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Poly Chlorinated Biphenyls (PCBs) in Power Transformers - An Indian Scenario

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The Polychlorinated Biphenyls (PCBs) one of the Persistent Organic Pollutants (POPs) has been used as dielectric fluids in transformers and capacitors, as plasticizers and in hydraulic fluids. Though PCBs never produced in India, the usage of PCB oils began in 1960 in India and PCBs have been imported mainly for transformers and capacitors applications. The imported PCBs-containing electrical devices were mostly distributed in large enterprises and the rest were distributed in the electrical power sector. The transformers that were installed prior to 1985 was identified and analyzed using GC/ECD technique. Around 1617 transformers are found to containing PCBs and out of which, 1150 transformers are declared as pure PCBs filled Transformers. From the analysis carried out on the 467 transformers, 225 were containing >500 ppm of PCBs and the remaining 242 transformers containing < 500ppm of PCBs. The major sector that owns PCBs containing equipment is the power sector (71%) followed by the steel industries (18%). The total weight of the PCBs oils and PCB contaminated oil is around 10,000 tons, which is being updated.

Keywords: *Polychlorinated biphenyls, Transformer, Inventory, India.*

1.0 INTRODUCTION

Polychlorinated biphenyls (PCBs) are used in two types of applications, open and closed ones. The closed systems where PCBs used are transformers, capacitors, heat transfer and hydraulic system and on the other hand the substances are also openly used as pesticide extenders, sealant, industrial oils, paints adhesives, plastics and as flame retardants. The major electrical applications included transformers, capacitors, voltage regulators, switches, bushings and cable insulation [1]. The commercial production of PCBs were started in the year 1929 by Monsanto Company from Swann Chemical Company, USA. In 1972, PCB production plants existed in Austria, Germany, France, Great Britain, Italy, Japan, Spain, USSR, and USA [2]. Between 1929 and 1977, about 1.7 billions of PCBs were produced in U.S [3-5].

Most commercial PCB mixtures are known by their industrial trade names. PCBs are generally occurs as mixtures of congeners; the most common commercial mixtures are called Aroclors. Aroclor names reflect the percent chlorine (by weight) of the mixture (e.g., Aroclor 1242 is 42% chlorine by weight) and the percentage of chlorination in commercial mixtures of different oil formulations for transformers ranges from 38.2 to 63.6 % [6] and from 5 to 9 chlorine atoms per molecule [7]. The main mixture, known as Askarel, contains 70 % Aroclor 1260 and 30 % tri- and tetrachlorobenzene approximately [8]. The United Nations Environmental Program (UNEP) reported the main producers of PCBs and PCB-containing products [9].

By 1970, PCBs were recognized as persistent and possibly hazardous environmental contaminant

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[10] and in 1979, Environmental Protection Agency (EPA) banned the manufacture and use of PCBs because of their adverse environmental effects [11]. The PCBs one of the POPs, can be released into the environment from hazardous waste sites that contain PCBs, illegal or improper dumped of PCB wastes, and leaks from electrical transformers containing PCBs. Transformers containing oil with concentrations of PCBs in excess of 500 ppm are classified as PCB transformers; those which contain between 50 and 500 ppm PCBs are considered to be PCB contaminated; and those which contain less than 50 ppm PCB are categorized as non-PCB transformers [12]. Because of the persistence of PCBs in environmental media, analyzing the presence and concentration of PCBs is important in conducting ecological risk assessments.

The Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants (POPs), first held in May 2001, focuses on eliminating or reducing releases of 12 initial POPs chemicals and wastes. The Stockholm Convention is an international legally binding agreement that targets twelve priority chemicals including PCBs identified as persistent organic pollutants. To date, more than 154 countries have signed and or ratified the Convention since it has entered into force in May 2004. India signed the Convention on 14th May 2002 and ratified it on 13 January 2006 and became a Party to the Stockholm Convention on POPs. Parties to the Stockholm Convention are required to develop National Implementation Plans (NIPs) to demonstrate how their obligations to the Convention will be implemented. India recognizes its obligation, under Article 7 of the Convention to develop and submit a NIP to the Conference of Parties (COP). India after the ratification of the Stockholm Convention on 13th January 2006 has accelerated the preparatory activities for the National Implementation Plan (NIP). India is committed to prepare the National Implementation Plan (NIP). As such, the country invited the United Nations Industrial Development Organization (UNIDO) to act as the GEF Executing Agency with expanded opportunities for the development of the NIP and opted to undertake this work through the GEF project cycle. The Ministry of Environment and Forest (MOEF), Government of India is the nodal ministry to implement this NIP program in India. The MOEF has entrusted the Central Power Research Institute (CPRI) which is an autonomous body under ministry of Power, Government of India to undertake this project to and for the activities relating to developing inventories of PCB's, PCB containing equipment and wastes in India [13]. As reported in the survey [13], PCBs are regulated as Hazardous Waste by MOEF under the schedule-1, appended to rule 3(i)(a) categorized in waste 28.1 and 32.4 of Hazardous Waste Management Amendment Rules [2000]. The concentration limit for PCBs given under schedule-2, appended to rule 3(i)(b) categorized in class A (A16) of HWM amended rule [2000] is 50 mg/kg (9).

In this study, transformers that were installed prior to 1985 were identified and their PCB levels were assessed using the standard techniques like GC-ECD. The distribution of PCB containing transformers in various sectors was also discussed.

2.0 EXPERIMENTAL

2.1 Instrument Conditions for the PCB Analysis.

The PCB analysis was carried out by an integrated system of gas chromatography, equipped with automatic injection system and coupled with a Ni electron capture detector (ECD) and mass spectrometric (MS) system with quadrupole ion trap (GC-ECD/MS) Varian, Model: 450GC. The separations were done in a 30m X 0.25mm X0.25µm Agilent HP-5MP column. Helium was used as carrier gas at 18 psi pressure and 1.9mL/min flow. The initial oven temperature was set at 80^{o}C, held for 2min, then increased to 150^{o}C at a rate of 25^{o}C/min, then increased to 280^{o}C at a rate of 8^{o}C/min. The temperature of both the injector and the detector was kept at 250^{o}C with nitrogen as make-up gas at a flow rate of 65ml/min. The injector volume was 1µl in the split mode.

2.2 Calibration and Sample Preparation

The calibration standard mixtures obtained as Aroclors 1248,1254 and 1260 (Supelco Co) were used in this study. The calibration standard solutions of 6,4, and 2 µm/mL were prepared using Iso octane (HPLC grade). These standard solutions were analyzed using GC-ECD and each characteristic Aroclor peaks were used for quantification of calibration solution [14]. The identification of PCBs as Aroclor was based on the agreement between the retention times of the peaks in the sample chromatogram and the retention time windows established through the analysis of the standards of the target Aroclor [5,15]. The quantification of PCBs in transformer oil is obtained from comparison with standards [4,5,15,].

The solid phase extraction (SPE) procedure was followed for the extraction of PCBs from transformer oil [16]. In a typical procedure, for the extraction of PCBs in transformer oil, 500 µl of isooctane was added to 200 µl of oil and treated with 5ml of Conc.H_2SO_4. The H_2SO_4 phase was discarded and the process is repeated till the acid phase is clear. The extract was passes on to a two column superclean LC Florisil solid phase extraction tube. Then it was flushed through using 10 mL aliquots of isooctane and collected the eluent in a 10mL volumetric flask.

3.0 RESULTS AND DISCUSSION

The analytical methods for PCBs are currently on their separation by gas chromatography (GC) [17], thin layer chromatography [18], capillary columns [19,20], flame ionization detector (FID) [21], the electron capture detector (ECD) [22-25], and mass spectrometry (MS) [26-29,15]. Immunoassay [30] and Neutron Activation Analysis [31] was also has been used for the PCB analysis. This work highlights the PCB analysis in transformer oil using gas chromatography having electron capture detector (ECD) in comparison with the standard mixture of Aroclors 1242, 1254 and 1260. A wide range of concentrations were determined using a dedicated column and Electron Capture Detection (ECD). The solid phase extraction (SPE) technique was found to be highly effective sample preparation technique for rapidly extracting PCBs from oils by capillary GC [16].

The Figs.1, 2 and 3 depicts the electron capture detector chromatographs of analytical standards (2,4 and 6 ppm) of Aroclor 1242, 1254, and 1260 respectively. The total number of peaks and the characteristic peak patterns associated with each Aroclor can act as a "fingerprint" identification when analyzing samples containing unknown PCB concentration [11].

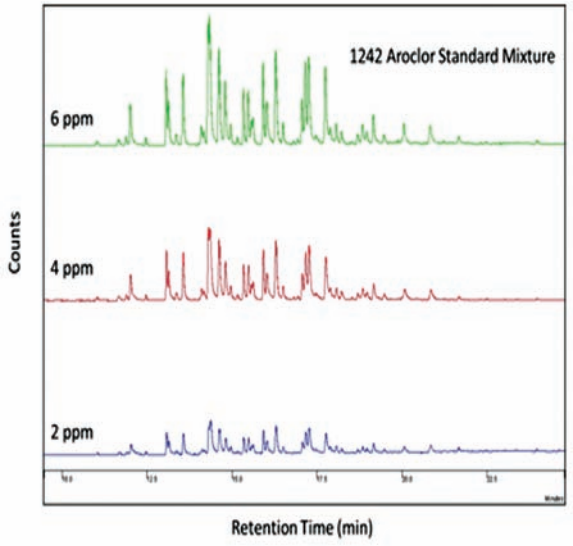

FIG.1 GC-ECD CHROMATOGRAMS OF 1242 AROCLOR STANDARD OF 2,4 AND 6 PPM.

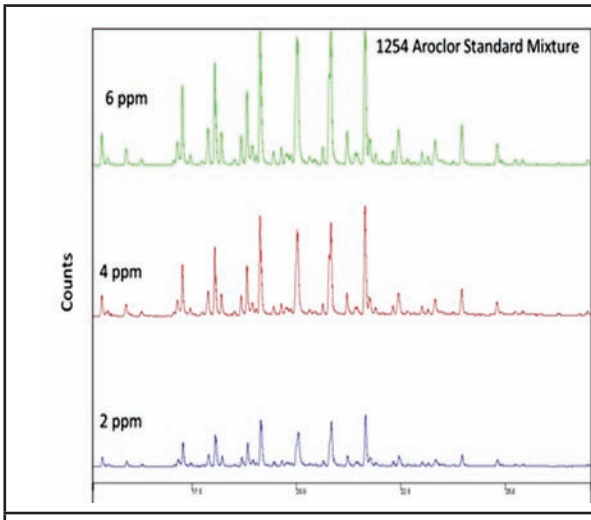

FIG.2 GC-ECD CHROMATOGRAMS OF 1254 AROCLOR STANDARD OF 2,4 AND 6 PPM.

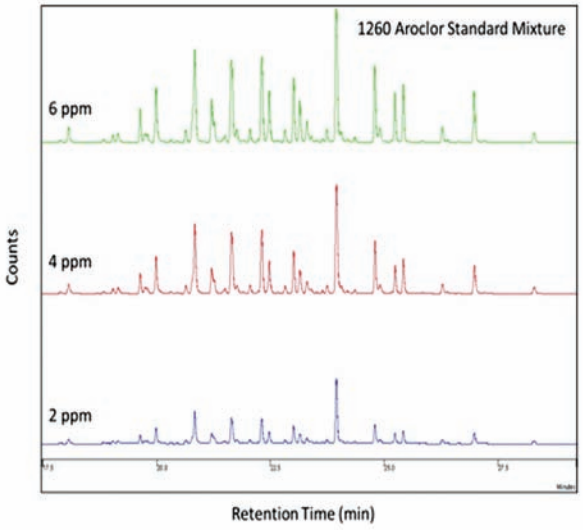

FIG.3. GC-ECD CHROMATOGRAMS OF 1260 AROCLOR STANDARD OF 2,4 AND 6 PPM.

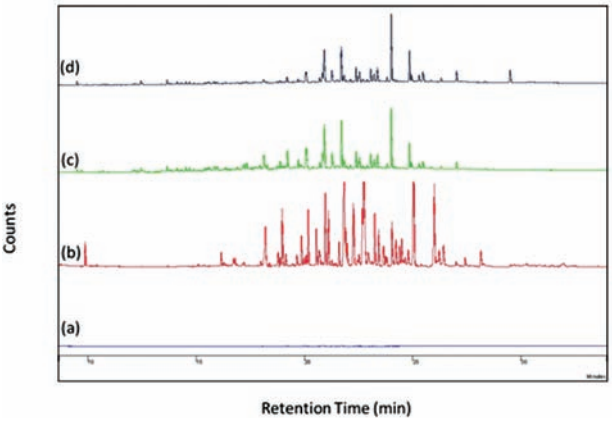

FIG.4. GC-ECD CHROMATOGRAMS OF (A) SOLVENT BLANK AND (B) TO (D) SAMPLES FROM VARIOUS SOURCES.

In order to check the analytical procedure, reagent blank was run and it is shown in the Fig.4(a). It is very clear that there are no peaks corresponding to PCBs were detected and hence no peaks would interfere with the qualitative or quantitative analysis of PCBs. All the PCB containing samples were analyzed in split injection mode in GC/ECD and hence, there were no peaks overlapping and especially, the high concentrated PCBs could be analyzed with better resolution. The Fig.4(b-d) represents the typical chromatographs of transformer oil containing PCBs.

Fig.5 gives a typical chromatograms obtained for the PCB containing transformer samples and were compared with those of the Aroclor standards. The retention times that are within ±0.1 were taken into account for matching the samples and the Aroclor pattern [5,15]. The analysis of PCBs in transformer oil and waste oil is obtained from comparison with standards in identical condition. For the quantification purpose, area summation of all components were done and compared to the summed area from the corresponding Aroclor standard. Alternatively, one can measure selected peaks (height or area) and compare them to corresponding peaks from Aroclor standards. Sometimes, a complex mixture of PCBs is difficult to identify and quantify. It has been observed that the peak pattern for a chemically or biologically degraded Aroclor mixture in the waste oil is significantly different from that of the manufactured form. When the sample of waste oil contains two or more Aroclor mixtures, it would be very difficult to quantify them. But, we did not notice such a situation during the analysis, since the transformer oil was drawn from different sources from all over India mainly from the operating transformers.

During the 1950's and the 1980's, India used to import PCBs-containing electrical equipment from other countries without being informed, most of which were transformers and capacitors for large facilities for specific application [13]. The imported PCBs-containing electrical devices were mostly distributed in large enterprises and the rest were distributed in the electrical power sector. It was noticed during the inventory that, around 500 PCB containing capacitors and about 500 PCB containing transformers were already discarded in the electrical power sector; but the data for the most of the imported PCBs-containing electrical devices, possibly in large enterprises in the non-power sector, are not available. The survey [13] shows that considerable amount of PCBs, PCB containing equipment and wastes exist in other sector such as cement, steel and paper etc.

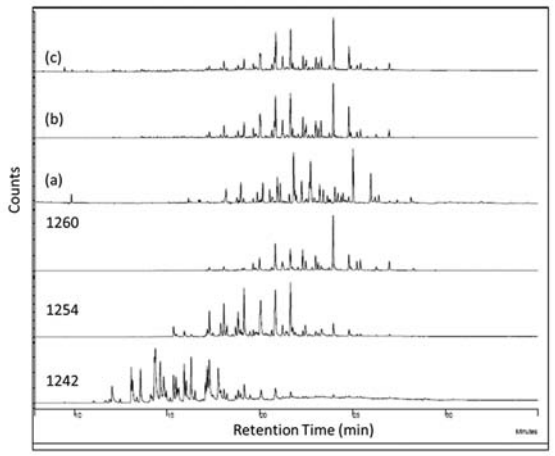

FIG.5. GC-ECD CHROMATOGRAMS PATTERN OF AROCLOR STANDARDS (1242, 1254 & 1260) WITH THAT OF THE SAMPLES FROM VARIOUS SOURCES.

TABLE 1

PCB TEST RESULTS OF SELECTED SAMPLES FROM DIFFERENT STATE LOCATIONS IN INDIA.

Name of the State.	Place/Area of Transformer located	Year	PCB concentration (ppm)
Karnataka	Karnataka Power Transmission Corporation Ltd.	1977	5109
Tamil Nadu	Ennore Thermal Power Station	1971	18900
Andhra Pradesh	Andhra Pradesh Generation Co Ltd.,	1967	1588
Uttar Pradesh	Panki Thermal Power Station	1975	257436
Maharastra	National Thermal Power Corporation	1977	8477
Gujarat	IFFCO	1972	1434
Assam	Nagaon Paper Mills (NPM)	1982	60 %
Kerala	Kerala State Electricity Board	1975	60 %
Haryana	Heidelberg Cement Power House -01	1958	60 %
Uttarakhand	Uttarakhand Jal Vidyut Nigam LTD	1985	60 %
Madhya Pradesh	M.P.POWER GENERATING CO.LTD, STPS,SARANI	1967	60 %
Orissa	ACC Limited	1984	60 %

Main owners of PCB containing equipment and PCBs oil in the public sector are the power generation and transmission companies (State Electricity Boards), heavy industries like cement, fertilizer and steel and in the private sector the mining, lubricant and ship-breaking industries.

The analysis carried out on the selected samples from the different locations is given in the Table.1. From the table, it is seen that the level of PCBs in some transformer are greater than 1000 ppm. The samples with 60% PCBs are declared by the concerned state locations.

The details of the transformers that were tested in the laboratory and the number of transformers declared as PCBs by the state locations are given in the Table.2. Around 1617 transformers are found to containing PCBs and out of which, 1150 transformers were declared as pure PCBs filled Transformers. From the analysis carried out on the 467 transformers, it is observed that there are 225 nos of transformers containing >500 ppm of PCBs and 242 transformers containing < 500ppm of PCBs.

TABLE 2

SHOWING THE TOTAL NUMBER OF TRANSFORMERS WITH DIFFERENT LEVELS OF PCBS IN VARIOUS STATE LOCATIONS.

STATE	No. of Transformers			Total no of transformers
	> 500 ppm	< 500 ppm	Pure PCBs	
Tamil Nadu	25	74	72	171
Karnataka	72	32	0	104
Kerala	0	0	7	7
Haryana	0	0	7	7
Gujarat	16	9	0	25
Maharastra	62	52	0	114
Andrapradesh	29	24	0	53
Assam	0	0	74	74
West Bengal	0	0	2	2
Uttarakhand	0	0	25	25
Utter Pradash	21	51	45	117
Sail Steel Plant	0	0	918	918
Total	**225**	**242**	**1150**	**1617**

For example, stake holders like Steel Authority of India (SAIL), has around 910 numbers of transformers installed at locations of their steel plants are declared as PCB containing transformers. Hence, based on the rating of the transformers and the volume of the oil, the total quantity of oil has been estimated. The sector wise distribution of PCB containing transformers is given in the fig.6. The highest quantities of PCB containing transformers are present in the steel industry. It is to be noted that some of the stake holders did not submitted the details of the PCB containing equipment.

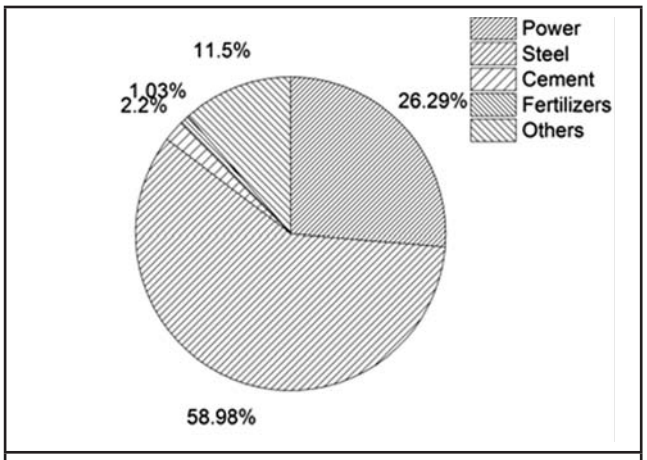

FIG.6. DISTRIBUTION OF PCBS CONTAINING TRANSFORMERS IN VARIOUS SECTORS.

It implies that the significant part of PCBs have not been identified yet. There are industries such as cement and steel which are installed prior to 1970 and the data of the transformers installed in their premises are to be received.

Most of the broken down transformers are recycled and reused. The out of service capacitors are stored at the owner's facilities. However, the PCB containing equipment and oil is not managed in an environmentally sound manner. Investigations show that out of service electrical devices in the Power Sector are temporarily stored in the yards throughout the country. However, due to limited monitoring, the concrete number of PCBs containing electricity devices is not available. Except PCBs-containing capacitors and transformers, no other electrical equipment (mainly small-sized devices) in use has been found containing PCBs. Though the analyses indicated that there are transformers installed prior to 1985 are non-PCB transformers, it is anticipated that the number of PCB containing transformers would go up once the inventory data is updated.

4.0 CONCLUSIONS

The inventory preparation of PCB's was undertaken covering 28 States and 6 Union Territories in India. PCBs were never produced in India and the import of PCBs into the country was banned in 1998. While the total amount of PCB-oils as well as PCB-containing equipment imported is unknown, the estimated quantity of PCB-containing equipment and pure PCB-oils in India today amounts to about 10,000 to 15,000 tonnes. Around 1617 transformers are found to containing PCBs and out of which, 1150 transformers were declared as pure PCBs filled Transformers. From the analysis carried out on the 467 transformers, it is observed that there are 225 nos of transformers containing >500 ppm of PCBs and 242 transformers containing < 500ppm of PCBs. However the data / information collected and collated to develop an inventory of PCBs in India clearly indicates that the amount of PCB and its waste exceeds the estimated quantity.

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