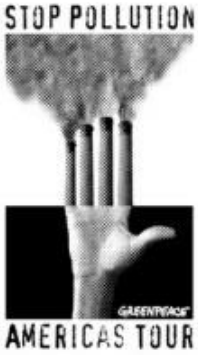

REPORT

Identification of organic pollutants and heavy metal contaminants in samples collected from the Petacol hazardous waste incinerator, Zarate, Argentina 2000

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December 2000

Technical Note: 19/00

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1 INTRODUCTION

The Petacol incinerator is located in an industrial estate in Zarate, Argentina. This incinerator is licensed to incinerate hazardous chemical wastes. The categories of wastes permitted to be incinerated at this facility are not known.

Ashes from the incinerator are stored in barrels within the Petacol incinerator grounds. Many of these barrels are rusting and in a poor condition.

2 SAMPLING PROGRAM

In May 2000, Greenpeace visited the Petacol incinerator facility and collected two samples of incinerator ash from storage barrels, and one sample of wastewater from a settling lagoon within the incinerator plant.

2.1 General Sampling Procedures

All samples were collected and stored in pre-cleaned glass bottles that had been rinsed with nitric acid and analytical grade pentane in order to remove all heavy metals and organic residues. Ash samples were collected in 100ml bottles, and the water sample was collected in a 1-litre bottle. All samples were immediately sealed and cooled upon collection. The samples were returned to the Greenpeace Research Laboratories for analysis. In addition, quantitative dioxin/furan analyses were conducted on a single ash sample (AM0007) by EUS Laboratories, Southampton (UK), according to UKAS accreditation standards. Further details on the analytical methods employed can be provided on request.

2.2 Sample Descriptions

Sample Number	Sample Description	Sample Location
AM0006	Wastewater	From one of two settling lagoons within the complex
AM0007	Ash	From a barrel within the complex [Labelled; Cenzas (ash)-TBA-Atanor]
AM0008	Ash	From a barrel within the complex [Labelled; Cenzas (ash)]

Table 1. Description of samples collected from the Petacol incinerator in an industrial complex, Zarate, Argentina 2000.

Descriptions of the samples are presented in Table 1. The two samples of ash were collected from two different barrels located within the incinerator plant. The barrels used to store the incinerator ashes were sealed with plastic lids. The ashes contained in the barrels are believed to be bottom ash or a mixture of bottom and fly ashes.

3 RESULTS AND DISCUSSION

Sample number	AM0006	AM0007	AM0008
Description	Wastewater	Incinerator ash	Incinerator ash
Location	Settling lagoon	Storage barrel within the plant	Storage barrel within the plant
Metals	ug/l	mg/kg (dw)	mg/kg (dw)
Cadmium (Cd)	38	<2	9
Chromium (Cr)	<20	371	158
Cobalt (Co)	<20	21	33
Copper (Cu)	327	2101	2827
Lead (Pb)	444	707	1418
Manganese (Mn)	<10	562	1628
Mercury (Hg)	8.6	0.36	1.71
Nickel (Ni)	<20	103	135
Zinc (Zn)	1222	2618	3242
No. of organic compounds isolated	4	23	102
No. of organic compounds reliably identified	0(0%)	10(43%)	20(20%)
ORGANOHALOGEN COMPOUNDS			
Benzene, 1,2-dichloro-		*	
Benzene, 1,3-dichloro-		*	
Benzene, 1,4-dichloro-		*	
Benzene, 1,2,3-trichloro-		*	
Benzene, 1,2,4-trichloro-		*	
Benzene, 1,2,3,5-tetrachloro-		*	
Benzene, 1,2,4,5-tetrachloro-		*	
Benzene, 1,2,3,4-tetrachloro-		*	
Benzene, pentachloro-		*	
Benzene, hexachloro-		*	
POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)			
Naphthalene and/or derivatives			✓(4)
Anthracene and/or derivatives			✓(3)
Phenanthrene and/or derivatives			✓(2)
Pyrene and/or derivatives			✓(3)
Triphenylene and/or derivatives			✓
OTHER AROMATIC COMPOUNDS			
Terphenyl and/or derivatives			✓
ORGANOSULPHUR COMPOUNDS			
Dibenzothiophene, 3-methyl-			✓
ALIPHATIC HYDROCARBONS			
Linear			✓(5)

*Table 2. Organic chemicals and heavy metals identified in samples from the Petacol incinerator, in an industrial complex, Zarate, Argentina 2000. For the groups of organic compounds reliably identified; ✓(#) signifies compounds identified using general GC/MS screening method, with the number of compound given in parentheses for groups with more than one compound; * signifies compounds identified only at trace levels using a selective ion monitoring (SIM) method. Metal concentrations are given in mg/kg dry weight for solid samples and ug/l for the liquid sample.*

The results of the organic screen analysis and heavy metals analysis are presented in Table 2, including a breakdown of the groups of organic compounds reliably identified in the samples.

3.1.1 Incinerator ashes

The two incinerator ash samples (AM0007 and AM0008) contained a number of toxic and potentially toxic heavy metals. The concentrations of these metals, other than chromium, were higher in sample AM0008 than in AM0007. The concentrations of copper, lead and zinc in both incinerator ashes are significantly elevated above background levels in the environment (see Table 3).

Heavy metals are not destroyed by incineration but are simply concentrated in the remaining ashes, or released to the environment via stack emissions. The concentrations of heavy metals in the ashes are highly dependent on the amounts of these metals in the wastes being incinerated.

Heavy metals can remain in their original form during incineration or may react to form new compounds such as metal oxides, chlorides or fluorides (Dempsey & Oppelt 1993). These changes are dependent on the composition of the wastes to be incinerated, and the forms that the metals are in. However, for the incineration of municipal wastes, the process of incineration has been shown to greatly enhance the mobility and bioavailability of toxic metals compared with the raw wastes (Schumacher *et al.* 1998).

Metal	Background concentrations in soil (mg/kg)	Factor by which sample AM007 exceeds the highest background concentration	Factor by which sample AM007 exceeds the highest background concentration	Reference
Cadmium (Cd)	0.01-2.0	<1	4.5	USPHS 1997, Alloway 1990
Chromium (Cr)	<1-100	3.7	1.6	Alloway 1990
Cobalt (Co)	1-40	0.5	0.8	Alloway 1990
Copper (Cu)	20 –30	70.0	94.2	Alloway 1990
Lead (Pb)	10-30	23.6	47.3	Alloway 1990
Manganese (Mn)	80-7000	0.1	0.2	Alloway 1990
Mercury (Hg)	0.02-0.625	0.6	2.7	Alloway 1990, WHO 1989
Nickel (Ni)	5-500 (50 average)	0.2 (2.1 average)	0.3 (2.7 average)	USPHS 1997
Zinc (Zn)	10-300 (50 average)	8.7 (52.4 average)	10.8 (64.8 average)	Alloway 1990

Table 3. Typical background concentrations of metals found in soil, and the elevation above these levels in the ash samples AM0007 and AM0008.

Heavy metals exert a broad range of toxic effects on humans, terrestrial and aquatic life and plants. A number of these metals also have the potential to bioaccumulate, including cadmium, chromium, lead, mercury and zinc (USPHS 1997, Kimbrough *et al.* 1999, MINDEC 1995). In addition, certain forms of cadmium and chromium have carcinogenic properties (USPHS 1998).

The two ash samples also contained a range of organic compounds. For both samples, it was only possible to identify a fraction of these compounds, particularly for sample AM0008.

Of the organic compounds identified in sample AM0007, the only compounds that could be identified were a range of chlorobenzenes. All of these compounds were present only at very low levels. The presence of these compounds suggests that a range of chlorinated benzenes have been incinerated at the Petacol facility. It is possible, however, that some or all of these compounds are products of incomplete combustion of other chlorinated wastes (Blumenstock *et al.* 2000).

The presence of these compounds may be indicative of elevated levels of dioxins and furans (PCDD/Fs) in this ash sample (AM0007). A subsequent quantitative dioxin/furan analyses at an independent laboratory confirmed the presence of 0.59 ng/g ITEQ (parts per billion) PCDD/Fs. Little research has been published concerning the dioxin content of hazardous waste incinerator ashes. Far more data have been published for ashes derived from municipal solid waste (MSW) incinerators. Bottom ashes and slags tend to contain lower concentrations of PCDD/Fs than fly ashes. Concentrations in bottom ashes are often in the part per trillion (ppt) range whereas in fly ashes they may range from parts per trillion (ppt) to parts per billion (ppb) (EEA 2000). For example, research on eight MSW incinerators in Spain found mean levels in fly ash between 0.07 and 3.5 ng I-TEQ/g (ppb) (Fabrellas *et al.* 1999). Another study on a MSW incinerator in Spain reported levels in fly ash from two analyses of 0.37 and 0.65 ng I-TEQ/g (ppb) (Abad *et al.* 2000). Particularly high levels were reported for one Spanish incinerator in 1997 (41 ppb TEQ) although levels recorded for the same installation in 1999 were lower (Stieglitz *et al.* 1999). At 0.59 ng/g TEQ, therefore, dioxin levels in the ash from the Petacol incinerator are not among the highest recorded, but nevertheless fall within the broad range reported for ashes from municipal incinerators. It is not possible to ascertain from the ash data alone whether the dioxins detected in the ash were unburned contaminants of the original waste feed, or whether they were formed during the incineration process.

Of the compounds identified in sample AM0008, the most were hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and alkyl benzenes. PAHs are commonly found as product of incomplete combustion of organic substances (Jones 1991, Overton 1994). Hydrocarbons, PAHs and alkyl benzenes are also components of crude oils or petroleum products, and are therefore very widespread environmental pollutants (Mackay 1988, Wang & Fingas 1995).

3.1.2 Wastewater

The sample of wastewater (AM0006) from the settling pool contained a number of heavy metals at concentration above typical freshwater background concentrations, including cadmium, copper, lead, mercury and zinc.

In the aquatic environment, these metals tends to bind to suspended material before finally accumulating in the bottom sediments (USPHS 1997, Bryan and Langston 1992). The high levels of these metals in the water, especially mercury and lead, indicate ongoing significant inputs of these metals to this settling pool. The discharge of wastewater from the incinerator scrubber to this pool could account for these high levels.

Only four organic compounds were isolated from this wastewater sample, though it was not possible to identify any of these.

3.1.3 Emissions to Air

The analysis of the samples from the Petacol incinerator shows the levels of pollutants in ashes formed as a result of the incineration of wastes at this facility. In addition to these ash outputs, a range of pollutants will also be released to air via the incinerator chimneys. It is highly likely that these will include particulates, heavy metals, and organic compounds including PAHs (EC 1998, Yasuda and Takahashi 1998, Magagni *et al*. 1991).

Certain metals, including cadmium, lead and mercury, are emitted from incinerator stacks in flue gases and as tiny particles (EEA 2000). The European Environment Agency (EEA 2000) notes that the separation of mercury is a special problem in incineration. Almost 100% of elemental mercury present in waste is emitted to stack gases because it does not bind well to filter dust or ashes. Elemental mercury constitutes about 20-50% of the total mercury emissions. The remainder is in the form of divalent mercury, which may be predominantly mercury chloride ($HgCl_2$). After emission to the atmosphere, divalent mercury, which is water soluble, may be deposited close to the incinerator. On the other hand, elemental mercury may be transported for long distances on air currents before it is eventually converted to the divalent form and then deposited on the ground (Carpi 1997).

The quantity of PAHs emitted is determined by waste composition, temperature and excess air during incineration. High emissions of PAHs have been shown to occur during start-up of incinerators (see Yasuda & Takahashi et *al*. 1998).

Analysis of sample AM0007 confirmed the presence of dioxins in ashes from the Petacol incinerator. Dioxins are inevitably synthesised during the incineration process. A proportion of the dioxins present in the waste incinerated may also pass through the incinerator unburned. As a consequence, the incinerator may be the source of dioxin contamination via the emitted flue gases and also through ny scrubber effluents or ashes that are released to the environment.

4 CONCLUSIONS

The ashes produced at the Petacol incinerator facility contain a wide range of toxic pollutants, including concentrated levels of a number of heavy metals. Analysis of sample AM0007 confirmed the presence of dioxins in ashes from the incinerator.

In addition to the detrimental effect placed on the environment by the release of incinerator ashes, it is highly likely that a wide range of pollutants are also being released to the environment via emissions to air from this facility.

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