Comunicaciones

IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

Alicante, 26-28 Junio 2013

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OLD SINS THROW LONG SHADOWS: PCBs – 40 YEARS AFTER RESTRICTIONS IN SWITZERLAND – STILL AN ENVIRONMENTAL PROBLEM?

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Introduction

In 1972, more than 40 years ago, Switzerland banned the application of polychlorinated biphenyls(PCB) in open systems. Further use in closed systems like transformers and condensers was only possible under an exemption clause which was then repealed in 1983. Since 1986, production, import, and use of PCB are completely banned in Switzerland. Nevertheless, several hundred tons of PCB are still present from older applications such as joint sealants[1], anti-corrosion coatings, industrially contaminated locations and disposal sites. From these and other diffuse reservoirs PCB can enter the environment via atmospheric deposition, waste water, and runoff[2]. In urban areas PCB air concentrations are higher compared to background locations, showing that PCB are emitted in cities from long-lived applications to the atmosphere[3,4].Due to the ban of PCB and the continuous elimination of PCB containing electrical equipment as well as ongoing improvement of waste water treatment, incineration and recycling processes, PCB levels in the Swiss environment have continuously decreased[5-8]. Nevertheless, in 2007 analyses of fish from the river Saane revealed extraordinary high levels of dioxin-like PCB (dl-PCB). Several fish species from this river exceeded by far the maximum level of 8 pg WHO-TEQ/g fresh weight (fw) set by the European Union[9]. A maximum of 97 pg WHO-TEQ/g fw was observed in a single fish sample. The former disposal site of La Pila was identified as the responsible point source for the PCB contamination of the river. La Pila was used as a landfill for domestic and industrial waste from 1952 to 1975. The landfill coversroughly 2 hectares and has a volume of approximately 195'000 m^3. Wastes are heterogeneously distributed and can be found downto a depth of 20 meters. The amount of PCB was estimated to be more than 20 tons. Solid samples taken at several spots of the landfill revealed PCB levels of more than 1000 mg/kg[10]. Based on the above mentioned findings and due to increasing political pressure the Federal Office of the Environment (FOEN) initiated a nationwide survey to obtain an overview of the PCB contamination of Swiss rivers and lakes. Hitherto unknown diffuse and point sources should be detected and identified by the monitoring of fish, water, and sediment. This data shall serve as a basis for immediate actions to protect humans, wildlife and the environment from the exposure to PCB.

Materials and Methods

Samples: Fish and sediment samples were taken by the responsible cantonal authorities, and analyses were carried out by contract laboratories or by Empa. PCB and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) were determined in fish, water and sediment. For the identification of unknown PCB point sources in contaminated rivers a method based on the use of polydimethylsiloxane(PDMS) passive samplers was developed[11,12].

Methods: All available data on PCB and PCDD/F in fish and sediment from Swiss lakes and rivers were collected resulting in 1300 data sets from the last 20 years. The compilation was published by the Swiss Federal Office of the Environment[13].
PDMS passive samplers were exposed in the PCB contaminated rivers for two to four weeks and then transported to the laboratory for analysis. After spiking with $^{13}C_{12}$-labelled PCBs the passive samplers were solvent extracted with methanol for 24 hours. The extracts were concentrated and cleaned up using acid treatment and chromatography on activated silica gel. Quantitative determination of PCB was carried out usinggas chromatography high resolution mass spectrometry (GC/HRMS) at a mass resolution of 10'000.

Results and Discussion

On the basis of PCB levels in fish, the Swiss water bodies were classified into three categories. The first category was defined as water bodies with PCB background contamination corresponding to levels below 4 pg WHO-TEQ/g fw (50% of the maximum level of 8 pg WHO-TEQ/g fw). The second category containing water bodies with levels of 4 to 8 pg WHO-TEQ/g fw in fish was defined as water bodies with diffuse to higher PCB load. In these water bodies, older individuals or fat rich fish species already may exceed the maximum level of 8 pg WHO-TEQ/g fw. The third category was defined as water bodies with high PCB contamination. In water bodies of this category, most fish species clearly exceed the permitted maximum level. The highest PCB concentrations of up to 329pg WHO-TEQ/g fw were found in fish from the river Saane downstream of the above mentioned landfill of La Pila[14]. Similarly high PCB levels up to 60 pg WHO-TEQ/g fw were detected in various fish species from the rivers Birs and Rhine close to Basel[13]. While the responsible source for the PCB contamination of the river Saane was known, the former landfill site La Pila, it remained unknown in case of the PCB contaminated river Birs. Therefore, a screening program was initiated in 2010 aimed at the identification of possible PCB point sources in the catchment of the river Birs. Polydimethylsiloxane (PDMS) passive samplers[15] deployed at 15 locations for approximately four weeks proved an excellent tool to identify the PCB source. Fig. 1 shows dl-PCB and PCDD/F levels in fish from the river Birs in Northwestern Switzerland measured in 2008 and 2009 in single and pooled samples of various fish species. The maximum level of 8 pg WHO-TEQ/g fw was clearly exceeded by almost 50% of the samples, most of them taken downstream of the barrage of Choindez. The highest value measured was 56 pg WHO-TEQ/g fw. In Fig. 2 the results from the PDMS passive sampler campaign are shown. A very similar trend,as noted in fish,was observed for the passive samplers. Highest concentrations were found close to Choindez highlighting this site as possible origin of the PCB contamination. Further analyses conducted with a closer grid of passive samplers in the vicinity of Choindez confirmed the first findings. An old industrial site in Choindez, producing cast iron pipes, was suspected to be responsible for the higher PCB input into the river Birs. Detailedinvestigations ofthisindustrial area brought to light, that PCB contaminated iron was used for the production of new cast iron pipes. Water from the river Birs was used to cool down exhaust gases from the iron melting procedure.This cooling water was not sufficiently cleaned and discharged into the river Birs intermittently. Inthis way highly PCB contaminated water entered into the river and led to the contamination of fish and sediment.

Figure 1: Concentrations of dl-PCB and PCDD/F in fish from the river Birsandother nearby rivers. Manually introduced trend curve (blue), highlighting the steep increase after Choindez.

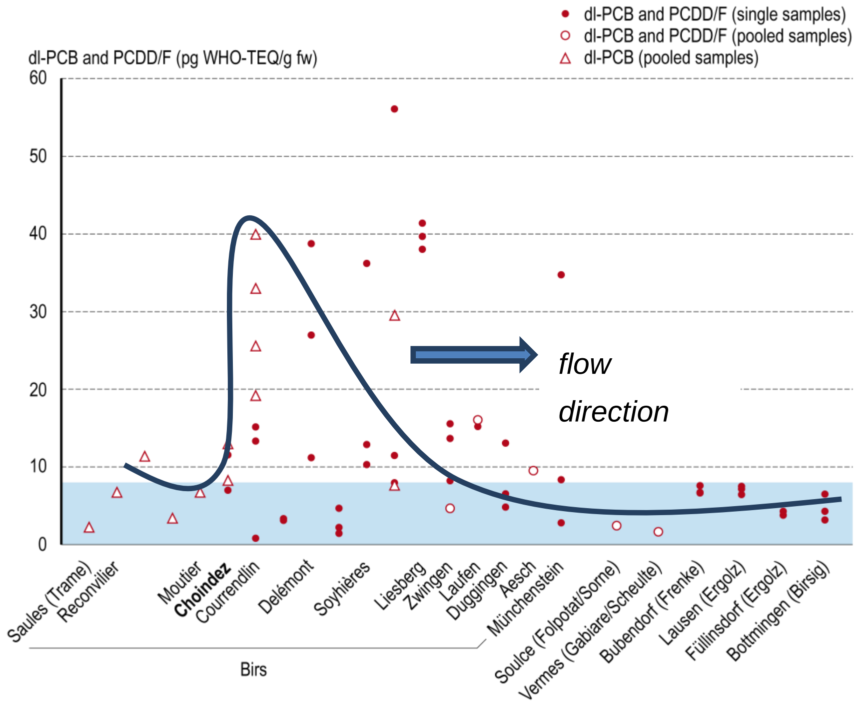
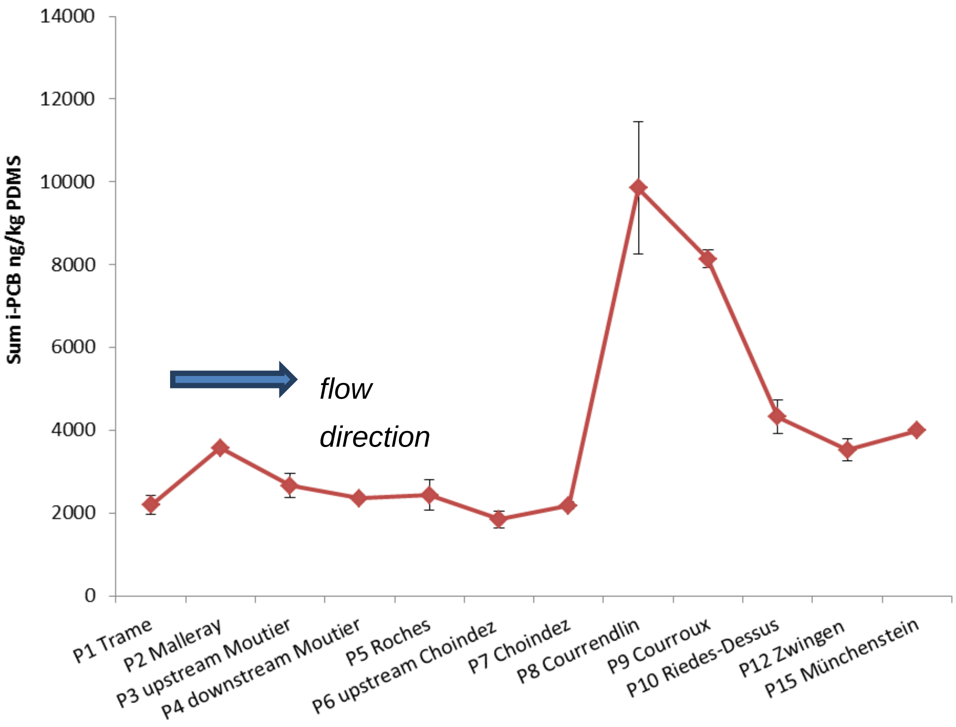


Figure 2: Sum of indicator PCB detected in the PDMS passive samplers exposed in the catchment area of the river Birs. Steep increase in PCB concentration after Choindez is visible.



Conclusions: Most of the Swiss water bodies can be categorized as background contaminated with PCB. However, there are still some PCB hot spots present in Switzerland. Two of them are the rivers Saane and Birs. In order to complete the overview on the PCB contamination of the Swiss aquatic environment, data gaps of several rivers and lakes should be closed in order to identify and eliminate activepoint sources. To this end, old landfills, former industrial production sites, and metal recycling plants (e.g. car and metal shredding) should be tracked. Special care has also to be taken in the demolition of buildings with suspected PCB legacies in building materials and electrical equipment. Furthermore, attention should be paid to dismantling, replacement, and recycling of steel constructions protected with PCB containing anti-corrosion coatings. Especially in recycling or deposition of old electrical equipment, PCB may still be released to the environment.
The landfill of La Pilaor the old industrial site of Choindez areonly two cases of many, showing clearly that old sins throw long shadows. After 40 years of restrictions ofthe use of PCB in Switzerland these old persistent organic pollutants are still a cause of concern. Therefore, based on today's knowledge on classical and emerging persistent organic pollutants a proper handling and disposal of contaminated wastes deserves top priority.

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