

# LEVELS OF POLYCHLORINATED BIPHENYL CONGENERS IN SEA WATER AND SURFACE SEDIMENT OF ALANG SHIP BREAKING SITE, BHAVNAGAR, GUJRAT, INDIA

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## Introduction

The ship breaking activity has a significant source of pollution from metal scraps, insulating materials, paint scrap, used oil/waste oil, insulating oils from electrical equipments, asbestos and various other solid waste. In past the insulating oils used in electrical equipments were impregnated with polychlorinated biphenyls (PCBs) to improve their flame resistance and thermal stability though they have been banned for many years now. Thus the old ships having electrical equipments with PCBs containing insulating fluids remain as potential source of pollution at and around any ship breaking site.

Alang Ship Breaking Site is the largest of its kind in the world and located at western coast of Gulf of Khambat (Cambay) of Arabian Sea. It is situated near Alang – Sosia village at about 50 km south east from Bhavnagar district in Gujrat state of India and it has a natural suitability for Ship breaking activities. The Gujrat Maritime Board has allocated 173 plots on lease to private companies for ship breaking activities. The site is about 10 km long stretching from Sosia in east to Alang in the west.

The news and concern related to permission to beach cruise ship SS Blue Lady and aircraft carrier Clemenceau at Alang Ship Breaking Site lead to attempt of assessing the levels of PCBs contamination, if any, at and near the site. In this study we sampled and analysed sediments from several plots of the ship breaking area and sea water from shore along the respective plots to evaluate the contamination of the area.

## Materials and Method

Ten locations (plots) were selected at ship breaking site including one location at about 10 km distance from ship breaking site as baseline location. Approximately 20 litres of seawater samples were collected during low tide from each location in stainless steel containers. Sediments were collected as sub-samples from ship breaking area of the respective plot towards the seawater and mixed to make composite sample. The composite sample from each sampling location was collected in wide mouth glass bottle with screw cap. Immediately after collection the samples were placed in ice boxes, transported to the laboratory and were refrigerated until further processing.

Sediment Samples of each location were extracted with mixture of dichloromethane and n-Hexane (1:1) in Soxhlet extraction assembly for about six hours. Extracts were concentrated by rotary vacuum evaporator (Buchi) and exchanged to cyclohexane.

Whole sample of seawater from each location was filtered through Whatman filter paper (No. 4), the filtrate aliquots were extracted thrice with dichloromethane and collected through anhydrous sodium sulphate. Extracts of aliquots of a sample were concentrated, combined and solvent exchanged to cyclohexane. Suspended solids collected on filter papers during filtration of water samples of each location were extracted similar to sediments.

Concentrated extracts were subjected to multi-layered column cleanup for removal of co-extracted interfering organic compounds and sulphur compounds. The collected elute from the cleanup were finally concentrated to 2 mL in n-Hexane.

**Table 1: Significant PCB Congeners**

Sl. No.	Group	Toxicity Significance	PCB Congeners (IUPAC #)
1	Group 1a	Sterically similar to 2,3,7,8-TCDD and purported to cause direct toxicity	77, 126, 169
2	Group 1b	Mixed-type inducers of somewhat lesser toxicity and frequently found in environmental samples	105, 118, 128, 138, 156, 170
3	Group 2	Phenobarbital – type (PB) inducers for Mixed-Function Oxidase enzymes are less toxic but most abundant in the environment	87, 99, 101, 153, 180, 183, 194
4	Group 3	Weak or non-inducers found at high concentration levels in environmental samples or animal tissues representing about 10% of the PCB content in tissues	18, 44, 49, 52, 70, 74, 151, 177, 187, 201
5	Group 4	Mixed type inducers having some potential for toxicity but usually present in tissues at low concentrations	37, 81, 114, 119, 123, 157, 158, 167, 168, 189

Pure PCB congeners were procured from Dr. Ehrenstorfer GmbH, Germany. Stock solutions of individual congeners were prepared in residue analysis grade n-Hexane. Individual congener solutions were serially diluted to working concentration. Mixture was prepared maintaining a concentration of 100 pg/ $\mu$ L of each congener in the solution. The mixture was diluted to make five different levels for multi-level calibration of the instrument.

Solutions of individual PCB congeners were injected to determine their retention time and mass spectra by operating the GC-MS in Electron Ionization and TIC (total ion chromatogram or scan) mode. Prominent ions and their relative abundance ratio were determined from mass spectra of individual congeners. The ions from the molecular ion cluster and the ions resulting from two chlorine losses from each chlorination level (one chlorine loss for monochlorobiphenyls) were selected for SIM (selected ion monitoring) mode of data acquisition. The ions for the data acquisition windows were selected such that window for each chlorination level also included ions characteristic of adjacent chlorination levels.

Quantitative analysis of sample extracts were performed by SIM (Selected Ion Monitoring) mode of data acquisition for 28 selected PCB congeners (Table 1). 1  $\mu$ l splitless injections of concentrated extract were made into split/splitless injector of Gas Chromatograph (Agilent 6890 PLUS Series) with Mass Spectrometer (Agilent 5973Network MSD).

Sample extracts were also analysed for qualitative screening for all chlorination levels of PCBs for assessment of congeners other than the 28 selected congeners. Three characteristic ions were selected for each chlorination level, some of these ions being common among two to three different chlorination levels, as a result, a total of twenty ions are monitored for screening of all chlorination levels of PCBs (Table 2).

**Table 2: Ions Selection for SIM Mode Data Acquisition (Qualitative)**

S. No.	Chlorination Level	Prominent Characteristic Ion(s)	Ion(s) resulting from chlorine loss
1	Mono chloro-	188, 186	152
2	Di chloro-	222	151, 150
3	Tri chloro-	254	186, 188
4	Tetra chloro-	292, 290	222
5	Penta chloro-	324, 326	254
6	Hexa chloro-	360, 362	290
7	Hepta chloro-	394, 396	324
8	Octa chloro-	428, 430	360
9	Nona chloro-	464, 462	394
10	Deca chloro-	498	428, 430

## Results and Discussion

### Congener Specific Analysis (28 Selected Congeners)

#### Seawater Samples

Quantities detected in suspended solids and filtrates were added to compute results for seawater samples. The contaminations of seawater of some locations were mainly contributed by suspended solids of the seawater of these locations. Total PCBs concentration detected (Table 3) for any location was highest as 463.07 ng/l at location #6 (22 congeners detected out of 28 congeners analysed). None of the congeners were detected at three locations (location #5, location #8 and location #10). Total PCBs concentrations in rest of the locations were ranged between 4.21 ng/l (at location #7) to 33.45 ng/l (location #3).

**Table 3: CONGENERS DETECTED AND RANGE OF CONCENTRATION IN SEAWATER**

S. No.	SEAWATER SAMPLE	CONGENERS DETECTED	RANGE (ng/l)		TOTAL (ng/l)
			Minimum (Congener)	Maximum (Congener)	
1	AW-1	4	2.46 (Congener 168)	4.13 (Congener 118)	12.86
2	AW-2	7	0.77 (Congener 70)	3.54 (Congener 18)	11.24
3	AW-3	14	1.11 (Congener 70)	3.63 (Congener 156)	33.45
4	AW-4	9	1.33 (Congener 77)	3.00 (Congener 128)	17.70
5	AW-5	NIL	ND	ND	ND
6	AW-6	22	1.39 (Congener 157)	86.96 (Congener 170)	463.07
7	AW-7	1	ND	4.21 (Congener 168)	4.21
8	AW-8	NIL	ND	ND	ND
9	AW-9	1	ND	5.01 (Congener 167)	5.01
10	AW-10	NIL	ND	ND	ND

ND – Not Detected

#### Sediment Samples

Total PCBs concentration detected (Table 4) for any location was highest as 570.45 ng/g at location #5 (8 congeners detected out of 28 congeners analysed). None of the congeners were detected at six locations (location #1, #2, #3, #4, #9 and #10). Total PCBs concentrations at rest of the locations were ranged between 11.92 ng/g (at location #8) to 150.95 ng/g (at location #6).

#### Aroclor Profiles

The congener profiles observed in the samples with some contaminations were indicative of Aroclor contamination, however the presence of more than one Aroclor poses extreme difficulty in identification and quantification of the Aroclors present.

Trace level contaminations observed in extracted ion chromatogramme (EIC) of some locations were not sufficient to draw any clear conclusion. However the trace levels of some congeners observed in samples of a few locations were mainly Trichloro and Tetrachloro biphenyls indicating possible contamination with Aroclors 1221, 1016 and 1232. The congeners observed in samples of locations #5 and location #6 were pentachloro through octachloro biphenyls indicating possible contamination with Aroclors 1242, 1254 and 1260.

In samples of some of the locations, though none of the congeners were detected out of the 28 congeners analysed, however trace level presence of congeners other than the selected 28 congeners (screening analysis by monitoring ions significant to chlorination levels) were observed but such congeners could not be quantified due to unavailability of standard reference materials for calibration.

**Table 4: CONGENERS DETECTED AND RANGE OF CONCENTRATION IN SEDIMENTS**

S. No.	SEDIMENT SAMPLE	CONGENERS DETECTED	RANGE (ng/g)*		TOTAL (ng/g)*
			Minimum (Congener)	Maximum (Congener)	
1	AS-1	NIL	ND	ND	ND
2	AS-2	NIL	ND	ND	ND
3	AS-3	NIL	ND	ND	ND
4	AS-4	NIL	ND	ND	ND
5	AS-5	8	16.88 (Congener 128)	166.50 (Congener 168)	570.45
6	AS-6	9	5.13 (Congener 105)	34.46 (Congener 170)	150.95
7	AS-7	2	5.80 (Congener 138)	8.39 (Congener 168)	14.19
8	AS-8	2	5.83 (congener 168)	6.09 (Congener 138)	11.92
9	AS-9	NIL	ND	ND	ND
10	AS-10	NIL	ND	ND	ND

\* Dry Weight Basis, ND – Not Detected

It appears from the analysis of seawater and sediment samples collected from selected plots at Alang Ship Breaking Site, Bhavnagar, Gujrat that the ship breaking activity at some of the plots have contaminated the sediment of the plot, nearby area towards sea and sea water with PCBs probably in the form of Aroclor mixtures which might have leaked from dismantling of electrical equipments, insulating materials and paint scraps released due to ship breaking. As the contamination is not widespread and not reflected in all the samples of seawater indicating that the contamination is probably location specific or specific to the ship being broken in the respective plot during the period of sampling.

When compared to Canadian Interim Sediment Quality Guidelines (ISQG) and Probable Effect Level (PEL) the total PCBs concentration observed in sediment samples at location #5 and at location #6 in the study were higher than ISQG (21.50 ng/g), which were however lower than the PEL(189 ng/g)<sup>1</sup>. The values at rest of the locations were below the ISQG level.

In a similar study conducted by Greenpeace Mediterranean in Aliaga Ship Breaking Yards, Izmir, Turkey in 2002 have reported sum of 7 indicator PCB congeners between <0.003 to 0.640 mg/kg of dry weight of sediments<sup>2</sup>. Guruge and Tanabe (2001) have studied PCBs and other organochlorines in remote coastal areas of Sri Lanka and reported PCBs levels as 4.4 ng/g dry weight of sediment<sup>3</sup>. Oliver Wurl and Obbard J. P. have reported sum of PCB congeners in the range of 0.05 to 1.8 ng/l (mean 0.5 ng/l) in seawater and 0.07 to 12.4 ng/l (mean 1.3 ng/l) in sea-surface microlayer (SML)<sup>4</sup>.

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