ANALYSIS OF PCB IN THE MINING SECTOR WITHIN THE LATIN AMERICAN REGION

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs)[1] requires parties to eliminate the use of polychlorinated biphenyls (PCB) in equipment by 2025 according to article 3, paragraph (1) (a). Moreover, Parties have to make determined efforts designed to lead to environmentally sound waste management of liquids containing PCB and equipment contaminated with PCB having a PCB content above 0.005 % as soon as possible but no later than 2028, subject to review by the COP (annex A, Part II, paragraph (e)) and dispose them off by 2028. Further, reports on progress in PCB management towards the 2025/2028 goals have to be submitted to the Conference of the Parties every five years. The governments of Chile and Peru have recognized in their national implementation plans (NIPs) the environmentally sound management of PCB and have prioritized action to be taken in the sector of the mining industry. Subsequently, under the leadership of the Basel Convention Regional Centre for Training and Technology Transfer for the South American Region in Argentina (BCRC-Argentina) and with the assistance of the United Nations Environment Programme (UNEP), the project 'Best Practices for PCB Management in the Mining Sector of South America'[2] has been developed and was implemented from 2010 to 2014.

The project included an "analytical component" with two objectives: (i) Identification of equipment and other items that contain PCB and (ii) Standardization of procedures for the analysis of soil, oils, contaminated materials, equipment and other applications. The later one included an interlaboratory assessment of laboratories analyzing PCB.

Materials and methods

POPs laboratories analyzing PCB were identified through UNEP's POPs Laboratory Database and an inquiry sent by the BCRC-Argentina. Laboratories were asked to fill out a questionnaire detailing their methods/protocols used for PCB analysis. The information obtained was transferred into UNEP database of operating POPs laboratories.

For screening purposes, an automated system was proposed and used in Chile and Peru. The samples resulting in concentrations higher than 50 mg/kg did undergo congener-specific analysis for six or seven indicator PCB. It was agreed that "real" samples from the mining sectors in Chile and Peru exhibiting the 50 highest concentrations from the screening will be subject for confirmatory instrumental analysis. The POPs laboratory at the EULA Centre, University of Concepción in Chile did undertake a training and evaluation of screening and confirmatory analytical methods.

Further, laboratories were trained in the analysis of PCB in technical matrices, such as transformer oils or soils, using either GC/ECD or GC/LRMS methods. A training session had been organized in Buenos Aires; the report is available from the following WebSite http://www.inti.gob.ar/pcb/documentos/informesReportesDocumentos/InformesReportes/UNEP-GEF_InformetrainingPCB_2013.pdf.

In order to test the performance of the PCB laboratories, laboratories trained under this project from Argentina, Chile and Peru were invited in August 2013 to participate in the UNEP-coordinated interlaboratory assessment. Laboratories that responded to this invitation were assigned the codes L201 to L206. Laboratories were to provide the analytical results according to the reporting scheme and within six weeks after receipt of the test

samples to the coordinator at MTM Research Centre, Örebro University. All results were evaluated together according to international standards, such as established by the International Organization for Standardization (ISO) or the International Laboratory Accreditation Cooperation, thus allowing a performance classification.

Two test samples were prepared and shipped to laboratories that had indicated their interest in participation at the UNEP-coordinated interlaboratory assessment as follows:
1. The indicator PCB standard solution consisted of a mixture of the six indicator PCB (congeners #28, #52, #101, #138, #153 and #180) in *iso*-octane. The concentration range per congener was from 1 µg/kg to 10 µg/kg;
2. The transformer oil was a dilution of an Aroclor 1254 (Lot LA79866) oil in toluene obtained from Wellington Laboratories (Guelph, ONT, Canada).

The Assigned Values (AV) were obtained from the 2nd Round of the Bi-ennial Global Interlaboratory Assessment on POPs[3] using the results of 15-18 laboratories. The AV was calculated using the main mode of the data of the Cofino Model , and is centered around the highest density of values. The data assessment was carried out according to the principles employed in the data assessment of the QUASIMEME proficiency testing organisation (www.quasimeme.org). The approach of the assessment is based on the standard, ISO 13528 (2005) and the IUPAC International Harmonised Protocol for Proficiency Testing.
The results of the interlaboratory assessment were presented at the final workshop of the project, which was held on 3 and 4 December 2013 in Santiago de Chile. The participants were given the results and evaluation sheets and two weeks to report any errors due to transfer of data or typing into the results sheets. No request for correction was received.

Results and discussion
A total of six laboratories participated in the training and analytical part of the GEF project, namely:

- Centro de Ciencias Ambientales de Chile – EULA, Concepción, Chile
- Laboratorios Hidronor S.A., Santiago, Chile
- DIGESA - Laboratorio de Control Ambiental, Ministry of Health, Lima, Peru
- Certificaciones del Perú S.A. - Cerper S.A.- Lima, Peru
- Corporación Laboratorios Ambientales del Perú SAC, CORPLAB, Lima, Peru
- SGS del Perú S.A.C., Lima, Peru

Typically, the laboratories had more than ten years of experience in the analysis of PCB and were accredited by their national bodies; *i.e.*, INN in Chile or IDECOPI in Peru.

The laboratories reported to apply either ASTM D4059–00-2010 or EPA 8082 methods. As a capacity building component of this project, laboratories were trained in the application of the European Union standard EN 12766/CEN. Table 1 presents an overview on the approaches for the analysis of PCB in different matrices used by the laboratories.

Table 1: Overview of methods used for extraction and analysis of PCB

Sample type	Extraction	Separation and detection
Transformer oils	Solid phase extraction, Dilution + Ultrasonic, Liquid-liquid	Capillary GC column + ECD
Solid residues/wastes	Soxhlet	Capillary GC column + ECD
Soils, sediments	Soxhlet y Ultrasonido	Capillary GC column + ECD Capillary GC column + LRMS
Effluents and water	Liquid-liquid, Solid phase extraction	Capillary GC column + ECD Capillary GC column + MS/MS
Human milk	Liquid-liquid	Capillary GC column + LRMS

In the year 2012, the above-mentioned six laboratories had analyzed a total of 4,602 samples; of these 91% were dielectric samples. It is important to note that the vast majority of these samples were generated from the electrical sector in Peru within a "sister" project 'Environmentally Sound Management and Disposal of PCBs' implemented by UNIDO and analyzed by DIGESA (Peru).

The EULA Centre at the University of Concepción compared the results of the screening exercise undertaken with (i) the Chlor N-Oil(R) test kit (a colometric method for concentrations above 50 mg/kg), (ii) the Dexsil L2000 analyser (quantitative electro-chemical method) of 30 most contaminated soil and 31 transformer oil samples with the results obtained from confirmatory analysis using GC/ECD according to method ASTM 4059D-00[4]. The results are displayed in Table 2.

Table 2: Semi-quantitative results of the three test methods (N/A = not analysed)

Matrix	Nº samples	Positive Clor-N-Oil® 50 ppm	Positive L2000DX	Positive GC-ECD	False positives	False negatives
Transformer oil	31	N/A	12	9	6	3
Soil	30	N/A	0	0	0	0
Transformer oil	674	63	N/A	14	49	N/A

Within the 61 samples analysed by EULA (31 transformer oil and 30 soil samples), 12 samples screened with the Analyzer L2000DX gave concentrations above the limit of 50 mg/kg (20% of all samples tested). Of these, 15% were confirmed by GC/ECD method (9 of the 61 samples). There were 10% of the samples found as false positives (9 out of 61) and 10% as false negatives (3 of the samples that were screened below the threshold). Within the 674 transformer oil samples that were analysed by DIGESA in Peru, 63 indicated concentrations above the threshold of 50 mg/kg (9% of all samples screened); however, only 14 samples were confirmed by GC/ECD analysis. There were 49 false negatives (2%); the samples that were below 50 mg/kg in the Chlor-N-Oil test did not undergo confirmatory analysis using GC/ECD.

Finally, the following laboratories participated in the interlaboratory assessment, which was conducted as part of the UNEP-coordinated 'Biennial Global Interlaboratory Assessment on Persistent Organic Pollutants – Second Round 2012/2013':
Argentina (2): Instituto Nacional de Tecnología Industrial (INTI), Buenos Aires and Kioshi, Avellaneda
Chile (3): Centro Nacional del Medio Ambiente (CENMA), Santiago; Centro Universitario Internacional Europa América Latina (EULA), Concepción; and Hidronor, Santiago de Chile
Peru (2): Corporación Laboratorio Ambiental del Perú, Lima and SGS, Callao
Spain (1): IDAEA CSIC, Barcelona.

Laboratories that responded to this invitation were assigned the codes L201 to L206. The following two tables show the z-scores of the laboratories for the two test samples. It should be noted that Laboratory L205 provided results obtained with the Analyzer L2000DX and therefore, was not able to provide congener-specific results.

Table 3: z-scores for standard solution

Indicator PCB	Lab 65	Lab 201	Lab 202	Lab 203	Lab 204	Lab 205	Lab 206
PCB 28	0.9	18.6	NA	NA	NA	NA	NA
PCB 52	1.6	30.2	281	NA	NA	NA	NA
PCB 101	1.2	18.0	62	0.5	NA	NA	NA
PCB 138	0.7	5.1	80	3.6	NA	NA	NA
PCB 153	1.7	7.8	58	2.9	NA	NA	NA
PCB 180	2.1	-0.9	-5.2	1.9	NA	NA	NA
□PCB LB (ND=0)	1.1	9.4	61	-0.1	897.2	NA	NA
□PCB UB (ND=LOD)	1.1	9.5	NA	NA	NA	NA	NA

Table 4: z-scores for the transformer oil test sample

Indicator PCB	Lab 65	Lab201	Lab 202	Lab 203	Lab 204	Lab 205	Lab 206
PCB 28	1.3	3.5	28151	NA	NA	NA	NA
PCB 52	-0.4	-3.0	413	NA	NA	NA	NA
PCB 101	-0.1	-2.9	37	0.3	NA	NA	NA
PCB 138	1.1	-4.4	165	1.0	NA	NA	NA
PCB 153	7.2	0.0	15	-1.0	NA	NA	NA
PCB 180	-0.4	-1.0	NA	0.4	NA	NA	NA
□PCB LB (ND=0)	0.7	-3.1	331	-2.2	63.1	-2.4	NA
□PCB UB (ND=LOD)	1.2	-2.8	NA	NA	NA	NA	NA

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References:

1 Stockholm Convention on Persistent Organic Pollutants (2001 and updates): www.pops.int
2 Project document available from www.thegef.org and from http://www.inti.gob.ar/pcb/ ; implementation reports from http://www.inti.gob.ar/pcb/informes.php
3 UNEP (2014): Bi-ennial Global Interlaboratory Assessment on POPs – Second round 2012/2013; available from http://www.unep.org/chemicalsandwaste/Portals/9/POPs/Interlab%20Assess/Second%20round/Interlaboratory%20Assessment%20POPs%20by%20UNEP-%20MAR2015_en.pdf
4 ASTM D4059–00 (2010): Standard Test Method for Analysis of Polychlorinated Biphenyls in Insulating Liquids by Gas Chromatography