

## DIOXIN AND DIOXIN-LIKE COMPOUNDS IN CHEMICAL LANDFILLS OF THE BASEL CHEMICAL INDUSTRY

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### Introduction

The contemporary scientific discussion regarding PCDD/PCDF sources focuses mainly on thermal emissions (e.g. waste incineration, sinter plants, secondary metal production), however, the history of contamination with dioxins and dioxin-like chemicals is closely related to the chlorine industry and the production of chlorine and chlorinated organics, including chlorinated pesticides.<sup>1-3</sup> In Switzerland, similar to elsewhere, the importance of the chlorine industry increased during the end of World War II and reached its' peak during the 1970s. The waste produced, for example during the production and utilization of chlorobenzenes and chlorophenols, were predominantly dumped by chemical companies such as Roche and predecessors of Novartis, Syngenta, Ciba and Clariant during the end of the 1940s to the mid 1970s. Even today a minimum of 35000 tonnes chemical waste is present in filled up gravel pits, small valleys and tracks in the region of Basel<sup>4</sup>. This chemical waste was often dumped in the 1950s without authorisation, and already at that time contaminated groundwater, streams and wells, representing a hazard for drinking water. Therefore, the chemical industry had to locate other areas where no prior experiences with chemical waste was made, and deposited 114000 tonnes in an old clay quarry of the community Bonfol (Kanton Jura), near the border to France, during 1961-1976.<sup>5,6</sup> Similar to the dumps of the region Basel, the toxic landfill in Bonfol (DBI) endangered drinking water and contaminates and presently continues to contaminate groundwater<sup>7</sup>. Therefore, the Basel Chemical Industry (BCI) was forced to fully remediate the landfill in Bonfol, i.e. to remove and incinerate the chemical waste. A remediation proposal was submitted to the relevant authorities in December 2003 by Novartis, Roche, Ciba, Syngenta and Clariant. This proposal contained key flaws, such as the non-adherence to Swiss laws regarding Workers Health and Safety and atmospheric pollution regulations<sup>8</sup>. In addition, the proposal asserted that dioxins, furans and PCBs would not be relevant for the remediation activities: „the concentrations [in the leaching water] of polychlorinated biphenyls (PCB) [...] are in the low ppb range, those of dioxins below 1 ng/l. Due to these low concentrations, these compounds are of little relevance for the assessment of emissions from the DBI [during the remediation work]“<sup>9</sup>. Those statements of the chemical industry were doubted by both the supervisory authority Swiss Kanton Jura<sup>10</sup> and by Greenpeace Switzerland. Hence, Greenpeace Switzerland commissioned a historical investigation of the chemical landfill Bonfol, both qualitatively and, as much as possible, quantitatively. The results from this investigation are summarised in this paper.

### Materials and Methods

Novartis, Ciba and Clariant chose not to collaborate to answer the question which compounds containing, and potentially containing dioxins were produced by the Basel chemical industry during the 1950s and 1970s<sup>11</sup>. In order to still obtain some overview on this question, I have utilised the listings of the German Environmental Agency (UBA) regarding dioxin-containing and potentially dioxin-containing substances from 1985<sup>12</sup> and supplemented these with additional literature relevant to substances containing dioxins, furans and PCBs. This list and data were compared and amended with information from:

- three lists of approximately 5000 substances, which were produced 1960, 1987 and 2003, respectively by the Basel chemical and pharmaceutical industry. These lists provided among other information on used educts and produced intermediates and products<sup>13</sup>.
- other non-published, internal documents from chemical companies containing for example production and synthesis methods, capacity calculations and company internal analysis reports
- newsletters and reports or other publications by company newsletters, newsletters from the chemical associations and further publications of and about the Basel chemical industry
- available analytical results from samples around the chemical waste disposal sites and 16 sites of the Basel chemical industry in Switzerland, France, Germany and the USA

Further, the lists and additional information were discussed with 21 chemists, chemical engineers and laboratory staff at Roche, Sandoz, Geigy, Ciba and Ciba-Geigy, or the predecessors of Novartis, Ciba SC, Syngenta and Clariant.

## Results and discussion

### *Dioxins, Furans and PCBs originating from production processes of the Basel chemical industry*

At least 38 of the substances produced and used during the 1950s to 70s within the chemical companies of Roche and the predecessors of Novartis, Syngenta, Ciba SC and Clariant contained or potentially contained dioxins, based on the dioxin list of the German Environmental Agency UBA<sup>12</sup>. These substances were used from the Basel chemical industry to produce several hundred products. For the processes used with four of these products, the dioxin and furan waste could be estimated for 1964-1975 (table 1): from production of trichlorophenol by Roche<sup>14</sup>, dioxazin pigments and paints<sup>15</sup>, Mitin LA as well as triclosan<sup>16</sup> by Geigy or Ciba-Geigy (compare Tab. 1).

Table 1: Order of magnitude estimates of the PCDD/PCDF wastes resulting during the production of four products by the Basel chemical industry during 1964-1975.

Production/usage of	Producing company	Period of time	Estimated PCDD/PCDF-amount (g)	Estimated 2,3,7,8-TCDD "Seveso-dioxin" (g)	Estimated TEQ-Int (g)
Trichlorophenol	Roche	End 1960s	Unclear	100	At least 100
Oxazin & Dioxazin: pigments and dyes	Ciba/Ciba-Geigy	1965-1975	Several 100'000		1000 to several 1000
Triclosan	Geigy/Ciba-Geigy	1966-1975	Several 10'000 to several 100'000	6-60	100 to 1000
Mitin LA	Ciba-Geigy	1974-1975	Unclear	10 to several 10	10 to several 10
Total			Several 100'000	110-200	1000 to several 1000

Further, according to a company intern substance list, at least 20 chlorophenol and at least 20 chlorobenzene containing substances were used during the 1950s to 70s by the Basel chemical industry<sup>17</sup>. Many of these were contaminated with dioxins, furans and PCBs. In addition, both of these substance groups are known to form dioxins and furans as well as PCBs during production processes. In particular during the relevant time period for the landfilling period in Bonfol (1961-1975), several thousand tons of products were produced from these chlorobenzenes and chlorophenols. The majority of dioxins and dioxin-like chemicals produced remained in the waste of these products, such as for example in the distillation residues from cleaning of chlorinated solvents. During 1961-1975, the quantity of PCDD/PCDF and PCB waste from such distillation residues would have been considerable, since approximately 1500-2000 tons of dichlorobenzene was used during this time according to previous workers at Geigy, Ciba and Ciba-Geigy. In addition, approximately 800-1000 tons trichlorobenzene were used for production processes by the same companies as well as Sandoz. The distillation residues resulting from the cleaning of these estimated 3000 tons of chlorinated solvents were dumped mainly in Bonfol. A more detailed quantitative assessment on the PCDD/F and PCB<sup>18</sup> wastes as a result of these processes could not be undertaken during this study.

### *Unintentionally formed PCBs – case example 2,6-dichloro-4-nitroaniline (DPNT)*

The production of 2,6-dichloro-4-nitroaniline (DPNT) by Sandoz highlights the production of large quantities of PCBs as unintentionally formed by-products during chemical processes. Approximately 100 kg PCB were produced as by-products during the production of 200 tons product in the year 1986<sup>19</sup>. It can, however, be assumed that in the case of DPNT production, the major proportion of PCB was emitted via waste water to the river Rhein, and from 1982 to sewage treatment plants. The example of DPNT production by Sandoz highlights, however, that only a few production processes are necessary to result in the emission of large quantities of unintentionally formed POPs (UPOPs) as by-products from chemical production.

### *Dioxins, furans and PCBs in the land fill Bonfol*

The majority of PCDD/PCDF and PCB impurities from educts and those formed during the production of trichlorophenol, triclosan, Mitin LA and Oxazin/Dioxazin pigments and paints ultimately ended up (via filtration and distillation of the chlorinated solvents) in the filtration and distillation residues. These solid wastes were dumped by the Basel chemical industry predominantly in the chemical landfill Bonfol during 1965-1975, since Bonfol was the only legal chemical waste-dumping site in Switzerland at that time operated by the Basel chemical industry.

Considering the PCDD/PCDF quantities resulting from the above 4 production processes, and considering that the Basel chemical industry in addition worked intensively with chlorinated solvents, it can be assumed that TEQ levels in the order of several tens of kilogram are to be expected in Bonfol. 2,3,7,8-TCDD would be present at levels of several 100 grams to kilograms, while the total quantity of PCDD/PCDFs and also PCBs may reach the magnitude of a ton.

### **Conclusions**

Despite the assertions of the Basel chemical industry in 2003 and 2005<sup>20</sup>, the qualitative and quantitative investigations of PCDD/PCDF and PCB waste resulting from relevant production processes indicate that large quantities of PCDD/PCDF and PCB waste had to be dumped at Bonfol. These toxins are not distributed homogeneous across the 114000 tons chemical waste present in the Bonfol landfill. On the contrary, since the major proportion of PCDD/PCDFs and PCB wastes remain bound to residues from e.g. distillation and filtration, the distribution would be expected to result in hotspots, i.e. concentrations which vary locally and reach relatively high levels. Hence, dioxins and dioxin-like compounds clearly belong to the chemical groups<sup>A</sup> which have to be considered carefully during a complete remediation with respect to emissions and industrial safety and workers protection. Previous experiences demonstrate that chemical waste sites are located in the vicinity of most chemical companies. The water-soluble compounds in such landfills often result in high contamination of groundwater. Containment solutions, which were often used for isolation of such wastes readily fail after 10-20 years as in the case of Bonfol. Considering the soluble compounds and their likelihood for contamination of groundwater, it is reasonable to remove and destroy these wastes, as is required in Switzerland<sup>21,22</sup>. From an economic point of view, complete remediation is often the most cost effective solution in the long-term.

During complete remediation, the less water-soluble compounds such as PCDDs/PCDFs and PCBs become relevant, since these substances can be emitted through removal of contaminated waste and/or additionally formed during thermal stress (e.g. fire or shredding activities) and are a health risk for staff operating the remediation. These risks and emissions are possible to avoid by careful planning and the implementation of appropriate technical measures. Avoiding such risks and emissions is a requirement for remediation of POPs waste under the POPs convention<sup>23</sup>.

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<sup>A</sup> Other substance classes relevant for the total remediation of Bonfol are for example aromatic compounds and polyaromatic compounds.

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