercial use.

Polychlorinated biphenyls are colourless or yellowish viscous liquids with distinct odour; depending on the number and position of chlorine atoms in the molecule, they have different physical, chemical and toxicity characteristics. PCBs have remarkable thermal stability and only break down at temperature of more than 1000 °C; they are highly resistant to acids, alkalis and oxidizers due to their high

[1] ppm = parts per million

chemical inertia. PCBs are insoluble in water and are semi-degradable with half-life proportional to their chlorination level and ranges between 10 - 15 years.



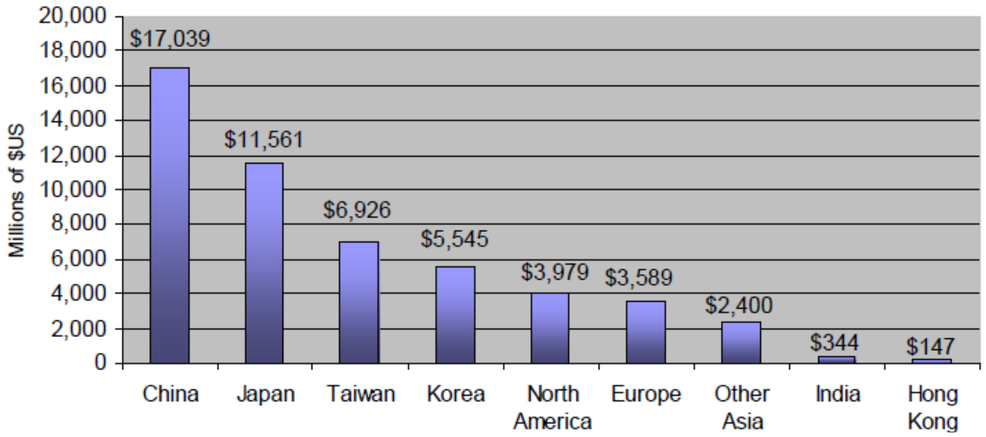
Graph 1: Molecular structure of PCBs

They are highly soluble in lipids, hydrocarbons and organic compounds and thus bio accumulate in fatty tissues of humans and other living organisms. This can cause a PCBs concentration of up to 70.000 times higher in the species of upper level in the food chain. In the process of global distillation (evaporation and deposition) PCBs could be transported over long distances even to such regions as Arctic. This process of evaporation, movement with the air streams, condensation and deposition on the ground is well known as the “grasshopper effect.”

Table 1: Characteristics of Polychlorinated Biphenyls

✓	Non-inflammable (complete combustion only at > 1000 °C), non-explosive
✓	High chemical resistance against acids, alkalis and oxidation and hydrolysis processes
✓	Excellent dielectric properties
✓	Good heat transfer properties
✓	Slightly soluble in water
✓	Well soluble in fat and organic solvents
✓	Low vapour pressure (low volatility)
✓	Unaffected by light
✓	

1.2 PCBs Production and Uses



Graph 2: PCB production by major PCB producing countries / regions in 2008 (WECC)

The total world production of PCBs between 1929 and 1989 was 1.5 million tonnes. After the ban of PCBs production and sale, except for closed system applications in the US in 1976, yearly PCBs production maintained at 16.000 tonnes from 1980 to 1984 and around 10.000 tonnes from 1984 to 1989. PCBs are still produced in North Korea.

PCBs have been manufactured as mixtures of congeners and were used in small quantities to form plastics, paints, ink, carbon papers, insecticides and lubricating oils; they were also used in formulations of dielectric fluids with PCBs concentration of up to 70% in transformers and capacitors, heating fluids and hydraulic fluids because of their remarkable dielectric potential, high heat absorption capacity and fire-resistant properties.

1.3 Risks and Impacts caused by PCBs

1.3.1 Health impacts

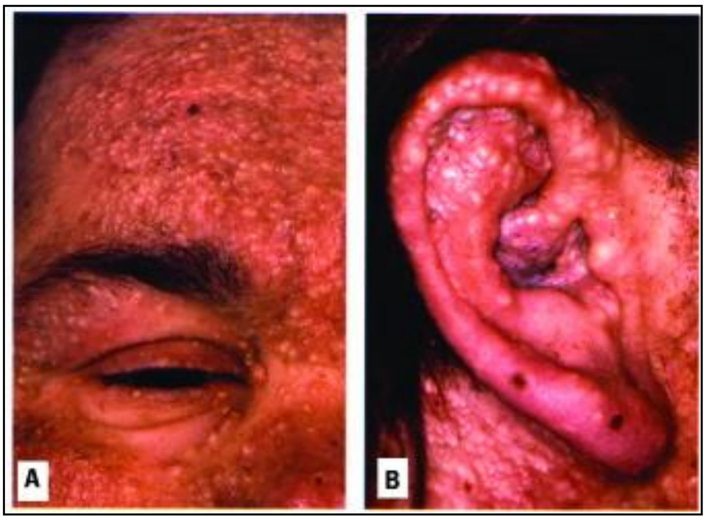
Human exposure to PCBs may occur through ingestion of contaminated food and/or water, inhalation of PCB vapour in the air and direct dermal contact. Being easily absorbed through all exposed area, PCBs will mostly be deposited and accumulate in fatty tissues and organs such as kidneys, lungs, adrenal glands, brain, heart, skin; and especially liver, which is favoured by PCBs.

The toxic potential of PCBs has been shown by preponderant data, which are based on studies of workers exposed to PCBs, consumption of contaminated fish or food products of animal origin as well as the famous Yusho (Japan) and Yu-Cheng (Taiwan) incidents; numerous laboratory mammal studies also provide broader and substantial evidence to adverse health effects caused by PCBs exposure. These include:

- **Hepatic effects** – increase in serum levels of some liver enzymes, possible liver damage;
- **Dermal effects** – skin irritation, chloracne, pigmentation of nails and skin;
- **Ocular effects** – hyper secretion of the Meibomian glands, abnormal pigmentation of the conjunctiva and swollen eyelids, these always accompany chloracne;
- **Immunological effects** – immune suppression, increased sensitivity towards infectious diseases, susceptibility to respiratory tract infectious;
- **Neurological effects** – neurodevelopment toxicity, abnormal reflexes and deficits in memory, learning and IQ of infants and children while no adverse neurological effects were found solely caused by PCBs exposure;
- **Reproductive effects** – possible menstrual disturbances in women, sperm morphology and production, difficulty in couple conceiving;

- **Cancer** – attested skin, digestive and liver tumours as well as leukaemia, but no significant relationship with increase of skin and pancreatic cancer.

Generally speaking, symptoms of PCBs poisoning, which will be seen firstly on skin and eyes, are acne, hyper pigmentation, keratosis, watering of eyes, liver disorders, bronchitis as well as certain peripheral neuropathies and endocrine disruptions; theses can recede in a year.



Graph 3: Chloracne – a typical sign for high PCB contamination

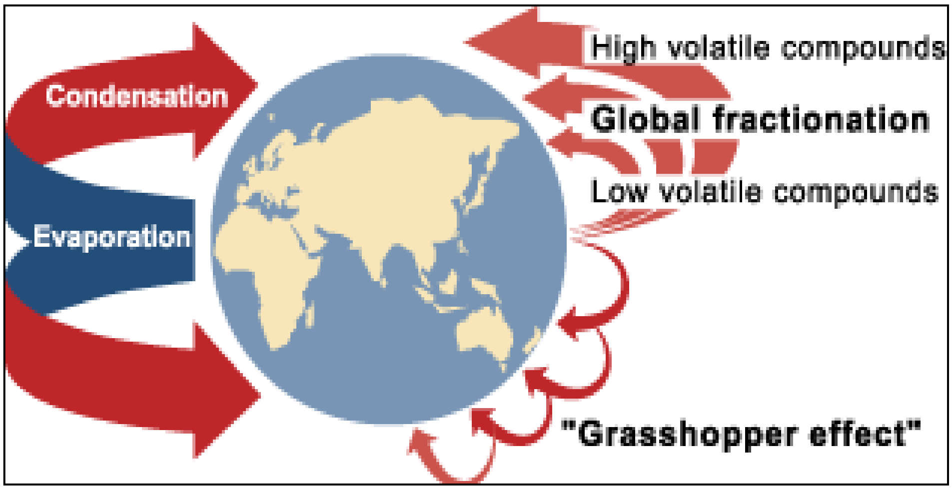
1.3.2 Environmental impacts

PCBs are still being produced and used in some developing and transition countries, human activities are the only source of PCBs released to the environment. PCBs find their way to the environment as a result of uncontrolled landfill, leakage of PCBs containing equipment, spills and emissions; industrial practices like improper "top up" or recharge mineral oil containing transformers with PCBs cause additional PCBs contamination in the environment.

Since manufacture and import/export of PCBs have been ceased and prohibited in the past years, these do not introduce large quantity of PCBs into the environment any more. Among the worldwide 1.2 million tons PCBs production in 1988, 4% of them were destroyed, 65% were still in use/storage (in electric transformers and capacitors) and 31% were in the environment.

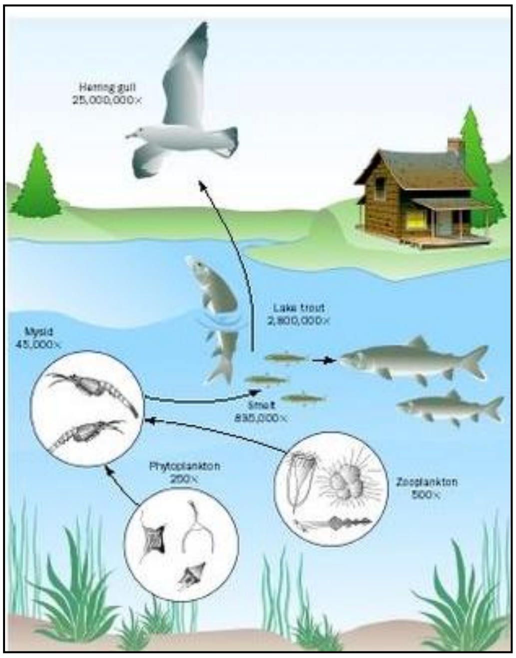
Once they got access into the environment, PCBs continue being redistributed among different environment compartments like air, water, soil and biota, by:

- Volatilization from soil and surface water into the air;
- Dry/wet deposition from air to soil or surface water; absorption/desorption by/from particles in the air or sediment in water body; Bioaccumulation,
- Bioaccumulation, which can cause a PCBs concentration of up to 70.000 times higher in the species of upper level in the food chain.



Graph 4: Bioaccumulation of PCBs

The less chlorinated PCBs congener is, the easier it can be volatized and migrate while highly chlorinated PCBs would tend to stay in the vicinity of contamination sources. Among these, atmospheric transport is regarded as the most import mechanism for global PCBs dispersion while PCBs could be transported over long distances even to such regions as Arctic. This process of evaporation, movement with the air streams, condensation and deposition on surface water and the ground is well known as the "grasshopper effect[2]."



The accumulate of PCBs in the fatty tissue of organisms low in a food chain are "magnified" when consumed by the animals in the higher level of the chain.

Even at low exposure levels, the concentration of PCBs in fatty tissue can accumulate to a high level.

Graph 5: Migration of PCBs

This process is termed biomagnifications. As PCBs bio-accumulate in organisms and bio-magnify in the **food chain**, they create health hazards at all levels. The short term health hazards associated with PCBs exposure for people include

[2] The **grasshopper effect** is a geochemical process by which certain chemicals, mostly persistent organic pollutants (POPs) are transported from the warmer regions of the world to the colder regions, particularly to the poles of the Earths.

1.4 Solutions

A series of international treaties have prohibited or regulated the production, use, import, export, transboundary movement or disposal of PCBs mainly regarding their toxic and persistent characters. These are:

- The **Basel Convention** on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal;
- The **Rotterdam Convention** on the Prior Informed Consent (PIC) Procedure for Certain Hazardous Chemicals and Pesticides in International Trade

The Stockholm Convention on Persistent Organic Pollutants

1.4.1 Basel Convention

Signed by 172 countries and entered into force in 1992, the Basel Convention endeavours to:

- **reduce transboundary movements**, especially movements from developed to less developed countries (LCDs), of hazardous wastes to a minimum consistent with their environmentally sound management (ESM);
- **minimize the generation of hazardous wastes** in terms of quantity and hazardousness;
- **dispose hazardous wastes** as closely as possible to their source of generation.
- **regulate import** and export of hazardous wastes with stringent requirements for notice, consent and tracking for transboundary movement of wastes;
- **prohibit export of hazardous waste** to LCDs that do not have suitable disposal technologies and assist LCDs in ESM of hazardous wastes.

1.4.2 Rotterdam Convention (PIC Convention)

Entered into force in 2004 and with 130 parties, this Convention controls the trade of a number of hazardous chemicals applying the so-called Prior Informed Consent procedure. Exporters of hazardous substances have to obtain the prior informed consent to the relevant agencies in the country of export as well as via the country of import before proceeding with the trade.

1.4.3 Stockholm Convention and POPs Chemicals

Entered into force in 2004 and with 167 parties, the Stockholm Convention engages to eliminate or restrict the production use of persistent organic pollutants (POPs). These originally include 12 chemicals: Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Hexachloro-benzene, Mirex, Toxaphene, PCBs as well as Dioxins and Furans (as unintentionally formed by-products as a result of incomplete combustion or chemical reactions of PCBs). On May 8th 2009, 9 so-

called New POPs chemicals, namely octaBDE, pentaBDE, PFOS, alpha HCH, beta HCH, Chlordecone, HBB, Lindane and PeCB, have been agreed to be added to the POPs list following procedures described by the Convention.
According to the convention, it is prohibited to produce, use, import and export PCBs, "except for the purpose of environmentally sound waste management". However, existing PCBs containing equipment (e.g. transformers and capacitors) are allowed to stay in service till 2025.

1.5 PCB Legislation based on the Stockholm Convention

The Law on the Environment is generally the basis for an overall environmentally sound management (ESM) in the country and should covers all characteristics regarding environmental issues, like,

Handling PCBs – according to the Stockholm Convention,

- It is forbidden:
  - to produce, import and export PCBs;
  - to reuse PCBs in other equipment of liquids;
  - to refill PCB equipment

- Legal and physical entities that possess and use PCBs and PCB equipment are obliged to report the origin, nature, content and quantity of PCBs and PCB containing/contaminated equipment to the responsible government agency / body for the professional activities in the field of environment not later than one year after this law enters into force.

- Legal and physical entities are obliged to proper labelling of the equipment of its PCB content

- Legal and physical entities handling PCBs, used PCBs and PCB equipments are obliged to keep records in accordance with this law and other regulations related to this issue.

2 PCBs Management

2.1 PCBs Application

PCBs have been found in three applications:

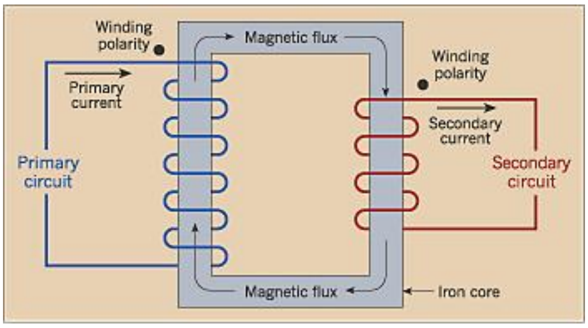
- **Closed system applications** – dielectric fluids, transformers, capacitors, microwave ovens, air conditioning, electric motors, ballasts for electric lights, electromagnets.

- **Partially closed system applications** – hydraulic fluids, rectifier, voltage regulators, circuit breakers, vacuum pumps, electrical cables.

- **Open applications** – inks, lubricants, waxes, flame retarders, adhesives, surface coatings, insulators, pesticides, dyes, paints, asphalts, pipeline condensates, plasticizers.

2.1.1 Transformers

A **transformer** is a power converter that transfers electric energy from one circuit to another through inductively coupled conductor's conductors—the transformer coils. A varying current in the *primary* winding creates a varying magnetic flux in the transformer's core and thus a varying magnetic field through the *secondary* winding. This varying magnetic field includes varying an electromotive force (EMF), or "voltage", in the secondary winding.



Graph 6: Principle of an electric transformer

Electricity is transferred from the generation plants (which usually produce electrical energy in high voltage level) and distributed to the end-users (which are of distance from generators and have demand on electricity of differently lower voltage levels, depending on concrete situations); in order to reduce energy loss, it is advantageous to keep the electrical current at a high voltage level during distant delivery.


Graph 7: Modern electric transformer

Transformers are thus used to raise and lower electrical voltage. They have the same basic design; i.e. a magnetic metallic core around which two sets of conducting (copper) wires are wounded. The ratio in the number of wires of those two separate coils decides the ratio of the input to the output voltage. Other important units of a transformer include **wooden struts** supporting the core, inlet electrodes for electrical connection to the outside and a metallic casing where the inner structure are immersed in dielectric fluid to prevent short-circuits and sparking.

With its outstanding dielectric and other stable properties, PCBs were popularly filled (in terms of oil mixture) in transformers before early 1980s. Finally, the transformer may be sealed or fitted with a "breathing device" which allows volumetric changes of the oil due to temperature fluctuations. The cooling fin helps evacuate the heat which is produced during operation of the transformer, since possible overheating decreases the electrical efficiency of the equipment and increases the risk of subsequent fire.

2.1.2 Capacitors

Capacitors are devices that can accumulate and hold electrical charge. Normally, they consist of two electrical conducting surfaces (coils of metallic foils) which are separated by a dielectric i.e. non-conducting material and fitted with contacts leading out of the capacitor. The dielectric material (fluid, paper, plastic, glass, mica or ceramic) increases the capacitor's capacitance while low capacitance devices are available with a vacuum as a dielectric material. PCBs are also found in some old, large oil-filled capacitors and in very old (pre 1975) fluorescent lamp ballasts and other applications.

Graph 8: Electric capacitors

Since capacitors are always sealed structures, they are not mainly subjected to maintenance and must be destroyed to eliminate the PCBs they contain, though some technologies allow their metals being recovered.

2.1.3 Contaminated Sites

PCBs contaminated soil or water bodies can be a result of leakages from PCB containing electrical equipment, mostly transformers when they are in service, storage or during their removal from the place of operation. Large PCBs contamination of soil and concrete floor pose acute risk to human and the environment.

2.1.4 Contaminated Material

Lubricants ▪ *Immersion oils for microscopes (mounting media)* ▪ *Brake linings* ▪ *Cutting oils* ▪ *Lubricating oils* - *Natural gas air compressors* *Casting Waxes* ▪ *Pattern waxes for investment castings* *Surface Coatings* ▪ *Paints* - *Paint on the undersides of ships* ▪ *Surface treatment of textiles* ▪ *Carbonless copy paper (pressure sensitive)*	*Adhesives* ▪ *Special adhesives* ▪ *Adhesives for waterproof wall coatings* *Plasticizers* ▪ *Gasket sealers* ▪ *Filling material in joints of concrete* ▪ *PVC (Polyvinyl chloride plastics)* ▪ *Rubber seals* - *Around vents* - *Around doors and windows* *Inks* ▪ *Dyes* ▪ *Printing inks* *Other uses*

▪ *Flame retardants* *- On ceiling tiles* *- On furniture and walls* ▪ *Dust control* *- Dust binders* *- Asphalt* *- Natural gas pipelines*	▪ *Insulating materials* ▪ *Pesticides*

Table 2. Other PCB contaminated material

2.2 PCBs Inventory

A PCB inventory relates to a list with detailed information about the owner and the site possessing the equipment, manufacturer, origin, serial number, PCB concentration and current PCBs quantities of the equipment, information of wastes on the site liable to contain PCB, etc. These information can be collected from electricity generating and electrical distribution companies as well as some supervisory agencies, or by establishing an own database. An inventory is the starting point for an environmentally sound management (ESM) of PCB containing equipment and material. By identifying, quantifying and recording total equipment and material that might contain PCBs, the inventory is essential for drawing a plan to manage, replace, dispose PCB equipment or material and to ensure final destruction of PCB appliances braced up to the prescribed time.

Because of dispersive uses of PCBs (e.g. use in inks, paint, lubricants etc.), it is impossible to produce a complete inventory for all PCBs. However, according to experiences, PCBs can be found in some industries or equipment such as: electric utilities (generation plants and transmission companies) that with transformers, capacitors, regulators, switches etc.; electrical equipment in buildings (industrial, office, apartments, schools, hospitals); electrical, communications, hydraulic equipment and fire suppressants in ships and aircraft; insulation in underground electrical cables; fluorescent light ballasts; painted objects like wallboard, wood; auto-shredder residue; contaminated mineral oil and other waste oils; barrels storing PCBs.

For example, in Macedonia, according to the Stockholm Convention, stakeholders which possess PCB equipment or PCB wastes are obliged to produce and maintain an inventory. Specially prepared forms with all the required data for the inventory have to be sent to the Ministry of Environment. Each equipment item, such as transformer, capacitor, vacuum pump, lamp ballast or electrical cable should have its own inventory number given by the MoEPP (Ministry of Environment and Physical Planning).

2.2.1 Identification of PCB Equipment

The Basel Convention has defined PCBs as any substances or material with a PCB concentration of above 50 ppm. Normally, PCBs constitute only part of the dielectric fluid in a transformer; as PCBs can be viscous, they are mixed with mineral oil or other chlorinated organic fluide, e.g. trichlorobenzene (TCB) or tetrachlorethylene, in order to reduce the viscosity and enhance the flow of liquid through the cooling ducts and thus cooling efficiency inside the transformer.

2.2.1.1 Transformer identifcation

Since different types of PCB transformers have been designed, there are no common guides when handling such equipment. Neverthless, there are several useful methods for external identification of potential PCB equipment:

(1) By reading data written on the name plate of the transformer, these include the rating of the transformer (power capacity in kVA) which can help to quantify the dielectric contained in the transformer (1 kVA = 1 litre of dielectric = 1.5 kg), operating frequency, rated current voltage, output power in kVA, type of insulation used, tranformation turns ratio, etc.

(2) To observe identification plate (in case it exists), which usually states PCBs (with their trade names such as AROCLOR, APIROLIO etc.) contained by the transformer and thus requirement for special precautions; there was a rule that PCB appliances had to be clearly labelled since 1975.

(3) To examin other technical information:

a. Type of cooling

The following type of cooling written on the transformer nameplate indicates the transformer has other than PCBs oil:

- Liquid Natural Cooling (LN)
- Liquid Natural Air Natural Cooling (LNAN)
- Synthetic Natural Cooling (SN)
- Oil Natural Cooling (ON)
- Oil Natural Air Natural Cooling (ONAN)

The first three cooling types also stand for no transformer oil applied since they only contain cooling fluids.

b) Density of transformer fluid

Specific weight of chlorinated organic liquids is around the value of 1.5 which is much higher than that of hydrocarbon, specific weight of mineral oil is less than 1.0 (about 0.85 - 0.9), information provided by the nameplate can also give a hint whether the transformer contains PCBs, taking the volume (normally in liter) of transformer into account.

(4) To distinguish the design of transformer. Because that PCBs were regarded as very stable, later designed transformers were totally or hermetically sealed without drainage vales or facilities for access**.**

Some industrial activities, however, have also caused transformers contaminated by PCBs as a result of negligence or unprofessional processes which cannot be identified simply by the methods described above. Among these, a common practice was to „top up" or recharge non-PCB (mineral oil) transformers with PCBs or servicing non-PCB transformers by renewing and adding mineral oil with PCBs contaminated pumps and tubing, which, for example, had been previously used to service PCB transformers.

Early decontamination attempts were merely replacing those "contaminated mineral oil" by adding new (non-PCB) mineral oil, while the PCB contaminated oil remaining in the windings, especially absorbed by woody structures, of the transformer gradually leach out. Therefore, it is necessary to test PCBs concentration of the oil in a flushed transformer again after several months and refill the transformer with mineral oil till the PCB concentration drop to less than 50 ppm.

2.2.1.2 Capacitor identification

In many cases, information about dielectric liquid can be found on the nameplate or a separate tag of a capacitor provided by the manufacturer. Especially after banning the PCBs for electrical equipment, most of the power capacitors were declared as PCB free/Non PCB either on the nameplate or with a separate tag*)*, and they can be disposed off as normal oil containing waste.

Graph 9: Identification plates and labels for identifying electrical equipment and containers with PCBs

2.2.2 Data collection

Information sources for an inventory can be electricity generating, supply and elimination companies as well as some supervisory agencies, or an own database. Data collected for an inventory must be detailed to provide the necessary information related to the particular type of PCB equipment or PCB waste such as:

(1) **In/out of service transformers**

- kVA rating
- Brand name
- Fluid quantity (qty)
- Type of fluid (brand of the fluid)
- Location of the transformer producer
- Number
- PCB concentration (not for refilled transformers)
- Year of manufacture
- Producer
- Weight of the transformer
- Status / owner

(2) In/out of service capacitors

- kVA rating
- Brand name
- Location of the capacitor producer
- Number
- Year of manufacture
- Weight of the transformer
- Status / owner

(3) Bulk storage tanks, drums and containers

- Type
- Location
- Weight
- Fluid quantity (qty)
- PCB concentration
- Status / owner

For transformer or capacitor, such information is sometimes available on its type plate. Data entry for status can include codes stand for leaking, stable, packed etc. which also could be found at the transformer nameplate.

All data, both gathered during the onsite visits by the inventory professionals and performed or received by the companies who possess potentially PCB contaminated equipment, should be entered in a specially prepared software database for PCB contaminated equipment; this software database is maintained by the POPs Unit of the Ministry of Environment and Physical Planning, and it is essential for organizing updated information on existing PCB contaminated equipment in the country and providing a picture of the current situation of PCB equipment.

2.2.3 Sampling

It is necessary to identify the type of cooling liquid before drawing sample from the equipment; normally, mineral oil without or with unknown percentage of PCBs and silicone fluids will be sampled

Personal protective equipment, such as overall protective clothes, air mask, goggles, gloves, protective hat and safety shoes shall be worn when taking sample from PCBs contaminated sites or equipment potentially contaminated with PCBs. Samples have to be representative and shall not be contaminated.

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2.2.3.1 Sampling of transformer

- Preparing

From safety aspects, a transformer has to be de-energized before sampling (some patents or technologies do allow extracting oil samples on-site while the transformer is still energized).

During sampling, the transformer shall be under positive pressure so that no air will be drawn into the transformer; in case it is sealed with an inert gas, its pressure gauge needs to be checked. Valve through which the sample is to be taken shall be flushed by certain amount of oil flowing to a waste container. Bottles for sampling have to be rinsed by partially filling, then gently swirling and emptying the oil into the waste container; no water droplets or foreign particles shall exist in the sample and overfilling is permitted for possible expansion of the sample during storage or transported. Moreover, if the sample is subjected to gas analysis, it is forbidden to let the sample under a vacuum (e.g. by pulling the plunger of a sampling syringe) which could degas the oil and lead to inaccurate results.

Taking sample from the transformer can be performed in two ways:

a. Taking a sample from the drain tap at the bottom of the transformer.

In case the transformer has been disconnected for more than 72 hours, the sample should be taken from the bottom, because of its higher density, PCBs tend to accumulate at lower part of the transformer. It is advisable to always have a spare gasket ready since the old one can be damaged when opening the drain tap. 50 ml of oil per sample is to be taken into bottles made of plastic, aluminium or glass,

b. Sampling from the oil filling cap by using a pump.

Procedure of sampling is the same as the one described above except that now a pump is used.
The pump consists of a plastic tube with diameter of around 1cm and length of around 1m; during sampling, one of end of the tube is connected to a syringe and the other is submerged into the transformer oil. Each time a sample with 50ml has to be drawn; this procedure needs to be repeated to take enough samples, since samples taken in this way cannot always be representative because the oil in transformer is not evenly mixed.

2.2.3.2 Sampling of capacitor

In case the nameplate or tag of a capacitor, which may contain information of inside fluid, is missing or damaged, the only way to know if the capacitor contains PCBs is to test the liquid.

A drip tray should be put under the capacitor to avoid any spillage. Afterwards a hole should be drilled in the casing on the top or the isolator should be dismantled for taking an oil sample by e.g. using a pipette. At the end, the hole should be sealed with a special paste and the capacitor should be placed in a drum. Once a capacitor is opened, it should be disposed because capacitors are always hermetically sealed.

Samples should be labelled with ID number, sampling date and location as well as type of the sampled material such as transformer oil, soil or sludge possibly containing PCBs. Plastic cap of the bottle should be tightened and each bottle should be put in a sealed plastic bag. All the samples will be packed into cardboard boxes and transported to the laboratory for analysis.

2.2.4 Analysis of Potential PCBs Oil

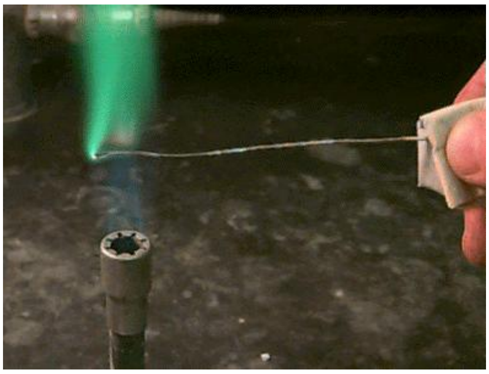
Identification of PCBs fluid can be done either in a simple way that can be carried out rapidly after sampling, or in laboratory for more precise outcomes. If not necessarily accurately, two methods can indicate the existence of PCBs rapidly:

a. Density test.

Containing the chlorine atoms, which are quite heavy element, PCB oils are with higher density of more than 1.5 g/ml; while mineral oils are usually with a density of less than 1.0 g/ml, a test can be simply done by putting an oil sample into water. PCBs containing oil will sink to the bottom of a mixture with water while mineral oil would float on the top.

b. Chlorine test.

The existence of chlorine can be either indicated by a green flame (result of volatilization of copper chloride which formed on the copper surface) when burning sample in the presence of copper. (Beilstein´s test)

The **Beilstein´s test** is a test for the determination of the presence of a halogen (chlorine, bromine, or iodine) in an organic compound. A piece of copper wire or gauze is pre-heated strongly in the oxidizing flame of a Bunsen burner (until the flame is no longer green) and the test substance placed on the wire or gauze, which is re-heated. A green flame indicates the presence of a halogen	 Graph 10: Beilstein´s test for chlorine

Chlorine can also be identified by using chlorine detection kits or specific instrument like L2000 DX analyzer, the both are based on separation of chlorine atoms from the PCBs by certain chemical reaction following by quantifying the chlorine concentration. Such tests however, cannot distinguish PCBs oils from other chlorine containing mineral oils.

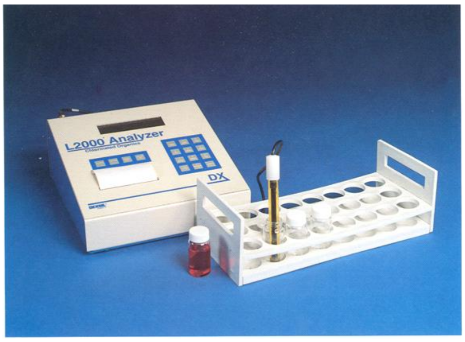
c. Clor-N-Oil 50 - PCB Screening kit for transformer oil from Dexil

Graph 11: PCB screening with a test kit

The Clor-N-Oil 50 Test kit works on the principle of chlorine determination and is ddesigned to be used in the field, Clor-N-Oil is a fast, accurate method to test electrical insulating fluids for the presence of PCB. Each pocket-sized kit contains everything necessary to perform the test in less than 5 minutes. All premeasured reagents are sealed in glass ampules for safe, fast, consistent and accurate results. Screening transformer oil with Clor-N-Oil can eliminate non-PCB fluids from costly laboratory analysis and allows a greater number of samples to be tested at less cost.Clor-N-Oil is available for testing transformer oil at four different action levels; 20 ppm, 50 ppm and 500 ppm.

d. <u>Instrumental Detection of the Chlorine Concentration</u>.

This method uses instruments for analyzing the chlorine content in the sample. The **L2000 DX** is such an analyser relying on the same principle as the test kits (separation of the chlorine atoms). However, instead of a colorimetric reaction, the analyser uses an ion specific electrode to quantify the chlorine concentration.



Graph 12: L2000 PCB analyzer

L2000 DX Analyzer

for testing chlorinated organic and PCBs

from Dexil Corp/US. The usable measurement range for oils and soils is 2-2000 ppm; 10 ppb-2000 ppm for water and 2-2000ug / 100cm2 for wipe samples.

e. Specific methods:

In order to gain more accurate results and precise dosages of PCBs, laboratory tests with different kinds of chromatography such as:

- packed column gas chromatography (GC)
- thin layer liquid chromatography (TLC)
- high performance liquid chromatography (HPLC)

Analysis using chromatography is indispensable, for example to confirm the present of chlorine is due to the existence of PCBs after the primary identification mentioned above.

Analytical chromatography refers to measuring relative proportions of the analyzed compounds in a mixture and requires only small sample amounts. Chromatography is a physical method for components separation with one mobile phase – namely the sample being separated together with the solvent, and one phase immobilized on the chromatographic column, which is the part of the chromatograph where the separation takes place. The sample is moved by the solvent through the chromatographic column – the stationary phase and consequently separated during the interaction with it. A gas chromatography (when the mobile phase is gas) however, needs very high temperature and is widely used in the field of chemical industry.

2.3 Labelling of PCBs Equipment

Identified equipment and containers with PCBs must have its own inventory number corresponding to the inventory form and its number in the database.

According the PCB concentration, equipment or material have to be labelled as “Non PCB”, “Suspected to contain PCB” or “PCB contaminated”, together with its inventory number.

Following labels are available depending on the PCB concentration (see picture 9)

- **Green label** for equipment or material without PCBs or with a PCBs concentration below 50 ppm;
- **Yellow label** for equipment or material suspected to contain PCBs (e.g. before the results of gas chromatography analysis come out)
- **Red label for** equipment or material with a PCB concentration of more than 50 ppm), also see Graph 13.

Graph 13: PCB labels

Graph 13: Electrical capacitors identified and labelled electrical capacitors

3 Storage

3.1 General Requirements

Setting and operating PCBs storage sites shall take into account possible impacts on human and the environment while reduce the risks caused by leaks, fire and other incidences to a minimum, following are some useful recommendation:

- Storage sites for PCBs must be secured from unauthorised entry and located in dedicated room or building;

- PCBs should not be stored in or closed to “sensitive sites” such as areas for food and animal feed storage and processing, schools, hospitals as well as residential places etc. Meanwhile, PCBs stocks must be separated with other (hazardous) material except similar chlorinated organic in some cases;

- According to their concrete characteristics, liquid or solid PCBs wastes have to be stored in dedicated containers; if transportation of these PCBs wastes are expected in the future, it is also advisable to choose containers which meet the corresponding transport requirements;

- The storage site shall have its own drainage system to avoid contamination of public sanitation network (e.g. sewerage system) and the environment, especially surface water; for the same reason, fire control measures are suggested to use non-water system;

- Retention system of the sites shall be designed with enough capacity (see 8.1), watertight and easy to decontaminate (storage sites for capacitor permeated with PCBs in form of gel is an exception); containers or constructions storing PCBs should be made of hard plastic or metal, i.e. do not choose fibreboard, wood, plaster or insulation material;

- Ventilation is necessary for storage sites where site visits or works would take place; storage sites with seldom entry could be completely sealed, with caution that the air must be examined for its oxygen, contaminants and explosive level every time before entry, supplied air with respiratory protection must be prepared;

- A fire alarm system should be installed; relevant emergency services (e.g. fire brigades) shall be informed about the PCBs storage for corresponding adaptation of emergency procedures;

- Any activities or appliances which would cause flame (e.g. smoking) or increase surface temperature of metal (e.g. welding operation) are forbidden; inflammable material (such as paper, rags, paint, solvents etc.) cannot be deposited together with the equipment or should be separated by fire-walls; PCB-filled units and flammable oil-filled units should be kept separate from each other;

- For transformers, the short circuit and over current protection devices should be checked and switched to a minimum. It is preferable to connect all customary alarming devices to the switching circuit of the contactor or the circuit breaker;

- For capacitors, the over current and unbalance protection devices and the possibility for resonance should be checked (the use of capacitors without over current protection should be discontinued). A visual inspection should be done at least once a year and all the leaking units should be changed; cable connections and discharge resistances should also be checked; the units' capacitances should be also measured if possible;

- Spill cleanup kits and personal decontamination materials must be on-site;

- All containers or constructions with PCBs must be properly labelled with required information such as contents of the container etc;

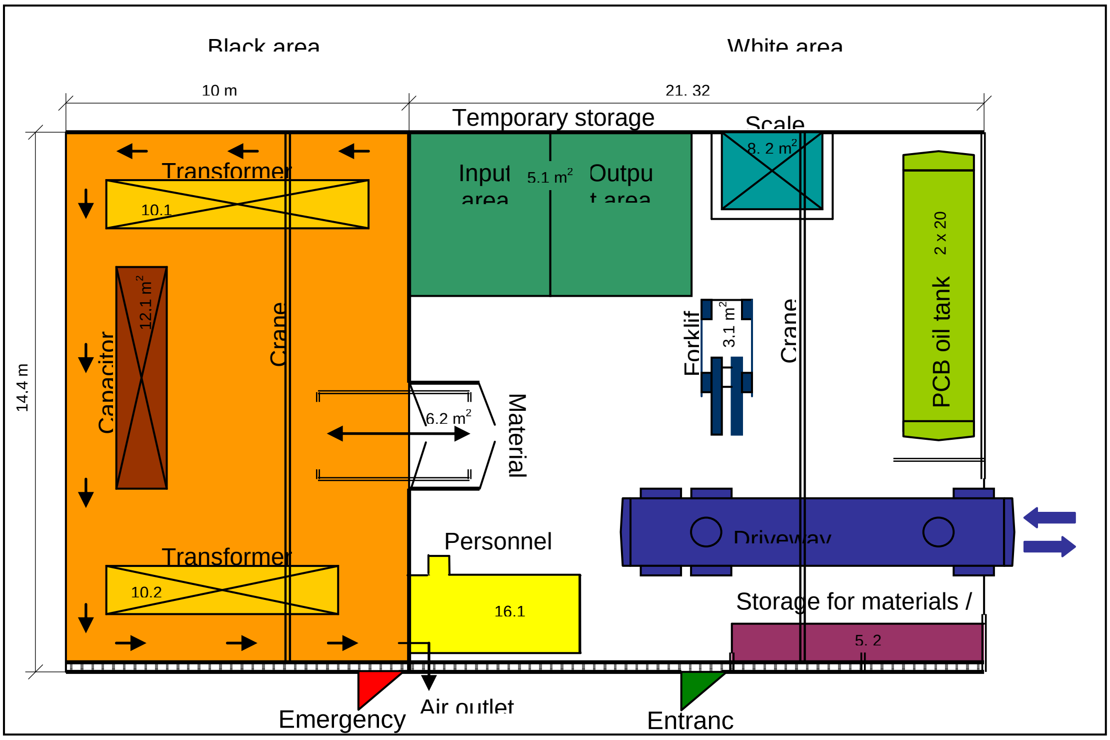
- An inventory of the total stock, an emergency plan as well as health and safety plan has to be made; regular site inspection regarding leaks, degradation of container and fire suppression system etc.

3.2 Temporary Storage Site

The temporary storage site (graph 14) consists of a black area (where all the activities involving PCBs will be carried out incl. draining, packing etc.), a white area (a clean area without work with PCBs equipment or material); an intermediate area made of a material sluice (where a transport carriage is placed) is set between the black and the white area; the material sluice has one door opening to the white area and one to the black area. The equipment from the input area of the temporary storage is transported by the forklift or the crane to the transport carriage in the material sluice. The door is closed and the other one opening in the black area is opened.

- An inventory of the total stock, an emergency plan as well as health and safety plan has to be made; regular site inspection regarding leaks, degradation of container and fire suppression system etc.;3.2 Temporary Storage Site,

- An inventory of the total stock, an emergency plan as well as health and safety plan has to be made; regular site inspection regarding leaks, degradation of container and fire suppression system etc.;



Graph 14: Sketch of a temporary storage site for PCB contaminated electrical equipment (transformers, capacitors)

- The PCB contaminated electrical equipment is collected from its owners at different locations in Macedonia by a specialized truck that fulfils the national transportation regulations (*see chapter 4*) and by applying the safety measures for handling PCBs described in 3.1 and 5.1.

- All necessary data of the electrical equipment in the storage should be noted and stored in the existing database for PCB-contaminated electrical equipment.

The truck has to be parked in the driveway of the white area of the storing site and unloaded using the crane and the forklift. The load is scaled using the weighing scale and placed in the input area of the temporary storage.
The equipment entering the black area is placed in the transformer or capacitor draining area by the crane. The drained equipment exits the black area the same way it enters using the crane in the black area, through the material sluice and by

the forklift in the white area. Afterwards it is placed in the output area of the temporary storage. The equipment from the output area is transported by the forklift back to the truck and exits the PCB storage on its way to permanent disposal.

The drained oil is stored in two transformer oil tanks with low PCB contamination equal to or less than 10.000 ppm and high PCB contamination of more than 10.000 ppm.

4 Transportation of PCBs

4.1 Preparing and Packaging

Transformers are recommended to be drained and sealed again before transportation. Selection of packaging shall base on the characteristics of the goods, risks caused by the goods as well as how they will be transported. Here are several packaging types suggested:

- Drained transformers: catch basins with absorbents;
- Capacitors: watertight metallic containers with pads;
- Solid PCBs material: open-top drums;
- Liquid PCBs material: sealed metallic drums with absorbents.

4.2 UN Proved Containers

UN approved containers for PCBs are designed, constructed, and operated with safety requirements for flammable and combustible liquids. Graph 12 is a steel drum without a removable head.

Graph 15: Imprinted UN Code of an UN approved drum

This container must be clearly marked with a specific label for the transport of hazardous chemicals with details of the contents and must be maintained in good condition.

If some of these materials are leaking, the container should be partially filled with an absorbent material, such as a commercial absorbent, kitty litter or a diatomaceous earth (see the list of absorbent materials in *chapter 8.3*).

The Intermediate Bulk Container (IBC) is another type of UN approved drums for packaging liquid PCBs material; it can be a plastic composite IBC container, steel IBC container, stainless steel IBC container or tank container or else in accordance with certain regulations. They are

Graph 16: an UN approved IBC

generally cubic in form and therefore can transport more material in the same area than cylindrically shaped containers and far more than might be shipped in the same space. IBCs differ in size but are generally between 700 mm and 2000 mm in height. The length and width of an IBC usually depend on the country's pallet dimension standard. An IBC can have a weight between 90 kg and 1200 kg depending on its size.

4.3 Transportation

Beside various national regulations depending on the countries, there are several regional and international treaties (or instructions) in charge of different types of transportation; these are:

The European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR);
it is a simple and short agreement with the key article stating that apart from some excessively dangerous goods, other dangerous goods may be carried internationally in road vehicles subject to compliance with the conditions laid down in Annex A (in particular as regards the packaging and labelling of the goods) and the conditions laid down in Annex B (in particular as regards the construction, equipment and operation of the vehicle carrying the goods in question).

- **The European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways**;

- **The Regulations concerning the International Carriage of Dangerous Goods by Rail (RID);** it is part of the Convention concerning International Carriage by Rail.

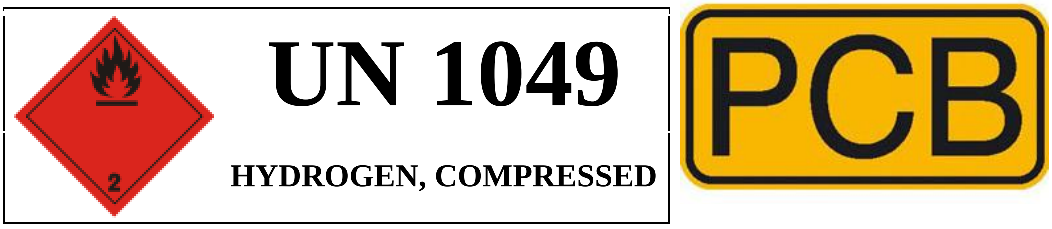
- **The International Maritime Dangerous Goods Code (IMDG);**

- **The Technical Instructions for the Safe Transport of Dangerous Goods by Air;** it is part of the International Convention for the Safety of Life at Sea

- **UN Recommendations on the Transport of Dangerous Goods.**

Generally speaking, the treaties (or instruction, recommendation) pointed out above share a consistent structure and thus are practical to be followed. While some are not obligatory or legally binding on individual countries, these treaties or instructions have laid down general requirements on transporting, including relevant operations like packaging and labelling, of hazardous wastes by dividing them into several classifications (e.g. 9 classes as to the UN Recommendations on the Transport of Dangerous Goods) according to the transport hazards they pose. Thus, it is in principle to classify the goods for the purpose of packaging, transportation and storage.

Graph 13 is an example of the simplest form of transport label according to the UN code, with its four-digit numbers (“1049” in the example), namely the UN number, identifying the common hazardous substances or articles. The UN numbers that range from UN0001 to UN3500 are published in the Recommendations on the Transport of Dangerous Goods, which has been adopted by different regulations of transport.



Graph 16: A set of Transport labels for PCB material

Graph 16 represents an example of the simplest form of transport label: The red diamond and the flame symbol indicate that the main transport hazard is the flammability of the product, and the number "2" at the bottom of the diamond indicates that the product is a gas under ambient temperatures and pressures.

Meanwhile, according to the Basel Convention and Rotterdam Convention as described hereinbefore, a trans-boundary movement of hazardous wastes can take place only upon prior notification of the competent authorities of the states of export, import and transit that the mentioned transport will take place. In addition, each shipment of hazardous waste must be accompanied by a trans-frontier shipment document stating the starting point of the transport (the place of export) and the final point of disposal (the place or disposal factory of import). This document also carries other information such as the shipment type, date and company of export and import, etc. Moreover, it is always indispensable to underline the safety measures during transportation.

For instance, for road transport vehicles, with reference from the ADR:

- When PCBs material is packed in UN approved container, a normal truck with a protective metal basin would be enough for the transport; otherwise, a special truck with an UN approved trailer and big metal box with lid on its top should be used;
- The driver should have a special licence for driving an ADR truck in addition to his driving license;

- To inform relevant personal, e.g. the driver, about the type of goods and the risks it pose; in the context of this guideline, it is therefore necessary to made the driver aware of the safety instruction of PCBs;
- Emergency plan has to be prepared; fire controlling instruments (using foam, halocarbons, carbon dioxide or chemical powders etc.) need to be equipped; no inflammable material can be transported together with PCBs;
- Other equipments that might be useful are: speed restrictors, hydraulic hoses, tachometers, personal protective equipment, empty containers, plastic sheets etc.;
- Precautionary labels or warning plates have to be displayed on the transportation vehicle;
- Relevant documents required are: ADR transport document, directions for special safety measures; ADR training certificate for drivers of vehicles transporting certain dangerous goods; certificate of approval for vehicles transporting certain dangerous goods;
- Competent measures have to be undertaken during loading, transport and unloading of dangerous goods, to prevent contamination of the environment or increase of risks of human exposure to the PCBs by any damage, spillages or leakage of PCB oil from the contaminated equipment.

5 Handling PCB Contaminated Equipment and Material

5.1 Health and Safety of Personnel

Personnel who handle or have contact with PCBs containing equipment or material have to wear personal protective equipment (PPE) and shall receive appropriate (health, safety and operational) training ahead; medical monitoring is also required for those who work with PCBs routinely.

A set of chemical resistant protection clothing include: overall cloths, respiratory mask, gloves, boots or shoes with disposable covers. Because of high permeability of PCBs, PPE made of chemical resistant laminated materials, fluorinated rubbers (instead of natural rubbers) or fluorine elastomers would be optimal choices; do not use PPE made of polyvinyl chloride (PVC). Even so, all PPE have to be changed regularly since no material can be totally impervious against PCBs.

Graph 17: A set of personnel protective equipment (PPE)

Adequate ventilation is required to ensure a non-explosive atmosphere with contaminant concentration under acceptable exposure limits; respiratory protective equipment are advisable in case the work is in poorly ventilated area or area with high temperature, to work with aerosol formation or more volatile PCBs. Because of PCBs vapours and aerosol are heavier than air; experiences suggest a down-draught formed by supplying (instead of extracting) fresh air from a higher level of the ventilated area. Besides, an air capture or even treatment system is required to prevent contamination of the environment, for example, by utilizing fabric or electrostatic filters to remove aerosol while activated carbon filter to absorb vapour.

5.2 Maintain and evaluate In-service transformers

It is necessary to inspect and de-energize (sometimes de-pressurize) the equipment before starting any maintenance activities. Competent personnel or authorized workshop and specific instrument have to be applied for maintenance operations such as decanting or transferring the dielectrics, rewinding of coils, taking samples, replacing leaking seals, repairing holes, to top-up internal components as well as retrofilling the transformers etc. Besides, these activities shall not be carried out at high temperature, usually no more than 25°C, to avoid volatilization of the PCBs.
With the objects to minimize risks caused by leakage, fire or malfunction of in-service transformers, periodical examination has to be carried out, regarding their electrical performance, possible electrical overload during operation, oil deterioration and oil level of the equipment. Two examples of tests which take into account these aspects are:

- Dielectric test: measures the voltage value under which the dielectric can be broken down;
- Oil acidity test: oil acidity will be counted in the way how much (in terms of mg) potassium hydroxide (KOH) would be needed to neutralize 1 gram oil.

Accessed air or moisture through seals, gaskets or holes (e.g. pin-hole of welding parts) and large temperature variation of the transformer will lead to oil degradation, like increased oil acidity, which favours corrosion of some sensitive or thin structures of the transformer, such as cooling fins, welding areas etc.
Any used material or equipment contaminated by PCBs, including dedicated tools for PCBs, disposable PPE and absorbents, must be decontaminated or properly treated as PCBs wastes.

5.3 Retrofilling

Retrofilling is to replace PCBs contained in a transformer by non-PCB dielectric fluid. To be pointed out is that, Basel and Stockholm Convention does try to prohibit transboundary movements of hazardous wastes and encourage complete phase-out of PCBs; besides, due to the complicated structure of transformer and specific properties required regarding the dielectric fluid, it is necessary to consider following aspects to evaluate feasibility of such processing and realize it:

a) Duration of the process versus rest service time of the transformer
   Normal transformers have service life of ca. 30 years, it is therefore necessary to figure out whether it still worth to carry out such time consuming process.
   Because some porous structure such as wood and paper etc. will retain quite an amount of PCBs oil, even when the transformer is firstly drained, it takes a period to repeat the operation until the concentration of PCBs, which will be leaked from those porous structure after retrofilling, reach an equilibrium of below certain limit. According to some report, ca. 50 ppm PCBs is estimated for a loading transformer 90 days after its first retrofilling, if 500 ppm is the original concentration, based on the assumption that ca. 10% of the original PCBs were retained in the core and coils.

b) Costs of retrofilling versus costs of purchasing a new transformer
   Besides basic expense of the operation, other costs regarding transport, destruction or disposal of contaminated oil and other equipment or material generated during the operation should also be taken into account; for instance, if there are no qualified technologies in the vicinity and thus transboundary movement of these materials are required.

c) Availability of suitable non-PCBs fluid
   Depending on the transformer structure, its designed electrical function and safety consideration etc., some important parameters to be taken into account when choosing alternative dielectric fluids are: dielectric constant, breakdown point, coefficient of thermal expansion (especially for transformers which do not have an expansion chamber to allow volumetric change of the fluid), density, viscosity (mainly regarding its fluidity when cycling through the cooling fins), flash point, flammability, properties of fire-resistance etc.

d) Others include measures to deal with problems caused by de-energizing the transformer during retrofilling etc.

Retrofilling should be carried out by authorized workshops or competent facilities with sufficient safety consideration; transformers are recommended to be drained before transport for retrofilling. Since it involves dismantling of the transformer which would lead to surface temperature increase of the transformer, beside ordinary requirements described in 3.1 and 5.1 regarding personal and site safety, fully attention and measures should be undertaken to avoid generation of

PCBs vapours, fumes, aerosols as well as spillage; it is therefore better to forbid flame cutting or welding activities, to control and slow down mechanical cutting speed. It is also recommended to cover the dismantling area with wooden or fibreboard pads to slower contamination of the floor.

6 Destruction and Disposal of PCBs

Despite the cessation of PCBs production in many countries from the mid 70s, PCBs remain a pollutant of major concern on international scale. There is still a substantial amount of PCBs in use worldwide, as a result of the long service time of electrical equipment such as transformers and since these are allowed to be used in many countries till the end of their lifetime. At the same time, there are relatively high quantities of PCBs in storage awaiting disposal, whilst a substantial proportion has been released into the environment.

Because high concentration PCBs wastes consist more than 90% of the total mass shown by inventories, they shall be firstly targeted to manage and destroy; especially for those in liquid form, which are more movable and permeable and thus cause far-reaching contamination of soil, water more easily, for example in case of spill. Depending on the: ,

a) **types or forms of the wastes** – PCBs (contaminated) oil with different percentage of PCBs; solid equipment, wastes and soil contaminated by PCBs; air or gases from PCBs treatment processes.
b) **hazards or risks** that the wastes pose – regarding their concentration, leakage rate, volatility etc.
c) **technical availabilities** as well as.
d) **economical conditions**, there are various ways for destruction or disposal of PCBs.

6.1 Pre-treatment

It refers to a series of physical processes that engage to separate (carrier of) targeted contaminants from the contaminated equipment or material, or to improve their physical quality for the upcoming procedures. Advantages of these are to significantly reduce the amount or volume and thus the costs of contaminated material to be treated or to simplify the process of destruction; also, they allow companies to collect and storage the contaminants till certain amount before their final destruction in certain facilities.

Technologies for these purposes can be categorized into:

6.1.1 Mechanical Pre-treatment

These are processes such as dewatering, grounding, size or density separation of the contaminated equipment or material etc.

6.1.2 Thermal Desorption

A common characteristic of these technologies are to separate organic compounds (through evaporation) from the contaminated material by heating before subsequent treatment of the gaseous PCBs, such as catalysed dehalogenation, pyrolysis etc.

6.1.3 Solvent Extraction

Contaminants are removed from the surface or matrix of soils or equipment components, extracted by either water based solvent (water with surfactants and so on) or organic solvent.

6.2 Destruction technologies

Technologies in this section refer to a breakdown or change of PCBs compounds, e.g. by adding oxidants, reducing agents, alkaline metal or other catalysts etc., with thermal or chemical energy input;

6.2.1 High Temperature Incineration (HTI) and co-processing

At a temperature between 870°C – 1200°C, contaminated wastes are combusted and completely oxidized into innocuous substances. Such system typically consists of rotary kiln, combustion chamber with afterburner, quench tower and flue gas treatment system. Certain conditions, i.e. 1.5s – 2s residence times at temperature of 1600°C – 1200°C and with 2% – 3% excess oxygen, are required to avoid the formation of toxic compounds like dioxins in stack gas.

With a PCBs removal efficiency of up to 99.9999%, HTI is the most common and proven destruction technology by now, especially for high-level concentration PCBs; however, it seems to be the most expensive treatments regarding its energy demand as well as necessary emission control, while some non-combustion technologies are reported as more efficient then HTI.

Working at temperature up to 1450°C, the co-processing in cement plants is another similar way to incinerate those contaminated wastes; during this operation, analysis and selection of wastes (regarded as AFR, Alternative Fuels and Raw Material) will be carried out, which can be fed into the kiln as source of energy or material; by properly controlling constituents proportion and adding point of the AFR, process temperature, residence times and emission, this could be a good choice to treat hazardous wastes. However, caution should be taken when treating wastes containing chlorine; either a pre-treatment like de-halogenation or modification of the rotary kiln is required; besides, this technology is not suitable to treat wastes containing mercury.

6.2.2 Thermal reduction

Operating in almost the same temperature as HTI, wastes are reduced by injected hydrogen (in the absence of oxygen) and converted into products of less toxic and molecular weight, e.g. hydrochloride. However, this is quite an expensive treatment (estimated as $4500 – $6000 / ton liquids) and again, emission control is required.

6.2.3 Chemical treatment

Based on ordinary chemical reactions such as oxidation/reduction and ion exchange etc., sometimes also assisted by physical interactions (e.g. evaporation/condensation), these technologies engage to extract and detoxify the contaminants or directly destroy and change the structure of toxic compounds.

6.2.3.1 De-halogenation

These are methods to remove halogens from the organic compounds, using hydrogen or other reducing agents that act as hydrogen donor:

- **Base Catalysed Decomposition (BCD)**

After mixing sodium bicarbonate and the contaminated material (with a proportion of 1:10) at 200°C – 400°C in the reactor, halogenated compounds will evaporate and be separated from the contaminated material, following by dehalogenation by sodium hydroxide.

- **Glycolate De-halogenation (APEG Plus; A: alkali metal hydroxide, PEG: polyethylene glycol**)

Soluble products such as glycol ether, hydroxylated compound and alkali metal salt are formed at the end of this process, through the reaction between alkali metal hydroxide (e.g. NaOH, KOH) and halogens contained in the contaminants) in heating condition.

- **ECO LOGIC**

This is a gas-phase reductive process, which undergoes at 850°C or higher and hydrogenizes carbon, a breakdown product of fed organic compounds, to methane; other products include light hydrocarbons, hydrogen chloride which requires further treatment (e.g. by adding caustic soda) and in case of non-optimal operation, carbon monoxide and carbon dioxide can form through reaction between methane and water steam.

6.2.3.2 Processes with Alkaline Metals or their Salts

These are mainly some innovative technologies which utilize earth metals, usually sodium and potassium, or their salts to convert contaminants to non-toxic molecules.

- **Molten Salt Oxidation**
  Being oxidized by molten alkaline salts at 900°C – 1000°C, organic compounds are converted to inorganic salts; for example, chlorine to sodium chloride.

- **Solvated Electron Technology (SoL™)**
  Alkali metal, usually sodium, can be immediately dissolved in liquid anhydrous ammonia and becomes free electrons, which is the strongest reducing agents known; these solvated electrons will then instantaneously neutralize the halogenated compounds that have been added into the solution. In the case of PCBs, sodium chloride (with chlorine atom from the PCBs) will be formed and the nitrogen content of treated soil will be raised.

6.2.3.3 Others technical options

- **Super Critical Oxidation (SCWO)**
  Under high pressure (e.g. 200 to 270 atmospheres) and temperature (e.g. 370°C – 480°C), supercritical water is able to dissolve gases including oxygen and organic compounds, which allow sufficient contact between oxygen and organic substances. In the presence of certain oxidant (e.g. oxygen), chlorine atoms of PCBs will be derived to chloride ions, carbon will be converted into carbon dioxide, nitro-compounds to nitrates etc.

- **Electrochemical Oxidation**
  Under low temperature (less than 80°C) and atmosphere pressure, oxidizers can be generated at the anode in an acid solution (e.g. nitric acid); organic compounds, in liquid or solid form with various water contents, are then converted into carbon dioxide, water and inorganic ions.

- **Advanced Oxidative Process (AOP)**
  Free radicals from oxidizers like O_2, H_2O_2, TiO_2, UV light and electrons etc. are used to destroy PCBs as well as other organic compounds.

6.2.4 Catalytic oxidation

- **Catalytic Extraction Process (CEP)**
  Acting as catalyst and solvent at temperature of 1300°C – 1600°C, metals like iron are able to destruct contaminants to primary elements, which then

be separated through different extraction processes (e.g. in the form of gases, ceramics etc.)

- **Catalytic Hydrogenation**
  Based on metal sulphides, hydrogenation catalyst is used to destruct PCBs into hydrogen chloride and some hydrocarbons of low molecular weight.

6.2.5 Biological Treatment

- Such technologies refer to decontamination of soils by microorganisms under various controlled temperature, nutrients concentration and oxygen level (aerobic or anaerobic) etc.

6.2.6 Other Treatment Processes

- **Vitrification**
  This is a thermal process to melt and immobilize metallic wastes with silica, while generated gas-form contaminants will be burned afterwards.

- **Plasma Arc**
  A thermal plasma field (resulted by introducing electric current through low-pressure gas) which can provide heat energy for combustion, pyrolysis or decompose contaminants to their atomic elements.

- **Ultrasonic Technology**
  By using ultrasonic for in-situ detoxification, this technology is still under development; its costs are supposed to be lower than incineration of PCBs contaminated soils.

- **Solar Detoxification – Photochemical Degradation**
  Short wave part (295nm – 400nm) of the solar radiation is concentrated to produce high temperature for the decomposition of PCBs contaminated soil and surface waters, while 750°C is regarded as optimal for the degradation process.

6.3 Disposal

Principally, disposal is the last choice of treating PCBs wastes, unless it is more environmentally sound than destruction of such toxic compounds. There are generally three ways under this category, namely:

- **Immobilization**
  Contaminants are chemically bound or physically solidified and placed in controlled sites or used in limited extent.

- **Landfill Cap System**
  Landfill can be applied on non-toxic products after destruction of PCBs wastes; this can also be a subsequent step after immobilization of the wastes. Important components of a landfill system are its capping, barrier and drainage layers; these should prevent hazardous substances from leaking out of the system and can range from simply a vegetated soil layer to multi-layers made of clay, plastics etc., with leakage detecting system as well as gas and laechate collection system. Comparing with wet climate zone which favours leakage of the hazardous wastes by precipitation, dry climate zones might require a less complex landfill system.

7 Recycling of PCBs

De-chlorination processes allow reuse/recycling of chlorine free oil as well as PCB-decontaminated equipment and material. Several companies already use such technologies in their commercial facilities for PCB disposal, whereas some technologies are still being developed and will soon enter the stage of commercial application.

The non-combustion technologies for PCBs decontamination in table 3 are approved and commercially available for PCBs disposal:

Table 3. Non combustion technologies for PCBs decontamination

BCD	(Base Catalyzed Decomposition)	Czech Republic, Spolana Neratovice
GPCR	(Gas-Phase Chemical Reduction)	Demonstration plant in Canada
SR	(Sodium reduction)	Envio Recycling, Germany
LTR²	(Solvent washing)	Envio Recycling, Germany

The LTR^2 technology (Low-Temperature Rinsing and Re-Use/Recovery) was developed by the ABB group in 2004 and it is now promoted by ENVIO. The technology is applied for decontaminating electrical equipment and other materials containing PCBs.

After draining the PCB liquid, PCB residues remaining in the transformer, mainly in the transformer core and windings, are removed by using a cleaning fluid; sodium metal which contained in the cleaning fluid will reaction with the C–Cl bond of the PCB molecule, generating sodium chloride and an organic molecule without any chlorine. To make it ready for use in the environmental field, it is necessary to convert it to a form with a highly accessible surface. This can be achieved by dividing the liquefied sodium in an inert organic solvent to produce fine particles of about 5-10 µm size. It has been found that the chemistry properties of extremely fine sodium particles differs remarkably from that of molten fused sodium. Many reactions take place under very mild conditions if the sodium has a very large surface, as realized in dispersion in oil with particles of 1-10 µm.

Generally, the operation temperatures vary between 100 ^{0}C and 160 ^{0}C, depending on the compound being destroyed, with temperatures of 120 ^{0}C to 140 ^{0}C being more typical. This relatively low operation temperature provides an important safety feature for application of the technology, since the rate of reaction can be quickly reduced in an emergency by removing the applied heat and cooling the treatment vessel.

This process of de-chlorination of the chlorinated biphenyl is designated as most common technology to de-chlorinate the PCB molecules and yield oil which can be re-used. When the process is completed, the reusable secondary materials such as copper, steel, oil, etc., will have a residual PCB contamination level of less than 5 ppm.

The residues from the treatment process include sodium salts and various aromatic, non-halogenated hydrocarbons. The quantity of residues generated by the de-chlorination procedure is proportional to the PCB content of the treated liquid. For oil with a PCB content of 1000 ppm, for instance, the total amount of residues is less than 1% of the oil weight.

Organic by-products are either landfilled or recovered following refinement for appropriate post-treatment uses (e.g., energy recovery). The inorganic by-products (together with the excess sodium added initially to the system) are typically recovered and disposed off in an appropriate manner. The LTR^2 technology allows the re-classification of many PCB transformers, including the Askarel, so that they can be put back into use.

8 Emergency Measures

8.1 Non-fire PCBs accidents

Caused by mechanical or electrical defects, these incidents only lead to physical damage of the equipment or container, without resulting in any fire or decomposition of the dielectric fluid.

Typical example is PCBs contamination due to leakage or spillage of the container or equipment like transformer. To avoid and deal with such incidences, technical safety measures have to be carried out, beside basic those requirements mentioned in 3.1 and 5.1; it is advantageous to install a retention system which with a capacity of at least 100% of the largest container and at least 50% of the total storage volume respectively.

As response to these incidences, relevant authorities or personal (e.g. doctor) should be informed immediately; measures have to be taken to prevent or stop continuance or expansion of the contamination or contaminated area; for example, by sealing the breakage with plastic films or rag.

8.2 PCBs Accidents involving fire

These are accidents accompanied by decomposition of the dielectric, sometimes even fires, for which increased voltage imbalance is the main reason. As a result of electrical arc caused by voltage surges or other insulation defects, hydrochloric gas or acid can be generated; in some more serious cases involving fire, highly toxic chemicals such as PCDFs, PCDDs and PCDPs can be formed in the presence of oxygen.

It is therefore a matter of course to have competent fire prevention system and to forbid any fire inducing activities in the vicinity of the PCBs container of equipment; for example, to ensure PCBs appliances will not operate under electrical overload or in case of any internal defects, to keep PCB-filled units and flammable oil-filled units separate from each other.
In the event of an accident, the device should be disconnected and tested with precautions before any further activities; to call fire fighters and other authorities, dry ice instead of water should be used to control the fire; strictly control any access to the accident site, personal who enter the site should be equipped with protective devices and wear protective clothing; take proper measures to stop and limit any pollution of the surrounding environment, e.g. to cut off all possible connection between the site and non-contaminated area; all equipment used in fire fighting and cleaning should be treated as contaminated waste.

8.3 Clean-up of contaminated sites

In the simplest cases, namely with impermeable surfaces such as sealed concrete and asphalt, decontamination can be done by a triple solvent scrub process followed by a sorbent clean-up each time.

A list of a few absorbent materials is given bellow:

- *Activated carbon* - a form of carbon with an extremely porous consistence and thus having a very large surface area available for adsorption

- *Diatomaceous earth* – a naturally occurring, soft and chalk-like sedimentary rock, usually in a form of a powder with great porosity used as an adsorbent

- *Imbiber beds* – spherical, plastic particles, with a size of salt or sugar granules that absorb a broad range of organic chemicals. The absorbed liquid cannot be released even under pressure or even if cut. Used for picking up and transporting spilled chemicals

- *Oil-Dri* – a company supplying granular absorbents and a complete line of synthetic absorbents such as polypropylene pads, socks, rolls, pillows, booms and emergency response spill kits

- *Peat moss* - a hydrophobic, biodegradable, granular, environmental and user friendly hydrocarbon absorbent that absorbs 15 times its weight

- *Safe step* - an inert, inorganic blend of siliceous and other minerals, insoluble in practically all solvents and strong mineral acids (except hydrofluoric). It is non combustible and non-toxic to humans and the environment and is used for absorption of variety of spills with organic, inorganic, toxic and non toxic nature

- *Sawdust* – material composed of fine particles of wood, produced by cutting the wood with a saw. Among its applications is its usage for soaking up spills, allowing the spill to be easily swept out the door

  Vermiculite - a natural mineral (clay) with a medium capacity to shrink and swell in a contact with fluid

However, in many cases, clean-up of contaminated sites refers to capture or treatment of soil and groundwater contaminated through improper disposal, leaks, spills and fires. Normally, soil with a contamination level of higher than 100 ppm must be treated while those between 10 ppm – 100 ppm can be disposed or kept on-site; soil with a contamination level of lower than 10 ppm and water with lower than 0.5 ppm are regarded as non-contaminated.

Clean-up procedures vary depending on the location and the severity of the contamination. Following are some common on-site technologies regarding capturing or/and treating PCBs contaminated soils and water bodies:

8.3.1 Soil vapour extraction, pumping and treating

These are two treating methods with similar operation principle.
With an air injection and an air extraction well, the former one engages to capture volatile or semi-volatile contaminants which are absorbed to soil particles, by generating an air flow through the soil pores.

The later one however is to pump out contaminated groundwater through an extraction well, which is located to minimize escape of the contaminants flume, and then to treat these on-site; such decontamination can be improved by adding water or proper solvent mixtures to the contaminated flume through an injection well set in vicinity of the contamination source.

8.3.2 Filtration and permeable reactive barriers

PCBs are hydrophobic contaminants and tend to attach on suspended particles or sediments in water body, these can thus be caught by various filters, e.g. sand filters, bio-filters etc.; for dissolved PCBs contaminants, membrane filters with smaller pore size and electric charge can be used.

Based on similar principle, permeable reactive barriers engage to intercept and decontaminate groundwater at the same time, with reactants such as iron and compost etc filled in the intercepting structure.

8.3.3 Adsorption and settling

Suspended solids and dissolved contaminants can be chemically or physically bound by flocculants, activated carbons etc. and thus become easier to settle or be captured for subsequent treatment.

Some other on-site decontamination technologies include free product collection, oxidation with ultraviolet light and air/stream stripping etc. A concrete example is the technology of *PCB Disposal Inc.*, which pre-treats the water in multiple steps, i.e. to filtrate the water for removing suspended particles of various sizes, followed by an oil sorption column and finally an activated carbon filter system to absorb PCBs. The same company treats PCB contaminated waters up to a level of 5.000 ppm PCBs depending on the local legal requirements regarding its discharge into the environment. PCBs contaminated water containing emulsified mixture of different polluting substances, which cannot be separated, will be incinerated.

Table 4: Steps for Clean-up of PCBs

Steps Involved	Location of Spill			
	Leakage into Containment System	Spills on Concrete and Asphalt	Spills on Soil	Spills into Water
Notify plant personnel, provincial authorities and Environment Canada of spill and clean-up intentions	1	1	1	1
Take safety precautions and avoid personal contamination	2	2	2	2
Prevent pedestrians and/or vehicles from entering contaminated areas	3	3	3	3
Plug or dike all drains to sewers and ditches		4		
Build dikes to contain PCB fluid in small area			4	
Cover with plastic to minimize runoff from rain		5	5	
Dam area if possible, and close off to vessels in navigable waters				4
Use pump to transfer PCBs into drums and/or soak up PCBs with sorbents	4	6		5
Use dredges to collect contaminated sediment				6
Wipe area with rags and solvents	5	7		
Take core sample to determine penetration		8 (2.5 cm deep*)	6 (60 cm deep*)	
Remove surface area past level of contamination		9	7	
Dispose of contaminated materials and waste PCBs	6	10	8	7
Monitor wells and other bodies of water in the vicinity for PCB contamination			9	

* The core sample is taken at 25 cm concrete or asphalt depth / 60 cm soil depth. Number 1 is given to the first action to be taken in case of spill in the named location; accordingly, number 10 is given to the action to be taken the last.

Table 4 has outlined sequential clean-up steps while the proper sequence depends on the location of the spill. Numbers (colours) from 1 (lightest) to 10 (darkest) are given to specific actions indicating their priority.

9 Alternative Dielectric Fluids

Criteria of choosing a PCBs alternative for transformer should based on:

- Characteristics of the new dielectric fluid such as dielectric breakdown (Kv), viscosity (cSt) in different temperature, specific heat, thermal

expansion coefficient, flash point (°C), fire point (°C), pour point (°C), specific gravity and biological oxygen demand (ppm) etc.;
- Structure or design of the transformer, for example whether a modification of the transformer will be required due to different thermal expansion coefficient of the alternative dielectric fluid;
- Requirement regarding fire resistibility of the alternative, depending on the concrete situation;
- Costs of the new dielectric fluid;
- Local or regional practices etc.

Several important PCBs alternatives are listed below:

9.1 Mineral oils

It is once the conventional oil used as dielectric before PCBs' popularity. Because of its high flammability, the application of such alternative has been limited. However, since mineral oils have their advantages such as low costs, low toxicity and high fluidity, it can be filled in transformers which are located in or operate in conditions allowing existence of relatively high fire risk.

9.2 Silicon oils

Though this kind of dielectric oils is non-toxic and without chlorine, it does have many disadvantages such as: high viscosity thus not convenient for cooling; high thermal expansion coefficient which may require modification of the transformer; sensitivity to water; form of silica during incineration which complexes the gas treatment; besides, transformers refilled with silicon oils have to operate at a lower rating, which means a lower electrical performance.

9.3 Ester material

Both synthetic and natural ester are ideal dielectric fluids for the replacement of PCBs, because their many advantageous characteristics, i.e. low viscosity, relatively high specific heat, high flash point and fire point comparing with mineral oil; besides, they are of good electrical properties and will not de-rate the transformer. Main drawback of ester material is their higher costs.

Other choices for PCBs replacement could be heavy oils, some chlorinated hydrocarbons, natural oils from biomass sources etc.

Abbreviations

BCD	Base Catalyzed Decomposition
CerOx	Mediated Electrochemical Oxidation
DDT	Dichloro Diphenyl Trichloroethane
DMCR	Dehalogenation by mechanochemical reaction
ELVS	End of Life Vehicle Solutions
GC	Gas Chromatography
GEF	Global Environmental Facility
GPCR	Gas Phase Chemical Reduction
HydroDec	Hydrodechlorination
IBC	Intermediate Bulk Containers
KVA	Kilovoltamper
LN	Liquid Natural Cooling
LNAN	Liquid Natural Air Natural Cooling
LTR^2	Low Temperature Rinsing and Re Use/Recovery
MCD	Mechanochemical hehalogenation
MoEPP	Ministry of Environment and Physical Planning
MSO	Molten Salt Oxidation
ON	Oil Natural
ONAN	Oil Natural Air Natural
PACT	Plasma Arc Centrifugal Treatment
PCBs	Polychlorinated Biphenyls
PCDDs	Polychlorinated Dibenzo-p-Dioxins
PCDFs	Polychlorinated Dibenzofurans
PIC	Prior Informed Consent
PLASCON	Plasma conversion
POPs	Persistent Organic Pollutants
ppm	parts per million
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PWC	Plasma Waste Converter
SCWO	Supercritical Water Oxidation
SET	Solvated Electron Technology
SN	Synthetic Natural Cooling
SPHTD	Self Propagating High Temperature Dehalogenation
SR	Sodium Reduction
TCB	Trichlorobenzene
UN	United Nations
WEEE	Waste Electrical and Electronic Equipment
WFPHA	World Federation of Public Health Associations