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Determination Of Unintentional Persistent Organic Pollutants (Upops) In Ecuador

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Abstract:
The results of the inventory of unintentionally produced persistent organic pollutants in Ecuador are presented and contrasted with the results of a sampling and analysis campaign at seven sites of interest to the country. The Stockholm Convention Toolkit was used to carry out the inventory, while the analytical results followed the methods of the U.S. Environmental Protection Agency (EPA). The inventory approaches made it possible to prioritize the sites of interest, thus reducing the amount of resources used in the national estimation process on the production of unintentional persistent organic pollutants UPOPs.
Materials and Methods*: In this work, a documentary review of the regulatory framework regarding hazardous waste in Ecuador was initially carried out. Subsequently, samples and laboratory analyze were carried out outside Ecuador in seven prioritized sites to release UPOPs.*
Results*: In 2018, estimated PCDDs and PCDFs emissions in Ecuador were 307 g TEQ/y corresponding to 4 groups: group 6 open burning processes: 63%, group 9 disposal and landfills (23%), group 2 ferrous and nonferrous metal production (9%), group 4 production of mineral products (2%), others sectors (3%).*
Conclusion: *With the results of the 2018 inventory, it was possible to identify that the main sectors that contribute PCDDs and PCDFs are the processes of open burning, disposal and landfills.*
Key Word*: UPOPs inventory; dioxins; furans; toolkit*

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I. Introduction

Persistent organic pollutants (POPs) have become one of the environmental issues of greatest concern at the international level. On May 22, 2001, the Stockholm Convention on Persistent Organic Pollutants (POPs) was adopted, laying the foundation for a concerted effort to reduce and eliminate POPs in a manner that protects health and the environment (Secretary of the Stockholm Convetion, 2019). The Convention entered into force on May 17, 2004 and was ratified by the Government of Ecuador on May 7, 2004.

Some POPs are by-products that are unintentionally produced and released into the environment during combustion or during some chemical processes of other POP substances. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), generally called dioxins and furans, are one of the original substances of the Stockholm Convention's "Dirty Dozen," which are typically produced during incineration. While pentachlorobenzene (PeCB) belongs to the chlorobenzene family, it can be produced in thermal and industrial processes.

The Stockholm Convention promotes the continued minimization and, where possible, ultimate elimination of unintentional POPs (UPOPs). The Parties to the Convention should develop an action plan to make progress towards achieving this objective and implement it. Each country should develop and maintain a national inventory of unintentionally produced POPs sources along with an estimate of releases (Secretaría del Convenio de Estocolmo, 2019).

Specifically, the Convention lists certain sources that have the potential for comparatively high formation and release of unintentionally produced POPs, such as PCDDs, PCDFs, hexachlorobenzene and polychlorinated biphenyls into the environment, as follows (Secretaría del Convenio de Estocolmo, n.d.):

- Incinerators for hazardous and medical waste and sewage sludge;
- Cement kilns that burn hazardous waste;
- Pulp production using chlorine bleach; and

- Certain thermal processes in the metallurgical industry: secondary copper production, sinter plants in iron and steel manufacturing, secondary aluminum production and secondary zinc production.

Developing emission inventories for POPs is a challenge, especially for UPOPs due to the lack of information on the amount of pollutants produced worldwide. Historically, many POPs have been deposited in soils and continue to be released as secondary emissions. These secondary emissions are difficult to estimate, as the magnitude and distribution of the original deposit and the resulting emissions are difficult to determine and calculate. Therefore, developing countries' UPOPs emissions are largely unknown and inventories have a high degree of uncertainty.

Ecuador in 2019, through the National Program for the Management of Chemical Substances (PNGQ) developed the "Diagnosis, action plans and capacity building to reduce emissions of unintentional persistent organic pollutants (UPOPs) in industrial sectors of Ecuador," within which the inventory of UPOPs was updated, and the main activities generating UPOPs were identified, as well as seven (7) geographic sites for sampling and subsequent analysis of PCDDs, PCDFs, and PeCBs.

II. Material And Methods

Document review

To diagnose the situation of UPOPs in Ecuador, an analysis of the regulatory framework for hazardous waste was carried out with local stakeholders (possible generators of UPOPs), and opportunities were identified to reduce emissions from the main sources of UPOPs. Through this study, the sources generating UPOPs were defined and their emissions were quantified following the methodology of the Stockholm Convention Toolkit for Emissions of PCDDs, PCDFs and other unintentional POPs (UNEP, 2013), the activity rates of the sources generating UPOPs were obtained from information gathered in the field and from secondary sources (National Program for the Management of Chemical Substances, 2019). With the Toolkit results, priority categories were obtained, which provided a guideline for the sectors with which sampling and laboratory analysis are performed to determine PCCD, PCDF and PeCB concentrations.

Sampling and Laboratory Analysis

Water, soil, air and leachate samples were taken at the seven (7) prioritized geographical sites (a botanical reserve that frequently suffers from forest fires, two landfills, a sugar mill, a steel and electroplating plant, a cement plant and a hazardous waste incineration plant). These samples were sent for analysis to laboratories in the United States to test for the presence or absence of UPOPs.

For soil sampling, the stubble, forest floor or other plant material found on the soil surface was separated to avoid contamination of the sample. Two samples of 100 grams of soil each were collected at every point. Meanwhile, for the water and leachate samples at the different points, a volume of two liters was taken for each point, in bottles of 1-liter capacity, trying to have an adequate representativeness for each sampling site.

Sampling for PCDDs and PCDFs was performed using two methods. At the steel and electroplating plant, Method TO-9a, which uses a high volume air sampler equipped with a quartz fiber filter and a polyurethane foam adsorbent (PUF), was used to sample 325 to 400 m^3 of ambient air over a 24-hour sampling period. EPA Method 23 was used for the other points, for which samples were taken isokinetically using a modified Method 5 train consisting of a glass fiber filter containing no organic binders, an XAD-2 resin trap and a series of clamps. The sampling train is rinsed with acetone and/or methylene chloride followed by toluene. Typically, all components of the train, including rinsates, are extracted and combined to produce an extract for analysis that represents the entire sampling train. This extract is split and 50% of it is stored in case there are problems and a new analysis is necessary. PCDDs/PCDFs are thoroughly cleaned prior to analysis.

EPA SW-846 Method 0023A is specific for PCDDs/PCDFs similar to 23. However, these methods are not identical. The main difference is that 0023A requires that the front half of the train consisting of the rinsates (nozzle, probe, front filter holder medium) and filter be removed and analyzed separately from the rear half of the train consisting of the rinsates (rear filter holder medium, condenser coil) and XAD-2 resin. In both cases the samples were analyzed by gas chromatography with high resolution mass spectrometry (HRGC/HRMS).

The methods used for the analysis of the samples sent were:

- PCCDs and PCDFs in Soil – EPA Method 8290A
- PCCDs and PCDFs in water and leachates – EPA Method 8290A
- PeCB in soil – Method 8270 D Solids
- PeCB in leachates – Method 8270 D Water
- PCCDs and PCDFs in air – EPA Method 23

Once the laboratory reports were available, a synthesis of the results was made in order to learn the values found by type of sample and sector.

III. Result

PCDDs/PCDFs Inventory

In 2018, estimated PCDDs and PCDFs emissions in Ecuador were 307 g TEQ/y corresponding to 4 groups:

- Group 6 Open burning processes: 63%
- Group 9 Disposal and landfills (23%)
- Group 2 Ferrous and nonferrous metal production (9%)
- Group 4 Production of mineral products (2%)
- Other sectors (3%).

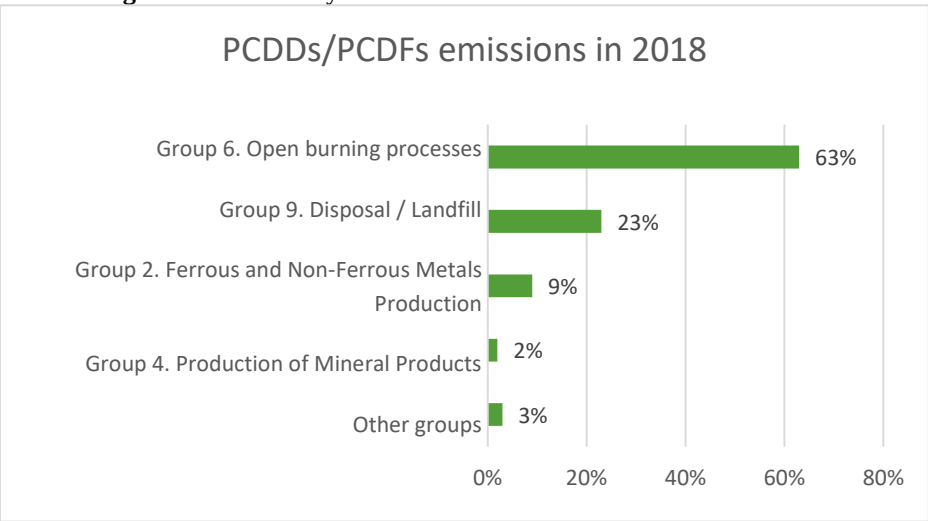
The air release pathway received 53% of the PCDD/PCDF emissions (164 g TEQ/y), residues 28% (85 g TEQ/y) and water 3% (10 g TEQ/y) (National Program for the Management of Chemical Substances, 2019). Table 1 summarizes the main PCDDs/PCDFs generating activities.

Table no 1. Summary of PCDDs/PCDFs generation results for 2018.

Source groups		Annual release (g TEQ/y)				
		Air	Water	Soil	Product	Residue
1	Waste incineration	1	-	-	-	4
2	Ferrous and Non-Ferrous Metals Production	7	0	-	-	20
3	Energy and Heat Generation	1	-	-	-	0
4	Production of Mineral Products	6	-	-	0	0
5	Transport	2	-	-	-	-
6	Open burning processes	147	-	48	-	-
7	Production of Chemicals and Consumer Goods	0	0	-	-	0
8	Miscellaneous	0	-	-	-	0
9	Disposal / Landfill	-	10	-	-	61
1-9	Total	164	10	48	0	85

The most important results for PCDD and PCDF emissions in Ecuador for 2018, using the Toolkit methodology, with the activity rates of the UPOPs generating sources, are shown in Figure 1.

Fig.1. Contribution by sector to PCDD and PCDF emissions in 2018



Industrial UPOPs Inventory

In 2018, emissions of industrial UPOPs in Ecuador were estimated at 11,637 g TEQ/y of HCB; 2,934 g TEQ/y of PeCB; 1,256 g TEQ/y of PCN and 16 g TEQ/y of PCBs, for a total of 15,846 g TEQ/y. Four groups of origin generated 100% of these emissions: Group 4. Production of mineral products (63%), Group 2. Production of ferrous and non-ferrous metals (24%), Group 6. Open burning processes (8%) and Group 5. Transportation

(4%). 73% of Industrial UPOPs emissions were HCB, 19% PeCB, 8% PCN and only 0.1% PCB. Table 2 presents the results of these emissions by source group and type of Industrial UPOPs.

Table no 2. Results summary of the generation of industrial UPOPs for 2018.

Source groups	Industrial UPOPs Emissions g TEQ/y					UPOPs%
	PCB	HCB	PeCB	PCN	UPOPs	
Waste incineration	0	14	51	24	90	1
Ferrous and Non-Ferrous Metals Production	0	2,371	1,413	0	3,785	24
Energy and Heat Generation	0	11	4	0	16	0
Production of Mineral Products	0	7,345	1,466	1,232	10,043	63
Transport	0	669	0	0	669	4
Open burning processes	16	1,211	0	0	1,227	8
Production of Chemicals and Consumer Goods	0	16	0	0	16	0
Miscellaneous	0	0	0	0	0	0
Disposal / Landfill	0	0	0	0	0	0
Total types of UPOPs	16	11,638	2,934	1,257	15,846	100
Totals by release pathway %	0.1	73	19	8		

Laboratory Sample Results

For the analysis of UPOPs, a total of 23 samples were taken (21 for PCDDs and PCDFs and 2 for PeCB) with their respective blanks: water, leachates, air and soil. Samples were taken at the seven prioritized sites. Table 3 below shows the results of the laboratory analyses ordered by company/site, matrix and data reported.

Table no 3. Laboratory analysis results

Sector and site	**Matrix**	**∑PCDD/PCDF pg/L**	**∑PCDD/PCDF pg TEQ/L**
Botanical reserve	water	n. d.	n. a.
Botanical reserve	soil	3.00	0.50
Botanical reserve	soil	2.00	0.50
Landfill	leachate	43.00	6.00
Landfill	leachate	38.50	7.00
Dump	leachate	1.63	24.00
Dump	leachate	1.39	12.00
Dump	leachate	928.00	10.00
Sugar mill	soil	29.00	0.70
Sugar mill	soil	4.00	0.50
Sugar mill	water	n. d.	n. a.
Steel plant	air in chimney	3.17	81.00
Steel plant	air in chimney	5.23	128.00
Steel plant	air in chimney	3.03	61.00
Electroplating plant	indoor air	11.60	141.00
Hazardous waste incineration plant	air in chimney	15.10	220.00
Hazardous waste incineration plant	air in chimney	22.30	508.00
Hazardous waste incineration plant	air in chimney	10.80	272.00
Cement plant	air in chimney	-	12.90
Cement plant	air in chimney	-	11.90
Cement plant	air in chimney	-	11.8

n. d.: Not detected

n. a.: Not applicable

IV. Discussion

Two samples were taken for PeCB analysis, one from the landfill leachate and the other from the soil of the sugar mill plantation. No concentrations were detected in any of these samples.

From the laboratory results, it can be stated that the steel and electroplating plant, as well as the hazardous waste incinerator report the highest amount of PCDDs/PCDFs pg TEQ/L; however, these results are not determinant, since they correspond to specific point values and, furthermore, it is important to take into account the particular conditions of the sampling sites in order to be considered as a source of generation and release of UPOPs. On the other hand, higher concentrations of UPOPs can be found in the sedimentation sludge from waste disposal sites.

For the geobotanical reserve and the sugar mill, the results of the soil samples show that UPOPs are unlikely to be deposited at the site where the fire or agricultural burning occurred, which is why, considering that the UPOPs generated are released and transported in the air over long distances, a sampling of emissions to the atmosphere would be more interesting to have information on this source.

V. Conclusion

The 2018 inventory was developed using the 2013 Standardized Toolkit methodology for the identification and quantification of releases of dioxins, furans and other unintentional POPs. The analysis of the results focused on the following variables: emissions of UPOPs by type, group, category, activity, release of UPOPs by type of matrix, activity rates and emission factors, considering the information available at the country level.

With the results of the 2018 inventory, it was possible to identify that the main sectors that contribute PCDDs and PCDFs are the processes of open burning, disposal and landfills. According to the results derived from the use of the Toolkit, open burning processes contributed the highest amount of PCDDs and PCDFs (about 147 g TEQ/y to air and 48 g TEQ/y to soil).

The results of the laboratory analyses suggest that the hazardous waste management sector (incineration plant) is an important point of interest, as it contributes the highest amount of pg TEQ of PCDDs and PCDFs (average of 333.33 in the 3 samples). A second sector of interest is the steel foundry, where 90 g TEQ of PCDDs and PCDFs were detected.

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