

The need of a Science-Policy exchange on POPs contamination risks and food safety

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BASEL / ROTTERDAM / STOCKHOLM CONVENTIONS

31 POPs listed in the Stockholm Convention (04/2023)

Chemical	Pesticides	Industrial chemicals	Unintentional production	Annex
DDT	+			В
Aldrine, Dieldrine, Endrine	+			А
Chlordane, Chlordecone, Toxaphene	+			А
Alpha-, Beta-, Gamma-HCH	+		By-product of lindane	А
Endosulfan, Heptachlor, Mirex	+			А
Pentachlorophenol (PCP), <u>Dicofol</u>	+	+		А
Commercial PentaBDE		+		А
Commercial OctaBDE (Hexa/HeptaBDE)		+		А
Commercial DecaBDE		+		А
Hexabromobiphenyl (HBB)		+		А
Hexabromocyclododecane (HBCD)		+		А
PFOS, its salts and PFOSF	+	+		В
PFOA and related compounds				А
PFHxS and related compounds		+		А
Short chain chlorinated paraffins		+		А
PCB PeCBz, HCB, PCN, <u>HCBD</u>	+	+	+	A/C
PCDD, PCDF			+	С

For most of the POPs, food is the major exposure pathway. Therefore for some of the POPs, food regulatory limits have been established for exposure control.

Regulatory limits in food drive the relevance for assessing food contamination and making the compound group relevant for the food and feed industry as well as relevant for contaminated sites (exposure relevance soil-feed-food)

Regulatory limits in food exist for

- (POP)Pesticides
- PCDD/PCDF (2001; EU)
- PCBs (2006; EU)
- PFOS, PFOA (12/2022 EU)

The EU regulatory limits are often applied by other countries to control imports.

POPRC: Chlorpyrífos, MCCP, LC-PFAA. COP: Methoxychlor; UV328, Dechlorane Plus

Protection of food and food-production-sector and human exposure as an important aim of POPs control – science & policy need

- South America has large food and feed production & exports as important industrial sector.
- E.g. Brazil & Argentina have a large meat production worth >34 billion and >12 billion\$ (2022) respectively. Total beef production in Argentina is predicted to reach >40 billion \$ by 2027. https://www.statista.com/outlook/cmo/food/meat/argentina#revenue
- Meat and other products of animal origin have a high risk for POPs exposure and contamination (Weber 2017; Weber et al 2018) and a stringent risk management is needed to avoid the extreme high costs of dioxin/POPs food crises (Behnisch & Brouwer 2020; Fiedler et al. 2000).
- Therefore some thoughts here on POPs in food & feed production and some science findings and related risks and potential relevance for GRULAC region which likely need (further) action by policy makers and further research by the scientific community.

Weber R (2017) Learning from Dioxin & PCBs in meat – problems ahead? *IOP Conf. Ser.: Earth Environ. Sci.* 85 012002.
https://iopscience.iop.org/article/10.1088/1755-1315/85/1/012002/pdf
Weber R, Herold C, Hollert H, Kamphues J, Blepp M, Ballschmiter K (2018) Reviewing the relevance of dioxin and PCB sources for food from animal origin and the need for their inventory, control and management. *Environ Sci Eur.* 30:42. https://rdcu.be/bax79
Lascano Alcoser et al (2011) Financial Impact of a Dioxin Incident in the Dutch Dairy Chain. *Journal of Food Protection*, 74(6), 967–979.
Fiedler H, Hutzinger O, Welsch-Pausch K, Schmiedinger A (2000) Evaluation of the Occurrence of PCDD/F and POPs in Wastes and Their Potential to Enter the Foodchain. Study on behalf of the European Commission, DG Environment, 30. September 2000.).

Assessment of risk of POPs for food & feed production of South America

- An increase in future risk for food/meat and feed might result for PCDD/F and PFOS/PFOA since the European Food and Safety Agency (EFSA) significantly reduced their Tolerable Daily/Weekly Intake (TDI/TWI) (EFSA 2018, 2020).
- For PCDD/F the TWI was reduced by a factor of seven. This might result in future reduction of PCDD/F limits in food of animal origin with associated higher risk for food production.
- Another increasing risk for food & feed production and consumption result from the reduction of Tolerable Weekly Intake (TWI) for PFOS and PFOA by a factor of 100 and 1500 respectively (EFSA 2020), resulting that a share of population is above this TWI.
- Therefore I will inform in the **first part** of presentation on Dioxin & PCB challenges with food and then in the **second part** on PFOS/PFOA risk for food and feed and related production.

EFSA (2018) Risk for animal and human health related to the presence of dioxins and dioxin-like PCBs in feed and food. *EFSA Journal* 2018;16:5333 https://www.efsa.europa.eu/en/efsajournal/pub/5333 EFSA (2020) Risk to human health related to the presence of perfluoroalkyl substances in food. *EFSA Journal* 2020;18(9):6223 https://doi.org/10.2903/j.efsa.2020.6223

Weber R (2017) Learning from Dioxin & PCBs in meat – problems ahead? IOP Conf. Ser.: Earth Environ. Sci. 85 012002. https://iopscience.iop.org/article/10.1088/1755-1315/85/1/012002/pdf

Weber R, et al. (2018) Reviewing the relevance of dioxin and PCB sources for food from animal origin and the need for their inventory, control and management. Environ Sci Eur. 30:42. https://rdcu.be/bax79

PCDD, PCDF and PCB Molecule $2 \rightarrow 0 \rightarrow 0^{9} \rightarrow 0^{8} \rightarrow 0^{7} \rightarrow$

• Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are highly **persistent** and **toxic** and **bioaccumulate** in meat, milk & eggs.

PCDF

- Due to these properties they were listed in the initial 12 POPs of the Stockholm Convention.
- PCDD/PCDFs were/are unintentionally formed in chlorine & organochlorine production, and thermal processes (e.g. waste incineration, metal industries etc.). Contaminated sites have been generated the last two centuries with risk for food and feed contamination.
- PCBs: 1.3 MT have been produced as technical PCB mixtures and more than 50% were released or disposed in landfills with related global contamination.

Weber, Gaus et al. (2008) Dioxin- and POP-contaminated sites—contemporary and future relevance and challenges Env Sci Pollut Res Int. 15, 363-393. <u>https://doi.org/10.1007/s11356-008-0024-1</u>

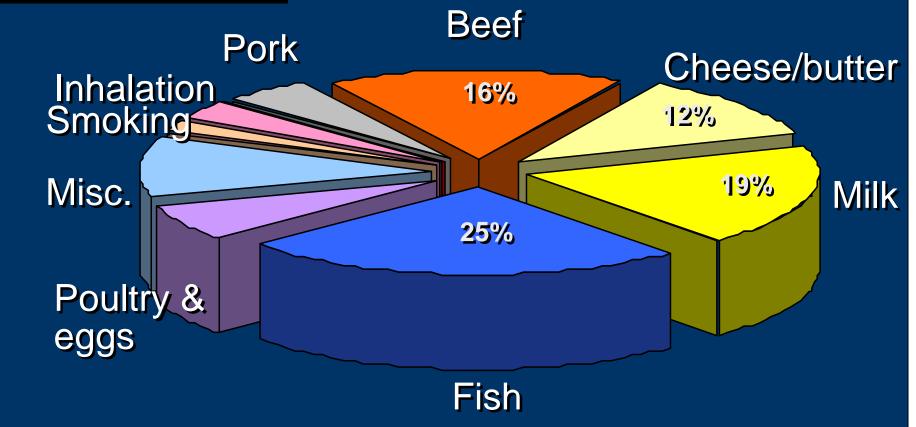
PCB

Human Background Exposure Dioxin/PCBs

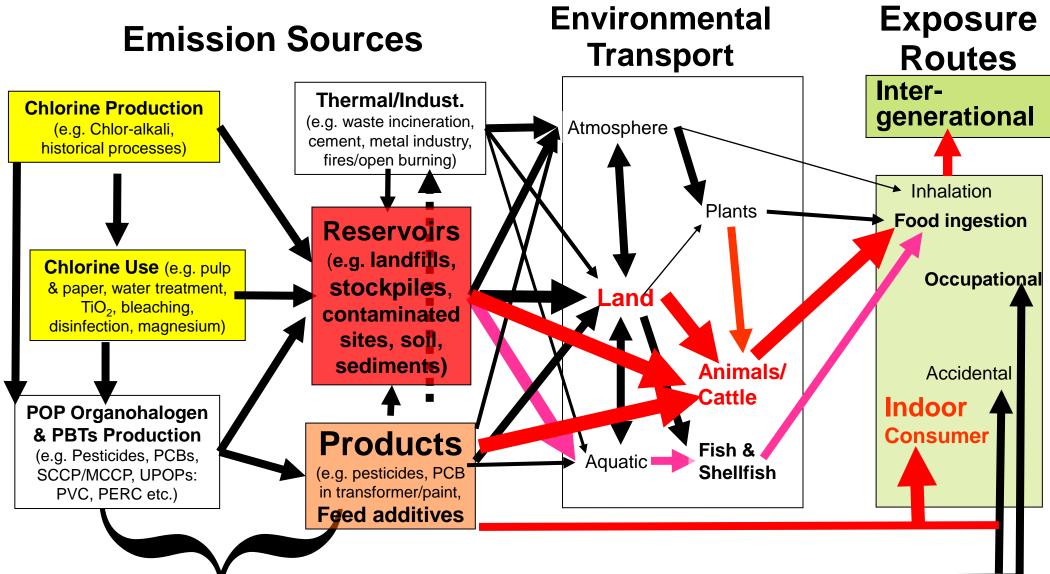


Human Dioxin exposure routes U.S.

- PCDD/F and PCBs are ubiquitous in fatty food.
- Bioaccumulate in top predators.
- Exposure depends on food habits.



"Life-Cycle" of PCDD/PCDF and other chlorinated POPs and Human Exposure



Weber et al. (2018) Reviewing dioxin/PCB sources for food. Environ Sci Eur. 30:42. https://rdcu.be/bax79

EU Regulation for PCDD/F and PCB

Regulations and limits are the legal base to define food as contaminated

- 2001: First EU maximum levels (ML) (only) for PCDD/F in food and feed 2375/2001/EC. Action level (AL) to trigger investigations.
- 2006: Additional maximum levels also for sum of PCDD/Fs and dioxin-like PCBs (dl-PCBs) in food and feed. ((EC) No 1881/2006)
- 2011: Amendments introducing WHO toxicity equivalency factors 2005 (TEF2005) and maximum levels for non-dioxin-like PCB (ndl-PCB) (Commission Regulation (EC) No 1259/2011).

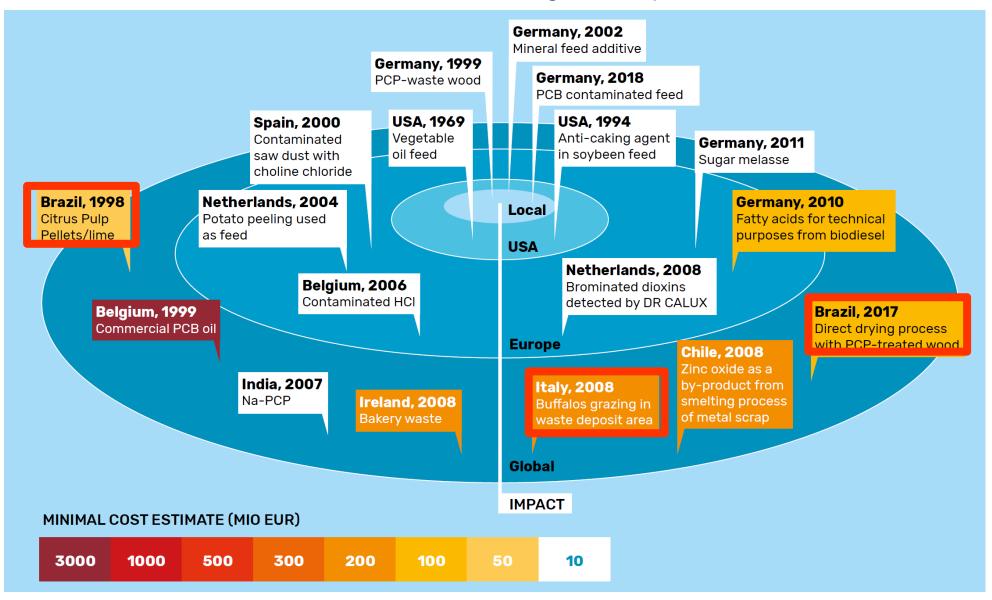
ML(I)	ML(I+II)	AL(I)	AL(II)
PCDD/F	PCDDF+PCB	PCDD/F	dl-PCB
2.5	4.0	1.75	1.75
1.75	3.0	1.25	0.75
1.0	1.25	0.75	0.5
2.5	4.0	1.75	1.75
2.5	5.5	1.75	2.0
	PCDD/F 2.5 1.75 1.0 2.5	PCDD/FPCDDF+PCB2.54.01.753.01.01.252.54.0	PCDD/FPCDDF+PCBPCDD/F2.54.01.751.753.01.251.01.250.752.54.01.75

The same levels apply to the fats derived from ruminants, poultry, and pork

South American meat is normally well below the EU regulatory limit but food contamination incidents.

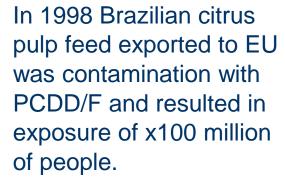
Dioxin and PCB Food and Feed Crises and Cost

• Dioxin food contamination in South America can have global impact and can costs in the 100 M\$ scale



Behnisch P, Brouwer B (2020) AFFIDIA - THE JOURNAL OF FOOD DIAGNOSTICS / 01 / 2020

Brazil Citrus Pulp case: Dioxin from contaminated sites contaminated international food chain



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The source was lime/CaO recovered/mined from a hazardous landfill of the organochlorine industry and sold to the feed and construction industry.

The case highlighted the lack of legislation, POP inventories and control of circular economy as well as the need of monitoring/ science capacity in Brazil. Changes happened then!

Torres et al. (2013) Env Sci Pollut Res. 20, 1958-1965

Dioxin in recycled ZnO contaminated meat in Chile & exports

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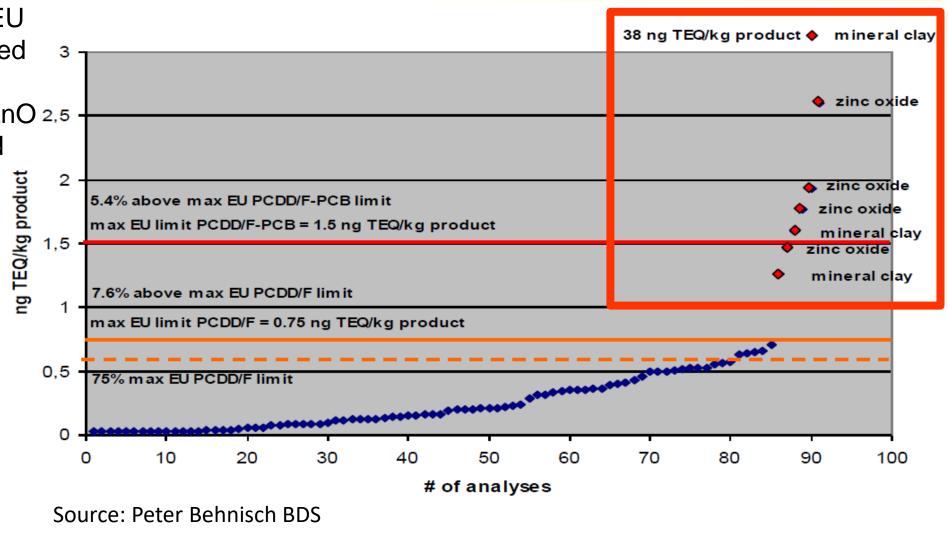
- Zinc oxide (ZnO) is partly used as feed additive, food supplement and fertilizer.
- ZnO can be produced from virgin ores or can be produced from recycling processes.
- The PCDD/F levels in ZnO produced from virgin ores for feed was between 0.008 ng TEQ/kg to 0.034 ng TEQ/kg and (CVUA Freiburg 2014).
- Contaminated ZnO used as feed additive in Chile was measured at 17,150 ng TEQ/kg (37,400 ng TEQ/kg considering non-detects) (Kim et al. 2009). This caused a large food contamination (mainly pork meat) in Chile resulting of ~200 million USD damage cost for meat production (Behnisch & Brouwer 2020).
- The source of such highly contaminated ZnO are zinc recycling processes such as the Waelz process. In the Waelz process a variety of scrap and secondary raw materials are used (e.g. ash from copper alloy production, EAF ash). Circular economy needs control & monitoring/science!



Kim (2009) Organohalogen Compounds 71, 173-176; CVUA (2014) Personal communication 6.11.2014 Behnisch P, Brouwer B (2020) AFFIDIA - THE JOURNAL OF FOOD DIAGNOSTICS / 01 / 2020 Chile established the dioxin bioassay in a laboratory and screened feed, feed additives and meat.

Several ZnO were above EU regulatory limit but contained 3 1000 times less PCDD/F compaired to the original ZnO 2.5 contaminating the pigs and pork meat.

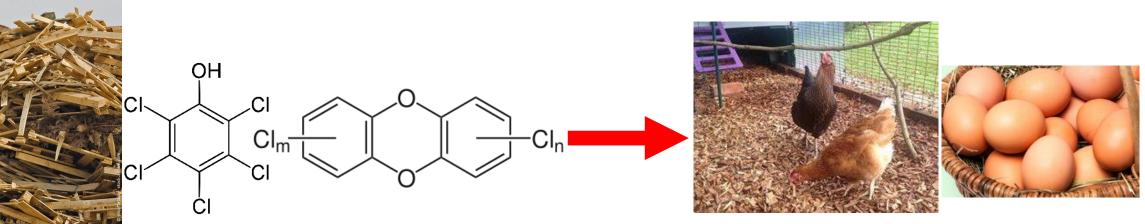




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PCP and dioxins in waste wood - Challenges with circular economy¹³

- Wood was/is (partly) treated with, PCP (contaminated with Dioxins), DDT, Lindan/HCH, Endosulfan, PCB, PCN, CCA & other hazardous chemicals.
- The use of PCP treated wood for drying of animal feed was the source of PCDD/PCDF contamination of Brazilian meat 2017 (~ 100 million USD) and other dioxin food cases in the EU (Behnisch P, Brouwer B (2020) AFFIDIA - THE JOURNAL OF FOOD DIAGNOSTICS / 01 / 2020)
- PCP treated waste wood has been recycled for bedding of chicken in Italy and Germany and resulted in dioxin contamination of eggs (Brambilla et al, 2010).
- PCP treated wood has been recycled as saw mill dust and used as a feed additive and contaminated chicken (Llerena et al. 2003).
- \Rightarrow Waste wood has several exposure pathways to livestock.
- Need legislation (in the EU limit for PCP in wood; regulation for waste wood in countries e.g Germany), Need of monitoring and a science based control of a circular economy (all three SA cases).



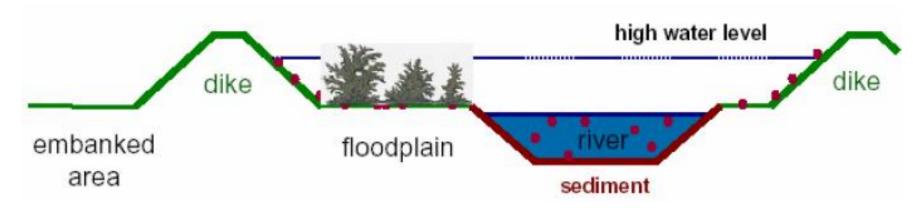
PCDD/F and **PCB – Feed** incidents and environmental exposure

- In the past: Often feed incidents were responsible for exceeding maximum levels of PCDD/Fs and PCBs in food of animal origin. This risk will continue in future (and the Chile pork crises showed)
- In recent years cattle/meat and chicken/eggs from free range production were found to exceed EU maximum limits.
 - E.g. Dioxins in food like mozzarella&meat in Campania region open waste burning "land of fire".
 - PCBs in cattle and dioxins/PCBs in chicken/egg in some areas in Germany
- The sources of contamination in Germany was often unclear. Therefore the German EPA issued a research project on investigating into contamination sources in the environment for livestock.
- Project report (Weber et al. 2015) including 80 pages research and policy needs.
 - (https://www.umweltbundesamt.de/publikationen/analysetrendabschaetzung-der-belastung-der-umwelt)
- Review article: Weber et al. (2018) Reviewing dioxin/PCB sources for food. Environ Sci Eur. 30:42. https://rdcu.be/bax79



Cattle & sheep raised on Elbe flood plains – research & science advice

- Alluvial soil in flood plains along 400 km of the river Elbe contaminated with high levels of PCDD/Fs (several 100 ng TEQ/kg dry matter in top layer and up to 7000 ng TEQ/kg in deep layer) from former magnesium production & organochlorine production in Bitterfeld region (released 1930s to 1950s).
 - PCDD/F levels in meat & milk of grazing cattle above EU maximum limit
 - Research to assess options for feed-harvest and cattle production on contaminated flood plains and for policy advice (Gude 2007, Kamphues 2011; Ungemach 2013)
 - Guidance document for agricultural use of flood-plain areas addressing e.g. restriction of grazing; cutting height for grass (for silage/hay) (Landwirtschaftskammer Niedersachsen 2010).



Source: Kamphues et al (2011) Organohalogen Compounds.

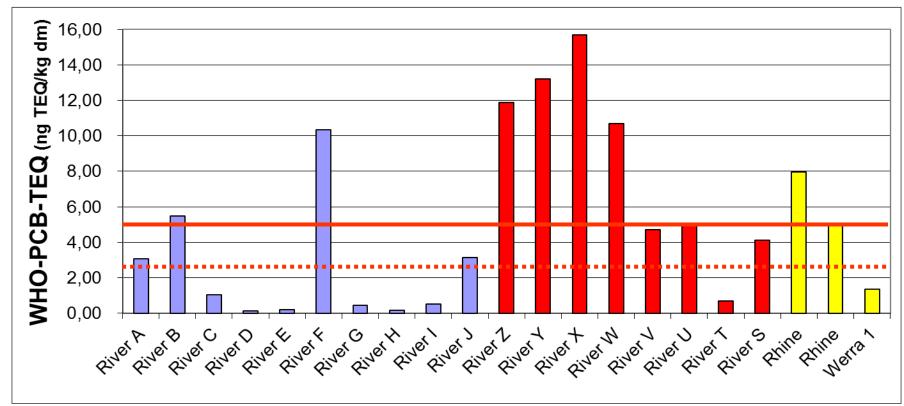
Cattle raised on flood plains impacted by industrially impacted rivers

- Further studies in flood plains of some German rivers: also on other floodplain of industrially impacted rivers meat of cattle and sheep exceeded the EU max. limits with dl-PCBs as main TEQ-contributor.
- Restriction/management of the use of the affected flood plains.



Systematic Assessment of contaminated areas: Flood plains of rivers in some German federal states From potentially contaminated soils only flood plains have been systematically assessed for dI-PCB/PCDD/F in some German federal states.

- Federal state A: 4 flood plain from 10 rivers had elevated dl-PCB-levels.
- Federal state B: 9 of 10 of assessed rivers had elevated dl-PCB-levels in soil.
- Federal state C: Elevated dI-PCB in flood plains of Rhine river (HLUG 2014).



Weber et al. (2018) Reviewing dioxin/PCB sources for food. Environ Sci Eur. 30:42. https://rdcu.be/bax79

PCB air emissions from open application and deposition on grass/feed and soils

Germany: 24000 t PCB in open uses sealants & paints from 1960 to 1970. Today still12000 t present releasing to 15 t of PCBs ever year to the environment pollutin soil and vegetation and livestock.



Exposure from soil



PCB paints Bild: Michael Bührket/pixelio.de

Bild: Thomas Max Müller/pixelio.de

PCB-Exposure

Direct exposure from point sources

Bild: Lunar Horse Media

Exposure from feed

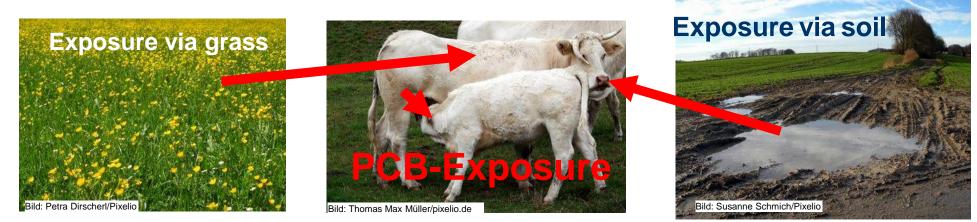


Weber et al. (2018) Life cycle of PCBs and contamination of the environment and of food products from animal origin Environ Sci Pollut Res Int. 25(17), 16325-16343 https://doi.org/10.1007/s11356-018-1811-y

d: Jochen Zellner /abfallbild.de

Problematic dl-PCB levels in soil and grass/feed for cattle

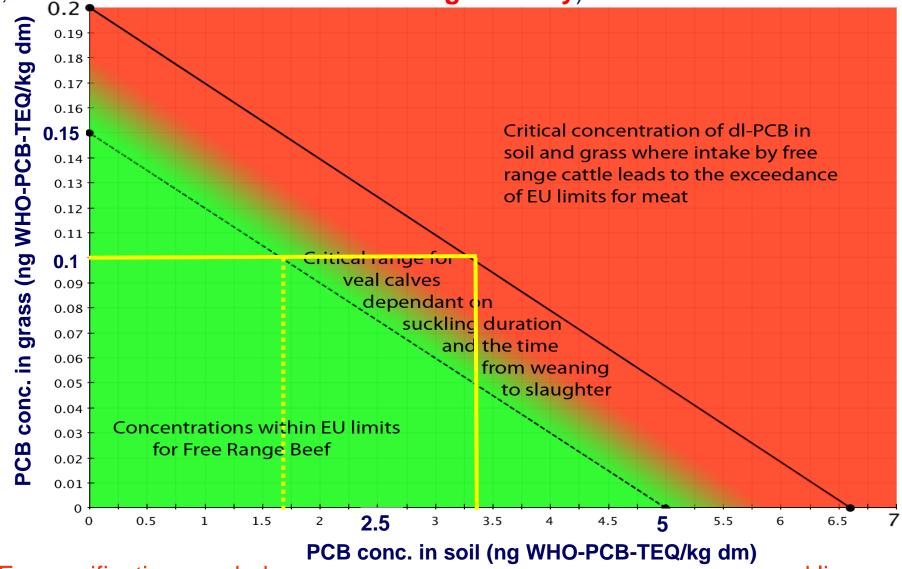
- Assessment of (dI-)PCB and PCDD/F levels in soil and grass/silages to derive critical exposure levels regarding exceedance of EU meat limits:
- dI-PCB levels in <u>soils</u> of flood plains and areas of other herds with dI-PCB TEQ levels exceeding EU standard without point sources were often between 2 to 6 ng WHO-PCB-TEQ/kg dm. Levels in <u>feed</u> in these cases were around/slightly below 0.2 ng WHO-PCB-TEQ/kg dm.
- Therefore meat of free range cattle (in particular when **calves are fed** by **milk of grazing cows** for a longer period) may exceed EU-regulatory limits at low soil levels (<5 ng PCB-TEQ/kg) and grass levels considerably below EU max. level (1.25 ng PCDD/F-dI-PCB-TEQ/kg).
 - Background soil levels are below 1 ng PCB-TEQ and not problematic.



Weber et al. (2018) Environ Sci Pollut Res Int. 25(17), 16325-16343 https://doi.org/10.1007/s11356-018-1811-y

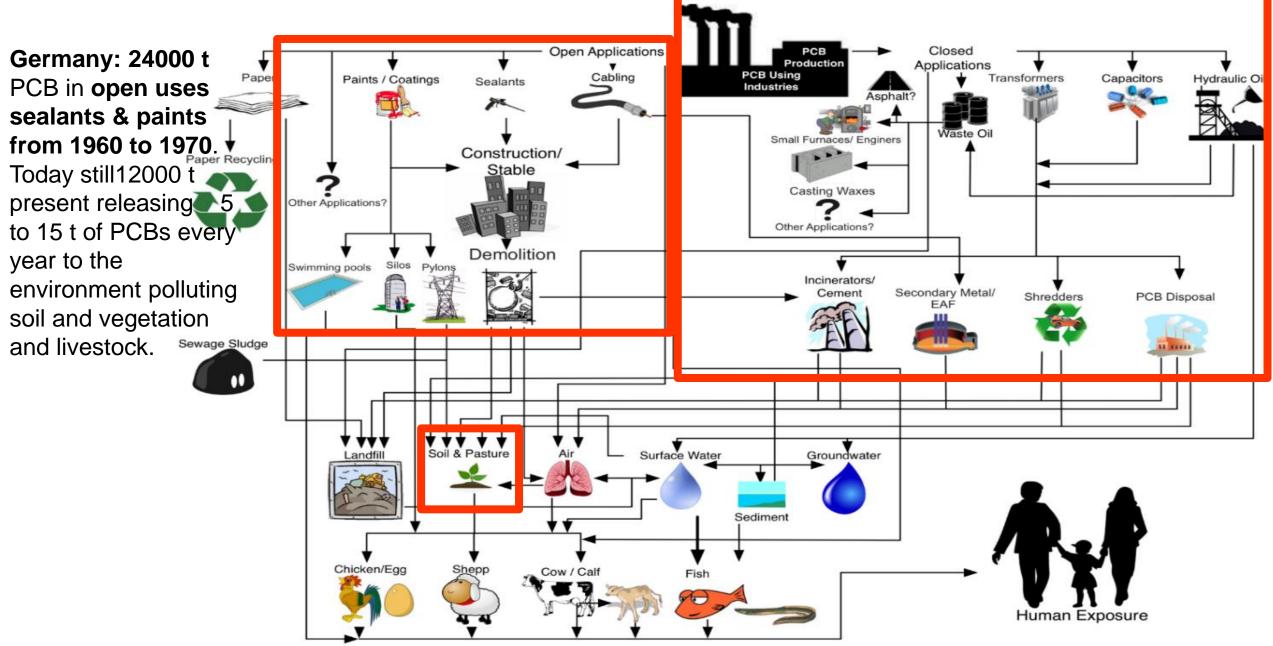
Problematic dl-PCB levels in grass and soil for cattle

Deduction of critical dI-PCB levels in grass and soil for **suckling cattle herds** (intake 10 kg grass/day with **3% soil**; based on **critical total intake of 2 ng TEQ/day**).



Exp. verification needed, particular for feeding in stable without long suckling period! Weber et al. (2018) Environ Sci Pollut Res Int. 25(17), 16325-16343 https://doi.org/10.1007/s11356-018-1811-y

Life cycle of PCBs - contamination of soils. food and human exposure⁴



Weber et al. (2018) Environ Sci Pollut Res Int. 25(17), 16325-16343 https://doi.org/10.1007/s11356-018-1811-y

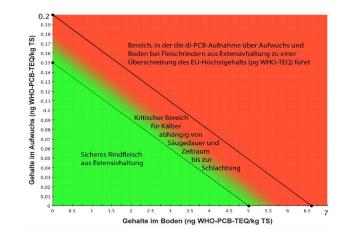
What is the reach of individual PCB and Dioxin emission sources (1)?

A key question is the reach of individual sources (considering the ca. 3 ng Dioxin/PCB-TEQ/kg soil; & 0.2 ng PCB-TEQ in grass). This is relevant to know if e.g. livestock breeding is impacted.

- For the PCB production sites the contamination and exposure via livestock in Brescia/Italy have been documented (Turrio-Baldassarri et al. 2009). Also for Anniston in the USA (ATSDR 2015).
- Emissions of the PCB production in Slovakia led to elevated PCB levels in humans up to 50 km in wind direction (Wimmerova et al. 2014).
- Assessment of details of soil contamination in the larger surrounding of most PCB production sites have not been published.

Kaneka





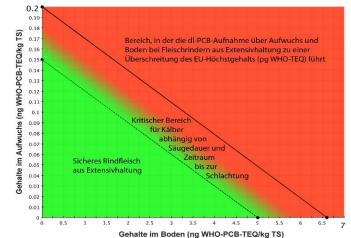
Weber et al. (2018) Environ Sci Pollut Res Int. 25(17), 16325-16343 https://doi.org/10.1007/s11356-018-1811-y

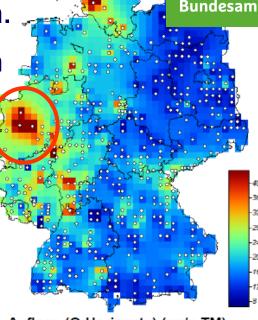
What is the reach of individual PCB and Dioxin emission sources (2)?

A key question is the reach of individual point sources (considering the ca. 2.5 ng PCB-TEQ/kg soil; and 0.2 ng PCB-TEQ in grass). This is in particular relevant to decide if livestock breeding is impacted /possible.

For a few sources the reach of the PCB-contamination has been assessed e.g.:

- Primary steel production Taranto/Italy: PCB/Dioxin-contamination led to the ban for grazing within 20 km from the industrial area (Esposito et al. 2014).
- Secondary steel production in Switzerland contaminated fishes with elevated PCB levels 30 km downstream (Zennegg et al 2011).
- Shredder plants contaminarte the surrounding a few hundred meters to km.
- PCB-release from Toronto/Canada had a measurable impact of 20 30 km into the surrounding. (Cziszar 2012; 2013)





Global review of PCDD/Fs & PCBs in free range eggs

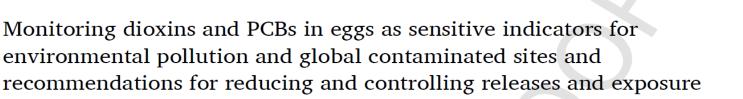


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Petrlik et al. (2022) Emerg. Contam. 8, 254-279 https://doi.org/10.1016/j.emcon.2022.05.001



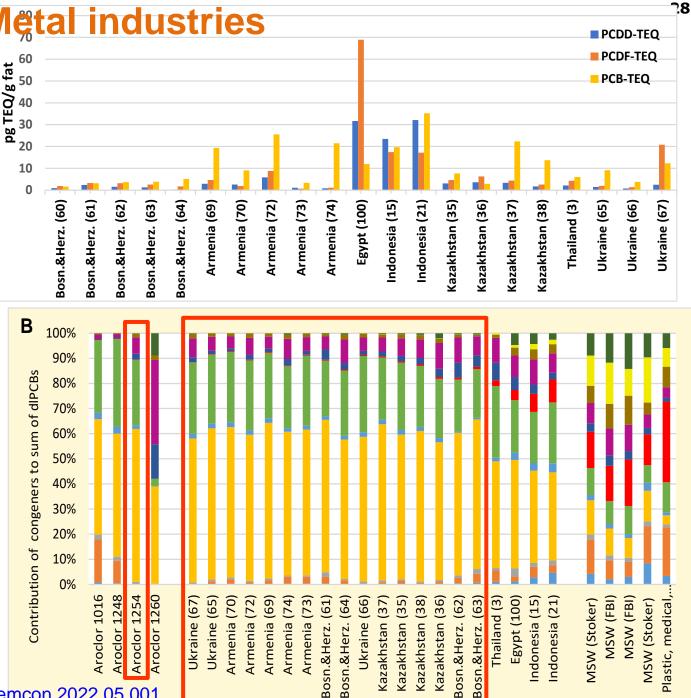
Rose Eckstein/ Pixelio

- Data on PCB & PCDD/F contaminated eggs were assessed from 20 years monitoring of IPEN & science literature.
- IPEN monitored 113 chicken flocks at potential PCDD/F- and PCB-contaminated sites and 88% of the pooled egg samples were above the EU maximum limits for PCDD/Fs (2.5 pg PCDD/F-TEQ/g fat) or the sum of PCDD/Fs and dioxin-like PCBs (5 pg PCDD/F-PCB-TEQ/g fat).
- Children consuming just one egg exceed the FAO/WHO TDI (based on 70 pg TEQ/kg month) and the EU tolerable weekly intake (TWI). This indicates that close to 90% of areas around these industrial emitters and open burning sources in developing countries were unsafe for the production of free-range eggs.

IPEN global egg study – Metal industries

- IPEN monitored 21 pooled chicken eggs around secondary metal smelters or steel industry in 7 countries (Armenia, Bosnia and Herzegovina, Egypt, Indonesia, Kazakhstan, Thailand, and Ukraine).
- All chicken flocks exceeded the EU regulatory limit with a high mean TEQ (26.0 pg TEQ/g fat). This indicates that all areas around these metal industries were unfit for free-range chicken farming.
- At 15 of the 21 sites commercial PCBs were the main TEQ contributor (mainly Arochlor 1254).
- This demonstrates that over the last 40 years PCBs have entered metal smelters on metal scrap with associated pollution of surrounding soils and chicken/eggs with exposure to humans.
- This highlights that the management of metals from PCB containing transformers, capacitors & other PCB contaminated metals need a better control and better cleaning of metal parts before they enter e.g. copper or aluminum smelters!!





Global egg study – E-waste recycling sites

- IPEN monitored 7 pooled eggs from chicken flocks at e-waste sites in 5 countries (Ghana, Kenya, Indonesia, Philippines, Thailand). The PCDD/F-PCB-TEQs were between 20.4 to 856 pg TEQ/g and therefore all eggs exceeded the EU regulatory limit. The mean TEQ was 308.4 pg TEQ/g fat and by far the highest mean/median TEQ of all source categories.
- Eggs at the Ngara e-waste dismantling market in Kenya were contaminated with 567.4 and 519.6 pg TEQ/g fat with 97.8 and 96.6% TEQ contribution from dI-PCB which are the highest dI-PCB levels ever measured in free-range eggs.
- With 855.8 pg TEQ/g fat in eggs from the e-waste site in Agbogbloshie (Ghana) where ewaste plastic parts/cables is frequently burned. The major TEQ contribution came from PCDD/Fs (661 pg TEQ/g fat) but also dl-PCBs were high (194.8 pg PCB-TEQ/g fat)
- This highlights that **e-waste sites in developing countries can be PCB hotspots** with associated exposure and stresses that PCB equipment need a better management there.





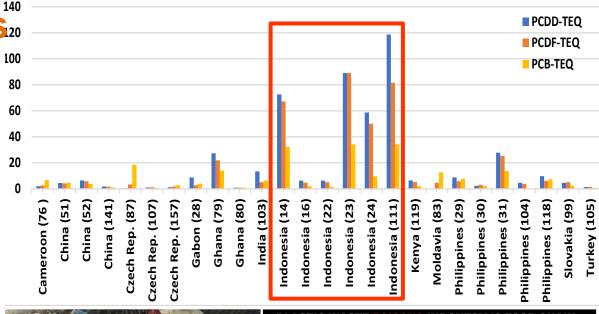
Petrlik et al. (2022) Emerging Contaminants https://doi.org/10.1016/j.emcon.2022.05.001



Global Egg Study – Waste Incinerators¹⁰

- 24 of 26 egg samples (92.3%) around waste incinerators in 12 countries (Cameroon, China (3), Czech Republic (3), Gabon, Ghana (3), India, Indonesia (6), Kenya, Moldova, Philippines (5), Slovakia, and Turkey) exceeded the EU limit for PCDD/Fs and dl-PCBs with a mean of 43.1 pg TEQ/g fat.
- Eggs in Tropodo/Indonesia where plastic wastes were used as fuel for tofu boilers had 234.4 and 172.0 pg TEQ/g fat. And two chicken flocks in Java, around lime kilns burning plastic waste as a fuel had 212.3 and 118.5 pg TEQ/g fat.
- The free-range chickens at both locations had access to ashes stored openly next to the kilns or used for paving sidewalks. The ashes contained PCDD/Fs at levels of 120 – 1300 ng TEQ/kg. This is up to 650 times above 2 ng TEQ/kg in soils considered acceptable for free-range chickens.
- This highlight that co-incineration of plastic waste in non-BAT facilities without air pollution control and ash management, releases high levels of PCDD/Fs in off gas and additionally via unmanaged ashes with associated environmental contamination and human exposure risk via chicken/eggs.

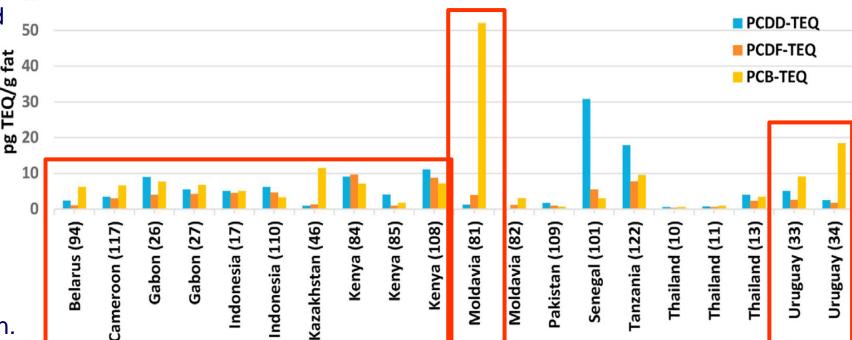
Petrlik et al. (2022) Emerging Contam. https://doi.org/10.1016/j.emcon.2022.05.001 & https://ipen.org/news/plastic-waste-poisons-indonesia%E2%80%99s-food-chain





Global Egg Study – landfills & dump sites (n=20)

- More than 50% of PCBs were not adequately managed and were disposed in landfills and dump sites in the past (Breivik et al. 2007). As semivolatile organic compounds PCB can migrate out of landfills over time.
- 16 of 20 pooled eggs sampled around landfills/dumps were above EU limit.
- In 12 of the 20 sites PCB-TEQ alone exceeded the EU TEQ-limit for eggs including two eggs from Uruguay.
- The highest contaminated eggs were sampled around a landfill in Moldova with 50 pg TEQ/g fat from dl-PCB.
- Also the eggs sampled around a landfill in Kazakhstan had more than 10 pg TEQ dl-PCB/g fat contamination.

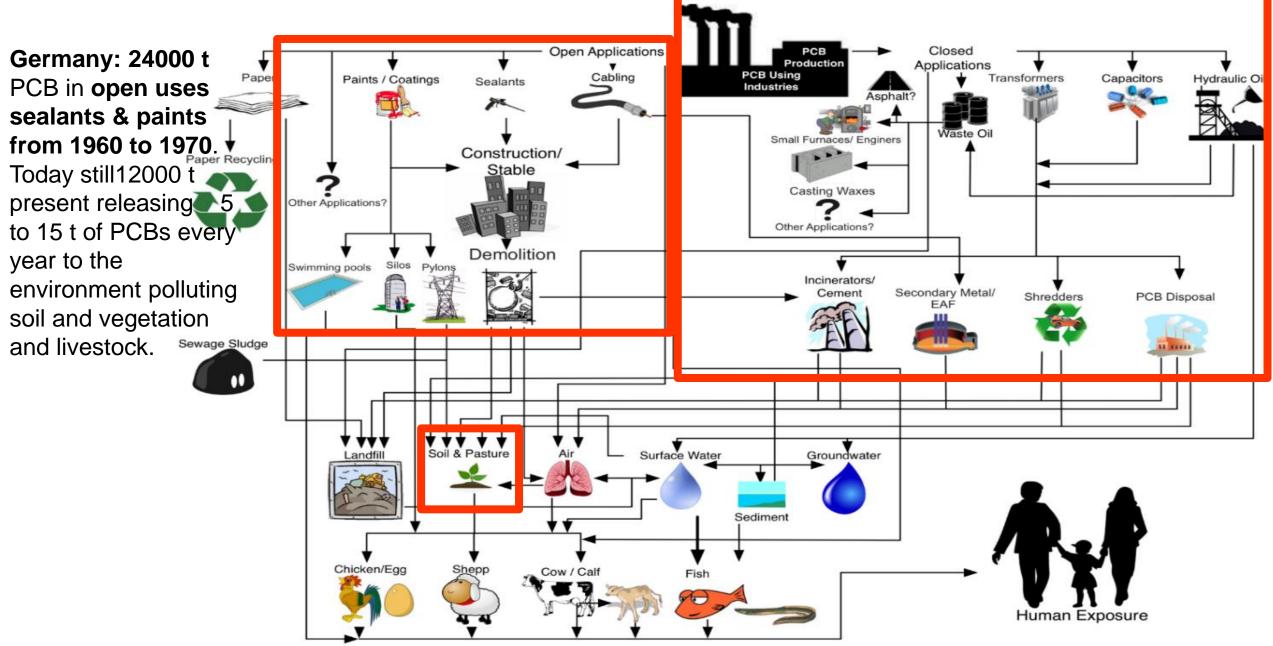


- Also in landfills in **Uruguay**, Belarus, Cameroon, and Gabon the TEQ contribution of PCBs was higher than the TEQ contribution of PCDD/PCDF.
- The high impact of PCB contamination in eggs around landfills and dump sites highlights that landfilling of PCB results in release and contamination of the surrounding with the very persistent and semivolatile PCBs. **Risk for livestock around landfills/dumps.**
- PCBs should not be disposed to landfills and dump sites since they evaporate over time and contaminated the surroundings.

Petrlik et al. (2022) Emerg. Contam. 8, 254-279 https://doi.org/10.1016/j.emcon.2022.05.001

Persistent Organic Pollutants (POPS) in Eggs: Report for Africa

Life cycle of PCBs - contamination of soils. food and human exposure²

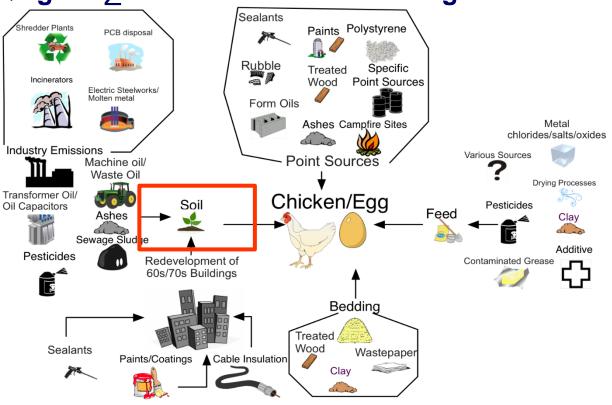


Weber et al. (2018) Environ Sci Pollut Res Int. 25(17), 16325-16343 https://doi.org/10.1007/s11356-018-1811-y

Science finding: Low PCDD/F & PCB levels in soil are already ³³ problematic for chicken egg/meat production – Policy action need

What are critical soil levels for impacting an egg above regulatory limit?

- With a total uptake of 25 pg (50 pg) TEQ/day a chicken reaches the current EU-limit of 2.5 pg (5 pg) for PCDD/F (sum PCDD/F-PCB) TEQ/g fat in egg.
- Free range chicken which spend a lot of time outdoor have a soil uptake of approx. 11-31 g soil/day.
- With a carry over of approx. 50% for TEQ-relevant PCB & PCDD/F the problematic levels in soils to reach EU limit for eggs (and meat) are approx. 3 to 7 ng TEQ/kg for ∑PCDD/F+PCB for free range chicken
- These problematic soil levels are low and **are exceeded in many areas of industrial emissions** and **can also be exceeded in residential areas or farms** (e.g. from ashes, pesticides, open burning or deposition).



Weber et al. (2018) Environ Sci Eur. 30:42. https://rdcu.be/bax79 ; Weber, Bell et al. (2019) Environ Pollut. 249, 703-715.

National PCDD/F limits in soil – need a better science base

34

 A major challenge is that the levels of contamination in the soil which result in contamination of chicken meat/egg above EU limits are below the current regulatory soil limits. Therefore an update is needed. What are Dioxin and PCB limit values in soil in GRULAC countries?

Canadian Environmental Quality Guidelines					
4 ng/kg TEQ	Alert level	ССМЕ, 2005а	а		
New Zealand Interim Accepta	nce Criteria				
10 ng/kg TEQ	Agricultural	MoE, 1997	b		
1,500 ng/kg TEQ	Residential	MoE, 1997	b		
18,000 ng/kg TEQ	Industrial	MoE, 1997	b		
Germany Federal and Lander	Germany Federal and Lander Ministers of the Environment recommendations				
5-40 ng/kg TEQ	Agriculture	EU, 1999	с		
100 ng/kg TEQ	Playgrounds	EU, 1999	с		
1,000 ng/kg TEQ	Residential areas	EU, 1999	с		
10,000 ng/kg TEQ	Industrial areas	EU, 1999	с		
The Netherlands Guidelines	The Netherlands Guidelines				
1,000 ng/kg TEQ	Residential and agricultural areas	EU, 1999	с		
10 ng/kg TEQ	Dairy farming	EU, 1999	с		
Sweden Generic Guidance Val	Sweden Generic Guidance Values				
10 ng/kg TEQ	Land with sensitive use	EU, 1999	с		

• In Germany and Netherland, for example, the regulatory limit for soil for residential areas is 1,000 ng PCDD/F-TEQ/kg dm. If chickens were kept on land with these levels, this could result in eggs with approx. 800 pg TEQ/g fat! For a 16 kg child a single egg (7 g fat) would exceed the TDI by 175 times.

Control/limit of PCDD/PCDF and dl-PCBs in fertilizers/biosolids³⁵

Fertilizer (including biosolids or ashes from biomass) can be a dioxin/POP source for agriculture.

- Therefore e.g. German developed a regulatory limits for fertilizers (DMG 2020) including limits for PCDD/s & dl-PCBs. Also a proposal for a fertilizer regulation in the EU has been developed.
- The "Basel low POP content" (15,000 ng TEQ/kg) is misleading and has also been derived with wrong assumptions (see Swedish EPA 2011; Lopez & Proença 2020; Wu et al. 2020; Weber et al. 2019).
- Need of science based unintentional trace limits for PCDD/PCDF (and PFOS/PFOA) in fertilizers.

Regulation	Pollutant	Limit value	Application/remark
Germany	a) PCDD/F + dl-PCB	30 ng TEQ/kg	All with exemption of b)
Germany	b) PCDD/F + dl-PCB	5 ng TEQ/kg	 b) pasture land and production of feed. & farmland without plowing
EU (2019)	PCDD/F	20 ng TEQ/kg	Fertilizer to land (JRC proposal)
Basel "low POP content"	PCDD/F	15,000 ng TEQ/kg	Misleading for further use; was wrongly derived!

JRC report EU fertilizer; ISBN 978-92-76-09888-1, doi:10.2760/186684, JRC117856

Swedish EPA (2011). *Low POP Content Limit of PCDD/F in Waste*. Report 6418; ISBN 978-91-620-6418. Lopes H, Proença S (2020) Appl. Sci. 2020, 10, 4951 https://doi.org/10.3390/app10144951; Wu et al. Emerg. Contam. 6, 235-249. https://doi.org/10.1016/j.emcon.2020.07.001; Weber et al. (2019) Environ Pollut. 249, 703-715.

• Regulatory limit for PCDD/F, PFOS/PFOA in fertilizer in any GRULAC country? Ash management?

31 POPs listed in the Stockholm Convention (04/2023)

Chemical	Pesticides	Industrial chemicals	Unintentional production	Annex
DDT	+			В
Aldrine, Dieldrine, Endrine	+			A
Chlordane, Chlordecone, Toxaphene	+			A
Alpha-, Beta-, Gamma-HCH	+		By-product of lindane	A
Endosulfan, Heptachlor, Mirex	+			A
Pentachlorophenol (PCP), <u>Dicofol</u>	+	+		A
Commercial PentaBDE		+		Α
Commercial OctaBDE (Hexa/HeptaBDE)		+		A
Commercial DecaBDE		+		A
Hexabromobiphenyl (HBB)		+		A
Hexabromocyclododecane (HBCD)		+		A
PFOS, its salts and PFOSF	+	+		В
PFOA and related compounds				A
PFHxS and related compounds		+		A
Short chain chlorinated paraffins		+		Α
PCB, PeCBz, HCB, PCN, <u>HCBD</u>	+	+	+	A/C
PCDD, PCDF			+	С

For most of the POPs, food is the major exposure pathway. Therefore for some POPs, food regulatory limits have been established for exposure control.

Regulatory limits in food drive the relevance for assessing food contamination and making the compound group relevant for the food and feed industry as well as relevant for contaminated sites (exposure relevant soil, feed, food).

Regulatory limits in food exist for

- (POP)Pesticides
- PCDD/PCDF (2001; EU)
- PCBs (2006; EU)
- PFOS, PFOA (12/2022 EU)

The EU regulatory limits are often applied by other countries to control imports.

POPRC: Chlorpyrífos, MCCP, LC-PFAA. COP: Methoxychlor; UV328, Dechlorane Plus

EU Maximum limits for PFOS, PFOA, PFHxS & PFNA in food

Regulations and limits are the legal base to define food as contaminated and the driver for monitoring

- 12/2022: First EU maximum levels (ML) (only) for PFAS in foodstuff "COMMISSION REGULATION (EU) 2022/2388 maximum levels of perfluoroalkyl substances in certain foodstuffs".
- Maximum levels in food for sum of PFOS, PFOA, PFHxS and PFNA were set to ensure a high level of human health protection taking the tolerable weekly intake of the EFSA (4.4 ng/kg ∑4 PFAS) in account.

			Maxim	um Levels µ	g/kg wet wei	ght
	Foodstuffs ⁽¹⁾	PFOS *	PFOA *	PFNA *	PFHxS *	Sum of PFOS, PFOA, PFNA and PFHxS * [,] **
10.3.1	Meat of bovine animals, pig and poultry	0,30	0,80	0,20	0,20	1,3
10.3.2	Meat of sheep	1,0	0,20	0,20	0,20	1,6
10.3.3	Offal of bovine animals, sheep, pig and poultry	6,0	0,70	0,40	0,50	8,0
10.3.4	Meat of game animals, with the exception of bear meat	5,0	3,5	1,5	0,60	9,0
10.3.5	Offal of game animals, with the exception of	50	25	45	3,0	50
10.1	Eggs	1,0	0,30	0,70	0,30	1,7

Due to the decrease in PFAS TWI - food and low detection limits

- Due to the decrease in PFAS TWI and exceedance of TWI, low food limits were set and the detection limits in the PFAS analysis needed to be lowered to low ppt (ng/g).
- This will result in frequent detection of PFAS in food (European and imported food/meat) with related risk of exceeding the food limits. Would be a nightmare for the food/meat industry.

Improved analytical methods to reduce PFAS detection limits in food (Netherlands)

Old method	New method
 -1 g sample -1 mL reconstitution -Old generation LC-MS/MS -Contaminated solvents -Slow elution on a small-particle column -2.5 ppb internal standard 	 -10 g sample -0.4 mL reconstitution -New generation LC-MS/MS -Higher quality solvents -Fast elution on an ultra small-particle column -5 ppt internal standard
Challenges - Lowering LOQs - Background contamination (mainly PFOA) - Contamination from isotopically labeled internal standards	Outcome Signal

Kause et al (2022) PFAS analysis at low ppt level in fruits and vegetables

Science: PFAS pollution crossed Planetary 100.000 Boundaries (the safe operating space of humanity) 100.000

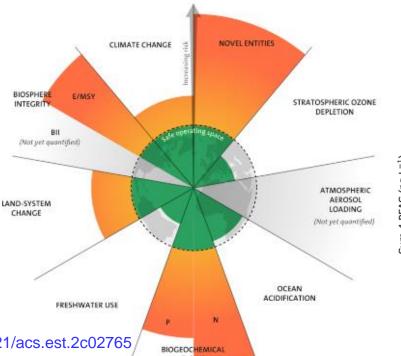
For four PFASs (PFOS, PFOA, PFHxS, PFNA), it is concluded that the global spread of these four PFASs has led to exceedance of the **planetary boundary for PFAS pollution because**:

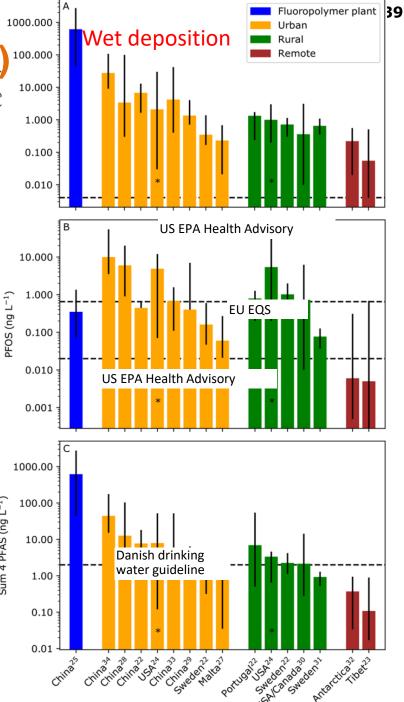
 levels of PFOA and PFOS in rainwater often greatly exceed US Environmental Protection Agency (EPA) suggested Lifetime Drinking Water Health Advisory levels (0.004 ng/L PFOA) and the Σ4 PFAS in rainwater is often above Danish drinking water limit of 2 ng/L Σ4 PFAS

2) levels of PFOS in rainwater are often above Environmental Quality Standard for Inland European Union Surface Water (0.65 ng/L PFOS);.

3) atmospheric deposition also leads to global soils being ubiquitously contaminated and to be often above proposed Dutch guideline values.

Cousins et al. (2022) Environ. Sci. Technol. https://doi.org/10.1021/acs.est.2c02765





Inventory of PFAS contaminated ground/drinking water in the US

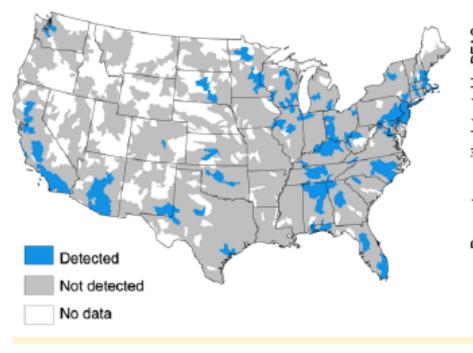
- Based on more than 36,000 water samples collected by the U.S. EPA (2013–2015), the drinking water supplies for 6 million U.S. residents exceed US EPA's lifetime health advisory of 2016 (70 ng/L) for PFOS and PFOA.
- Considering EFSA & CDC assessment, this was still 10-100 times too high (CDC 2017; EFSA 2020; Grandjean & Budtz-Jørgensen 2013).
- US EPA updated interim Health Advisory 2022: PFOA 0.004 ng/L







Hydrological units with detectable PFASs





Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

Xindi C. Hu,^{*,†,‡} David Q. Andrews,[§] Andrew B. Lindstrom,^{\parallel} Thomas A. Bruton,^{\perp} Laurel A. Schaider,[#] Philippe Grandjean,[†] Rainer Lohmann,[@] Courtney C. Carignan,[†] Arlene Blum,^{\perp, ∇} Simona A. Balan,[•] Hu et al. Environer Scherchridlereit. SDOI: 10. 1021/acs.estlett.6b00260; August 9, 2016

Assessment of PFAS contaminated drinking water US

Estimated population-wide exposure to PFOA and PFOS from drinking water in the United States

10

PFOA+PFOS concentration (ng/L)

41

300

250

200

150

100

50

0

Letter

millions

Population in

- Study estimate that 18-80 million people in the US receive tap water with 10 ng/L or greater concentration of ∑PFOA + PFOS, and
- Over 200 million people in US likely receive water with a ∑PFOA + PFOS concentration at or above 1 ng/L.
- Status of drinking water levels and limits for PFOS and PFOA in GRULAC countries?

100

Population-Wide Exposure to Per- and Polyfluoroalkyl Substances from Drinking Water in the United States

David Q. Andrews* and Olga V. Naidenko

Science & Technology | + | |+ K

pubs.acs.org/journal/estlcu

Andrews & Naidenko (2020) Environ. Sci. Technol. Lett https://doi.org/10.1021/acs.estlett.0c00713

Source of PFAS in water in USA: contaminated sites from 50 years of use ⁴² Presumptive Contamination Sites (n=57,412)

More than 57,000 sites of presumptive PFAS contamination were identified:

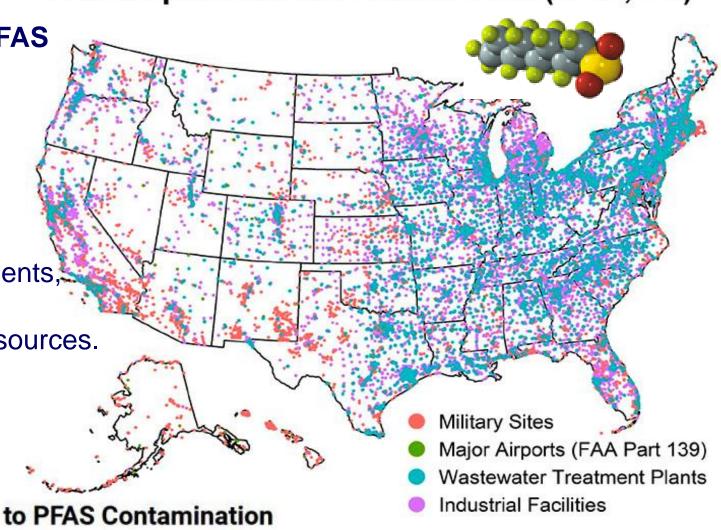
- 49,145 industrial facilities,
- 4,255 wastewater treatment plants,
- 3,493 current or former military sites, and
- 519 major airports.
- This conceptual approach allows governments, industries, and communities to rapidly and systematically identify potential exposure sources.



Presumptive Contamination: A New Approach to PFAS Contamination Based on Likely Sources

Derrick Salvatore, Kira Mok, Kimberly K. Garrett, Grace Poudrier, Phil Brown, Linda S. Birnbaum, Gretta Goldenman, Mark F. Miller, Sharyle Patton, Maddy Poehlein, Julia Varshavsky, and Alissa Cordner*

Salvatore et al. (2022) Environ. Sci. Technol. Lett. 9, 11, 983–990; https://doi.org/10.1021/acs.estlett.2c00502

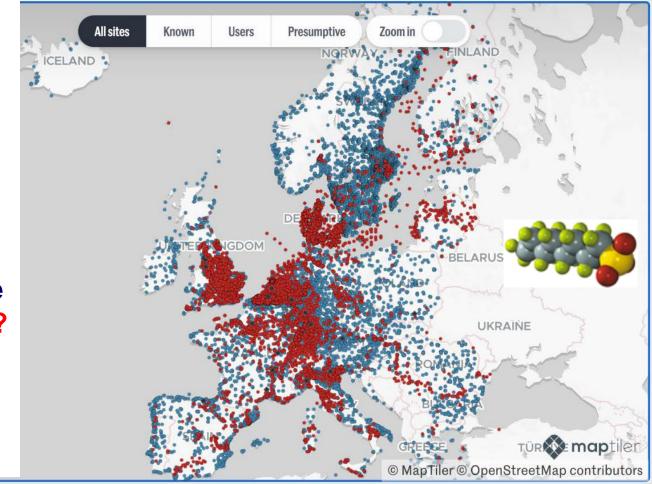


Presumptive PFAS contaminated sites in Europe "Map of Forever Pollution"

With the same methodology a European journalist consortium published 02/2023 a map of PFAS contaminated sites in Europe in major newspapers and website.

In total they documented:

- >17,000 known contaminated sites,
- > 2,100 hotspot clusters,
- Plus > 21,000 presumptive contaminated sites presumed to be contaminated on the basis of scientific investigations and expert advice without sampling data.
- How many PFAS contaminated & presumptive contaminated sites exists in GRULAC region?
- What are the risks for humans and livestock?
- Research need considering new EU limits!

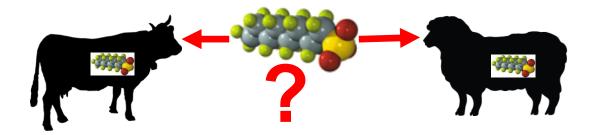


🛑 Known contamination 🛛 🛑 Known PFAS User 🔵 Presumptive contamination 🔶 PFAS manufacturing facility

https://www.lemonde.fr/en/les-decodeurs/article/2023/02/23/forever-pollution-explore-the-map-of-europe-s-pfas-contamination_6016905_8.html

POPs with high risk for food & feed production

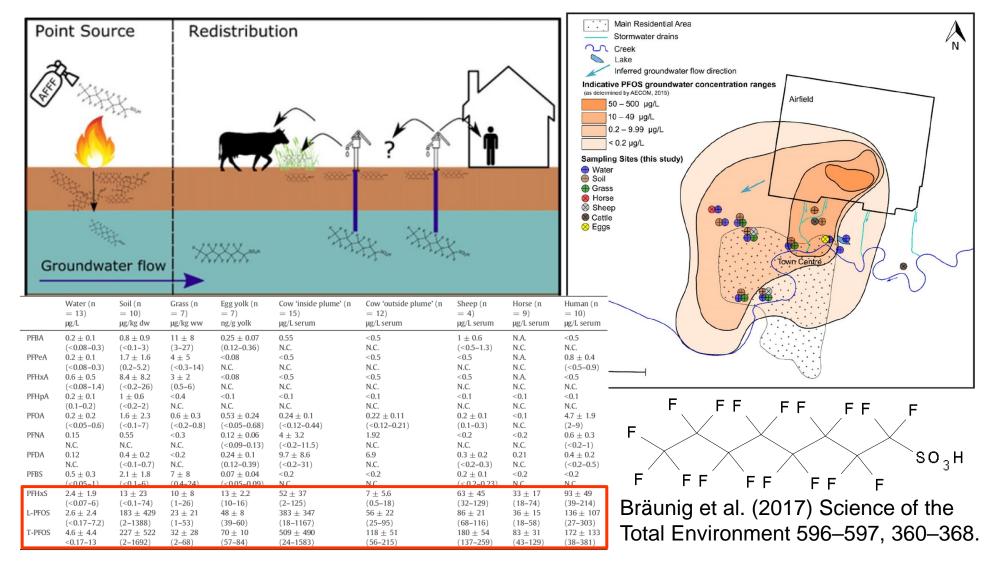
- The risk of PFOS and PFOA for food and feed considerable increased since the European Food and Safety Agency (EFSA) has significantly reduced the Tolerable Daily/Weekly Intake (TDI/TWI) by a factor of 100 and 1500 respectively, resulting that a (large) share of population now is above this TWI. (EFSA 2018 a,b). Food is likely a major contributor.
- The detection limit for PFOS and PFOA in meat/other food needed to be reduced from 1000 ng/kg to 10 ng/kg. Data from GRULAC region at this limit?
- The risk seems high in Brazil for PFOS where still large amounts of PFOS precursors are used against leaf cutting ants which released up to 487 t of PFOS to the Brazilian environment 2004 to 2015 (Loefstedt Gilljam et al 2016) with risk for PFOS exposure to food producing animals.
- Overall assessment needed for accumulation of the water-soluble PFOS/PFOA via different pathways in the food chain finally reaching cattle and chicken in food production.



EFSA (2020) Risk to human health related to the presence of perfluoroalkyl substances in food. *EFSA Journal 2020;18(9):6223* https://doi.org/10.2903/j.efsa.2020.6223 Loefstedt Gilljam (2016) Environ. Sci. Technol. 50 (2), 653–659;

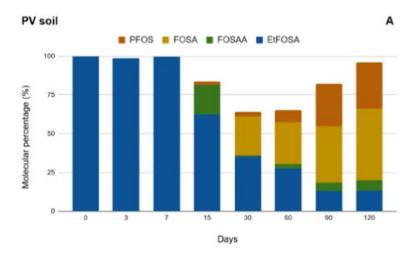
PFAS Contaminated ground water/soil – impact on farms

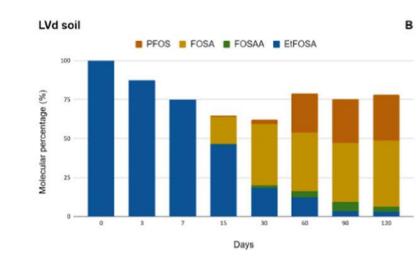
 Studies on farms where ground water/soil is contaminated resulted in high levels of PFOS and other PFAS in cattle. Also contaminated lakes/fish.



Risk from use of PFOS precursor sulfluramide pesticide in Brazil/SA ⁴⁷

- Brazil has granted an acceptable purpose exemption for using PFOSF to produce sulfluramid (EtFOSA) and to apply approx. 30 tonnes/year as insecticide to control leaf-cutting ants.
 EtFOSA used as ant baits release PFOS in Brazilian agricultural soils
- Sulfluramide degrade to PFOS within a few months and contaminate soils and the wider environment with long term risk for cattle and feed (e.g. soybeans).





Guida et al (2023) Chemosphere 325, 138370

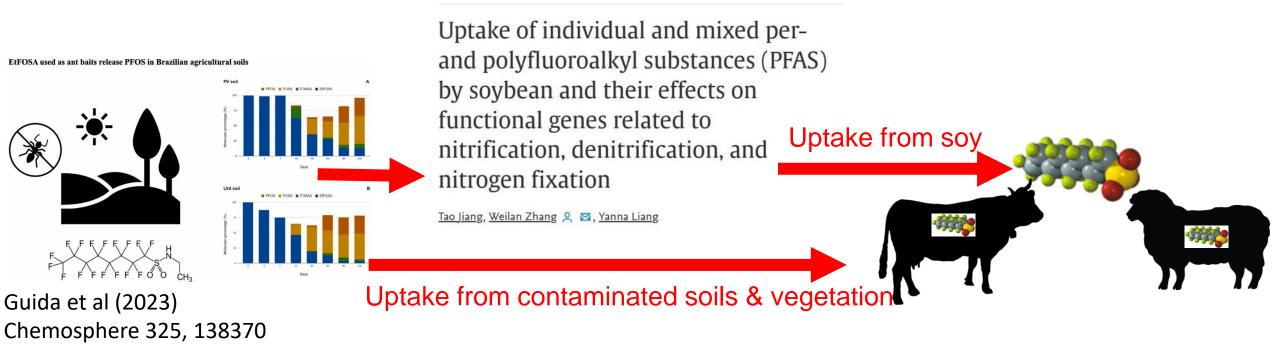
PFAS are taken up by soy beans – relevance for livestock?

• PFAS can be taken up by soybeans from soil and accumulate in the beans, roots and shoots.

48

- Shorter chain PFAS generally had a higher transfer factor than longer chain PFAS.
- Therefore PFOS, PFOA and other PFAS contamination in soils, groundwater and surface water are a risk for feed and food/meat production in Brazil and other South American countries.





Jiang et al. (2022). Science of The Total Environment, 838, 156640.

Challenges with PFOS/PFAS contaminated sites & exposure

- In our review article we compiled information on PFOS exposure pathways and transfer factors from environmental matrices (in particular soil) for different food producing animals.
- PFOS is accumulating in the foodchain and the exposure via soil and plant uptake of livestock can be the major exposure pathway for humans in areas where soil is contaminated.
- The same is true for PFOA and other bioaccumulative PFAS (PFHxS, PFNA).
- Short chain PFAS accumulate in plants.



Review

Pathways and factors for food safety and food security at PFOS contaminated sites within a problem based learning approach

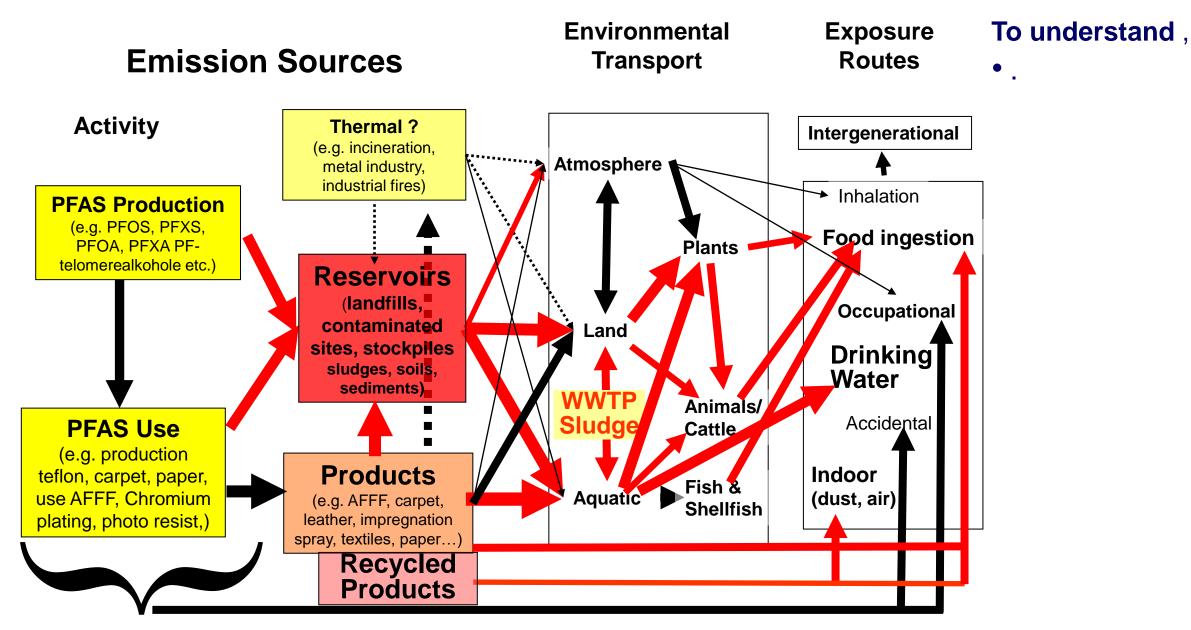


Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH

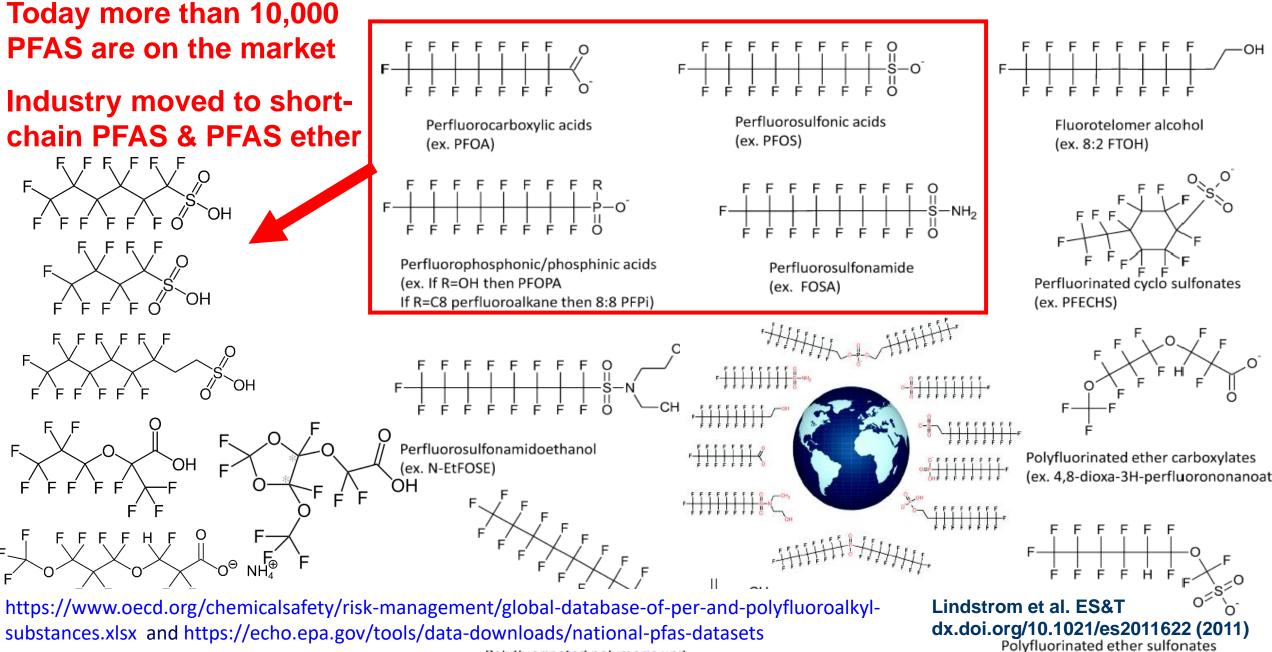
Stephan Brendel^{*}©, Éva Fetter, Claudia Staude, Lena Vierke and Annegret Biegel-Engler

Gianfranco Brambilla ^{a,*}, Wendy D'Hollander ^b, Fardin Oliaei ^c, Thorsten Stahl ^d, Roland Weber ^e

Life-Cycle of PFOS, PFOA and other PFAS



Other PFAS have substituted PFOS and PFOA



Polyfluorinated polymeric unit

Challenges with PFOS/PFAS contaminated sites & exposure

- In our review article we compiled information on PFOS exposure pathways and transfer factors from environmental matrices (in particular soil) for different food producing animals.
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- Short chain PFAS accumulate in plants.



Review

Pathways and factors for food safety and food security at PFOS contaminated sites within a problem based learning approach



Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH

Stephan Brendel^{*}©, Éva Fetter, Claudia Staude, Lena Vierke and Annegret Biegel-Engler

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The Madrid Statement on PFASs

The Madrid Science Statement on PFASs (2015):

- Documents the scientific consensus regarding the persistence and potential for harm of PFASs
- Lays out a roadmap to gather needed information and prevent further harm. <u>Recommendation to</u> <u>policy makers, industry, science...</u>
- Dialogue with industry (Fluorocouncil)

http://ehp.niehs.nih.gov/1509934/ http://ehp.niehs.nih.gov/1509910/ http://ehp.niehs.nih.gov/1510207/

Madrid Statement signed by >250 scientis and coordinated by Green Science Policy Institute http://greensciencepolicy.org/Madrid-Statement

Perspectives Brief Communication

2015: Environmental Health Perspectives

The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

http://dx.doi.org/10.1289/ehp.1509934

Arlene Blum,^{1,2} Simona A. Balan,² Martin Scheringer,^{3,4} Xenia Trier,⁵ Gretta Goldenman,⁶ Ian T. Cousins,⁷ Miriam Diamond,⁸ Tony Fletcher,⁹ Christopher Higgins,¹⁰ Avery E. Lindeman,² Graham Peaslee,¹¹ Pim de Voogt,¹² Zhanyun Wang,⁴ and Roland Weber¹³



Environ. Sci. Technol. Lett. 2020, 7, 532–543

pubs.acs.org/journal/estlcu https://doi.org/10.1021/acs.estlett.0c00255

Global Perspective

Scientific Basis for Managing PFAS as a Chemical Class

Carol F. Kwiatkowski,* David Q. Andrews, Linda S. Birnbaum, Thomas A. Bruton, Jamie C. DeWitt, Detlef R. U. Knappe, Maricel V. Maffini, Mark F. Miller, Katherine E. Pelch, Anna Reade, Anna Soehl, Xenia Trier, Marta Venier, Charlotte C. Wagner, Zhanyun Wang, and Arlene Blum

Regulate PFAS as a group and allow only essential use

Madrid Statement recommendations for policy makers:

• Enact legislation to require <u>only essential uses</u> of PFASs and <u>enforce labelling to indicate uses.</u>

Perspectives Brief Communication

http://ehp.niehs.nih.gov/1509934/ The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

http://dx.doi.org/10.1289/ehp.1509934

 The EU Commission in its chemicals strategy (2020) for sustainability towards a toxic-free environment suggests to address PFAS as a group. With the following action: phasing out the use of PFAS in the EU, <u>unless their use is essential.</u>

https://ec.europa.eu/environment/strategy/chemicals-strategy_en#ecl-inpage-238 PFAS: https://ec.europa.eu/environment/chemicals/pfas/index_en.htm

Brussels, 14.10.2020 COM(2020) 667 final



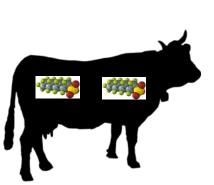
COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS

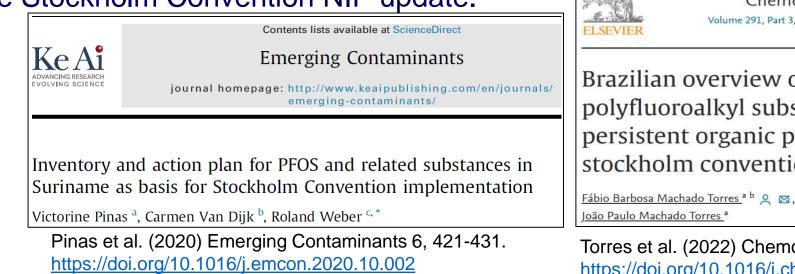
> Chemicals Strategy for Sustainability Towards a Toxic-Free Environment

• February 2023: ECHA publishes details of a **proposed restriction of around 10,000 PFASs!** Available on ECHA's website https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal ECHA's scientific committees will now start evaluating the proposal in terms of the risks to people and the environment, and the impacts on society. **Regulatory Activities in GRULAG?**

PFOS/PFOA and other **PFAS** research needs for GRULAG region

- What is the PFOS, PFOA and other PFAS situation in GRULAG region? Exposure level/risks?
- What is the status and long term risk and long term fate of PFOS from the approx. 500 tonnes of Sulfluramide use in Brazil in the past? What is the situation in other GRULAG countries?
- What are current PFOS and PFOA levels in South American meat (beef, chicken, pork)? Do they meet the new EU food standards? Future development considering PFAS mobility?
- What is the PFOS, PFOA and other PFAS contaminated site situation in GRULAG region and what is the risk for humans but also for food (meat/soy) production?
- GRULAG region has limited analytical capacity! How to assess PFOS, PFOA & other PFAS?
- The assessment could start with an inventory of PFOS, PFOA and PFHxS in the frame of the Stockholm Convention NIP update.





Chemosphere Volume 291, Part 3, March 2022, 132674

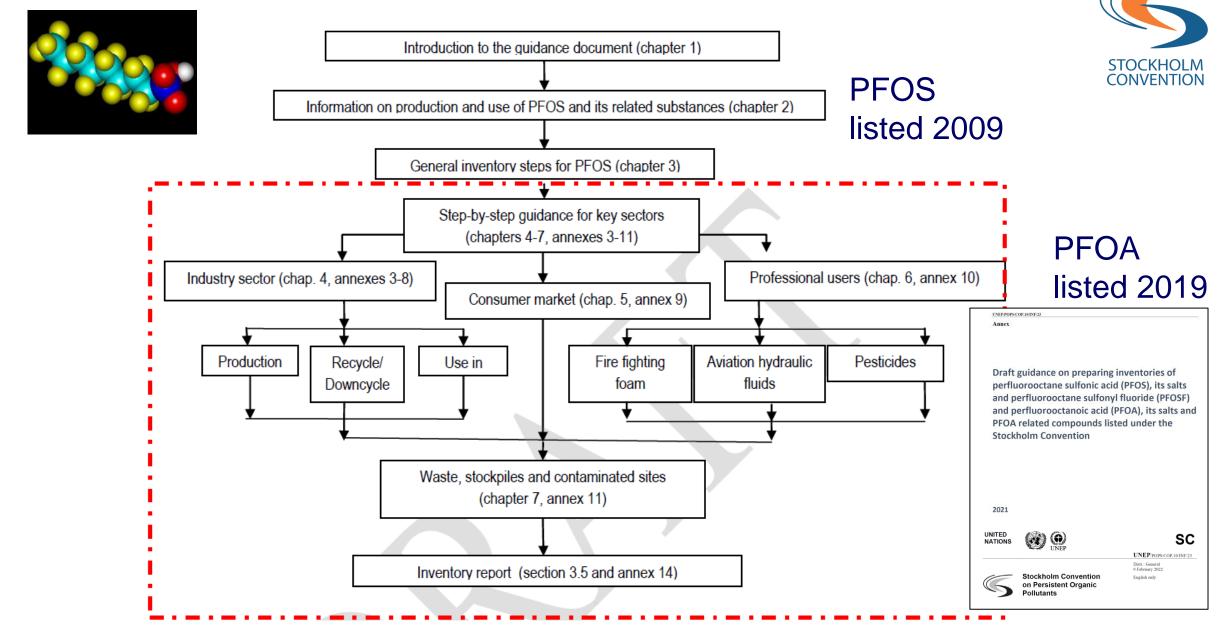


Brazilian overview of per- and polyfluoroalkyl substances listed as persistent organic pollutants in the stockholm convention

Fábio Barbosa Machado Torres ^{a b} 2 🖾 , Yago Guida ^{a b}, Roland Weber ^c,

Torres et al. (2022) Chemosphere 291, 132674. https://doi.org/10.1016/j.chemosphere.2021.132674

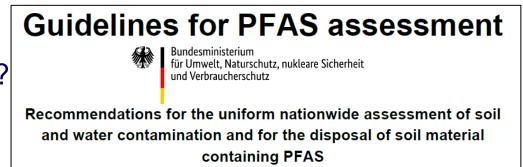
Inventory/Assessment of PFOS and PFOA in SC



http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/tabid/2882/Default.aspx

PFOS/PFAS assessment – policy needs and research opportunity

- How to control PFOS/PFAS in products that inventories and circular economy management becomes feasible (e.g. textiles, carpets)? Large challenges of PFOS, PFOA and overall PFAS inventory in articles and products – no/limited labelling. What are options/limitation?
- Only few country have developed standards for PFOS/PFOA in articles! EU did not succeed to develop a validated CEN standard for PFOS in products (waiting for validation since 5 years).
- There are several 100 PFOS and PFOA precursor chemical. For only a few of these precursors chemicals an analytical method is available.
- Research need: Developing validated measurement standards for PFOS/PFOA and precursors and other PFAS (research & industry). Options: Total Oxidizable Precursor (TOP) Assay.
- GRULAG region has limited analytical capacity! How to appropriately assess the threats and the pollution of PFOS, PFOA and other PFAS?
- What regulatory limits to set for PFOS, PFOA and other PFAS for drinking water, food or soil in GRULAC region? Science based assessment and selection.



Workshop on "From Science to Action" for the BRS and industrial chemicals guidance for the Stockholm Convention, 12-14 April 2023, Buenos Aires

Thank you for your attention! Questions?

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SCIENCE TO ACTION



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