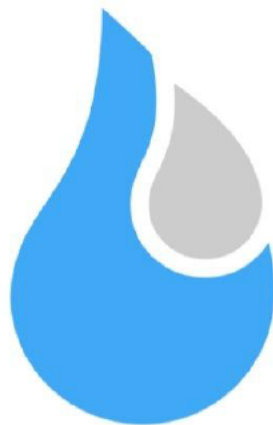


PFOS used in Paper Production

Consequences on drinking water and agricultural land in
Germany, Holland, Denmark and Sweden



GiertzTech AB

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Abstract

The chemical PFOS was forbidden in 2008. A ruthless chemical manufacturer uses a method where PFOS can be marketed as a “green chemical”. The manufacturer manipulates the product so that its actual content of PFOS is impossible to measure using the certified and standardized measurement method commonly used by government agencies and accredited institutes. The purpose is similar to Volkswagens Dieselgate; the product is manipulated in order to avoid government control and government regulations. The pulp and paper industry use hundreds of tons yearly of this “green chemical” and where PFOS remains in the produced paper. Paper end up in waste and which is burned in incineration plants. PFOS is not destroyed in the burning process. The result is that PFOS is spread with the flue gas to surface- ground- and drinking water as well as to agricultural land.

The supply of non toxic water and food belongs to basic infrastructure. This basic infrastructure has been destroyed beyond repair in parts of Germany, Holland, Denmark and Sweden.

1. Introduction

This report displays that a ruthless chemical manufacturer sells hundreds of tons yearly of the forbidden chemical PFOS in a way where the users, the pulp and paper industry, believe they purchase a “green chemical”.

This report shows that Swedish pulp and paper industry use approximately hundred tons PFOS yearly. All used PFOS end up in the environment.

This report shows that PFOS is not destroyed in incineration plants and therefore spread with the flue gas to surface- ground- and drinking water as well as to agricultural land. Incineration plants operate according to the EU directive 2010/75/EU. Consequently, there is a serious fault in the EU directive.

PFOS was measured in sewage and in produced paper from Swedish paper manufacturers. Furthermore, PFOS was measured in tap water in 40 cities in Germany, Holland, Denmark and Sweden. PFOS was also measured in vegetables produced in Holland and Sweden.

Water samples and vegetables were collected during April-June 2017 and analyzed in June 2017.

2. Use of PFAS/PFOS in papermaking

Paper is produced using the Fourdrinier process. Slurry of fibers, containing 98 % water, is spread on a rotating and perforated plastic mesh conveyor and where the water must be removed fast. This is achieved by adding a surfactant which reduces the water surface tension. Since 2015 a mix of four PFAS is used in Sweden: PFOS ($C_8F_{17}SO_3$), PFDS ($C_{10}F_{21}SO_3$), PFD_oDS ($C_{12}F_{25}SO_3$) and PFTeDS ($C_{14}F_{29}SO_3$). The mix contains equal amount of the molecules PFOS, PFDS, PFD_oDS and PFTeDS; hence, all four PFAS have the same concentration (measured in mol). A part of these four PFAS remain in the produced paper.

Paper produced in Sweden was analyzed. In all cases the paper displayed the same concentration (measured in mol) of PFOS, PFDS, PFD_oDS and PFTeDS; therefore only the concentration of PFOS is shown. The measurement accuracy is moderate and therefore the approximate concentration is displayed (400 mg/kg); however, results could vary between 300-500 mg/kg.

Producer and city	Type of paper	PFOS concentration, mg/kg
Unknown	Dagens Nyheter, newspaper	Approx. 400
Unknown	Svenska Dagbladet, newspaper	Approx. 400
Metsä Tissue AB, Pauliström	Lambi, toilet paper	Approx. 400
Metsä AB, Mariestad	Serla, kitchen paper	Approx. 400
SCA hygiene products, Edet	Edet Torky, kitchen paper	Approx. 400
SCA hygiene products, unknown	Libero Newborn, diaper	Approx. 400

Sewage from 4 paper mills was analyzed. All samples displayed the same concentration (measured in mol) of PFOS, PFDS, PFD_oDS and PFTeDS; therefore only the concentration of PFOS is shown.

Paper Mill	Place where sample was taken	PFOS concentration, mg/l
Stora Enso Fors (Avesta)	In river Forsån, 1 km downstream of the paper mill	40
Artic Paper Grycksbo AB Grycksbo	In lake Grycken, 1 km downstream of the paper mill	20
Stora Enso Kvarnsveden (Borlänge)	In river Dalälven, 1 km downstream of the paper mill	0.002 (2 µg/l)
Waggeryd Cell AB (Vaggeryd)	Tap water (ground water) in nearby city Vaggeryd	2

Note that river Dalälven is very large. Hence, the concentration is low although the total amount of PFOS, PFDS, PFDDoDS and PFTeDS is high.

The results prove that Swedish paper making industry use a mix of PFOS, PFDS, PFDDoDS and PFTeDS as surfactant and where PFOS was forbidden in 2008.

Analyses of produced paper from 2014, 2015 and 2016, display that the Swedish paper making industry introduced PFOS, PFDS, PFDDoDS and PFTeDS, as surfactant, during the third quarter 2015.

3. A method to mask PFOS and PFAS

The pulp and paper industry has used different types of PFAS as surfactants since the 1960ies. During 50 years a surfactant consisted of only one type of PFAS; often $C_{16}F_{33}SO_3$. From 2015, one surfactant dominates the market and it consists of a mix of four PFAS (PFOS, PFDS, PFDDoDS and PFTeDS). Why? The reason is that the chemical industry is now able to mask the presence of PFAS, including PFOS.

The chemical industry uses a method where PFOS, PFDS, PFDDoDS and PFTeDS are mixed in a way where they form clusters. The state of the art method used when analyzing PFOS, PFDS, PFDDoDS and PFTeDS is mass spectrometry (LC-MS/MS). This method analyzes single or solitary molecules; however, not PFOS, PFDS, PFDDoDS and PFTeDS which are part of a cluster. The consequence is that it is impossible to measure presence of these chemicals and the product can be promoted as a “green” surfactant.

Swedish companies must register import/use of chemicals to the Swedish Chemical Agency. The following paper manufacturers in Sweden use PFOS, PFDS, PFDDoDS and PFTeDS and the total import is hundreds of tons yearly (wherein approximately hundred ton is PFOS): Artic Paper Grycksbo AB, BillerudKorsnäs, Metsä AB, SCA, Stora Enso and Waggeryd Cell AB. According to the Swedish Chemical Agency their database contains no registration of PFOS, PFDS, PFDDoDS and PFTeDS imported/used by these companies or by the pulp and paper industry as a whole.

It is common knowledge within the pulp and paper business that the manufacturing process used since the 1960ies demands use of surfactants and where the dominating surfactant has been PFAS.

4. A novel method to measure PFAS/PFOS

The above clusters of PFOS, PFDS, PFDDoDS and PFTeDS disintegrate at very low concentration. Consequently, the method is to mix the sample with MQ-water (distilled water). This report displays

that tap water often contain 3-100 mg/l PFOS and which is a very high concentration. The method used is to mix the sample with 1000 times water, often 100 000 times water and sometimes with 1 million times water. That reduces the concentration to 30-1000 ng/l and which is the normal measurement range of state of the art methods.

5. Incineration plants

In Europe incineration plants operate according to the EU directive 2010/75/EU. In short, waste containing less than 1 % halogen compounds is burned in a process where the flue gas temperature must be increased to at least 850 °C during at least 2 seconds.

PFAS are known to be extremely persistent and there is reason to believe that they can sustain temperature up to approximately 1100 °C. The result is that PFOS, PFDS, PFD_oDS and PFTeDS are spread with the flue gas to lakes, groundwater and drinking water as well as to agricultural land which contaminates produced food.

Many reports display contamination of lakes, groundwater, drinking water and agricultural land by PFOS and PFDS caused by historic use of these chemicals in e.g. fire fighting foam (AFFF). The concentration is normally very low. The concentration of PFOS and PFDS in Stockholm tap water (lake Mälaren) has been approximately 4-5 ng/l of each of these chemicals.

Water samples from Stockholm tap water (Norsborg water plant) have been collected and stored since 2015. The table below displays concentration of PFOS, PFDS, PFD_oDS and PFTeDS during 2015 to 2017.

Time when sample was collected	PFOS, µg/l	PFDS, µg/l	PFD _o DS, µg/l	PFTeDS, µg/l
2015-01-01	0.005	0.004	0	0
2015-10-20	4	0.020	0.017	0.02
2016-02-23	15	13	15	18
2016-04-13	42	46	53	60
2016-05-18	160	190	210	240
2016-06-27	300	360	420	470
2016-08-01	480	580	670	750
2016-10-01	610	530	850	950
2016-12-22	2200	2600	3010	3500
2017-02-27	5200	6200	7300	8200
2017-03-20	8100	9700	11000	13000
2017-05-01	20000	24000	28000	31000

The sample from 2015-01-01 shows the historic contamination from AFFF; the concentration of PFOS and PFDS is very low (4-5 ng/l). The sample from 2015-10-20 shows the first sign of novel contamination from PFOS, PFDS, PFD_oDS and PFTeDS. Samples from 2016-02-23 display very large increase of PFOS, PFDS, PFD_oDS and PFTeDS. In all samples the four PFAS have the same concentration, measured in mol. However, they have different molecular weight and hence, e.g. PFTeDS has higher concentration measured in µg/l compared to PFOS.

The conclusion is that Stockholm tap water (lake Mälaren) started to contain increasing concentration of PFOS, PFDS, PFD_oDS and PFTeDS at the same time as these chemicals were introduced as surfactant by the Swedish paper making industry. All samples from 2016-02-23 to 2017-05-01 contain the same concentration (in mol) of all four PFAS; *i.e.* exactly the same mix as in produced paper and

in paper mill sewage. There is no paper making industry in the lake Mälaren region; consequently this contamination originates from burning of paper in incineration plants primarily in the Stockholm region.

6. PFOS in Sweden

Tap water from 13 Swedish cities, with incineration plants, has been analyzed with respect of PFOS, PFDS, PFD_oDS and PFTeDS. In all cases the water in a city displayed approx. the same concentration (measured in mol) of each of these four PFAS; therefore only the concentration of PFOS is shown.

City and type of water	PFOS concentration, mg/l
Avesta, ground water	6
Borlänge, ground water	80
Göteborg, lakes Delsjöarna	5
Halmstad	10
Linköping, river Motala ström	6
Ljungby, ground water	100
Norrköping, lake Glan	10
Nyköping, lake Yngaren	2
Stockholm Norrvatten, northern part of lake Mälaren	8
Stockholm Vatten, southern part of lake Mälaren	20
Södertälje, ground water	40
Uppsala, ground water, Gränby waterplant	40
Örebro, ground water	4

In Sweden water is unsuitable for consumption when the sum of PFOS and PFDS exceeds 900 ng/l. Consequently, the drinking water in these cities exceeds this level with 4 000 to 200 000 times.

Tap water from the cities Sala and Hedemora were analyzed as reference. Sala and Hedemora have no incineration plant and both reside approximately 50 km from the nearest incineration plant. The PFOS concentration was 3 µg/l in Sala and 4 µg/l in Hedemora, *i.e.* significantly lower than in cities with incineration plants. However, the PFOS and PFDS concentration was 6 to 8 times above the recommended level for unsuitable water.

7 different vegetables and root vegetables were randomly selected from two grocery stores (COOP and Hemköp). Wheat from farmland was also analyzed. Each vegetable displayed approx. the same concentration (measured in mol) of PFOS, PFDS, PFD_oDS and PFTeDS; therefore only PFOS is shown in the table.

Type of vegetable	Producer, city	PFOS concentration, µg/kg
Potato	Unknown, Västerås	30
Wheat	Grown outside Gnesta	6
Broccoli	Horna Gård, Åhus	2
Jerusalem artichoke	Mariannes Farm, Strövelstorp	8
Onion	Dalbo Gård, Oxie	10
Carrot	Steglinge Gården, Höganäs	20
Cucumber	Unknown, Järna	40
Cucumber	Växtkraft AB, Hälsingborg	60

Some of these vegetables were grown close to incineration plants. These vegetables display high concentration of PFOS, PFDS, PFD_oDS and PFTeDS (potato/Västerås, cucumber/Hälsingborg,

cucumber/Järna and carrot/Höganäs). The city Åhus is situated far away from incineration plants in Hässleholm and Malmö and consequently, broccoli produced there has lower PFOS, PFDS, PFDoDS and PFTeDS concentration. The results display correlation between concentration and distance to incineration plants.

7. PFOS in Germany

Tap water in 10 German cities, with incineration plants, has been analyzed with respect of PFOS, PFDS, PFDoDS and PFTeDS. In all cases the water in a city displayed approx. the same concentration (measured in mol) of each of these four PFAS; therefore only the concentration of PFOS is shown.

City and place where sample was taken	PFOS concentration, mg/l
Bielefeld, Ost	10
Bremen, Zentrum	8
Dortmund, Westfalenhalle	6
Düsseldorf, Zentrum	9
Hannover, Langenhagen	20
Hamburg, Stillhorn	100
Krefeld, Zentrum	20
Neustadt, Zentrum	70
Remscheid, Zentrum	40
Wuppertal, Zentrum	50

Note that the concentration is mg/l, *i.e.* extremely high. The recommended PFOS level for drinking water in Germany is 300 ng/l. Hence, this level is exceeded with 10 000 to 300 000 times.

Tap water from the cities Lübeck (Stockelsdorf) and Neumünster (Brokenlande) were analyzed as reference. Lübeck and Neumünster do not have incineration plants. The PFOS concentration was 1 respectively 6 µg/l, *i.e.* significantly lower than in cities with incineration plants. However, the PFOS concentration was 3 respectively 20 times above recommended level.

8. PFOS in Holland

Tap water in 7 Dutch cities close to incineration plants has been analyzed with respect of PFOS, PFDS, PFDoDS and PFTeDS. In all cases the water in a city displayed approx. the same concentration (measured in mol) of each of these four PFAS; therefore only the concentration of PFOS is shown.

City and place where sample was taken	PFOS concentration, mg/l
Amsterdam, city centre	40
Arnhem, city centre	10
Dordrecht, city centre	8
Enschede, city centre	60
Hengelo, city centre	20
Roosendaal, city centre	100
Rotterdam, city centre	60

Note that the concentration is mg/l, *i.e.* extremely high.

Vegetables from Holland, bought in Sweden, have been analyzed with respect of PFOS, PFDS, PFDoDS and PFTeDS. In all cases the vegetable displayed approx. the same concentration (measured in mol) of each of these four PFAS; therefore only the concentration of PFOS is shown.

Type of vegetable	PFOS concentration, µg/kg
Bell pepper (paprika)	240
Egg plant (aubergine)	140
Leek	200
Tomato	120

9. PFOS in Denmark

Tap water in 5 Danish cities with incineration plants has been analyzed with respect of PFOS, PFDS, PFDoDS and PFTeDS. In all cases the water in a city displayed approx. the same concentration (measured in mol) of each of these four PFAS; therefore only the concentration of PFOS is shown.

City and place where sample was taken	PFOS concentration, mg/l
Copenhagen, Kastrup	10
Kolding, city centre	20
Odense, city centre	90
Nästved, city centre	10
Slagelse, city centre	30

Tap water from the city Greve was analyzed as reference. Greve has no incineration plant and resides 30 km south of Copenhagen. The PFOS concentration was 30 µg/l, *i.e.* significantly lower than in cities with incineration plants. However, the PFOS concentration is far above recommended level.

10. PFOS in China

Tap water from Chinese cities was collected 2013, 2014, 2015 and 2016. Tap water from Beijing Xidan 2013-06 and from Tianjin 2014-04 contains very small concentration of PFOS, PFDS and no measurable PFDoDS and PFTeDS.

The table below displays PFOS, PFDS, PFDoDS and PFTeDS in tap water collected 2015-04.

City where sample was collected	PFOS, µg/l	PFDS, µg/l	PFDoDS, µg/l	PFTeDS, µg/l
Beijing, north	65	75	84	95
Beijing, Xidan	84	100	110	120
Kenli	36	40	46	52
Tianjin	12	14	14	16
Tiantongguan	8	9	10	11

The results display that the all water samples contain approx. equal amount of the four PFAS (PFOS, PFDS, PFDoDS and PFTeDS) measured in mol.

The table below displays PFOS, PFDS, PFD_oDS and PFTeDS in tap water collected 2016-11.

City where sample was collected	PFOS, µg/l	PFDS, µg/l	PFD _o DS, µg/l	PFTeDS, µg/l
Beijing, north	52000	62000	73000	82000
Beijing, Xidan	26000	31000	36000	41000
Suqian	70000	84000	98000	110000
Kenli	36000	43000	50000	57000
Nanjing	21000	25000	29000	33000
Yang Zhou	28000	33000	39000	44000

The results display that all water samples contain equal amount of the four PFAS (PFOS, PFDS, PFD_oDS and PFTeDS) measured in mol.

The news paper “China Daily” from 2015-04 and 2016-11 contains PFOS, PFDS, PFD_oDS and PFTeDS and where these four PFAS have the same concentration measured in mol.

Analyses made on newspaper and water samples from 2015-04 and 2016-11 prove that a surfactant, consisting of a mix of equal amount of PFOS, PFDS, PFD_oDS and PFTeDS, is used in China; *i.e.* exactly the same surfactant which used in Sweden and described in section 2. However, this surfactant was introduced large scale in China late 2014 or early 2015, *i.e.* approx. one year earlier than in Sweden.

It is reasonable to assume that this surfactant originates from China. The rapid increase of PFOS, PFDS, PFD_oDS and PFTeDS in Chinese tap water during 2016 indicates that the launch was successful and that the chemical manufacturer gained large market share during relatively short time. Subsequently, this surfactant was marketed in EU where it rapidly gained large market share.

11. Action levels

As far as the author understands the recommended level for PFOS in drinking water in Germany is 300 ng/l. As far as the author understands TDI for PFOS in food in Germany is 150 ng/kg/day. Sweden has two levels for drinking water. Action must be taken when the sum of 11 PFAS (including PFOS and PFDS) exceeds 90 ng/l and water is unsuitable for consumption when the sum of 11 PFAS exceeds 900 ng/l. There is no recommended level for food in Sweden.

The directive 2013/39/EU sets the PFOS limit in inland water to 0.65 ng/l. Lake Mälaren and lake Grycken exceeds this value by 30 million times and Dalälven exceeds the limit by 3 000 times.

12. Swedish government and science

Swedish scientists and government agencies are convinced that contamination of PFOS is primarily caused by historic use of PFOS in fire fighting foam (AFFF) and leakage of PFOS from e.g. military airfields. That is what they look for and that is what they find.

The chemical industry knows how to “package” PFAS (including PFOS) where its presence is masked and can be marketed as “green chemicals”. Government agencies must adapt to this and learn how to measure in a way where PFAS, including PFOS, can be analyzed.

13. Conclusions

The study provides evidence that Swedish paper manufacturers use a mix of PFOS, PFDS, PFDDoDS and PFTeDS as surfactant in paper production. PFOS was forbidden 2008.

The study provides evidence that PFOS, PFDS, PFDDoDS and PFTeDS are spread by incineration plants to drinking water reservoirs and to agricultural land and where the result is huge contamination of tap water and food.

The study provides evidence that incineration plants do not operate as expected and hence, the EU directive 2010/75/EU must be changed accordingly.

Illegal import of surfactants containing PFOS must stop immediately.

PFDS, PFDDoDS and PFTeDS are not forbidden; however, it is highly questionable to use them in a way where they pollute paper mill sewage and the produced paper.

The study displays that a chemical manufacturer manipulates its product in a way where it is impossible to measure its contents of PFOS, PFDS, PFDDoDS and PFTeDS, using state of the art methods. The result is a devastating environment catastrophe. The origin of this surfactant is probably China.