REDUCING THE EMISSIONS OF PERFLUORINATED CHEMICALS: THE ENFORCEMENT APPROACH

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Abstract

The Flemish Environmental Inspectorate Division investigated the emissions of 13 compounds of PFC, especially PFOS and PFOA, by 53 companies which were identified as potential users of these chemical substances and by 11 sludge processing plants. In total 51 sludge samples, 5 compost samples and 73 waste water samples were analysed. PFC concentrations ranged from less than 0,01 mg/kg dw to 107,6 mg/kg dw in sludge and from less than 0,1 µg/l to 2211 µg/l in discharged waste water. The EID initiated administrative and judicial procedures to diminish the emissions of these substances and forwarded some suggestions to the policy makers for decreasing the emission risk of PFC in the environment.

Introduction

Until a few years ago perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were produced in large amounts. Both compounds are part of the family of perfluorinated chemicals (PFC) which specific technological properties made them used widely as surfactants, lubricants, paper and textile coatings, polishes, food packaging, and fire-retarding foams over the past fifty years. However, concern about PFC is growing. Several studies suggest these compounds to be globally distributed, environmentally persistent, bio accumulative and potentially harmful to the environment. The toxicity of these compounds is still being investigated[1].

In 2006 German scientists revealed the occurrence of PFC in surface and drinking waters in remarkable high concentrations. Concentrations up to 446 ng/l were found in the Ruhr (tributary of the Rhine) and up to 4385 ng/l in the Möhne (tributary of he Ruhr). Normal concentrations in the Rhine river and its main tributaries were determined below 100 ng/l. The high river water concentrations were assumed to originate from leaching of PFC-contaminated sludge applied illegally to agricultural land and woodland[2].

One of the possible sources of the contaminated sludge could be a waste trader from the Flemish Region in Belgium. These German findings were the immediate cause for the EID to start an investigation which focused on the actual discharge of PFC in industrial waste water and the presence of PFC in sludge from industrial waste water treatment installations.

Materials and Methods

The EID is the authority responsible for the enforcement of the Flemish environmental health legislation. The 1985 Environmental License Decree and its implementing orders, Vlarem I and II, describe the integrated environmental license and the general and sector-related environmental conditions for industrial activities. The Flemish environmental legislation is based upon the principle of prevention of pollution, nuisance and damage. The EID aims to reach a high-level, planned and co-ordinated enforcement, by combining a preventive and a repressive approach[3]. Each year different enforcement campaigns and actions are planned and executed[4]. The presented action was not planned but since its importance, immediate action was necessary. The supervision of the discharge of industrial waste water and waste has always been an important item.

In a first step, the EID defined the industrial activities which use relevant quantities of PFOS or PFOA in their production process. A 2004 environmental risk evaluation report of PFOS-related substances lists as main use areas of PFOS-related substances: chromium plating, photolithography, photography, production of film, aviation, fire fighting foams, fabric treatment, paper treatment and coatings[5]. In these industrial sectors PFOS-

related substances are used either as an acid, as a polymer or as a substance. Although fire fighting foams are responsible for important PFOS releases to the environment, they are further not considered as they are not a continuous emission source of PFOS. Fluor polymer production plants were included in the investigation.

Subsequently, the EID selected 53 companies from the above mentioned areas (table 1) and collected 66 water and 34 sludge samples at the selected companies and had them analysed on 13 compounds of PFC (table 2). Special attention was paid to the removal of the teflon seals from the screw caps of the sample recipients. The analyses were performed by the Flemish Institute for Technological Research (VITO) which is appointed as the Flemish reference laboratory for environmental analyses.

Table 1: *Overview of the selected companies*

Area	*Number*
Textile	27
Paper	8
Chromium plating	3
Photography	2
Various	13
Total	**53**

Table 2: *Analysed compounds of PFC*

Perfluorobutane sulfonate (C4)	Perfluorononanoic acid (C9)
Perfluorohexanoic acid (C6)	Perfluorodecanoic acid (C10)
Perfluorohexane sulfonate (C6)	Perfluorodecane sulfonate (C10)
Perfluoroheptanoic acid (C7)	Perfluoroundecanoic acid (C11)
Perfluorooctanoic acid (C8)	Perfluorododecanoic acid (C12)
Perfluorooctane sulfonate (C8)	Perfluorotetradecanoic acid (C14)
Perfluorooctanesulfonamide (C8)	

As the PFC-contamination in Germany was assumed to be caused by contaminated sludge, also 11 sludge processing plants were involved in the investigation. 17 samples were taken from filter cakes, 5 samples of composted material and 7 samples of waste water.

Results and Discussion

Potential PFC-users: During the inspections, the EID took samples of the discharged waste water and from either the sludge before it was dewatered or from the filter cakes of the dewatered sludge. In some plants only sludge or only waste water was sampled. The operators of the plants were thoroughly questioned about the use of PFC-containing raw materials. Nearly half of the operators (23 companies) affirmed the use of PFC-containing products in the production process, of whom 14 in the textile area. They declared a yearly use of PFC-containing substances ranging from 1160 kg to 87000 kg to impart the produced fabrics or carpets oil, water or dirt repellence. Textile companies reported a discharge of PFC in the waste water of 0,006 kg/yr to 4,5 kg/yr. Other companies reported a use of 10 kg/yr to 10000 kg/yr. PFC were found in the waste water or in the sludge of all these companies but one (a producer of air conditioning applications who used only 5 l/yr PFC).

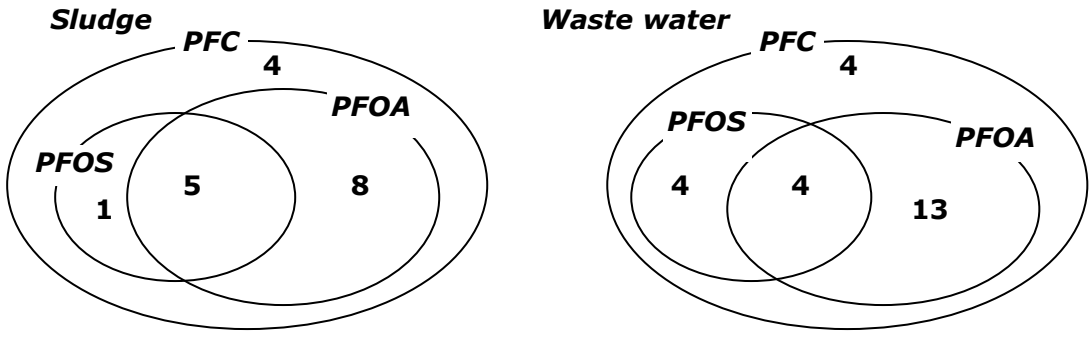

Figure 1: *The number of companies from potential PFC-users in whose sludge or waste water PFOS, PFOA or other PFC were found*

Operators of the 30 other companies denied the use of PFC-containing materials in their production processes. Although PFOA was found in the sludge of 3 of these companies in very low concentrations (0,01 to 0,90 mg/kg dw). In the waste water of two companies PFOS was found (1 µg/l and 2,3 µg/l), and of another company PFOA (5,6 µg/l). Figure 1 gives an overview of the presence of PFOA, PFOS and other PFC in the 53 sampled companies.

Tables 3 and 4 show how the concentration of PFC (13 compounds) is distributed in the 34 samples taken from the sludge of the industrial waste water treatment installations. In 41% of the samples concentrations of PFC were below the detection limit. PFOA was found in more samples than PFOS. From the 20 samples containing PFC, only 4 contained PFC other than PFOA or PFOS. In 8 sludge samples (24%) PFOA was present and no PFOS was found. Only one sample (sludge from a chrome plating plant) the PFOS content was significant high (25 mg/kg dw) while there was no PFOA detected. Maximum concentrations of PFC of 107,6 mg/kg dw and 65,3 mg/kg dw were found in sludge originating from a producer of fluorinated organic compounds.

The analyses from the discharged waste water samples revealed the same trends. In 20 waste water samples (30%) PFOA was present while no PFOS was found. The opposite was the case in 4 samples. The same chrome plating plant discharged water with a concentration of 231 µg/l PFOS, while no PFOA was found. This is not surprising while PFOS-salts are used to lower the surface tension of metal plating solutions to prevent the formation of mists containing potentially harmful components from the baths[5]. Waste water with a total PFC-concentration of 1160 µg/l to 2211 µg/l was discharged by the above mentioned producer of fluorinated organic compounds. Although these values are very high, they are still below the emission standard led down in the environmental permit of this company.

Table 3: *Distribution of the concentration of total PFC, PFOS and PFOA in 34 sludge samples of potential users of PFC*

Concentration (mg/kg dw)	*number of results*		
	PFC	PFOS	PFOA
Not detected	14	26	19
0,01 – 0,1	6	3	6
0,1 – 1	7	1	4
1 – 10	1	1	0
10 – 50	4	3	5
> 50	2	0	0

Table 4: *Distribution of the concentration of total PFC, PFOS and PFOA in 66 waste water samples of potential users of PFC*

Concentration (µg/l)	*number of results*		
	PFC	PFOS	PFOA
Not detected	30	54	38
0,1 – 5	12	8	12
5 – 20	13	0	9
20 – 100	2	0	0
100 – 500	6	5	7
> 500	4	0	1

In 27 companies, PFOA or PFOS was detected. Amongst them, there were 19 companies where both the waste water and the sludge were sampled and analysed. In 42% (8) of the companies PFOS or PFOA was found in the sludge sample, but was not detected in the sample of discharged waste water. In 32% (6) of these companies the waste water contained PFOS (2 samples) or PFOA (5 samples) while these contaminants were not found in the sludge. These results may confirm that sorption is higher for sulfonates than for carboxylates[6]. It may be clear that the investigation on the emissions of PFC in the environment may not be limited to the analysis of discharged waste water samples.

Sludge processing plants: The EID also sampled in 7 sludge processing plants filter cakes which were processed either for incineration or further processing in composting plants. In 6 plants PFOS or PFOA was found in the discharged waste water (PFOS: 1,78 µg/l – 9,98 µg/l; PFOA: 1,35 – 36,44 µg/l), or in the filter cakes (PFOS: 1,78 – 17,97 mg/kg dw; PFOA: 0,27 – 21,08 mg/kg dw). In one plant where no PFOS/PFOA was found, EID measured 0,89 µg/l PFC_6A.

Because part of the processed filter cakes were transported to composting plants for converting it into a soil improver, the EID also sampled compost in 4 composting plants. Two of them seemed to have processed

contaminated sludge since PFOS was detected in concentrations of 0,2 mg/kg dw en 0,59 mg/kg dw. Taking into account these results we must conclude that compost containing traces of PFC might have been introduced by these companies.

Enforcement actions of EID: The EID used these results to initiate an administrative and judicial procedure to diminish the emissions of these substances. Since PFC are part of the list of 'dangerous substances' as mentioned in the European Directive 76/464/EEC of 4 May 1976 – recently transformed into the European Directive 2006/11/EC of the European Parliament and of the Council of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (i.e. families and groups of substances, selected mainly on the basis of their toxicity, persistence and bioaccumulation and individual substances and categories of substances belonging to the families and groups of substances listed in the annex of the European legislation, and which have a deleterious effect on the aquatic environment), the EID exhorted 15 companies in whose discharged waste water PFC was found, to inventory the fluorinated organic compounds used in their production processes, to report about alternatives for these products and to take measures for ceasing the discharge of PFC-containing waste water. Based on the 1981 Decree on the prevention and management of Waste, the EID took measures to prevent that sludge originating from non-food industry, and thus potentially containing substances which are harmful for the environment, could end up in soil improver. The EID will further follow the actions of the different companies.

Suggestions to the policymaker: From this investigation, it is clear that PFC are still widely used and present in industrial emissions to the environment. The EID formulated some suggestions to the Flemish minister of Environment:

- Since the Flemish environmental legislation does not provide for PFC-standards in discharged waste water, it is recommended to provide for standards in the environmental permit for the individual compounds of PFC. Because of the important differences in properties and ecotoxicity between the different PFC-compounds a group standard is not assumed to be relevant.
- The European Community recently took measures 'to restrict the use and the placing on the market of PFOS' by the European Directive 2006/122/EC of 12 December 2006. From 27 June 2008, PFOS may not be commercialised or used as a substance or constituent of preparations in a concentration equal to or higher than 0,005 % by mass. Some exceptions are provided for. Since the directive does not apply to PFC other than PFOS, the EID recommended to implement a formal prohibition to use sludge originating from non-food industry in or as a soil improver. From this rule could be departed if the sludge producer can prove his sludge to arise from a homogeneous, steady process not involving contaminants that are harmful for the environment.
- The EID also argues in favour of the processing of sludge at different plants depending on its destination, either incineration or soil improver.

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