

PFOS/PFOA Contaminated Megasites From Sludge Application of a PFAS Producer Polluting The Drinking Water Supply of 5 Million People in Germany

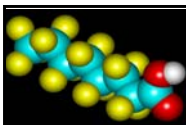
Roland Weber*, Dirk Skutlarek**, Harald Färber**,
Paul Kröfges*** Claudia Baitinger***, Ingo Gödeke***

*POPs Environmental Consulting, Göppingen, Germany

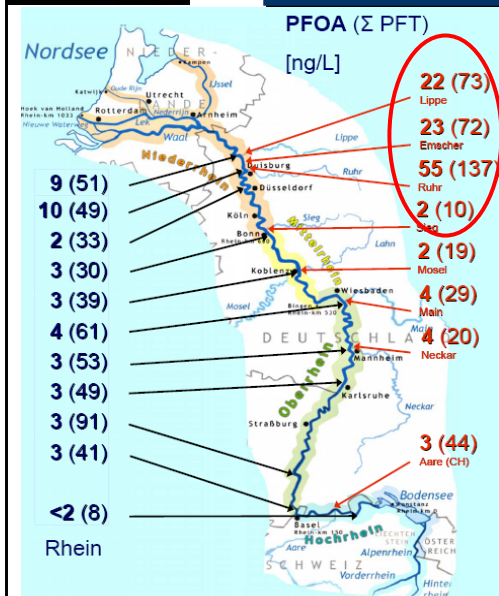
**University Bonn, Institute for Hygiene and Public Health, Bonn, Germany

***BUND (FoE Germany) Nordrheinwestfalen e.V., Düsseldorf, Germany

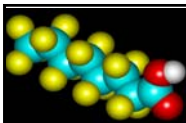
<http://www.dioxin20xx.org/pdfs/2007/07-634.pdf>



Perfluoro Alkyl Substances (PFAS) in Rhine and Tributary Rivers (2006)

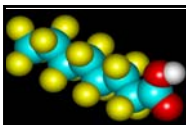
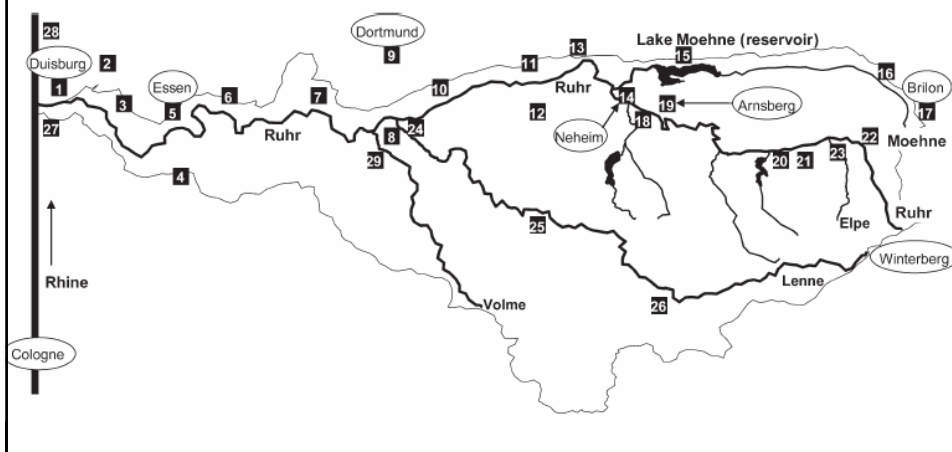


- Screening of PFOS, PFOA and other PFAS in the Rhine river and tributaries (Skutlarek, Färber, Exner, Univ. Bonn, March 2006)
- High PFAS-contamination in Rhein tributary rivers Ruhr, Emscher and Lippe (near the city of Essen).



PFOS, PFOA & other PFAS Pollution Ruhr/Moehne and tributaries (2006)

Tracing the PFAS- contamination in the Ruhr
back to Möhne river and tributary creeks.



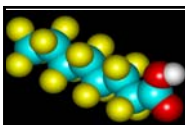
PFOS, PFOA & other PFAS Pollution Moehne river and tributaries (2006)

Extreme high concentrations of PFOA and other
PFAS in the Moehne river and tributaries.

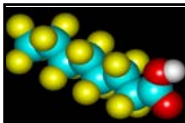
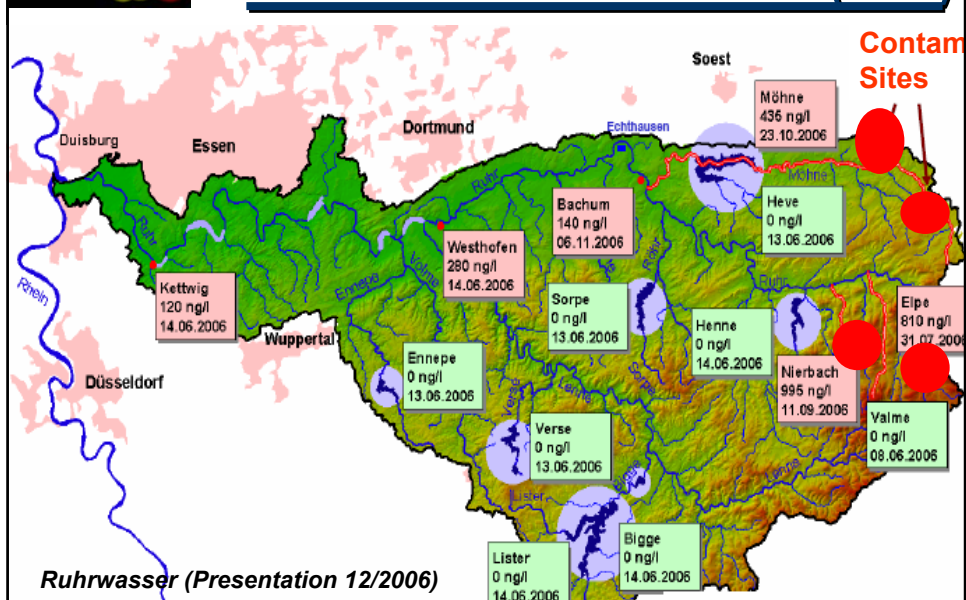
Sampling site (river)	PFBuA [ng/L]	PFPeA [ng/L]	PFHxA [ng/L]	PFHpA [ng/L]	PFOA [ng/L]	PFBS [ng/L]	PFOS [ng/L]	Σ [ng/L]
Klossiepen	—	—	—	—	11	—	—	11
Steinbecke	500	2670	2630	621	16800	1450	5900	30571
Hoebecke	—	—	—	—	—	—	—	—
Klossiepen	—	—	—	46	1860	17	2	2032
Bermecke	—	—	—	—	—	—	—	—
Bermecke (mo)	—	—	—	110	6530	146	507	8301
Moehne	—	—	—	50	1930	38	135	2375
Steinbecke (mo)	—	—	—	189	33900	669	3160	43348
Moehne	—	—	—	80	7070	87	405	8318
Moehne	—	—	—	58	5990	79	370	7157
Hengelsbach	—	—	—	—	—	—	—	—
Moehne	—	—	—	46	5570	67	311	6595



Skutlarek, Exner, Färber, *Environ Sci Pollut Res* 13 (5) 299 – 307 (2006)



PFOS, PFOA & other PFAS Pollution Ruhr/Moehne and tributaries (2006)



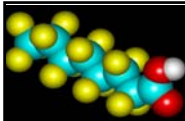
Activities for Population Protection - PFAS in Moehne Reservoir (2006/2007)

Lake Moehne (drinking water reservoir for ca. 5 million people) with a volume of 134.5 million m³, was contaminated with Σ PFAS of 822 ng/l. Calculated concentration in the lake: **110.5 kg PFAS**.

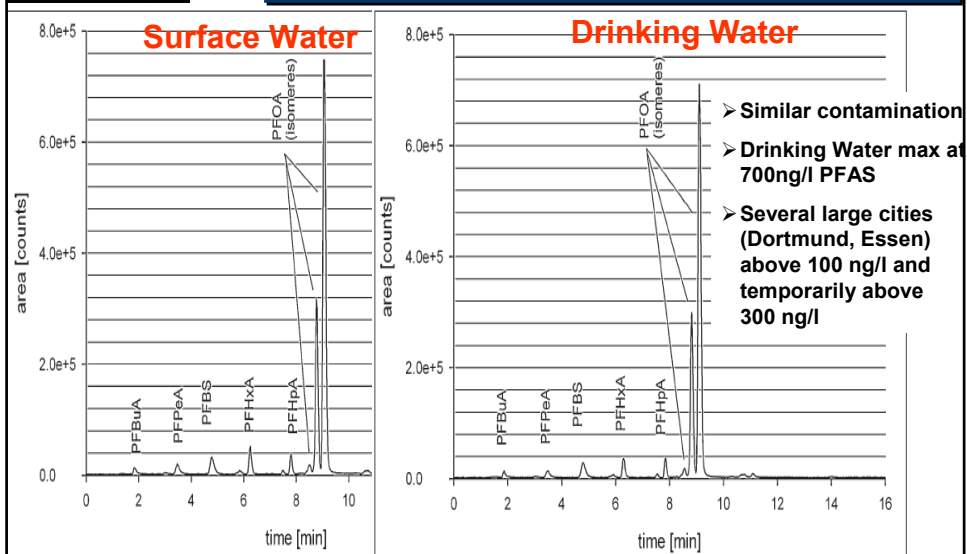
- After July 2006: use of two other dams with non contaminated water to dilute high concentrations of the Moehne dam to adjust the concentration in the Ruhr to below 300 ng PFAS/l (just meeting the preliminarily established drinking water limits).
- The Moehne Reservoir released slowly the approx. 110 kg PFAS into the Ruhr and via Rhein finally into the North Sea contaminating on their way drinking water and fish.

Source PFOS/PFOA Contamination in Ruhr and Tributary Rivers (2006)

- The PFOS/PFOA contaminated agricultural fields resulted from mismanagement of PFAS contaminated sludge of a PFAS producer which was imported via a Dutch trader to a German company (in accordance with EU hazardous Waste Shipment Regulation (EEC 259/93).
- In a criminal act the German company (GW Umwelt) then labelled the sludge as “bio-solids” and gave it to farmers. In September 2006 the BUND (FoE Germany) accused the company and also the local authority Soest.
- After the contamination was revealed the company proclaimed bankruptcy and the former owner and CEO of the company went to court. Court investigation ongoing.



Comparison of PFAS Levels in Surface and Drinking Water



Investment of 100 million Euro in water works in the region !

Guidelines/Regulation Limits for PFAS

Local/State governments approached German Health Agency for clarification and help (05/2006).

- No drinking water guideline worldwide for PFC.
- No comprehensive Risk Assessment that would have allowed a straight forward decision for limits (after 50 years high volume production of PFOS/PFOA used in daily life/household!!!).
- German Health Agency made a preliminary recommendation for drinking water limits PFAS. (21.06.2006)

Prel. Recommendation of German Health Agency for Drinking Water

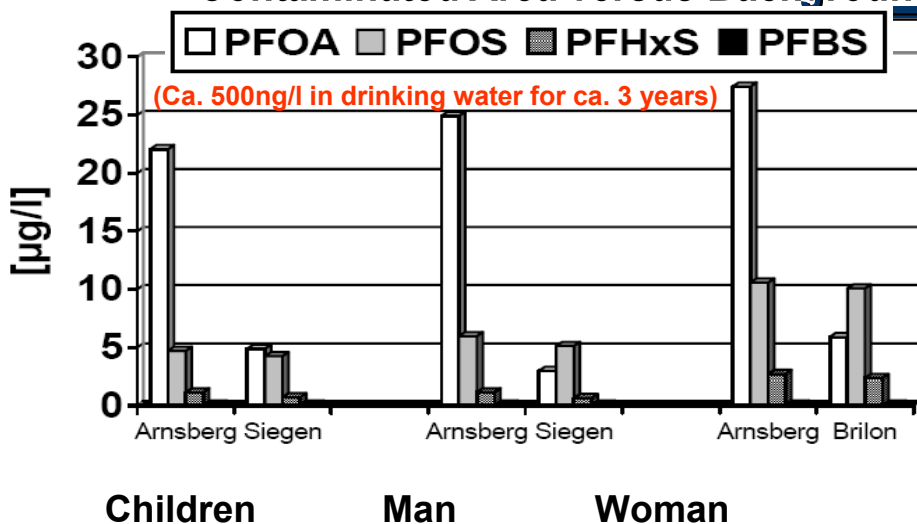
Type of Limits	Abrev.	PFOA	Reasoning
Target value (minimum quality)	GOV	$\leq 0.1 \mu\text{g/l}$	Health precaution (Life span)
Health guiding value	LW	$\leq 0.3 \mu\text{g/l}$	Acceptable value (Life span)
Precautionary action value infants	VMW _s	0.5 $\mu\text{g/l}$	Precautionary protection infants
Action value adults	MW = VMW ₀	5.0 $\mu\text{g/l}$	Recom: Not use for nutrition purpose

Stellungnahme Trinkwasserkommission BMG (beim UBA) 21.06.06; revised 13.07.06

Risk assessment New Jersey state (2007):

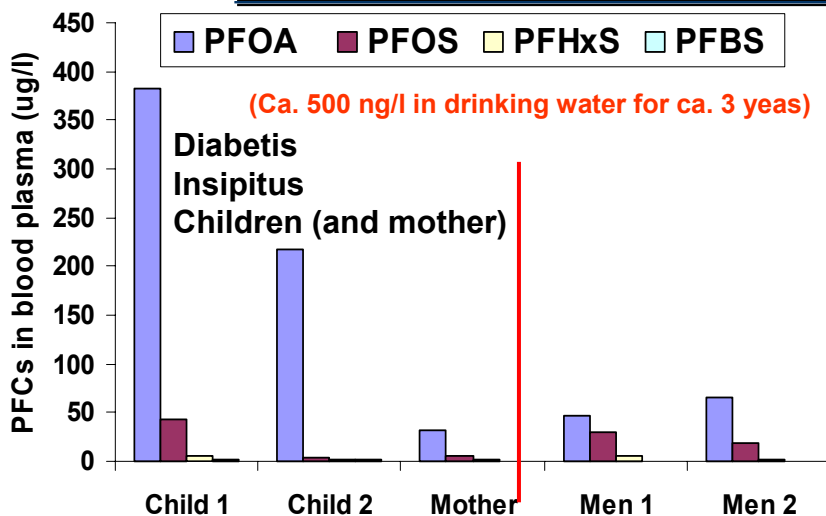
Limit drinking water PFOA* 40 ng/l.

PS in Human Blood Plasma (3/2007)- Contaminated Area versus Background



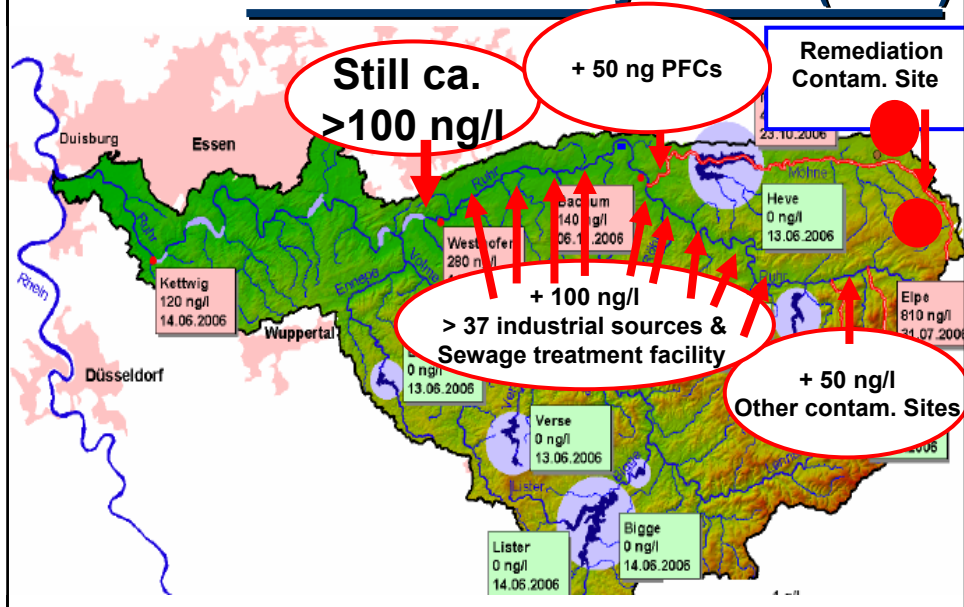
University Bochum/Erlangen-Nürnberg, LUA NRW Study on human PS contam. in areas with elevated PS drinking water contamination. 3/2007

PFCs in Human Blood Plasma (3/2007)- Some High Water Consuming Individuals



University Bochum/Erlangen-Nürnberg, LUA NRW Study on human PS contam. in areas with elevated PS drinking water contamination. 05/2007

Perfluorinated Surfactants in Ruhr and Tributary Rivers (2008)

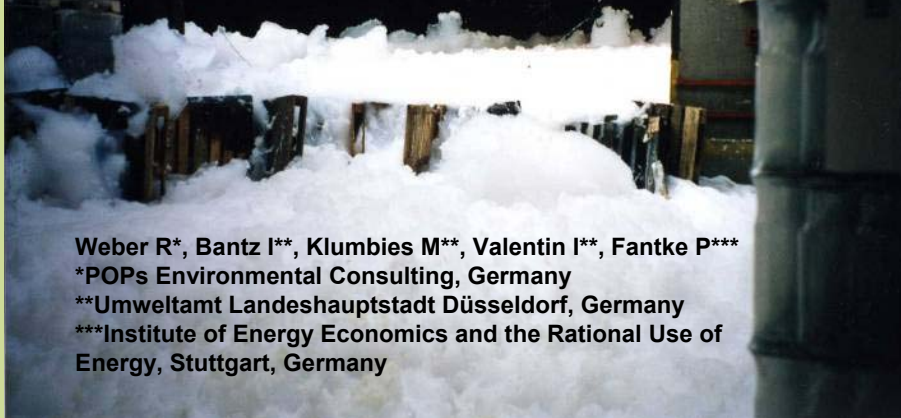


Dimension of Contamination - Further Monitoring Efforts

- Approximately 250,000 tons of imported sludge were distributed as “Soil Improver” on approx. 1300 sites in Germany including agricultural land, grazing fields and forests. Luckily only a minor part contained high levels of PFAS (what did the other sludge include?).
- Start of national monitoring activities for PFOS/PFOA contamination in German rivers and water works.
- In course of this screening several other contaminated surface waters were detected.
- Also discovered that a large share of German sewage sludges contain PFOS/PFAS (from industries, households and run off).



PFOS/PFAS POLLUTION FROM USE OF FIRE FIGHTING FOAM IN A MAJOR FIRE IN DÜSSELDORF/GERMANY – HUMAN EXPOSURE AND REGULATORY ACTIONS



Weber R*, Bantz I**, Klumbies M**, Valentin I**, Fantke P***
*POPs Environmental Consulting, Germany
**Umweltamt Landeshauptstadt Düsseldorf, Germany
***Institute of Energy Economics and the Rational Use of
Energy, Stuttgart, Germany

<http://www.dioxin20xx.org/pdfs/2010/10-1379.pdf>

klü 12.08.2010

PFOS/PFAS Pollution from AFFF Use (Düsseldorf/Germany 05/2001)



Germany & Federal States

klü 12.08.2010

PFOS/PFAS Pollution from AFFF Use (Düsseldorf/Germany 05/2001)



Umweltamt
Landeshauptstadt Düsseldorf



Federal State Capital Düsseldorf

Area: 217 km²

Population: 585 000 Inh.

Population density: 2700 I/km²

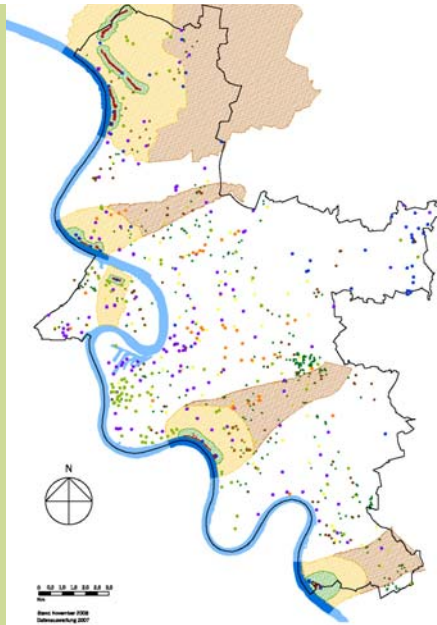
klu 12.08.2010



Ground water use in the city area of Düsseldorf/Germany



Umweltamt
Landeshauptstadt Düsseldorf



LEGENDE Wasserrechte

- Gartenbrunnen
- Erdsonden
- Trinkwassernotbrunnen
- Trinkwasser
- Brauchwasser
- Feldberieselung
- Sanierung

Wasserschutzzonen

- Wasserschutzzone I
- Wasserschutzzone II
- Wasserschutzzone IIIa
- Wasserschutzzone IIIb
- Sonderschutzzone Rhein

Major Fire Event Extinguished by AFFF (Düsseldorf/Germany 05/2001)



Umweltamt
Landeshauptstadt Düsseldorf

- Düsseldorf (district Gerresheim) faced a major fire in a depot for plastic crates for beverage bottles in May 2001.



- The blaze was extinguished by using a 42 m³ of AFFF foam, containing perfluoroalkyl substances (PFAS) including PFOS.
- Assuming 1-3 % PFAS would mean a use of total 420 kg to 1260 kg PFAS in the fire event.

Run-Off AFFF Contaminated Water (Düsseldorf/Germany 05/2001)



Umweltamt
Landeshauptstadt Düsseldorf

Despite the ground fixation with asphalt and brick flooring at the time of the fire, PFAS in the fire water extensively infiltrated into the soil through joints and cracks, run-off from the fire place into soils bordering the area and through the partly damaged sewer system.



After the fire, the depot was pulled down and the whole terrain was unsealed (2002).

klü 12.08.2010

PFOS/PFAS Pollution Germany Start of National Monitoring Activities



Umweltamt
Landeshauptstadt Düsseldorf

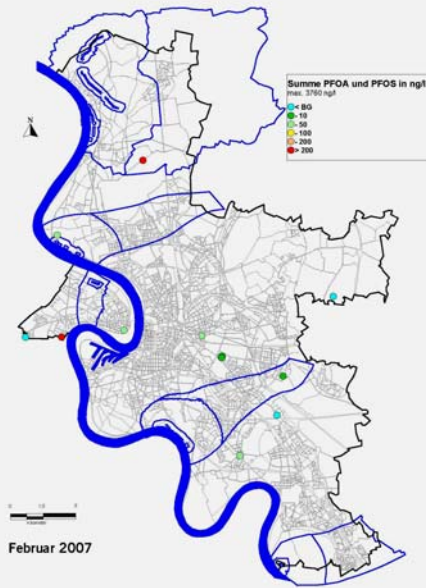


- For 6 years no monitoring activity at that fire place
- 2006: Discovery of drinking water contamination of rivers Möhne/Ruhr being the drinking water reservoir for 5 Million people (the main sources were PFOS/PFOA and other PFAS contaminated agricultural area)
- Here the challenge to manage PFC contamination in drinking water works became obvious:
Investment of 100 Million Euro!
- Start of monitoring on PFAS pollution in Germany by competent authorities (2007 on)

klü 12.08.2010



Umweltamt
Landeshauptstadt Düsseldorf

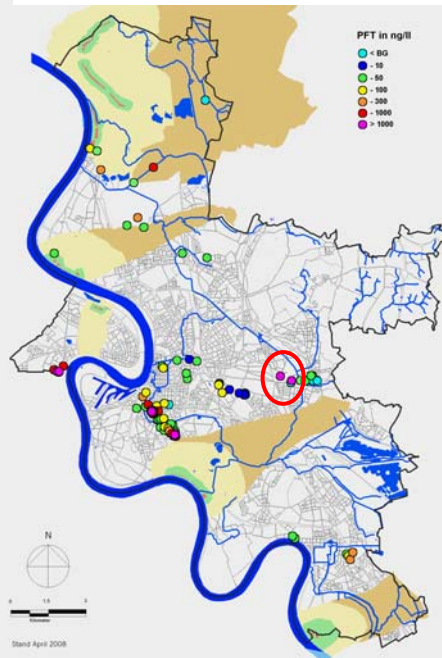


Februar 2007

PFAS Groundwater screening in the city area of Düsseldorf (Februar 2007)



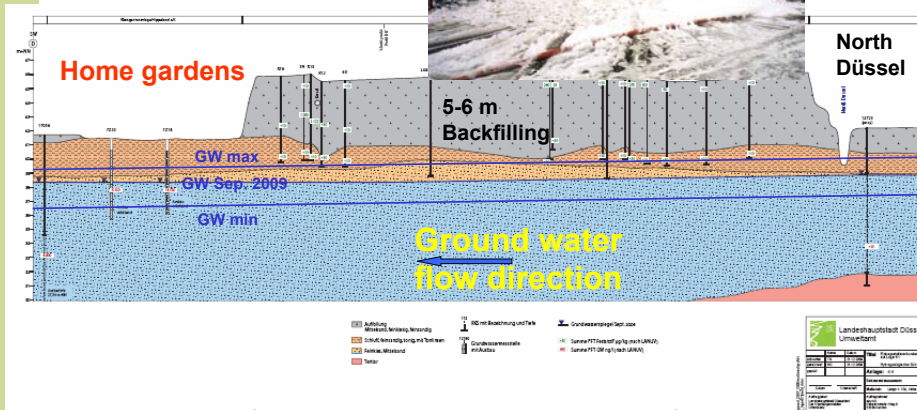
Umweltamt
Landeshauptstadt Düsseldorf



Stand April 2008

PFAS Groundwater screening in the city area of Düsseldorf (End of 2007)

Umweltamt
Landeshauptstadt Düsseldorf



Umweltamt
Landeshauptstadt Düsseldorf

- **40 ground water samples from dedicated ground water wells and private wells from gardens were analyzed (02/2009 – 03/2010).**
- **265 soil samples from 120 bore holes, 14 surface soil samples from vegetables gardens were taken.**
- **& Vegetable and fruit samples**



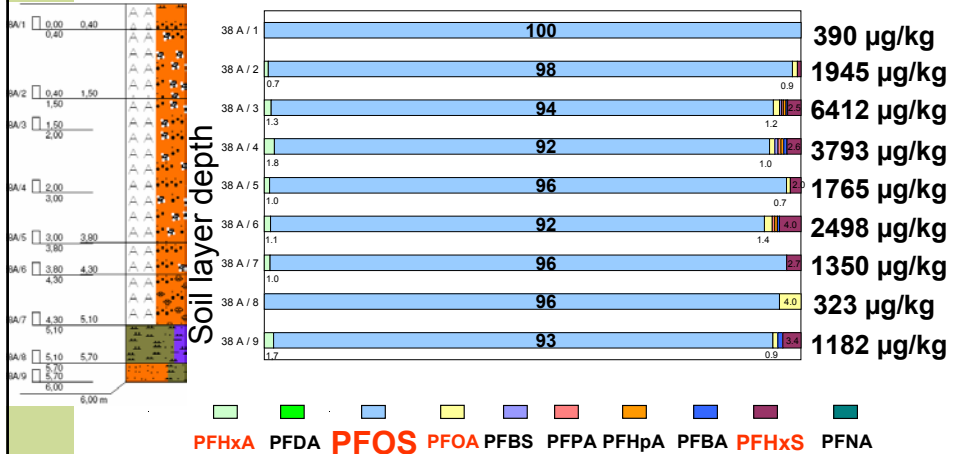
PFOS/PFAS Pollution AFFF Düsseldorf

PFC Soil Contamination and Profile



Umweltamt
Landeshauptstadt Düsseldorf

- PFOS is main contaminant in the polluted soil (>90%)
- PFAS profile does not change significantly with depth



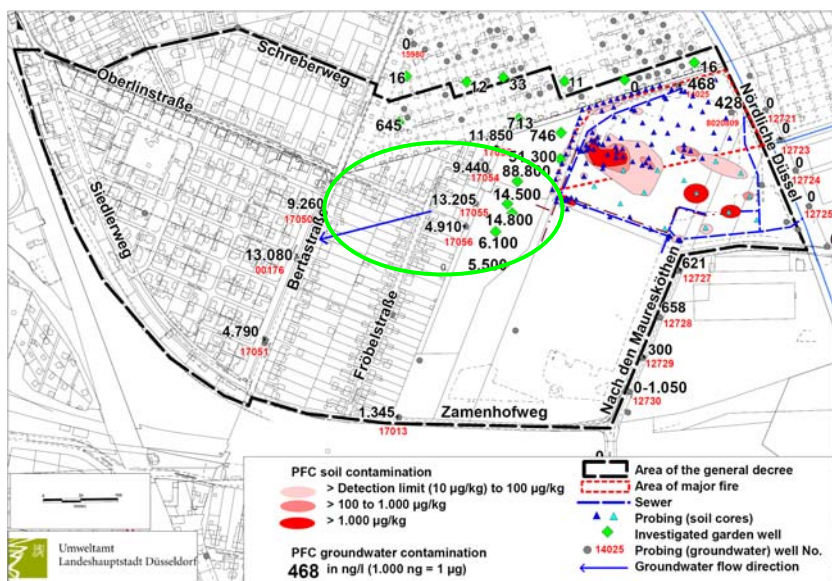
klu 13.01.2010

PFOS/PFAS Pollution AFFF Düsseldorf

Soil and Ground Water Level (03/2010)



Umweltamt
Landeshauptstadt Düsseldorf



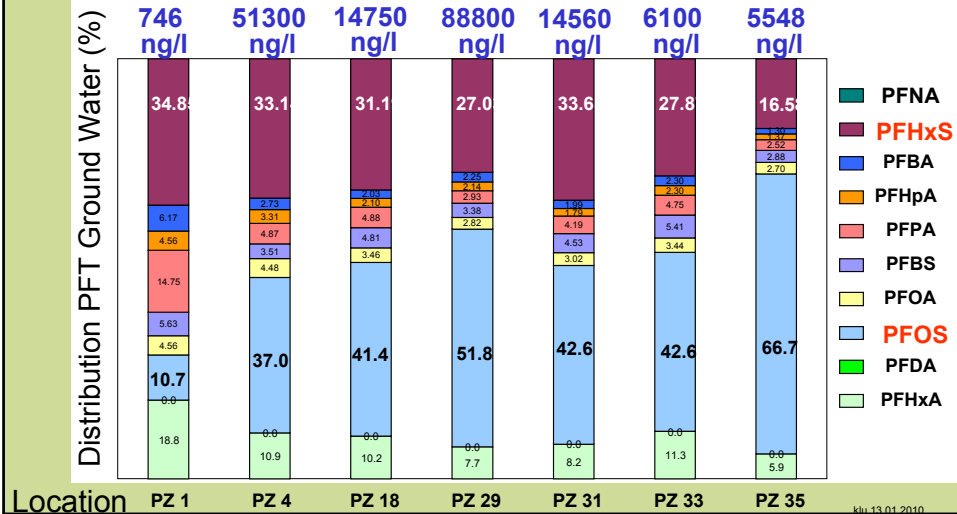
klu 12.08.2010

PFOS/PFAS Pollution AFFF Düsseldorf PFC in Ground Water Vegetable Gardens



Umweltamt
Landeshauptstadt Düsseldorf

- PFAS profiles differ significantly from the soil samples
- PFOS and PFHxS are main contaminants in the polluted ground water (together approx. >70%)

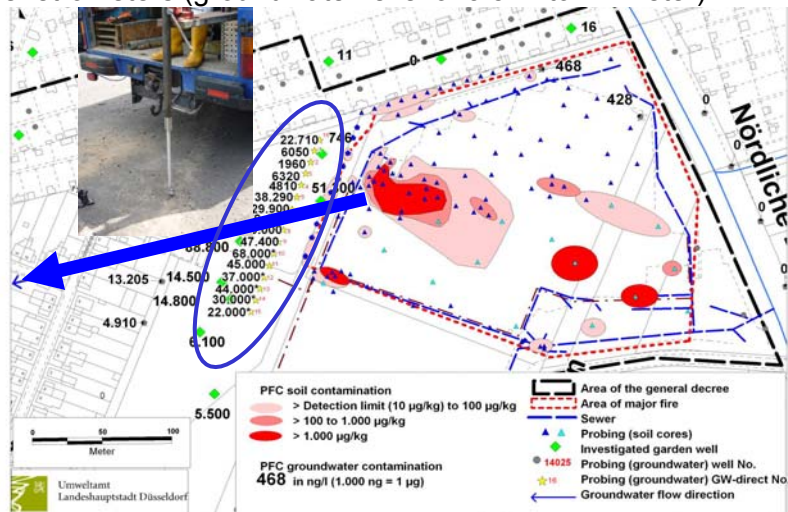


PFOS/PFAS Pollution AFFF Düsseldorf Groundwater Profile Monitoring (06/2010)



Umweltamt
Landeshauptstadt Düsseldorf

- For monitoring of the ground water migration from the site, 16 locations in a row distance of 7 to 8 m where measured with penetrometers (groundwater level of 3.5 m to 12 meter).



PFOS/PFAS Pollution AFFF Düsseldorf Groundwater Profile Monitoring (06/2010)



Umweltamt
Landeshauptstadt Düsseldorf

PFAS-distribution in ground water downstream of the contaminated site (Sum PFAS in ng/l)

Sampling Position	North No.16	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
3.5 m	22.710	6.050	1.960	6.320	4.810	38.290	29.900	159.400
5.0 m	18.000			5.910				47.000
7.0 m	950	560	430	600	1.220	3.650	10.030	14.150
9.0 m			330					
11.0 m	330	230	420	380	460	600	3.360	3.920
12.0 m	150	20	670	1.310	210	4.710	3.900	470

Sampling Position	No. 8	No. 9	No. 10	No. 11	No. 12	No. 13	No. 14	No. 15 - South
3.5 m	183.620	11.720	66.620	30.970	20.550	19.580	6.800	4.400
5.0 m								
7.0 m	95.330	47.400	67.800	37.430	37.400	43.740	16.630	22.200
9.0 m								
11.0 m	37.410	38.400	44.400	40.570	28.900	35.400	29.830	22.230
12.0 m		34.650	42.200	45.030	25.440	36.320	16.180	21.510

klw 12.08.2010

PFOS/PFC Pollution AFFF Düsseldorf Risk Assessment Consumers



Umweltamt
Landeshauptstadt Düsseldorf

- A preliminary risk assessment with focus on the users of the gardens was carried out according to the tolerable daily intake (TDI).
- The German Federal Institute for Risk Assessment (BfR) has set in 2006 a TDI for PFOS and PFOA of 0.1 µg/kg body weight per day, respectively (according to EFSA).
- Considering recent epidemiological studies (sperm, fertility) this value is probably more then an order of magnitude too high !!

klw 12.08.2010

PFOS/PFAS Pollution AFFF Düsseldorf

Results of Monitoring (09/2010)



Umweltamt
Landeshauptstadt Düsseldorf

PFAS content in vegetables and fruits from gardens irrigated with contaminated ground water and exposure risk (calculated for a child 10 kg; TDI 100 ng/kg day⁻¹).

	Sampling-date	PFC- content in µg/kg	Main PFC substance	Consumption within TDI ¹⁾
Apple	17.12.2009	18	PFDoA	20 kg/year
Figs	17.12.2009	<BG (10 µg/kg)		
Celery	17.12.2009	32	PFOS & PFHxS	11.4 kg/year
Radish	23.06.2010	<DL (4 µg/kg)		
Cherry	23.06.2010	<DL (2 µg/kg)		
Spring onions	23.06.2010	2.2	PFBA	165 kg/year
Kohlrabi	23.06.2010	7.6	PFBA und PFPA	48 kg/year
Cherry	08.07.2010	3.7	PFBA	98 kg/year
Zucchini	08.07.2010	4.5	PFBA	81 kg/year

< DL: Detection limit

¹⁾ TDI: Tolerable daily intake

klu 12.08.2010

PFOS/PFC Pollution AFFF Düsseldorf

Actions for Soil & Consumer Protection



Umweltamt
Landeshauptstadt Düsseldorf

- For reasons of precautionary soil conservation and health protection a General Decree was remitted for the sites of known and assumed PFAS groundwater contamination, interdicting the extraction and usage of groundwater as well as the irrigation of soils with groundwater.
- The interdiction is initially imposed for 15 years and shall be regularly adapted according to the findings of further investigations.
-

klu 12.08.2010

PFOS/PFAS Pollution AFFF Düsseldorf Actions on PFOS/PFC Foam



Umweltamt
Landeshauptstadt Düsseldorf

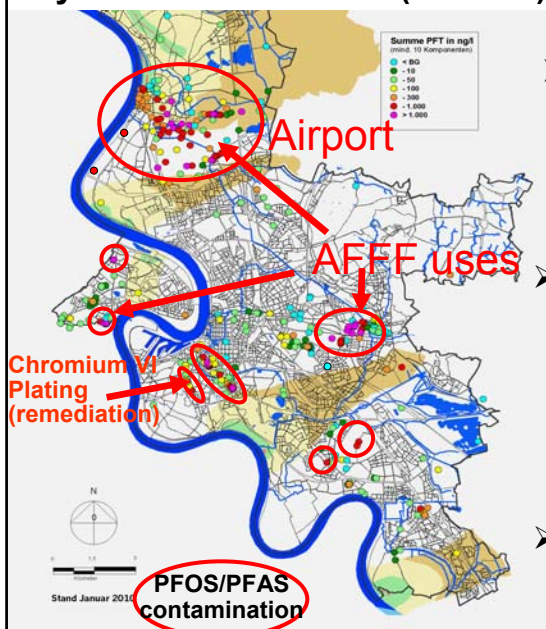
- Düsseldorf has an ongoing program and develop methodology to assess PFOS/PFAS contaminated sites
- PFOS/PFAS contaminations were discovered
 - At other sites of major fires
 - At fire fighting practice areas
 - At chromium plating factories
- The respective assessments have started

klw 12.08.2010

PFAS groundwater screening city area of Düsseldorf (01/2010)



Umweltamt
Landeshauptstadt Düsseldorf

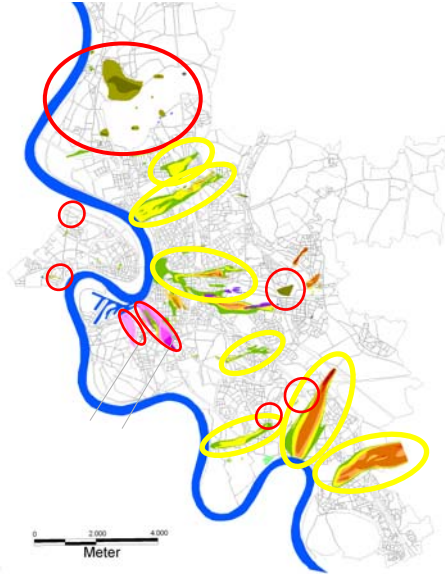


- Düsseldorf has an ongoing program and develop methodology to assess PFOS/PFAS contaminated sites
- PFOS/PFAS contamination
 - Sites of major fires
 - Fire fighting practice areas
 - Airport (AFFF + other?)
 - At chromium plating factories
- Respective assessments have started

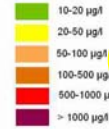
Overview on PFC & PCC Ground Water Pollution in Düsseldorf (2010)



Umweltamt
Landeshauptstadt Düsseldorf



CKW-Konzentrationen



**Chlorinated
Organics (TeCE,
TrCE, VCM, etc)**

**PFOS/
PFAS**



Perfluorierte Tenside (PFT):



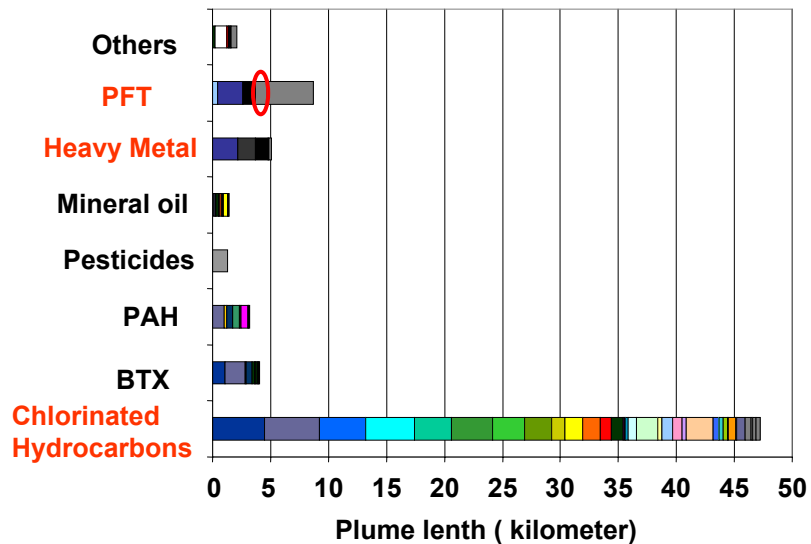
Stand 2009

Contamination plumes of Pollutant Classes in Düsseldorf City (5/2010)



Umweltamt
Landeshauptstadt Düsseldorf

Pollutant Classes



PFOS/PFC Pollution AFFF Düsseldorf Actions PFOS/PFC Foam Use Düsseldorf



Umweltamt
Landeshauptstadt Düsseldorf

- In consequence of the knowledge on PFOS/PFAS related damages and challenges caused by recent fires, the complete old stock of extinguishing foam containing PFOS, which was available in the municipal fire department, has been destroyed.
- Moreover, the use of PFAS containing extinguishing foams that are allowed to be used as substitutes for PFOS containing foams is largely omitted.
- Control of fire fighting practice (only practice foam)
- Extinguishing water in fires (with AFFF use) is either collected or the affected area will be investigated in a timely manner to avoid the formation of new groundwater damages.

klu 12.08.2010

Umweltamt
Landeshauptstadt Düsseldorf



**PFAS in a
Belgium beer
(108 ng/l)!**

Pulkrabova et al. Dioxin 2011,
Brussels 21-25 Sep 2011.

(In Düsseldorf groundwater is
not used for brewing beer!)

Please take care
that the „wrong foam“
does not end up in the
„right stuff“!



PFOS/PFOA – Water as Final Sink Contamination of the Oceans/Sea

