DIOXINS IN WASTE FROM CHLOR-ALKALI PLANT: A CASE STUDY

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Introduction

Many chlor-alkali plants used or still use mercury for chlorine and caustic soda production. The Minamata Convention requires a phase out of the use of mercury in chlor-alkali plants by 2025[1]. Although the mercury cell process is being phased out, as of 2019 there were at least 12 plants still using the process in six countries [2].

Elemental chlorine is produced in chlor-alkali plants by the same processes which unintentionally form and release hexachlorobenzene (HCB), pentachlorobenzene (PeCB), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). The chlor-alkali process is listed among Part III, Annex C sources of unintentionally formed persistent organic pollutants (POPs) under the Stockholm Convention[3]. Among these, PCDD/Fs have never been used as commercial products, nor were intentionally manufactured for any reason other than laboratory purposes. PCBs, HCB and PeCB are also unintentionally formed, usually from the same sources that produce PCDD/Fs. However, unlike PCDD/Fs, they have also been manufactured and used for specific purposes. HCB and PeCB were produced for sale or use and/or transferred in wastes (so called hexa-residues) from subsequently discontinued production of pesticides at the Spolana chlor-alkali plant[4,5].

It was well established that significant releases of PCDD/Fs occurred in the Leblanc and graphite electrolysis processes during chlorine production[6-10]. High concentrations of PCDD/Fs were measured in residues and/or contaminated soils at the facilities using these processes. Less information is available about PCDD/Fs and other unintentional POPs concentrations in waste produced by more recent amalgam electrolysis chlor-alkali plants and/or the levels of PCDD/Fs in residues after production ends. However, this information can be important for decision-makers planning the phase-out of chlorine production which uses mercury. In addition to assessing mercury contamination, it is also important to determine the extent of HCB, PeCB and PCBs contamination when elevated PCDD/F concentrations are found in residues. Remediation should be adjusted according to the identified chemicals to prevent further spread of POPs pollution.

Spolana, one of two chlor-alkali plants in the Czech Republic, measured PCDD/Fs, PeCB, HCB and PCBs levels in several different wastes from amalgam electrolysis. This data became available in annual reports for Spolana's compliance with its permit under the International Plant Protection Convention (IPPC) permit compliance. The objective of this study is to bring further information about the occurrence of PCDD/Fs and other POPs in waste produced by amalgam electrolysis units in chlor-alkali plants so that any further spread into the environment of these POPs during dismantling of these units in closed and/or abandoned chlorine production plants.

Materials and methods

Protocols provided by the Spolana chlor-alkali plant to the public authorities and Arnika were followed for the analysis of several waste groups from an amalgam electrolysis unit in chlor-alkali plant based in the Czech Republic. PCDD/Fs analyses were conducted using EPA Method 1613B for PCBs by using modified method EPA 1668 with high resolution GC-MS. HCB and PeCB were analyzed by using EPA Method 8081 for the analysis of organochlorine pesticides (OCPs) and halogenated compounds with GC-ECD. Toxic Equivalency Factors (TEFs) established by the WHO expert group in 2005 were used for calculation of WHO-Toxic Equivalency (TEQ) levels of PCDD/Fs and dioxin-like PCBs (dl PCBs)[11].

Information from literature and previous reports about production of waste and its description[12] was used as an additional source about the annual volume of waste classes and the production capacity of the chlor-alkali plant.

Persistent Organic Pollutants (POPs) concentrations were available for four basic waste groups classified under four waste classification codes as they are defined in the European waste catalog[13]. These waste groups are: 060404 Waste containing mercury; 061302 Spent activated carbon (except 060702); 160709 Waste containing dangerous substances; and 190211 Other wastes containing dangerous substances. In most cases both brine and floor sweepings from the electrolysis hall were in waste group 060404. Spent activated carbon from the roasting process of used brine was in waste group code 061302. In 2007, sludge was in waste group 160709, and brine roasting residues were in waste group 190211.

History of the Spolana chlor-alkali plant

Electrolysis: The Spolana chlor-alkali plant used graphite electrolysis from 1950 – 1975[12,14]. That unit was abandoned and buried under a sarcophagus-like edifice in 2012 - 2013. Chlorine production was switched to the new amalgam electrolysis process in 1970s. In 2017, Hg use was phased out, but remediation continued until 2020, generating waste similar to that from its operation but arising from deposits in the demolished unit and the

demolition process. Roasting of part of the wastes was used for mercury recovery to supplement mercury inputs into the chlor-alkali production. After the discovery that this process leads to unintentional production of PCDD/Fs, it was shut down by the end of 2013, according to the IPPC permit renewal[15]. The chlor-alkali plant in Spolana had a production capacity of 135,000 elemental chlorine units (ECU) per year in 2013[15].

Production at Spolana was gradually broadened in 1950-ies to produce chlorine and sodium hydroxide, and other facilities were built for the production of bone glue, fat, cellophane, and HCl[14]. Final products of the plant changed throughout time. It produced organochlorine pesticides, including technical HCH and lindane between 1961-72[4,16]. Between 1965-68 it produced the herbicide 2,4,5-T and chlorinated phenols. A part of the 2,4,5-T production was even exported to the USA and was applied as a component of "Agent Orange" in Vietnam. During the production of these chemicals, a huge amount of PCDD/Fs (in particular, the most toxic 2,3,7,8-TCDD) was formed and former factory buildings containing products, intermediates, etc. belonged to the most PCDD/F-contaminated sites on the globe[5]. Major production at the facility is now focused on PVC and caprolactam which are also known sources of PCDD/F contamination[17-20].

Base-catalysed decomposition (BCD) in combination with an indirect thermal desorption unit (ITU) were used to clean up abandoned buildings used for pesticides production in Spolana. The remediation process consisted of the decontamination and demolition of three buildings, excavation and treatment of surrounding soils of these buildings, and treatment of chemicals stored closed to the main building. BCD technology has been in operation at the Spolana site for several years. Performance of the technology was evaluated by expert groups which found that the residual amounts of PCDD/Fs in the output oil were less than 0.016 ng TEQ g^{-1} and HCB <0.2 μg g^{-1}. Levels of POPs in the process off-gas were as follows: PCDD/Fs, between 0.013 and 0.031 ng TEQ $m^{-3}N$; PCBs, between 0.0014 and 0.005ng TEQ $m^{-3}N$; HCB, between <6.7 and 187 ng $m^{-3}N$; and total organochlorine pesticides, between 17 and 235 μg $m^{-3}N$[21-22].

Results and discussion

Analytical results for each of the waste groups were obtained in the years 2007 – 2009, and 2014 – 2020.

As shown in Table 1, the same number of measurements is not available for each waste group because the company stores the wastes and takes samples for analysis when they are transported for disposal. As a consequence, analytical results appear in the reports occasionally rather than annually. Used activated carbon was measured in 2009 and then again after the roasting process was shut down, in 2014 and 2016. Results for PCDD/Fs, dl PCBs, and HCB and PeCB are summarized in Table 1. PeCB was measured in two samples of waste only during demolition of the amalgam electrolysis unit. Sludge, waste group 160709 and waste containing mercury, waste group 060404, contained 424 and 866 ng g^{-1} dw of PeCB respectively.

Table 1. Levels of PCDD/Fs, dl PCBs, and HCB in wastes from amalgam electrolysis in chlor-alkali plant during the period of 2007 – 2020.

Waste Code	060404	060404 (swee-pings)	061302 (used activ. carbon from roasting)	061302 (used activ. carbon)	160709 (sludge)	190211 (roast. residue)
	Wastes generated during operation of amalgam electrolysis unit					
PCDD/Fs (ng WHO-TEQ g^{-1} dw)	0.16 – 9.8	NA	13.35	ND-0.05	0.00005- 11.6	0.11
Number of samples analyzed, (2008) 2009 and 2014-2017	5	0	1	2	3	1
Year of analysis	All	-	2008	2014 & 2016	2009,2016,2017	2009
	Wastes from demolition of amalgam electrolysis unit					
PCDD/Fs (ng WHO-TEQ g^{-1} dw)	1.1 – 4.1	11.45	NA	<LOQ	4.7-6.3	NA
Number of samples analyzed 2018-2020	2	1	0	1	2	0
Year of analysis	2019,2020	2018	-	2018	2018 & 2019	-
	Wastes generated during operation of amalgam electrolysis unit					
dl PCBs (ng WHO-TEQ g^{-1} dw)	0.03 - 0.42	NA	0.56	<LOQ	0.13-0.19	NA
Number of samples, 2014-2017	5	0	1	2	2	1
Year of analysis	2014-2017	-	2008	2014 & 2016	2016 & 2017	2007
	Waste from demolition of amalgam electrolysis unit					
dl PCBs (ng WHO-TEQ g^{-1} dw)	0.13 - 0.24	0.43	NA	<LOQ	NA	NA
Number of samples analyzed, 2018-2020	2	1	0	1	0	0
Year of analysis	2019,2020	2018	-	2018	-	-

	Wastes generated during operation of amalgam electrolysis unit					
HCB (in ng g^{-1} dw)	<5 - 3,490	NA	5,800	<5	837 - 2,240	<10
Number of samples, 2008-2017	4	0	1	2	3	1
Year of analysis	2014-2017	-	2008	2014 & 2016	2009,2016,2017	2007
	Waste from demolition of amalgam electrolysis unit					
HCB (in ng g^{-1} dw)	13,000 - 18,800	<5	NA	NA	61 - 1,670	NA
Number of samples analyzed, 2018-2020	2	1	0	0	2	0
Year of analysis	2019,2020	2018	-	-	2018 & 2019	-

The highest concentration of PCDD/Fs was measured in used activated carbon (061302) from the roasting process when it was in operation, i.e. until the end of 2013. This can be easily explained by the fact that there was a process of further thermal treatment of waste, comparable to the process defined in the literature as direct thermal desorption. At the request of Arnika, this technology was closed by a decision of the authorities[15]. It is possible that other amalgam electrolysis plants around the world are running a similar technology because chemical companies are trying to recover mercury from waste and are unaware of the side effect of PCDD/F formation in the process. Roasting of mercury-containing waste in chlor-alkali plants should be considered a significant source of PCDD/Fs. The used activated carbon had the PCDD/Fs content of 13.35 ppb, very close to the limit for Low POPs Content Level (LPCL)[a], i.e., 15 ppb as applied in the EU, and close to the PCDD/F concentrations from graphite electrodes found in Sweden (see Table 2).
Other wastes from the amalgam electrolysis plant also contained relatively high concentrations of PCDD/Fs in the range of 1 to 11.6 ng WHO-TEQ g^{-1}, corresponding for example to concentrations in fly ash from waste incinerators or from metallurgical plants. However, they are lower compared to PCDD/F concentrations in sludge from chlor-alkali production using graphite electrodes (see Table 2). PCDD/F congener pattern in the analyzed wastes is at Figure 1. It is different in roasted brine residues (190211) from other three classes of waste.

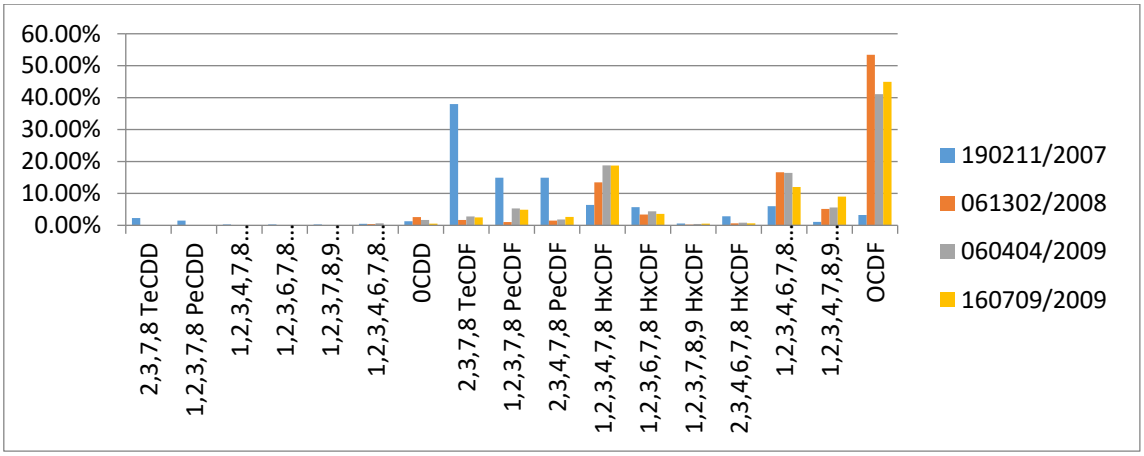

Figure 1. PCDD/F congeners pattern in wastes from amalgam electrolysis of chlor-alkali plant in the Czech Republic. Absolute levels of congeners from the chemical analyses results were used in this graph.

Table 2. PCDD/PCDF concentrations in sludge from chlor-alkali production using graphite electrodes

	Germany[24]	Sweden[9]	China[10]
PCDD/Fs in sludge	Up to 3,985 ng I-TEQ g^{-1}	13 – 28 ng N-TEQ g^{-1}	21.65 ng I-TEQ g^{-1}

There were high levels of PCDD/Fs and HCB in wastes from demolished amalgam electrolysis, produced in 2018 – 2020 (see Table 1).
We estimated the total amount of PCDD/Fs per year leaving the amalgam electrolysis process in Spolana during its former operation. From older studies and documentation submitted in the IPPC permit compliance reports, we obtained data on the total amount of waste in individual categories transferred from the operation for processing elsewhere. The overview compiled from the data for the years 2004 - 2008 is summarized in Table 3.

[a] LPCL is the level of POP content that defines the POPs containing wastes for which mesures in Article 6 of the Stockholm Convention apply[3]. These levels are defined for each POP in General Technical Guidelines for POPs wastes updated regularly by Basel Convention [23].

Table 3. Monitored groups of wastes annual production and range of the PCDD/Fs transferred per annum

	060404 (Hg waste)	061302 (used activ. carbon)	160709 (sludge)	190211 (roasting residues)
Years 2004 - 2008	35 t/a	2 - 8 t/a	28 - 47 t/a	6 - 13 t/a
Range of PCDD/Fs in waste (mg TEQ/a)	118	27 – 107	155 - 261	0.66 – 1.43

Based on information on PCDD/F concentrations in individual waste groups (see Table 1) and data on their amount transmitted per year, we estimated the total amount of PCDD/Fs transported in wastes during 2004-2008 to range from 301 to 487 mg WHO-TEQ / year. The Dioxin Toolkit lists emission factors in waste (residues) from chlor-alkali plants in terms of elemental chlorine units (ECU). The EF for waste for electrolysis in Spolana in 2004-2008 would be approximately between 2.2 and 3.6 µg WHO-TEQ / ECU. It is slightly more than estimated by the Dioxin Toolkit for Class 2b, 1.7 µg TEQ / ECU. For metal electrodes, Dyke and Amendola[25] reported transfers to secure landfill that ranged from 0.2 to 18 µg TEQ / ECU capacity (Median = 1.1 µg I - TEQ / ECU capacity) based on data gathered in 2000 and 2002.

Use of decontamination technology

The BCD technology used in Spolana for remediation of PCDD/F-contaminated sites has also dealt with other POPs, including HCB, which is another important POP contained in chlor-alkali waste. BCD had to deal with tens of thousands of tonnes of treated material and it would cope with a few tens of tons of extra waste from the chlor-alkali plant. This opportunity was not used because there was no legal obligation to clean up the waste presented in this study because the LPCL for PCDD/Fs (15 ppb) has been set too high.

Conclusions

The documented flow of PCDD/Fs in wastes from a chlor-alkali plant in the Czech Republic using mercury demonstrates the need to tighten the limits for the definition of POPs wastes in the EU and to lower the LPCL for PCDD/Fs. Half a gram of PCDD/Fs, expressed in the WHO-TEQ, transferred annually in tens of tonnes of waste from the chlorine chemical factory demonstrates the need to lower the level for the definition of POPs waste (LPCL) in order to avoid the creation of new sites contaminated with POPs..

Acknowledgements

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