Anthropogenic Pollutants in the Environment

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What are the questions ?

What is a contaminant ?

Chemical which is foreign to the environment in which it is released, or which significantly raises the background concentration of the natural chemical in the environment.

How mobile is it ?

Is it transported in the atmosphere ? In water ? On particles ? At what rate ? What slows it down ?

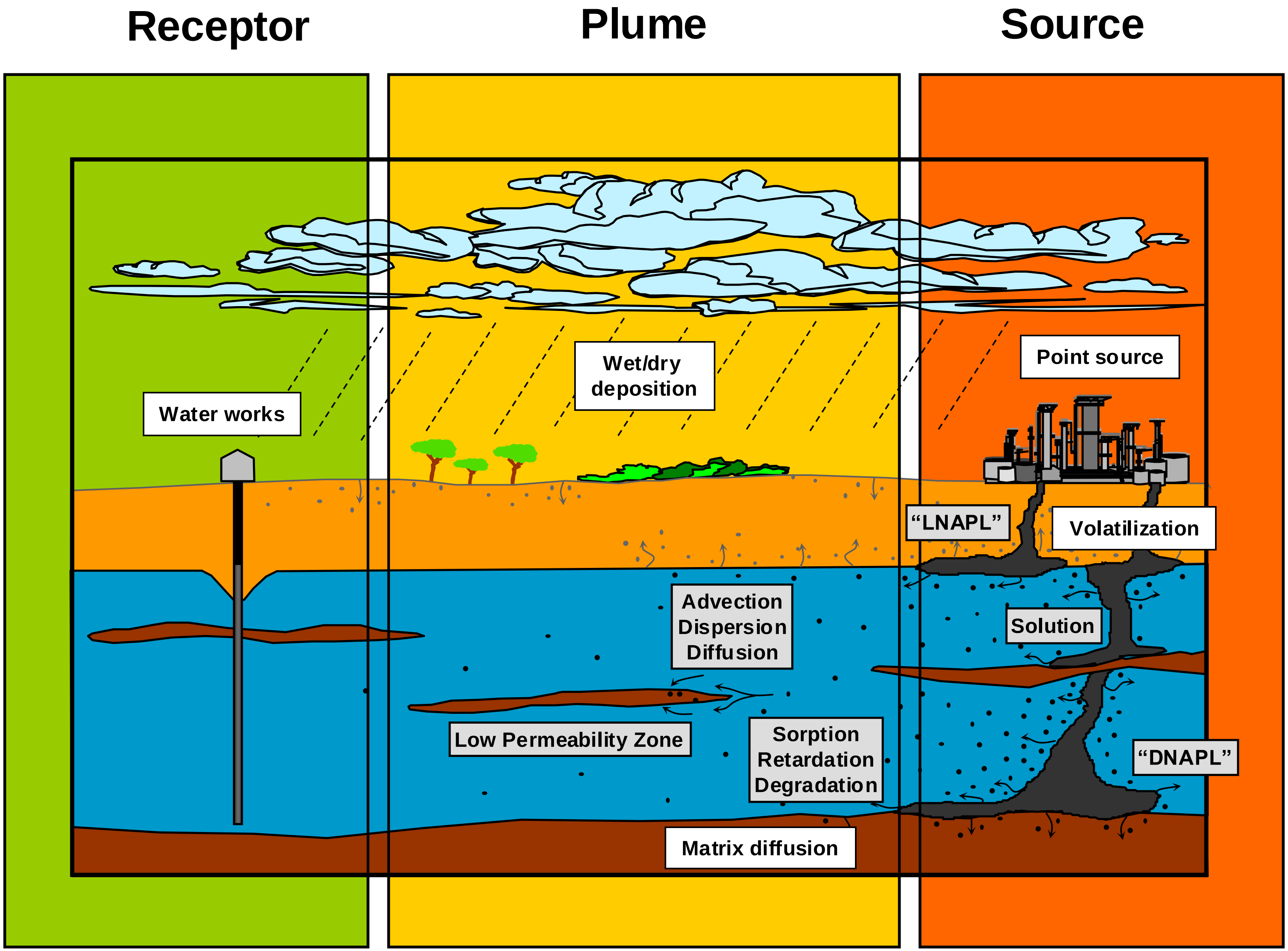
Where does it end up ?

Does it accumulate in soils ? Does it accumulate in biological tissue ? Is it persistent ? Does it degrade ?

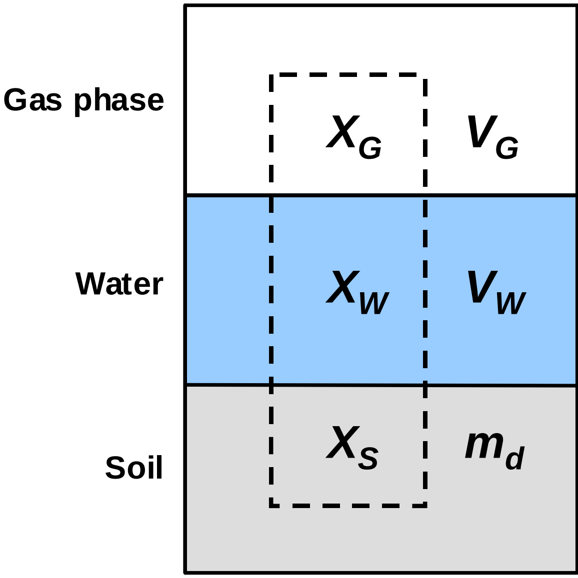
How can we remove it?

Remediation techniques, natural attenuation, soil washing, etc…

Distribution of contaminants in the subsurface



Distribution of contaminants in the subsurface



$$\frac{X_G}{V_G} = C_G \qquad \frac{X_W}{V_W} = C_W \qquad \frac{X_S}{m_d} = q$$

$$\frac{C_G}{C_W} = H \qquad \frac{q}{C_W} = K_d$$

$$\frac{q}{C_G} = K_{SG} = \frac{K_d}{H}$$

$$K_d = K_{OC}\, f_{OC}$$

$$K_{OC} = a \log K_{OW} + b$$

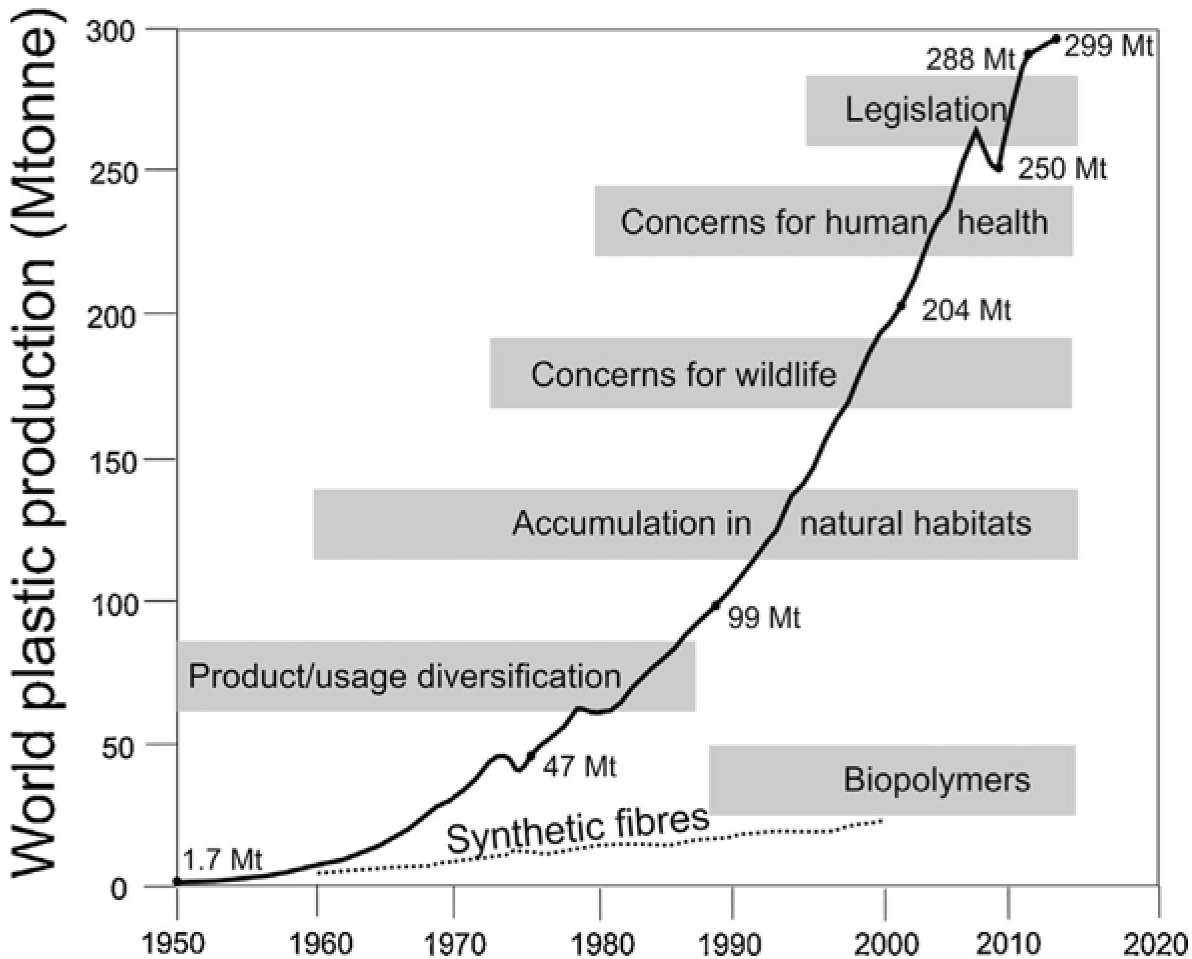
X_G; X_W; X_S	Contaminant mass in the gas phase (X_G), water (X_W) and soil (X_S)
V_G; V_W; m_d	Volume of the gas phase (V_G), water (V_W) and mass of soil (m_d)
C_G; C_W; q	Contaminant concentration in the gas phase (C_G), water (C_W) and soil (q)
H	Partition coefficient gas phase - water (Henry‘s constant)
K_d	Partition coefficient soil - water
K_{SG}	Partition coefficient soil - gas phase
K_{OC}	Partition coefficient soil organic carbon - water
K_{OW}	Partition coefficient octanol - water
f_{OC}	Mass of organic carbon in the soil with respect to the total mass of the soil
a; b	Empirical constants

<u>Organic</u> contaminants in the environment

What are Contaminants?

"Dosis sola facit venenum"
(Paracelsus - Theophrastus Bombastus v. Hohenheim, 1493 - 1541)

Exponential production of synthetic polymers and evolving concerns…



Zalasiewicz et al. 2019. The geological cycle of plastics and their use as a stratigraphic indicator of the Anthropocene. Anthropocene, http://dx.doi.org/10.1016/j.ancene.2016.01.002

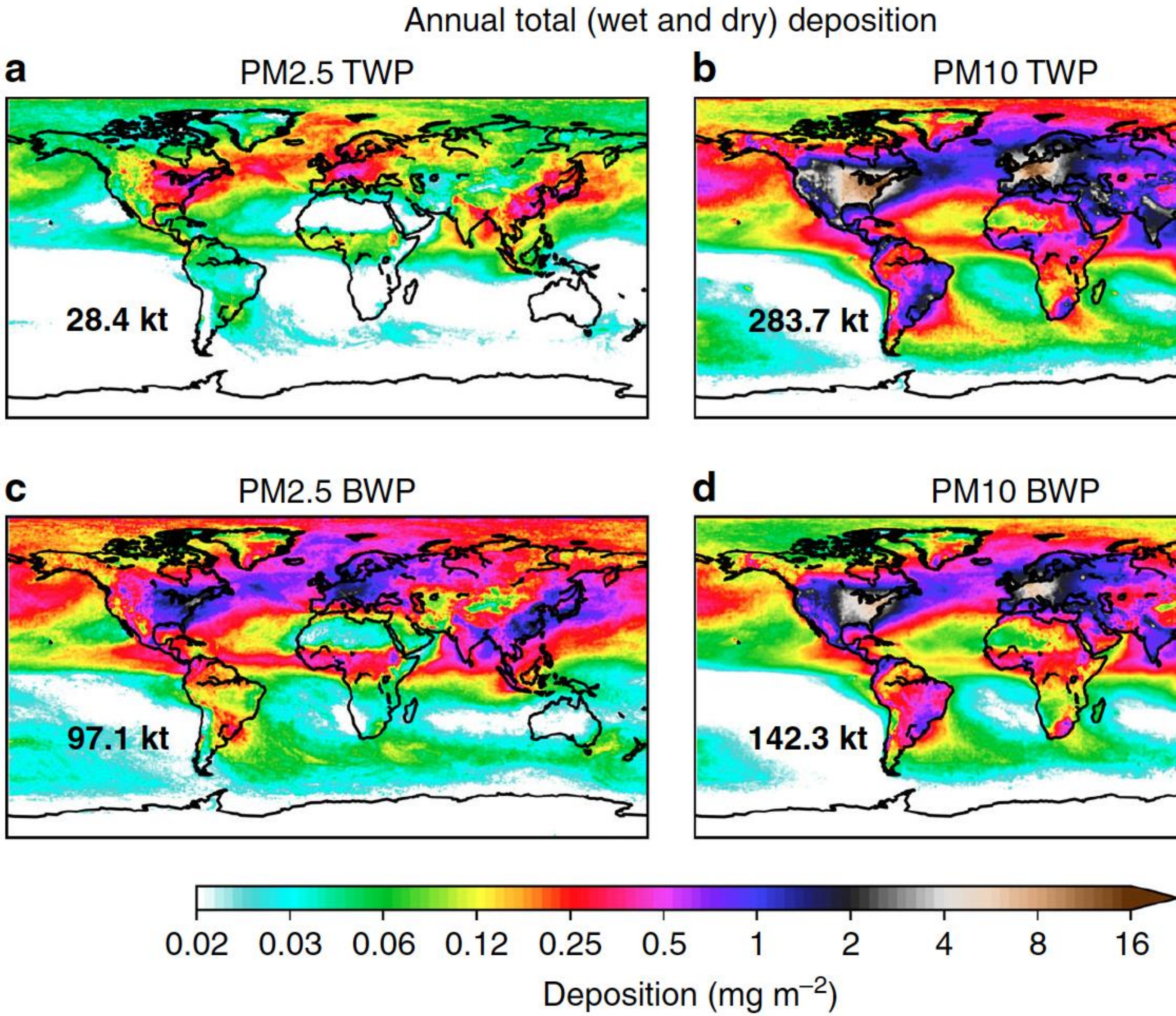
Plastic waste generation

Table 1. Countries with the highest plastic waste generation in 2016. Calculations using data reported in (*18*), with a refined estimate for the United States (bold text). EU-28 countries are reported collectively (italics).

Country	Plastic waste generation (metric tons)	Total waste generation (metric tons)	% Plastic in solid waste	2016 Population (millions)	Per capita plastic waste generation (kg/year)
United States	**42,027,215**	**320,818,436**	**13.1**	**323.1**	**130.09**
United States	34,020,748	263,726,732	12.9	323.1	105.30
EU-28	*29,890,143*	*243,737,466*	*11.7*	*511.2*	*54.56*
India	26,327,933	277,136,133	9.5	1,324.5	19.88
China	21,599,465	220,402,706	9.8	1,378.7	15.67
Brazil	10,675,989	79,081,401	13.5	206.2	51.78
Indonesia	9,128,000	65,200,000	14.0	261.6	34.90
Russian Federation	8,467,156	59,585,899	14.2	144.3	58.66
Germany	6,683,412	51,410,863	13.0	82.3	81.16
United Kingdom	6,471,650	32,037,871	20.2	65.6	98.66
Mexico	5,902,490	54,151,287	10.9	123.3	47.86
Japan	4,881,161	44,374,189	11.0	127.0	38.44
Thailand	4,796,494	27,268,302	17.6	69.0	69.54
Korea, Rep.	4,514,186	18,576,898	24.3	51.2	88.09
Italy	3,365,130	29,009,742	11.6	60.6	55.51
Egypt, Arab Rep.	3,037,675	23,366,729	13.0	94.4	32.16
France	2,929,042	32,544,914	9.0	66.9	43.81
Pakistan	2,731,768	30,352,981	9.0	203.6	13.42
Argentina	2,656,771	18,184,606	14.6	43.6	60.95
Algeria	2,092,007	12,378,740	16.9	40.6	51.59
Malaysia	2,058,501	13,723,342	15.0	30.7	67.09
Spain	1,832,533	20,361,483	9.0	46.5	39.42

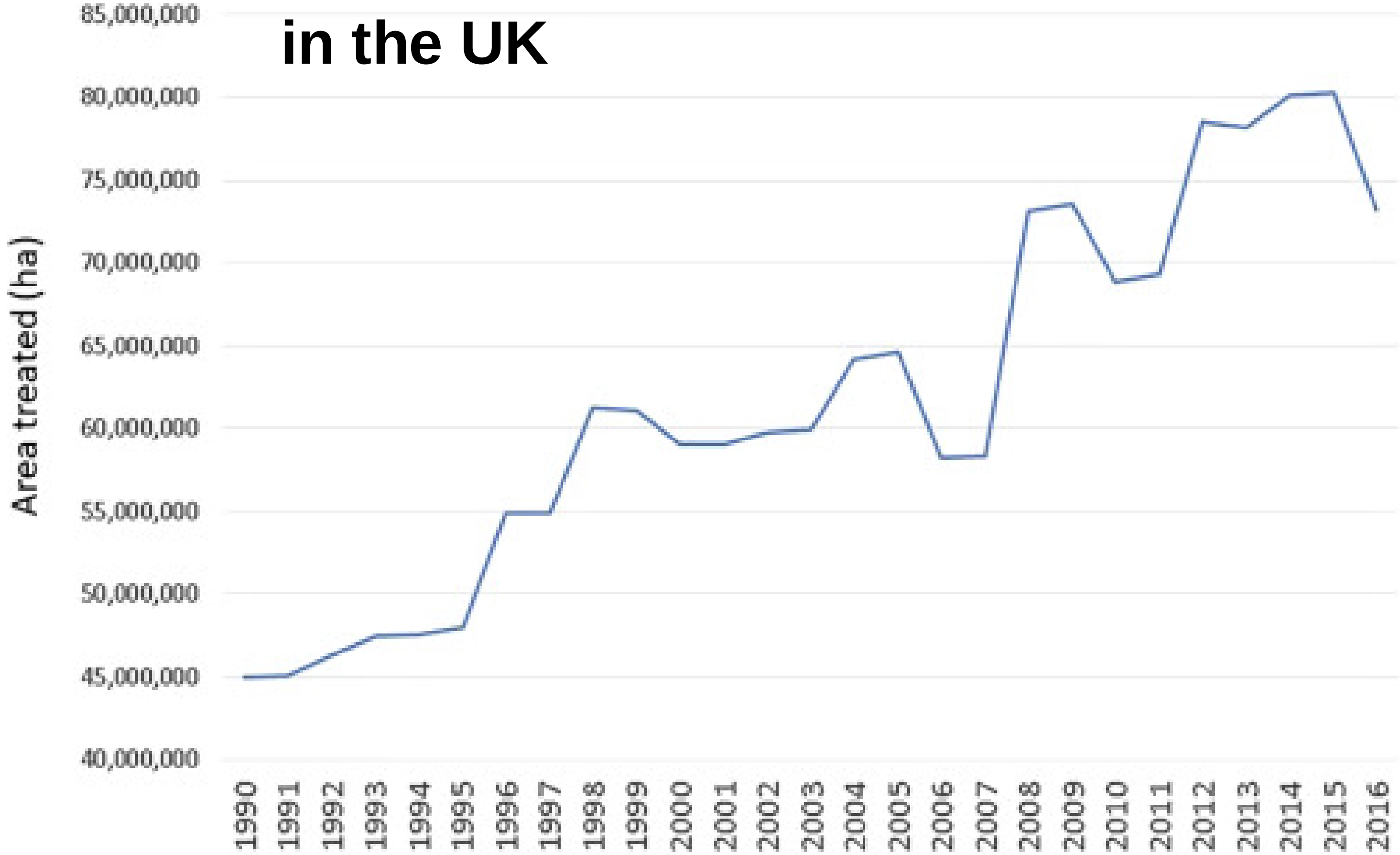
from Law et al. 2020: The United States' contribution of plastic waste to land and ocean. Sci. Adv. 6, eabd0288 (2020).

Global emission and depostion of tyre and break wear particles (TWP, BWP)



Evangeliou et al. 2020. Atmospheric transport is a major pathway of microplastics to remote regions
https://doi.org/10.1038/s41467-020-17201-9 | www.nature.com/naturecommunications

Pesticide treated area in the UK



The total area of crops treated with pesticides each year has approximately doubled between 1990 and 2015. There are about 4.5 million hectares of cropped land, and this area remained almost unchanged over this period. Each field is now, on average, treated about 17 times
https://www.cell.com/one-earth/fulltext/S2590-3322(20)30140-8

Most frequently detected groundwater contaminants at hazardous waste sites [NRC, 1994].

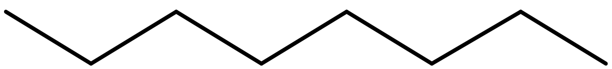
Rank	Compound	Common Sources
1	**Trichloroethene**	**Dry cleaning; metal degreasing**
2	Lead	Gasoline (prior to 1975); mining; construction material (pipes); manuf[illegible]uring
3	**Tetrachloroethene**	**Dry cleaning; metal [illegible]ng**
4	**Benzene**	**Gasoline; manu[illegible]**
5	**Toluene**	**Gasoline; m[illegible]**
6	Chromium	Metal p[illegible]
7	**Methylene chloride**	**De[illegible] paint removal**
8	Zinc	[illegible]ing
9	**1,1,1-Trichloroethane**	**[illegible]stic cleaning**
10	Arsenic	[illegible]anufacturing
11	**Chloroform**	**[illegible]ents**
12	**1,1-Dichlor[illegible]**	**[illegible]egreasing; solvents**
13	**1,2-tra[illegible]**	**Transformation product of 1,1,1-Trichloroethane**
14	C[illegible]	Mining; plating
15	[illegible]	Manufacturing; mining; occurs in nature as oxide
16	[illegible]	Manufacturing; mining
17	**[illegible]oroethene**	**Manufacturing**
18	**[illegible]chloride**	**Plastic and record manufacturing**
19	Barium	Manufacturing; energy production
20	**1,2-Dichloroethane**	**Metal degreasing; paint removal**
21	**Ethylbenzene**	**Styrene and asphalt manufacturing; gasoline**
22	Nickel	Manufacturing; mining
23	**Di(2-ethylhexyl)phthalate**	**Plastics manufacturing**
24	**Xylenes**	**Solvents; gasoline**
25	**Phenol**	**Wood treating; medicines**

New class of compounds: Per- and polyfluoroalkyl substances (PFAS)

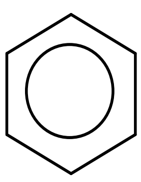
Organic Contaminants - Hydrocarbons:
Origin- Natural/Anthropogenic

Hydrocarbons

Aliphatic hydrocarbons (non-cyclic)



Aromatic Hydrocarbons
(BTEX - Benzene - Toluene - Ethylbenzene - Xylene)



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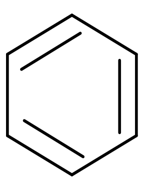
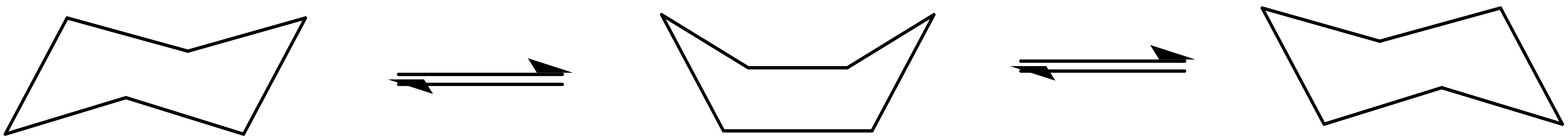
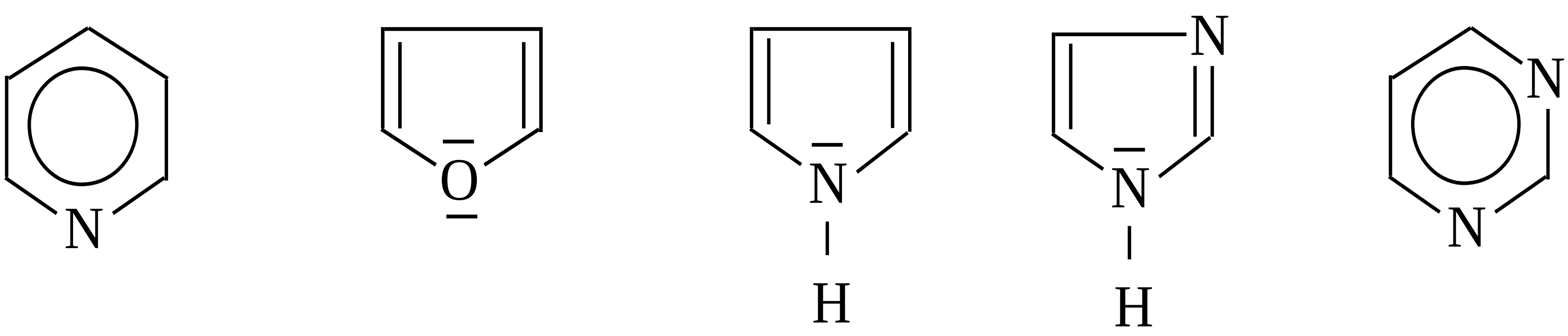


Organic Contaminants - Hydrocarbons: Origin- Natural/Anthropogenic cont.

Alicyclic hydrocarbons (non-aromatic rings, e.g. cyclohexane)



Heterocyclic hydrocarbons
(rings with heteroatoms, e.g. pyridine, furane, pyrrol, imidazol, pyrimidin)

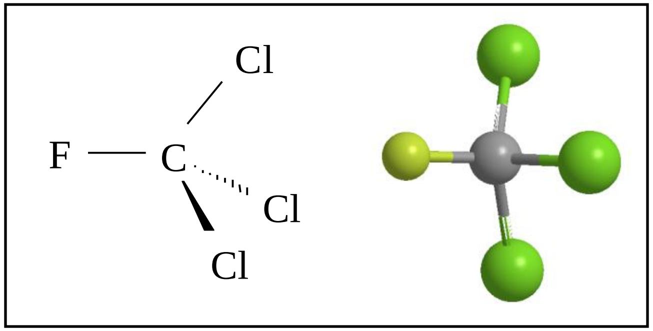


Frequent Contaminants: Structure - Occurrence

Compound	Application/Production	Geogenic/Biogenic

Freons:

Fluorochlorohydrocarbons

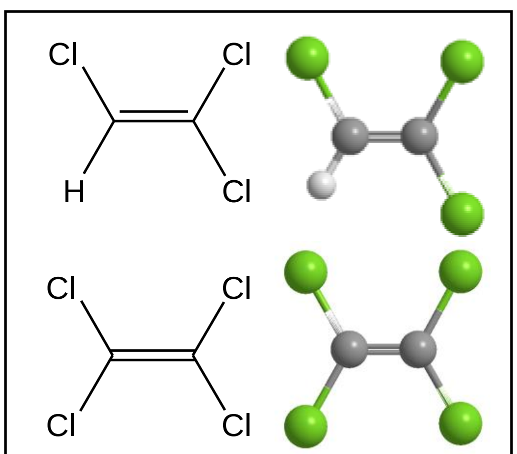


propellants, solvents

(volcanic)

VCH: Volatile chlorinated hydrocarbons

Trichloroethene (TCE),
Per(tetra)chloroethene (PCE)

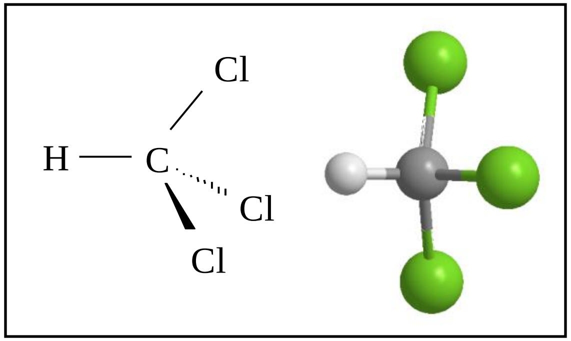


Solvents:
dry cleaning,
degreasing of metals,
electronics, etc

(volcanic)

Frequent Contaminants: Structure - Occurrence cont.

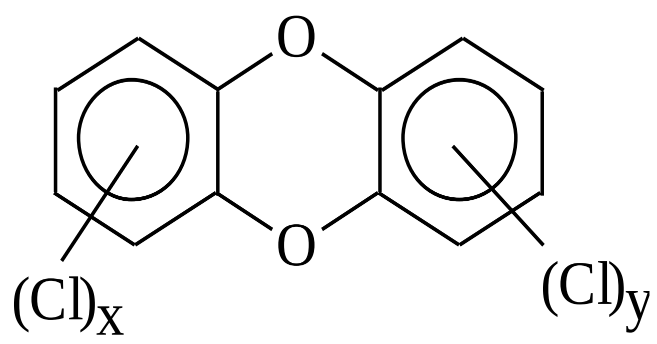
Compound	Application/Production	Geogenic/Biogenic
Dichloromethane (DCM)	propellants, solvents	(volcanic)
Trichloromethane (TCM) Chloroform		(volcanic) from dissolved organic matter during chlorination of drinking water
Methylchloride Monochloromethane	Intermediate 26 000 t/a	5 000 000 t/a Biogenic ("giant kelp")



Frequent Contaminants: Structure - Occurrence cont.

Compound	Application/Production	Geogenic/Biogenic
Dioxins	PCP – agent orange prodcution incinerators	Forest fires (approx. 60 kg/a in Canada)

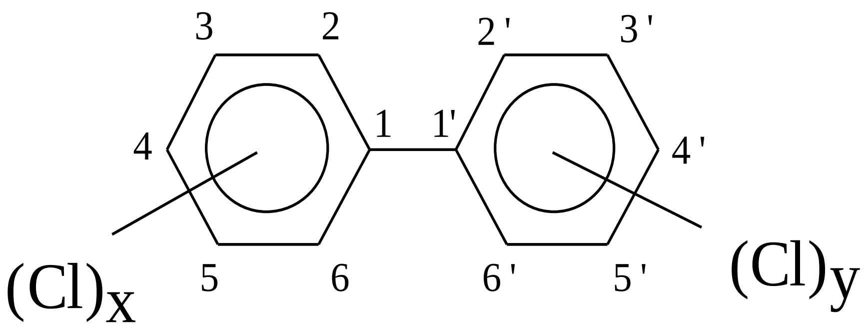
"Dioxins" refers to a group of chemical compounds that share certain chemical structures and biochemical characteristics: polychlorinated dibenzo-p-dioxins (PCDDs - dioxins) and polychlorinated dibenzofurans (PCDFs - furanes) are double carbon ringed molecules with a varying amount of chlorination and an additional single (furanes) or double (dioxins) oxygen connection creating a tricyclic planar molecule. Depending on the number of chlorines, varying from 1 to 8, a total of 210 closely related molecules 'congeners' theoretically exist.



Frequent Contaminants: Structure - Occurrence cont.

Compound	Application/Production	Geogenic/Biogenic
PCBs PCBs are mixtures of synthetic organic chemicals with the same basic chemical structure and similar physical properties ranging from oily liquids to waxy solids. Due to their non-flammability, chemical stability, high boiling point and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics and rubber products; in pigments, dyes and carbonless copy paper and many other applications. More than 1.5 billion pounds of PCBs were manufactured in the United States prior to cessation of production in 1977.	Transformer oil Hydraulic oil	(volcanic)

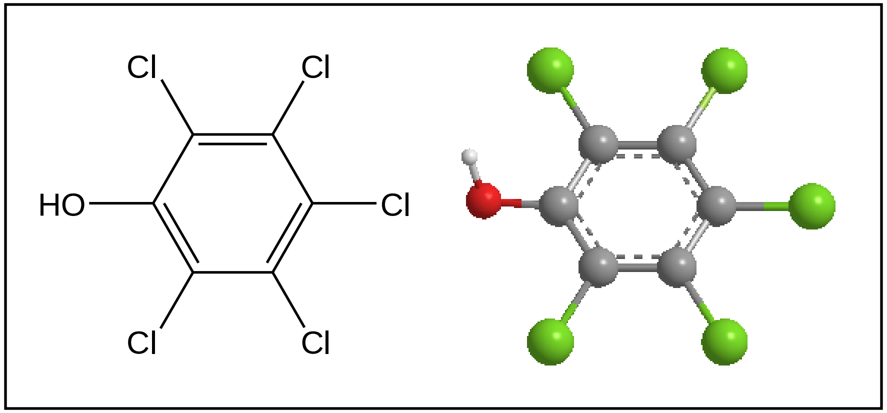
PCBs: Polychlorinated Biphenyls



Frequent Contaminants: Structure - Occurrence cont.

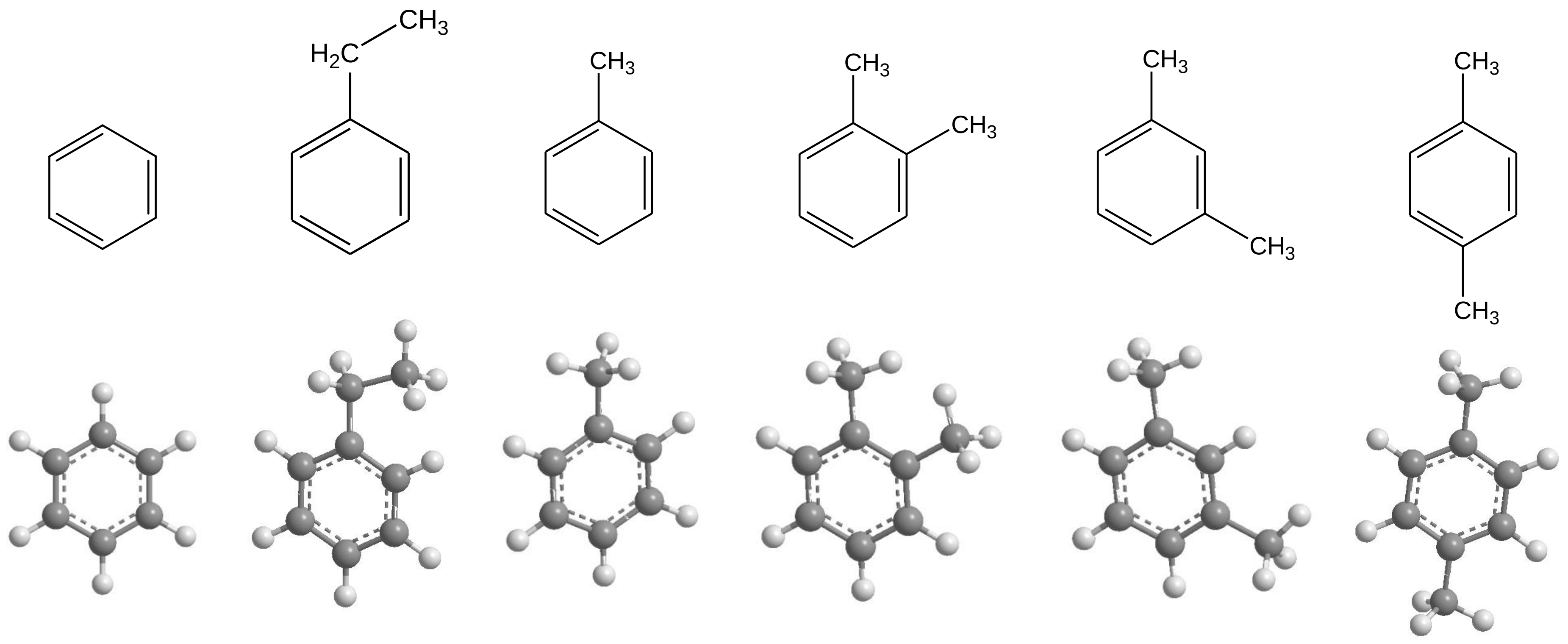
Compound	Application/Production	Geogenic/Biogenic
Chlorophenols Chlorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. Phenol is an aromatic compound derived from benzene, the simplest aromatic hydrocarbon, by adding a hydroxy group to a carbon to replace a hydrogen. There are five basic types of chlorophenols: mono[one]chlorophenols, di[two]-chlorophenols, tri[three]chloro-phenols, tetra[four]chlorophenols, and penta[five]chlorophenols. In all, there are 19 different chlorophenols.	pulp and paper industry (PCP: wood preservatives)	swamps, peat bogs (fungi and lichen) 2,6-dichlorophenol: Sexual lure of ticks; ant repellant of grass hoppers (nat. >> anthropogenic)

(e.g. Pentachlorophenol: PCP)



Frequent Contaminants: Structure - Occurrence cont.

Compound	Application/Production	Geogenic/Biogenic
BTX, BTEX: Benzene, Toluene, (Ethyl-benzene) Xylenes	solvents, fuel, traffic	Crude oil, coal

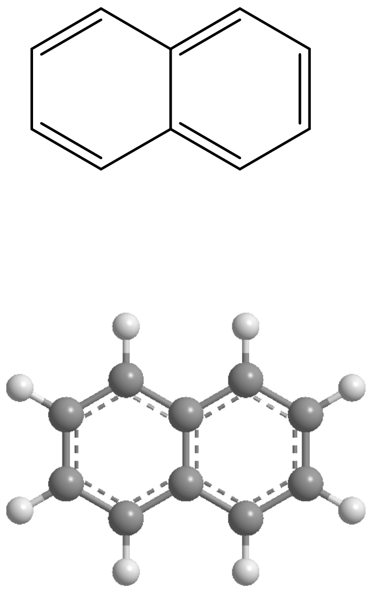


Benzene **Ethylbenzene** **Toluene** **o-Xylene** **m-Xylene** **p-Xylene**

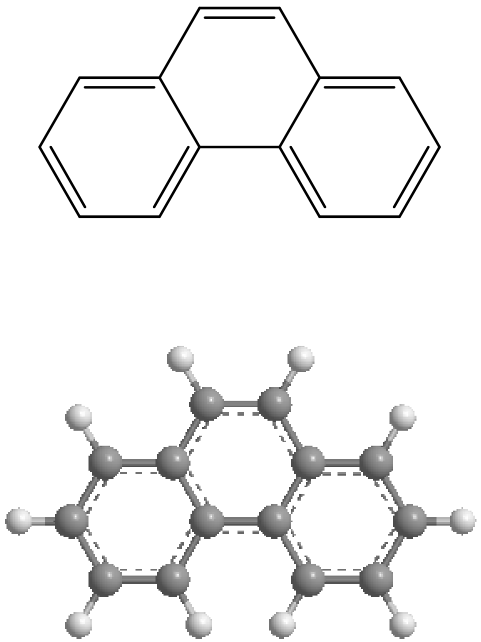
Frequent Contaminants: Structure - Occurrence cont.

Compound	Application/Production	Geogenic/Biogenic
Polycylic Aromatic Hydrocarbons: PAH	cokeries, manufactured gas plants, diesel emission	wildfires crude oil kerogen coal (chondrites - meteorites)

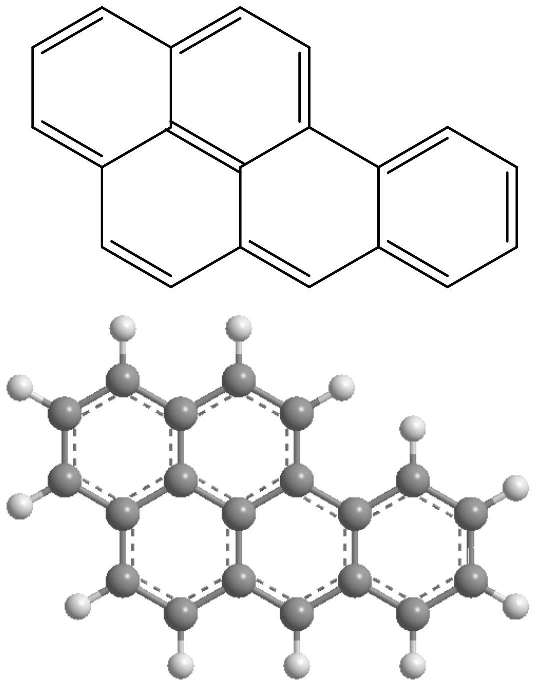
e.g.



Naphthalene



Phenanthrene



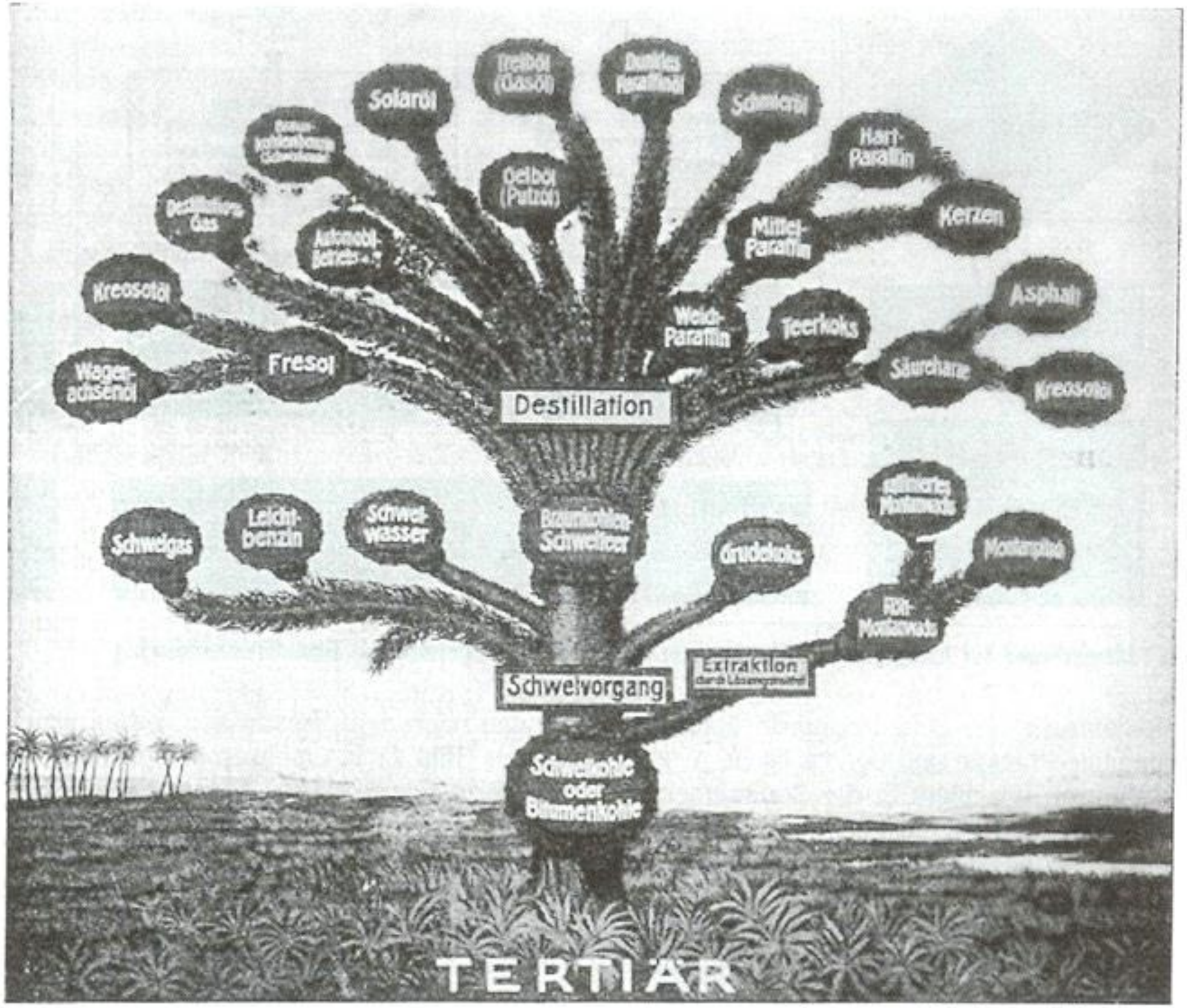
Benzo(a)pyrene

Frequent Contaminants: Structure - Occurrence cont.

16 EPA PAH:

2 ring: Naphthalene
3 ring: Acenaphthylene; Acenaphthene, Fluorene, Phenanthrene, Anthracene,
4 ring: Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene
5 ring: Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benz(a)pyrene, Dibenz(a)anthracene,
6 ring: Indeno(1,2,3-cd)pyrene, Benzo(g,h,i)perylene

2 - 4 ring PAH frequently in groundwater (cokeries, gas plants, tar destillation products)



Deutsches Museum, München

Stammbaum der Braunkohlenprodukte

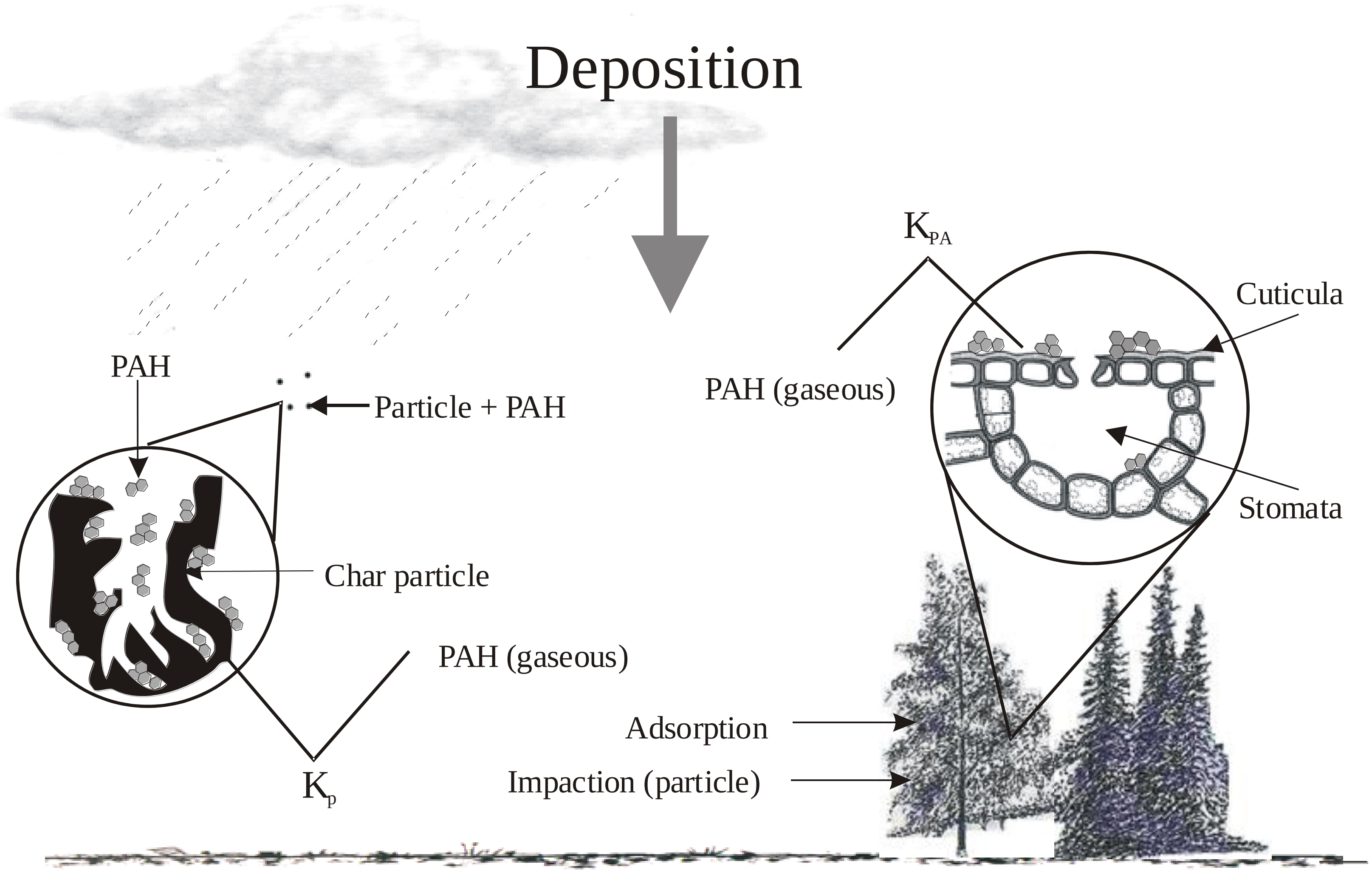
Aus dem Tertiär erwachsen uns durch die Verarbeitung der Schwelkohle zahlreiche technisch wertvolle Produkte: Gase, Leichtbenzin, Grudekoks, Montanwachs, Kreosot, Automobilbetriebstoffe, Schmieröl, Solaröl, Gasöl, Hartparaffin, Kerzen, Putzöl, Kreosotöl, Teerkoks, Säureharze usw.

1: Stammbaum der Braunkohlenprodukte

Contaminants
or
Resources?

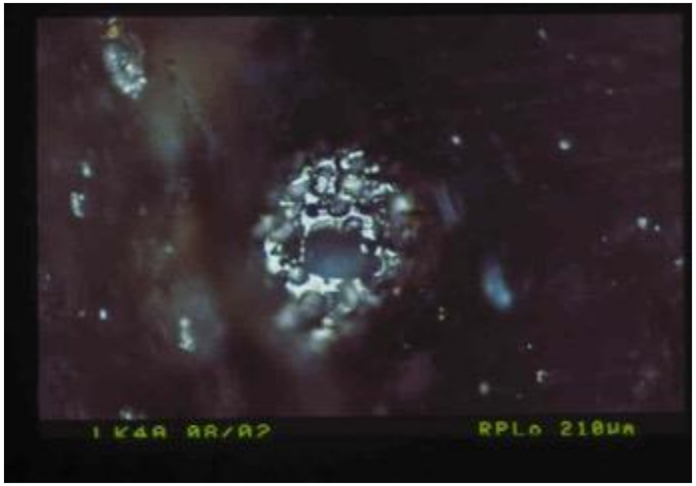
Lignite coal, tar
and tar distillates
as resources

Black Carbon and PAHs in the air



Carbonaceous particles in atmosphere / soils

Deposition Schönbuch

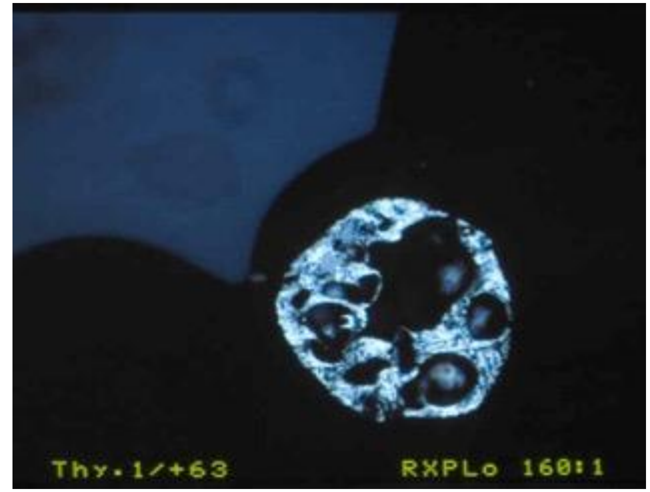


Char

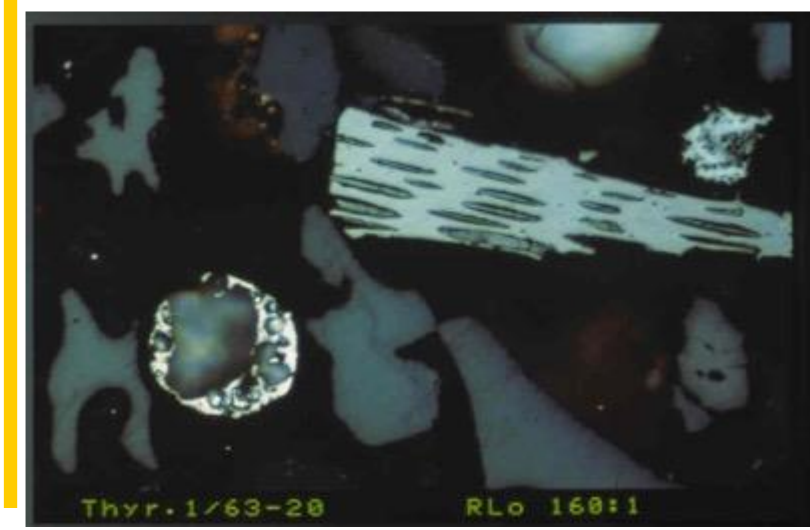
Charcoal

Soot

Soil sample, southwest Berlin

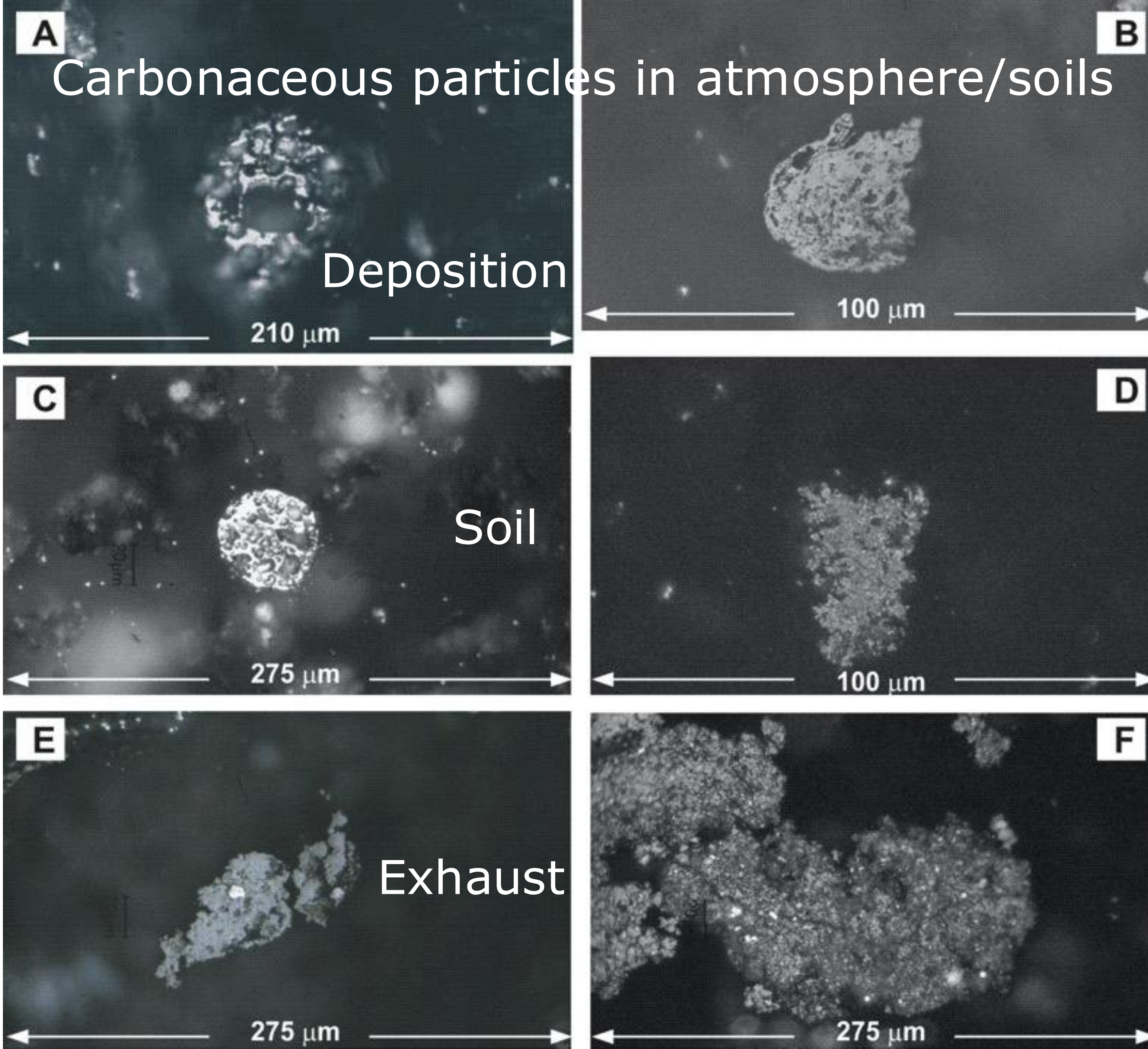


Char



Charcoal and char

Carbonaceous particles in atmosphere/soils



PAHs in Space (C&EN, 10/18)

ASTROCHEMISTRY

Titan's haze chemistry explored

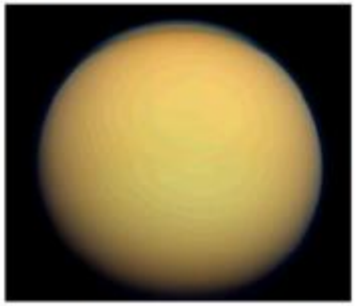
Lab experiments suggest low-temperature photochemistry produces hazy PAHs

The thick, hazy atmosphere of Saturn's moon Titan has provided a curious mystery for scientists. In 2005, the European Space Agency's *Huygens* lander detected atmospheric benzene on Titan via mass spectrometry, and evidence from other sources has suggested the presence of polycyclic aromatic hydrocarbons (PAHs)—possible sources of Titan's haze.

PAHs create haze here on Earth, and chemists have long understood how benzene forms the multiringed molecules at high temperature, but conditions on Titan are downright frigid, ranging from about −70 to −200 °C. Now, scientists using laboratory experiments and theoretical calculations have shown how these reactions could happen at low temperatures (*Nat. Astron.* 2018, DOI: 10.1038/s41550-018-0585-y).

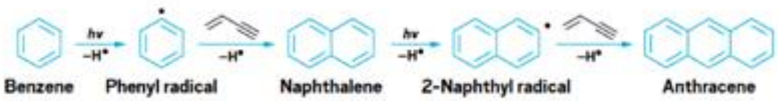
Some aromatic chemistry in Titan's atmosphere is already understood. Solar ultraviolet radiation penetrates hundreds of kilometers into Titan's atmosphere, possibly photolyzing benzene to a phenyl radical, which reacts with vinyl acetylene to make naphthalene. To figure out how that process could produce more complex PAHs, a team led by Ralf I. Kaiser of the University of Hawaii, Manoa, and Musahid Ahmed of Lawrence Berkeley National Laboratory reacted naphthyl radical with vinyl acetylene under conditions that simulate Titan's low temperature. Through radical intermediates, those reactions produced three-ringed anthracene and phenanthrene molecules—identified by mass spectrometry.

To explain how these products could form at low temperatures, Kaiser and Ahmed collaborated with Alexander M. Mebel of Samara University and Florida International University and colleagues to calculate energetically feasible reaction pathways from naphthalene and vinyl acetylene to the three-ringed PAHs. Mebel says he was surprised to find four pathways with surmountable energy barriers that led from each of the possible naphthyl radicals to both anthracene and phenanthrene.



Polycyclic aromatic hydrocarbons could contribute to Titan's characteristic yellow haze.

"This is a new route towards PAH formation," says Xander Tielens of Leiden University, who studies PAHs in interstellar space. He explains that the results show how solar UV photons can create radicals at low temperatures, avoiding the high energy barrier to PAH formation seen in combustion and other high-temperature processes. And Tielens says this mechanism could explain PAH formation elsewhere in space, like in molecular clouds.



Solar photons (*hν*) create radical intermediates that can react with vinyl acetylene to build polycyclic aromatic hydrocarbons at low temperatures.

The group is now adapting its experiments to explore formation of larger PAHs, including molecular cages and other three-dimensional structures, as well as aromatic molecules containing nitrogen, the major component of Titan's atmosphere.—SAM LEMONICK

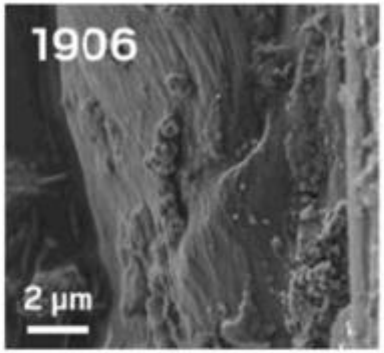
Regulation helps!

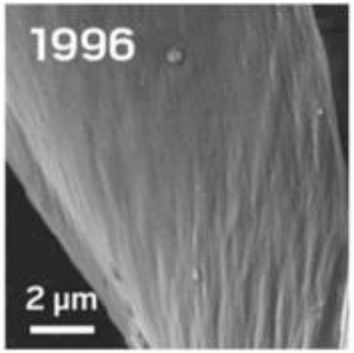
POLLUTION

▶ Dirty sparrows provide a historic look at soot

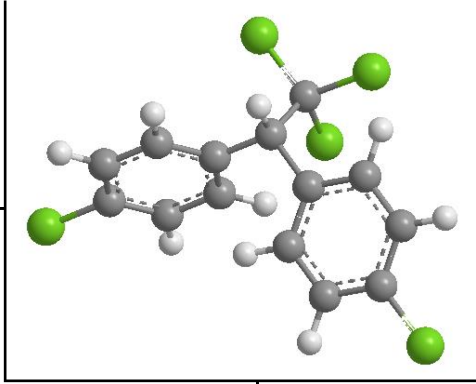
Evolutionary biologist Shane G. DuBay and art historian and photographer Carl C. Fuldner of the University of Chicago were studying bird specimens in natural history museum collections when they began noticing that birds collected more than 100 years ago are much dirtier than recently collected birds. That observation led them in a new direction to use the soot embedded in bird feathers to estimate past black carbon aerosol pollution stemming from burning wood and coal (*Proc. Natl. Acad. Sci. USA* 2017, DOI: 10.1073/pnas.1710239114). The team used electron microscopy to gather photometric reflectance data on feathers from more than 1,300 bird specimens collected from 1880 to 2015 in the U.S. manufacturing belt, which includes Chicago, Detroit, and Pittsburgh. The researchers used the data to estimate black carbon concentrations, finding that levels peaked between 1900 and 1910 and that levels before 1910 were higher than previously thought—estimates were inexact until the mid-1950s when atmospheric sampling became common. Black carbon remained relatively high in the sampling region until about 1960, when concentrations began to fall because of more efficient coal burning, environmental regulations, and a shift to cleaner-burning natural gas. Besides noting the reduced breathing hazard to people and wildlife over time, the researchers say their findings suggest black carbon's contribution to past climate change has been underestimated and that the results should help improve models estimating future climate change.—STEVE RITTER

These micrographs reveal that a feather from a field sparrow collected in Chicago in 1906 is darkened and speckled with soot particles, whereas a feather from a field sparrow collected in the same area in 1996 is relatively clean.



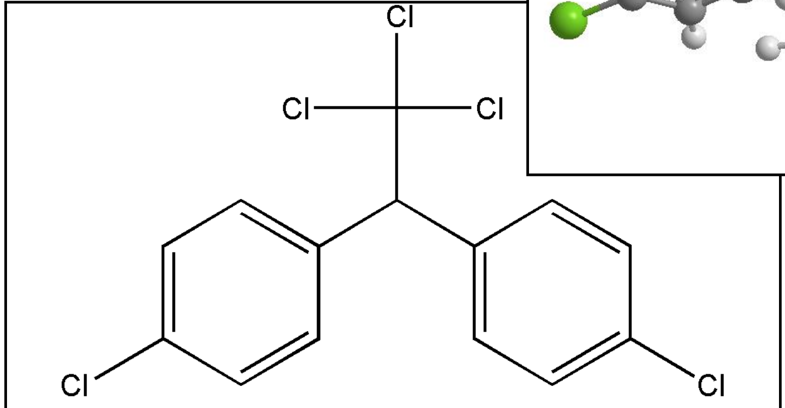


"Brief History" of DDT



1948

Nobel Prize to Paul Müller (Switzerland) for the discovery of the insecticidal properties of DDT.



Benzene, 1,1'-(2,2,2-trichloroethylidene)bis 4-chloro-

DDT acts as a nerve poison, accumulates in the cell membranes (higher K_{OW}) and blocks signal transmission (respiratory failure); still being utilized to combat Malaria.

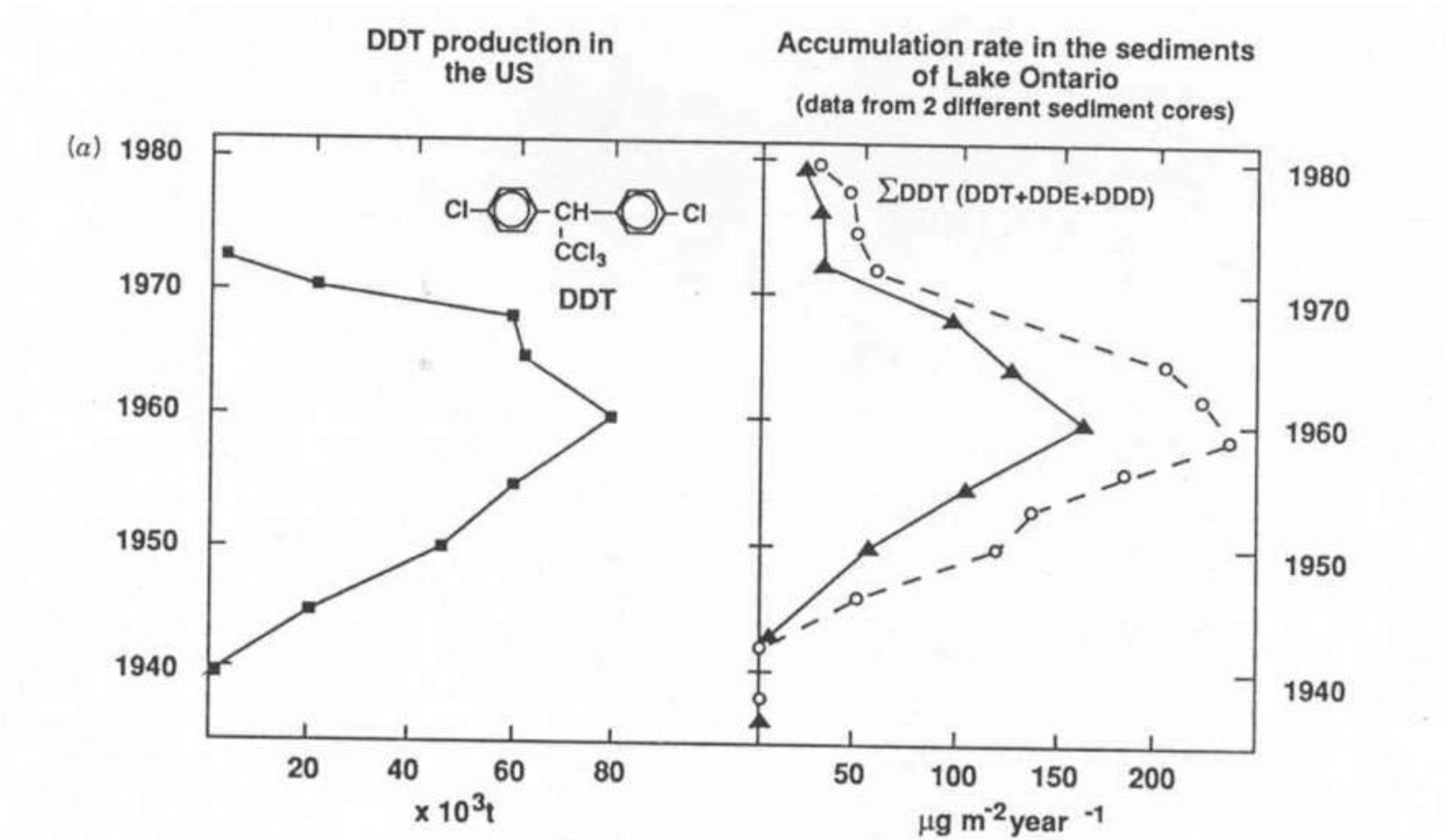
Global distribution in the atmosphere (bound to particles)

Accumulation in the fatty tissues of organisms

DDT transfer through milk and eggs; especially affected is the end of the food chain (e.g. birds of prey through selective hunting of the "old and weak")

Similarly applicable to PCBs and PAHs (enrichment in soils – a record of the history of industrialization)

DDT in the environment



Schwarzenbach et al. 1993

DDT discussions…

SCIENTIFIC AMERICAN

News - May 4, 2009

Should DDT Be Used to Combat Malaria?

DDT should be used "with caution" in combating malaria, a panel of scientists reported today

By Marla Cone and Environmental Health News

A panel of scientists recommended today that the spraying of DDT in malaria-plagued Africa and Asia should be greatly reduced because people are exposed in their homes to high levels that may cause serious health effects.

The scientists from the United States and South Africa said the insecticide, banned decades ago in most of the world, should only be used as a last resort in combating malaria.

The stance of the panel, led by a University of California epidemiologist, is likely to be controversial with public health officials. Use of DDT to fight malaria has been increasing since it was endorsed in 2006 by the World Health Organization and the President's Malaria Initiative, a U.S. aid program launched by former President Bush.

In many African countries, as well as India and North Korea, the pesticide is sprayed inside homes and buildings to kill mosquitoes that carry malaria.

Malaria is one of the world's most deadly diseases, each year killing about 880,000 people, mostly children in sub-Saharan Africa, according to the World Health Organization.

The 15 environmental health experts, who reviewed almost 500 health studies, concluded that DDT "should be used with caution, only when needed, and when no other effective, safe and affordable alternatives are locally available."

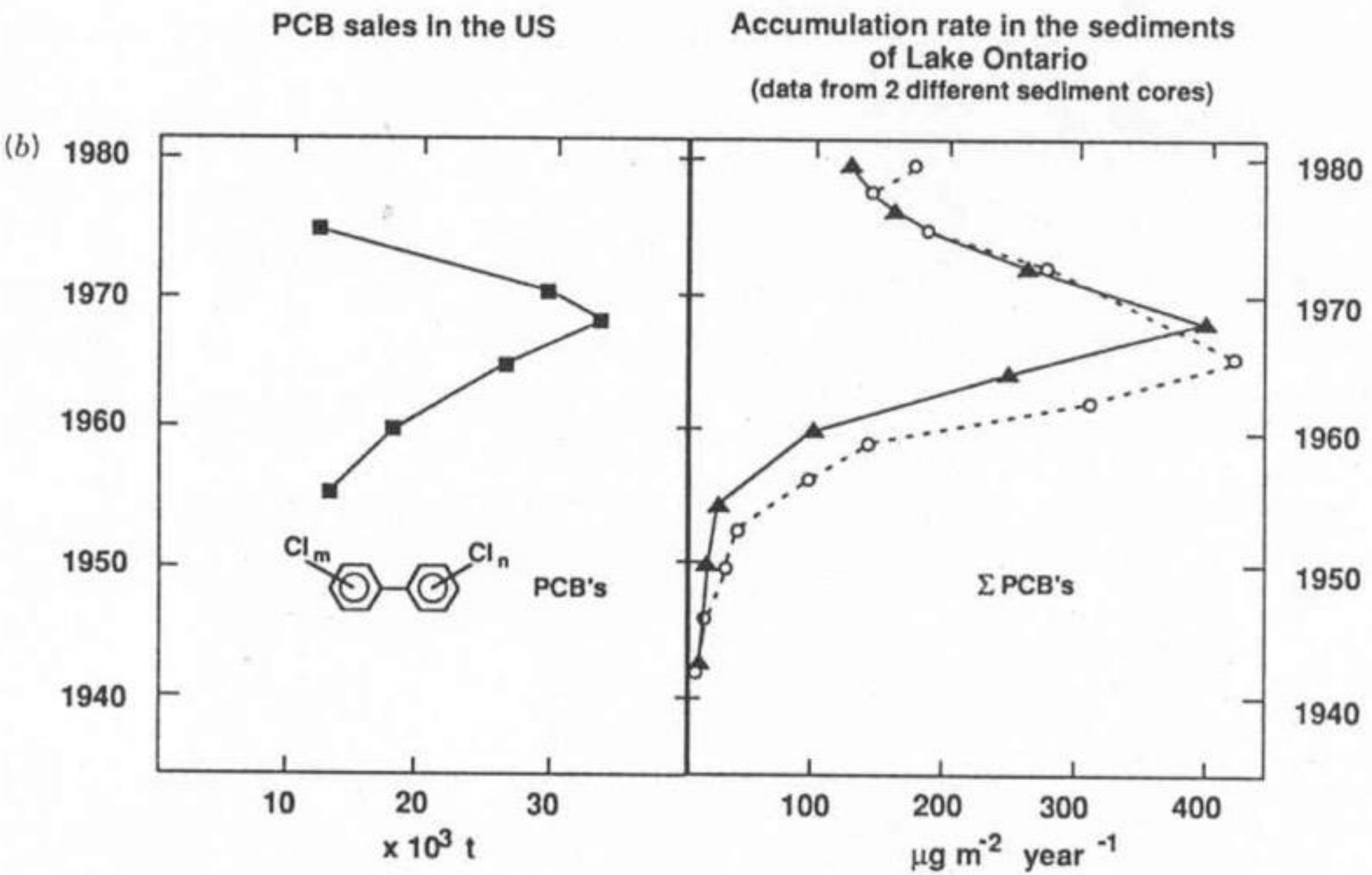
We cannot allow people to die from malaria, but we also cannot continue using DDT if we know about the health risks," said Tiaan de Jager, a member of the panel who is a professor at the School of Health Systems & Public Health at the University of Pretoria in South Africa. "Safer alternatives should be tested first and if successful, DDT should be phased out without putting people at risk."

The scientists reported that DDT may have a variety of human health effects, including reduced fertility, genital birth defects, breast cancer, diabetes and damage to developing brains. Its metabolite, DDE, can block male hormones.

"Based on recent studies, we conclude that humans are exposed to DDT and DDE, that indoor residual spraying can result in substantial exposure and that DDT may pose a risk for human populations," the scientists wrote in their consensus statement, published online today in the journal *Environmental Health Perspectives*.

"We are concerned about the health of children and adults given the persistence of DDT and its active metabolites in the environment and in the body, and we are particularly concerned about the potential effects of continued DDT use on future generations."

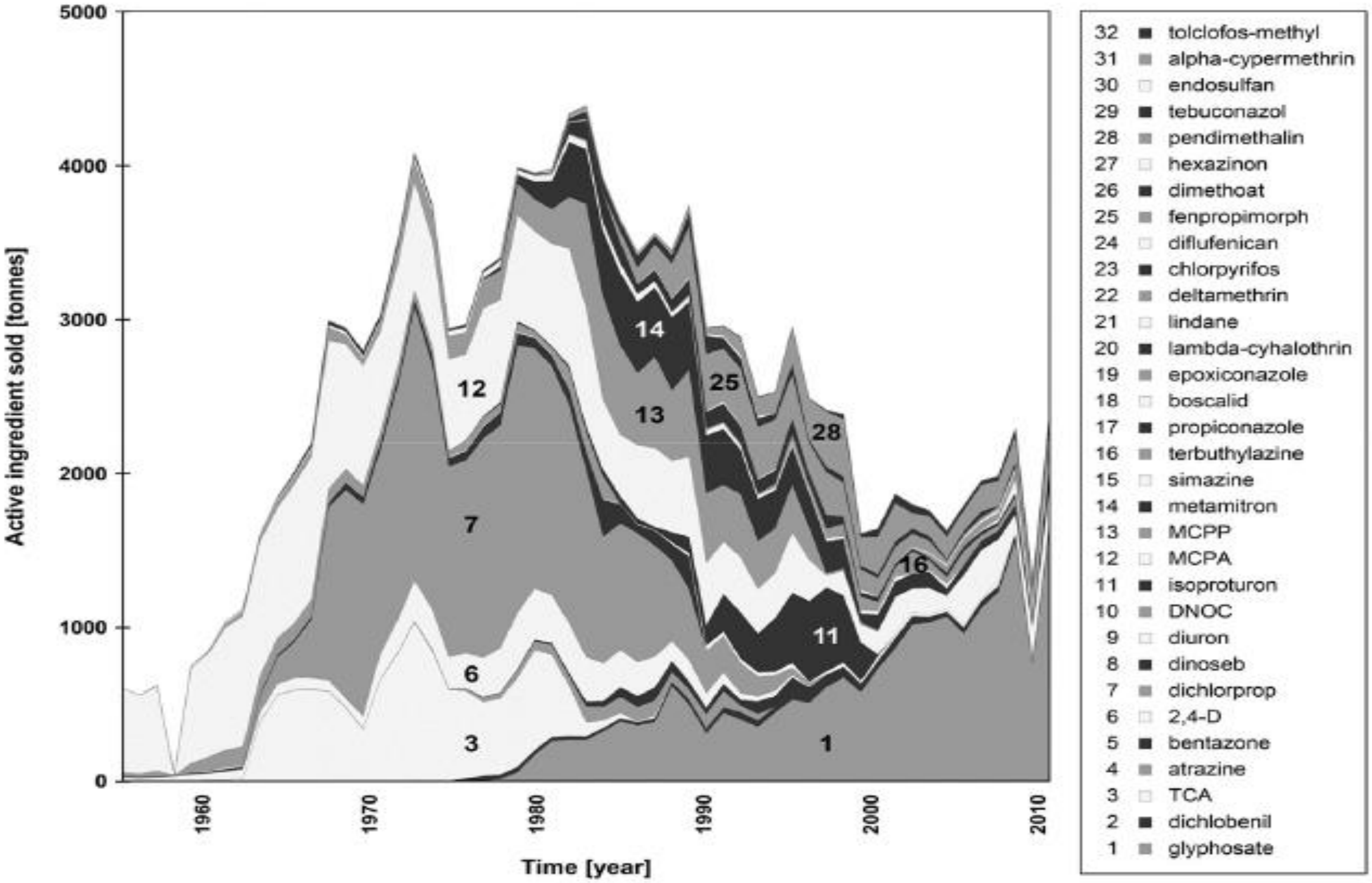
PCB in the environment



Schwarzenbach et al. 1993

Pesticides: Glyphosate takes over…

U.S. McKnight et al. / Environmental Pollution 200 (2015) 64–76



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In The News / Nov 29

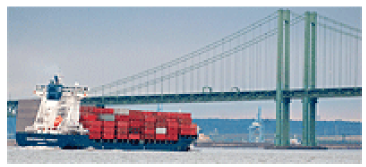
Bhopal: The victims are still being born.
Bhopal is a calamity without end. On 3 December 1984, clouds of poison leaking from a Union Carbide pesticides plant brought death to thousands in this central Indian city. Today, fully a quarter of a century later, victims of this, the world's worst industrial disaster, are still being born. London Independent, United Kingdom

Bhopal's women still bear scars of gas hell.
Many women were twice afflicted by the world's worst industrial accident. Those who lost family have had to nurse their grief and themselves; some 43 per cent of pregnant survivors lost their babies, and there has since been an epidemic of gynaecological diseases. Edinburgh Scotsman, United Kingdom

Tenaska coal power plant water use to face public hearing.
Many factors could derail a proposed coal-fired plant near Sweetwater, including environmental and economic concerns. But Thursday, the focus will be on water. Abilene Reporter-News, Texas

Irondequoit residents living above

Dredging battle pits jobs vs. river.
By Jeff Montgomery Wilmington News Journal 29 November 2009



cwalker71/flickr
Container ship on the Delaware River.

Nearly 28 years after Congress authorized the Army Corps of Engineers to deepen the Delaware River's main shipping channel, the only thing about the project that has deepened is the controversy.

The latest showdown over the $300 million plan to increase the depth of the shipping channel from 40 to 45 feet is scheduled for Dec. 8 in federal court, when Delaware and New Jersey will try to block the corps from carrying out its threat to start dredging without permits from either state.

more...

Monsanto's control over seed market prompts antitrust inquiry.
By Peter Whoriskey Washington Post
29 November 2009

Today, the vast majority of the nation's two primary crops grow from Monsanto's genetically altered seeds: 93% of soybeans and 80% of corn. Monsanto's dominant role in the nation's agriculture has not unfolded without complaint.

Monsanto says it has done nothing wrong.

"Farmers choose these products because of the value they deliver on farm," Monsanto said in a statement. "Given the phenomenally broad adoption of these technologies by farmers, such questions are normal and to be expected."

more...

New Science
Understand the latest scientific findings

Pesticide levels in blood associated with prostate cancer. 25 November 2009
Blood levels of three types of banned organochlorine pesticides are associated with prostate cancer in the general US population, researchers report in a recent study. Researchers who analyzed data from a large, long-term national study coordinated by the CDC found that levels of organochlorine pesticides in the blood are

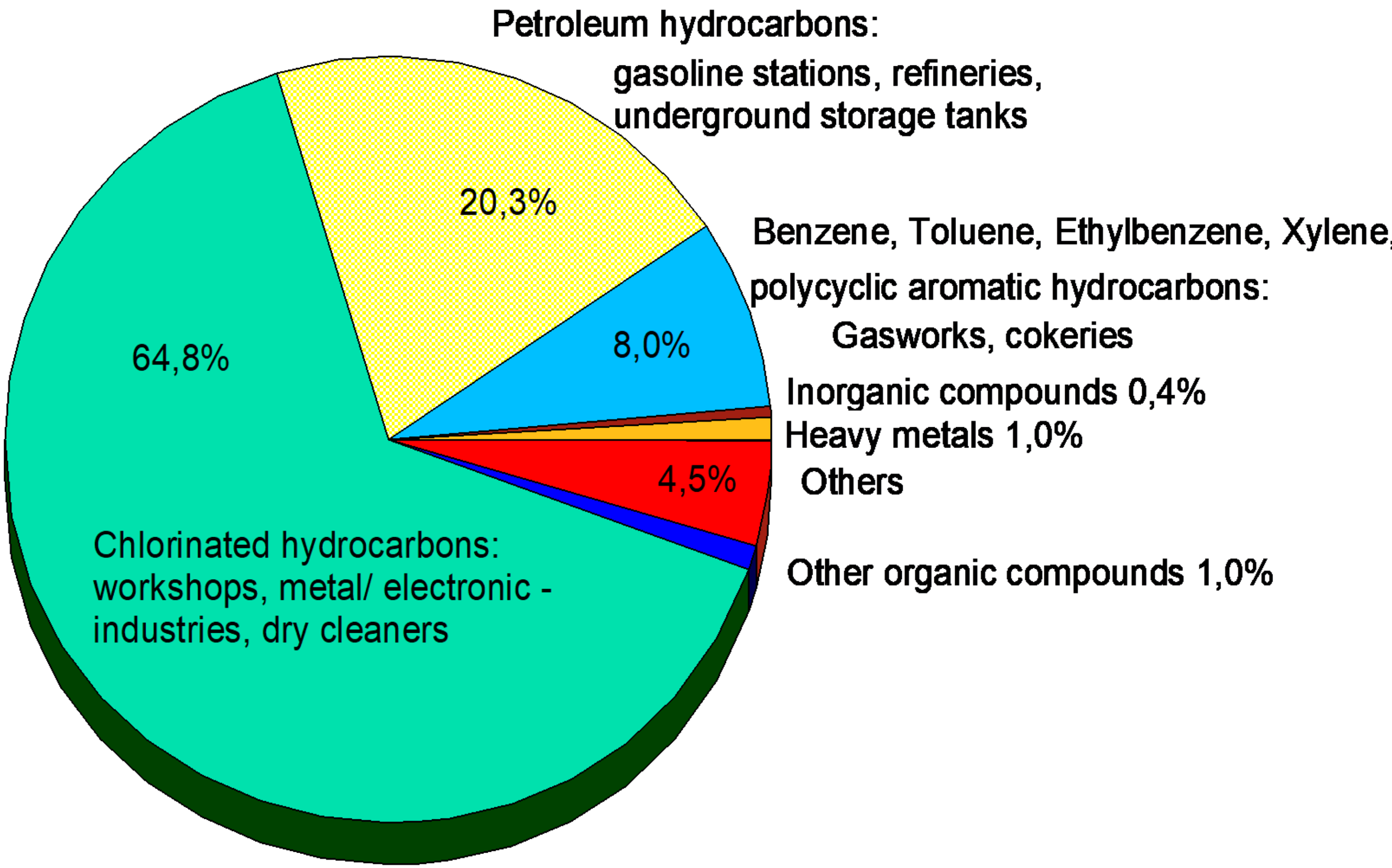
Media Review
Scientists critique media coverage

Article should better explain the threat posed by environmental PCBs. Nov 24
A Los Angeles Times article fails to highlight what PCBs are and why they are such a problem in the first place. more...

An article lists the pros – but not the cons – of a bed bug pesticide. Nov 19

Contaminants in Groundwater
(Baden-Württemberg, LfU, 09/96)

About 1.900 Reported Cases of Groundwater Pollution in the State of Baden-Württemberg

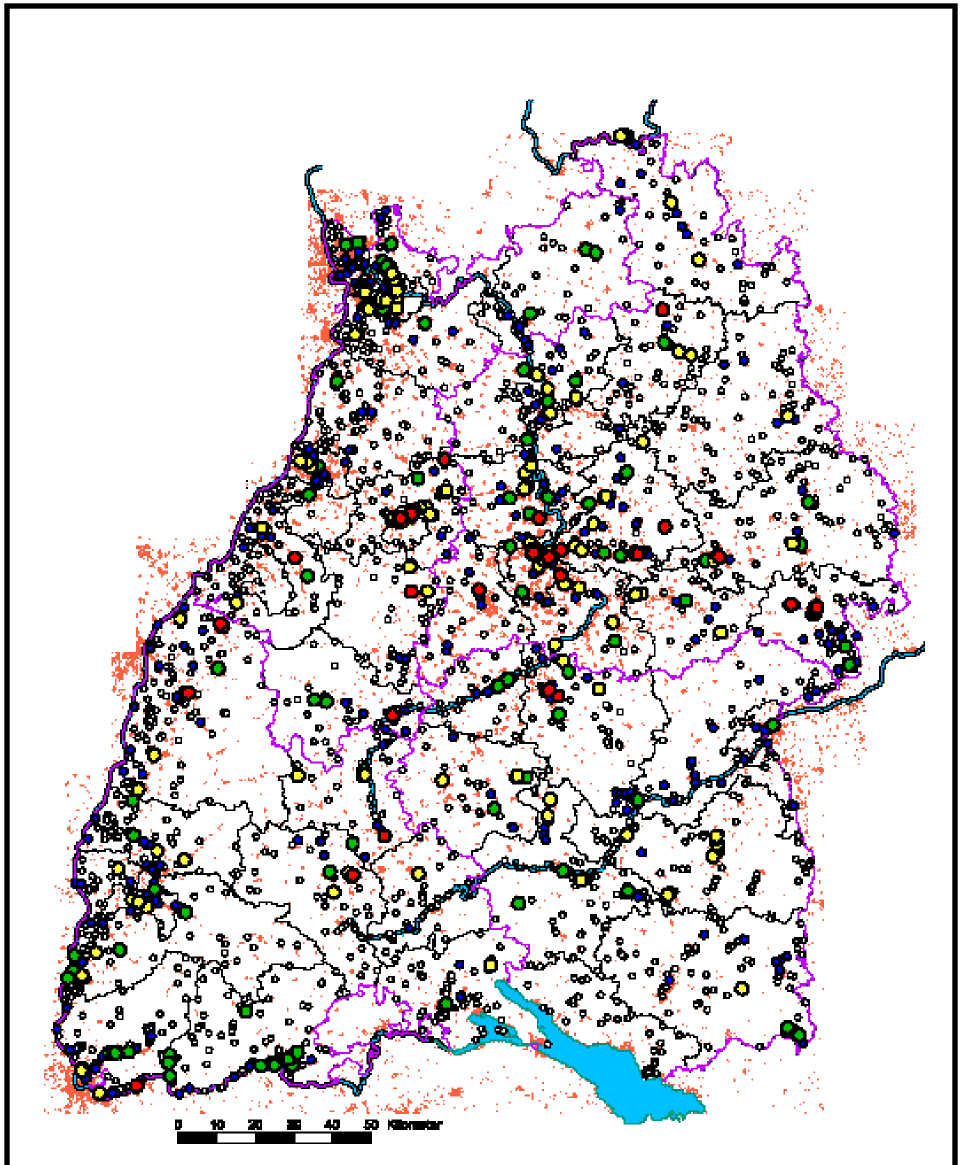


"Brief History" of (Chlorinated) Solvents (textile cleaning, degreasing)

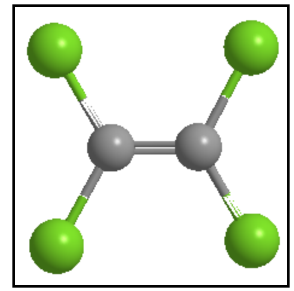
1825 – 1900	**Benzene (carcinogenic, weakly flammable)**
1870 – 1930	**Light gasoline (weakly flammable)**
1900 - 1960	**Heavy gasoline (flammable, less poisonous)**
1880 - 1950	**Carbontetrachloride (not flammable, carcinogenic)**
1930 -	**Per-, Trichloroethene (poor flammability, “non poisonous”)**
1960 -	**CFC, Freons (non poisonous)**
1974	**CFCs degrade ozone (Molina & Rowland)**
1974, 1976	**Haloforms (e.g. chloroform) in drinking water**
1976	**VOC in river water (Rhine)**
1977	**VOC in drinking water, groundwater and mineral waters, TCE carcinogenic?**
1975, 1977	**Formation of HCl, Phosgene and carbontetrachloride through photooxidation of VOCs in the atmosphere**
1984, 1990	**Formation of trichloroacetic acid (through photooxidation of VOC in the atmosphere (connected to forest dieback)**
1986	**Utilization of CFC in textile cleaning (replacement of "per")**
1987	**Montreal Protocol for the banning of ozone degrading chemicals**
1995	**Nobel Prize for Chemistry to Mario Molina, F. Sherwood Rowland (together with Paul Crutzen)**
1996	**End of the production of ozone degrading chemicals in industr. countries**
1996	**Proof of the ubiquitous appearance of trifluoroacetate from HFC (partially fluorinated ethane, CFC replacement, Frank et al., *Nature*, 382, 34)**

................???

PCE in groundwater



Tetrachloroethene (PCE)



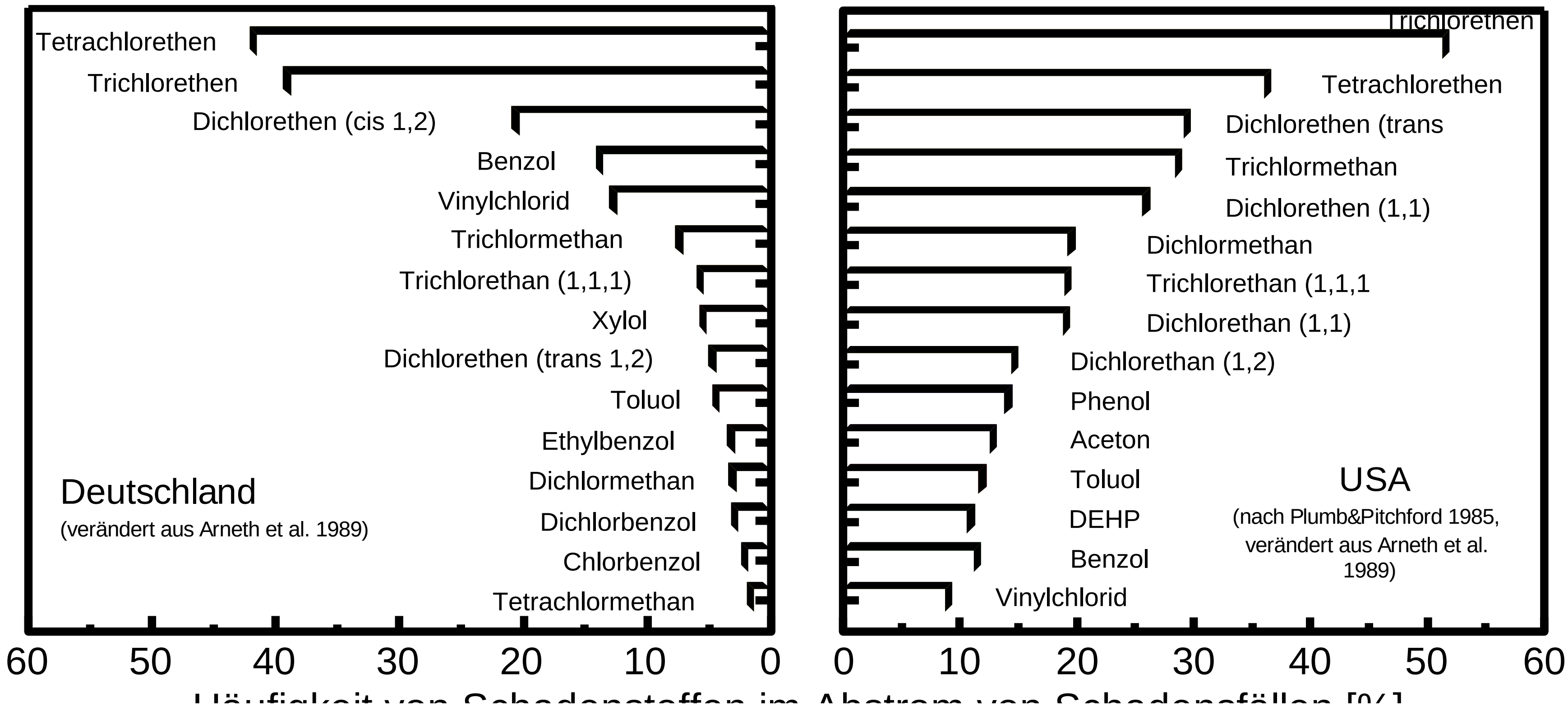
Sampling campaign 1998

Conc. in mg/l

- n.d.
- < 0.0010
- 0.0011 – 0.0050
- 0.0051- 0.1000
- > 0.1000

LFU - Baden Württemberg

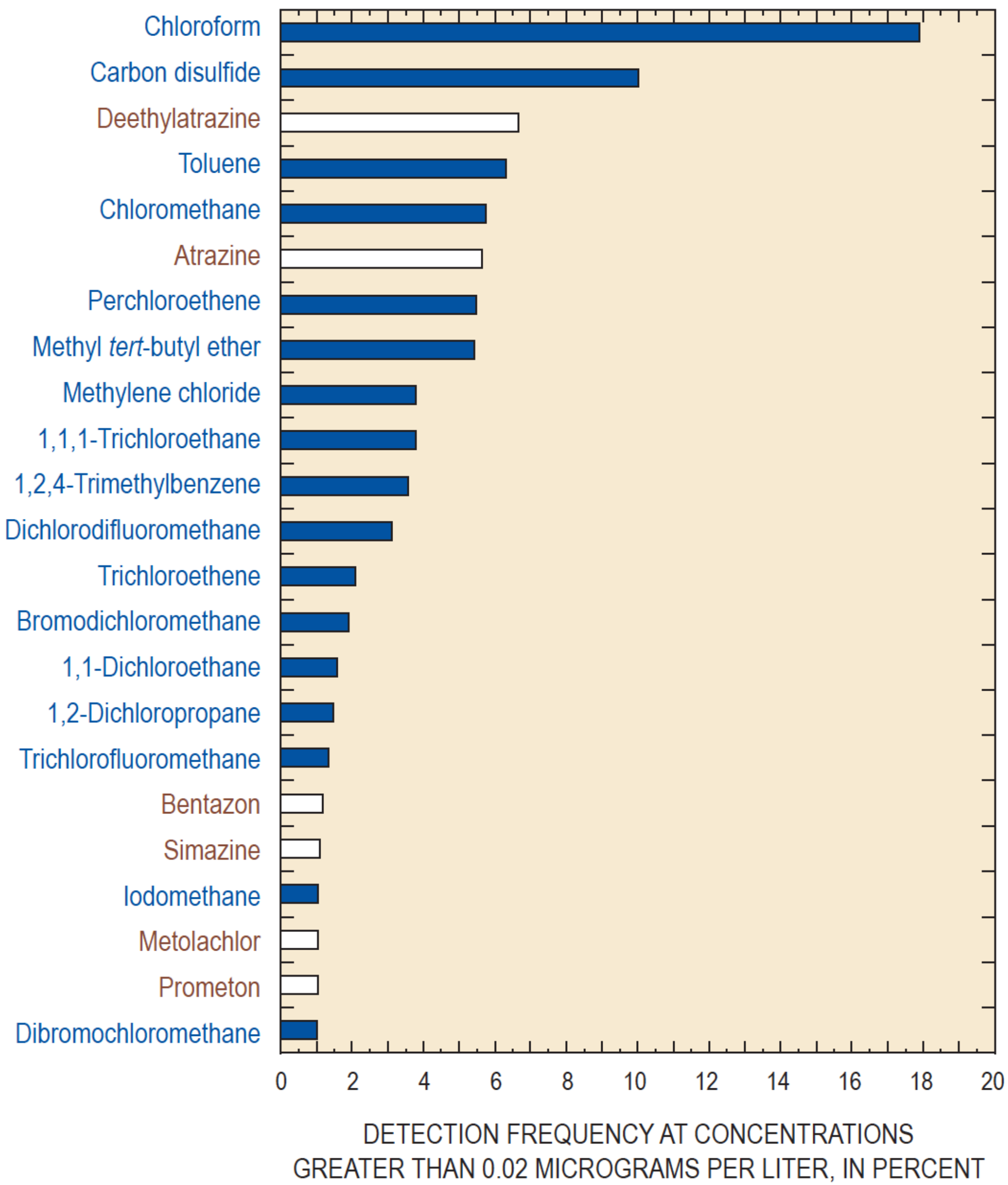
Contaminants in Groundwater - Germany *vs* USA



Occurence of contaminants in plumes [%]

Schiedek et al. 1997

Contaminants in Groundwater Update 2009 (USA)



Detection frequency of VOCs (white) and pesticides (white) at concentrations > 0.02 µg/l in more than 1% of domestic wells.

National Research Council 2013. Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites. Washington, DC: The National Academies Press. https://doi.org/10.17226/14668.

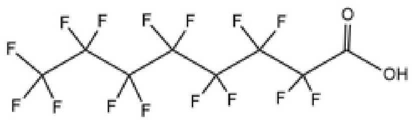
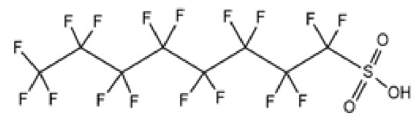
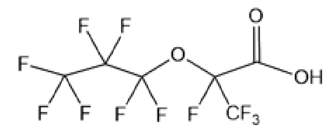
New classes of compounds are released into the environment?

- **Pesticides**
- **Pharmaceuticals**
- **Genetically engineered biochemicals**

“New” contaminants: Per- polyfluoroalkyl subst. (PFAS)

“New” contaminants: Per- and polyfluoroalkyl subst. (PFAS)

Table 1. Physicochemical properties of selected PFCs.

Chemicals	PFOA	PFOS	HFPO-DA
Chemical Formula	$C_8HF_{15}O_2$	$C_8HF_{17}O_3S$	$C_6HF_{11}O_3$
Chemical Structure			
Molecular weight (g mol^{-1}))	414.00[a]	500.10[a]	330.05[b]
Solubility (g L^{-1})	3.40[a]	0.57[a]	7.10[d]
pK_a (-)	-0.20[a]	-3.30[a]	0.06[d]
H (-)	3.71[e]	0.449[e]	0.07[e]
$log\ K_{ow}$ (-)	4.59[a]	5.26[a]	3.95[f]
$log\ K_{oc}$ (-)	-2.90[c]	2.57[h]	1.05[g]

[a] (Milinovic et al., 2015); [b] CAMPRO SCIENTIFIC GmbH; [c] (Barton, Kaiser, & Russell, 2007); [d] (Heydebreck et al., 2015); [e] HENRYWIN v3.10 (Bone Method); [f] KOWWIN v1.67; [g] (Gomis, Wang, Scheringer, & Cousins, 2015); [h] (EPA, 2014)

Everybody uses them…..

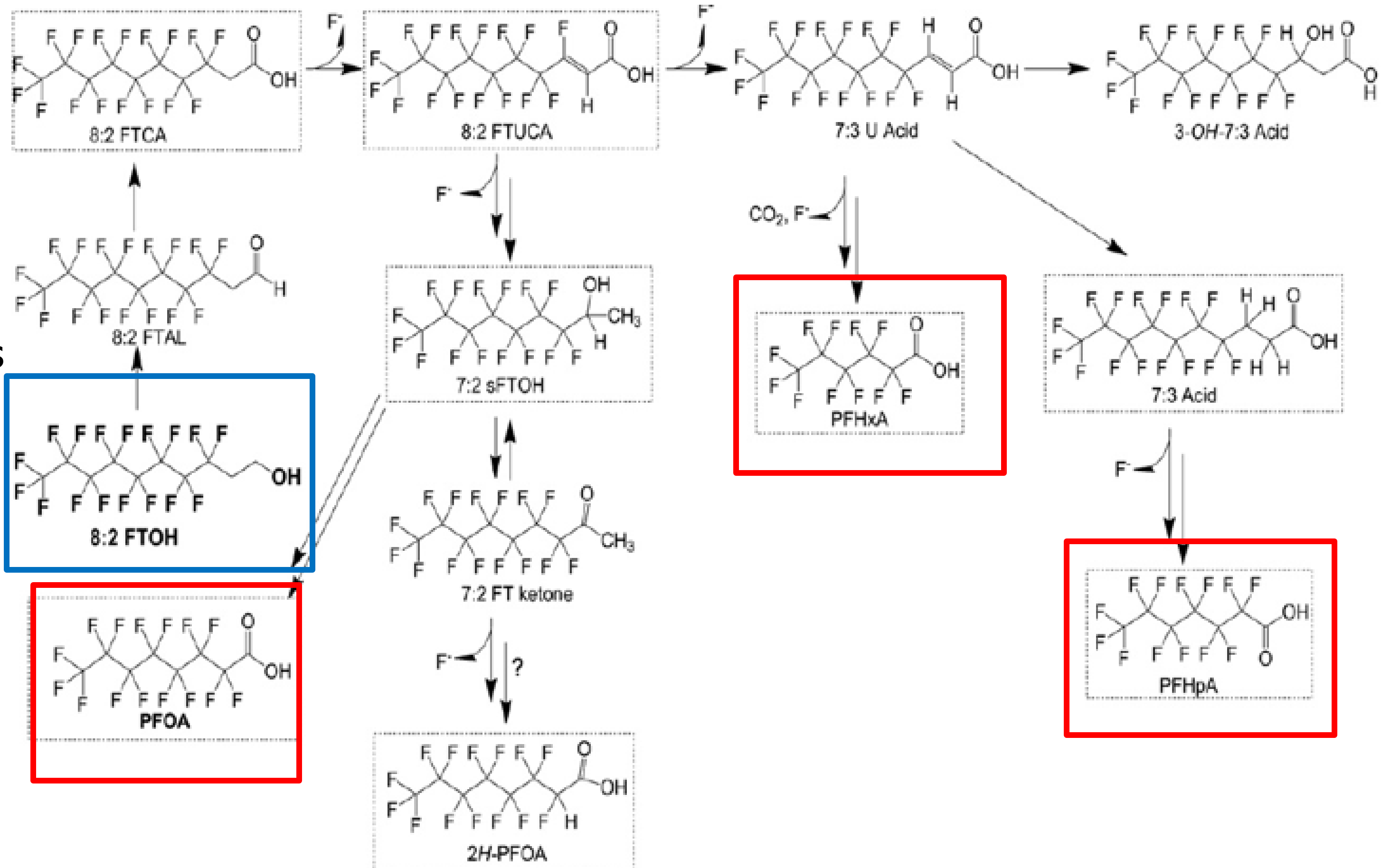
Background - Where do we find PFASs?

- Oil and water-repellent
- Stain-resistant upholstery, carpeting
- Non-stick coatings in cookware (Teflon®)
- Breathable, all weather clothing (Gore-tex®)
- Paper and packaging protectors (food packaging)
- Paints and adhesives
- Fluoro-elastomers (gaskets, O-rings, Hoses)
- Mining and oil surfactants
- Metal plating baths (chromium)
- Pesticides/Insecticides
- Aqueous film-forming foams (AFFF) for fire fighting

PFAS - Precursors

Per- and polyfluorinated alkyl substances (PFAS) comprise >3000 individual compounds

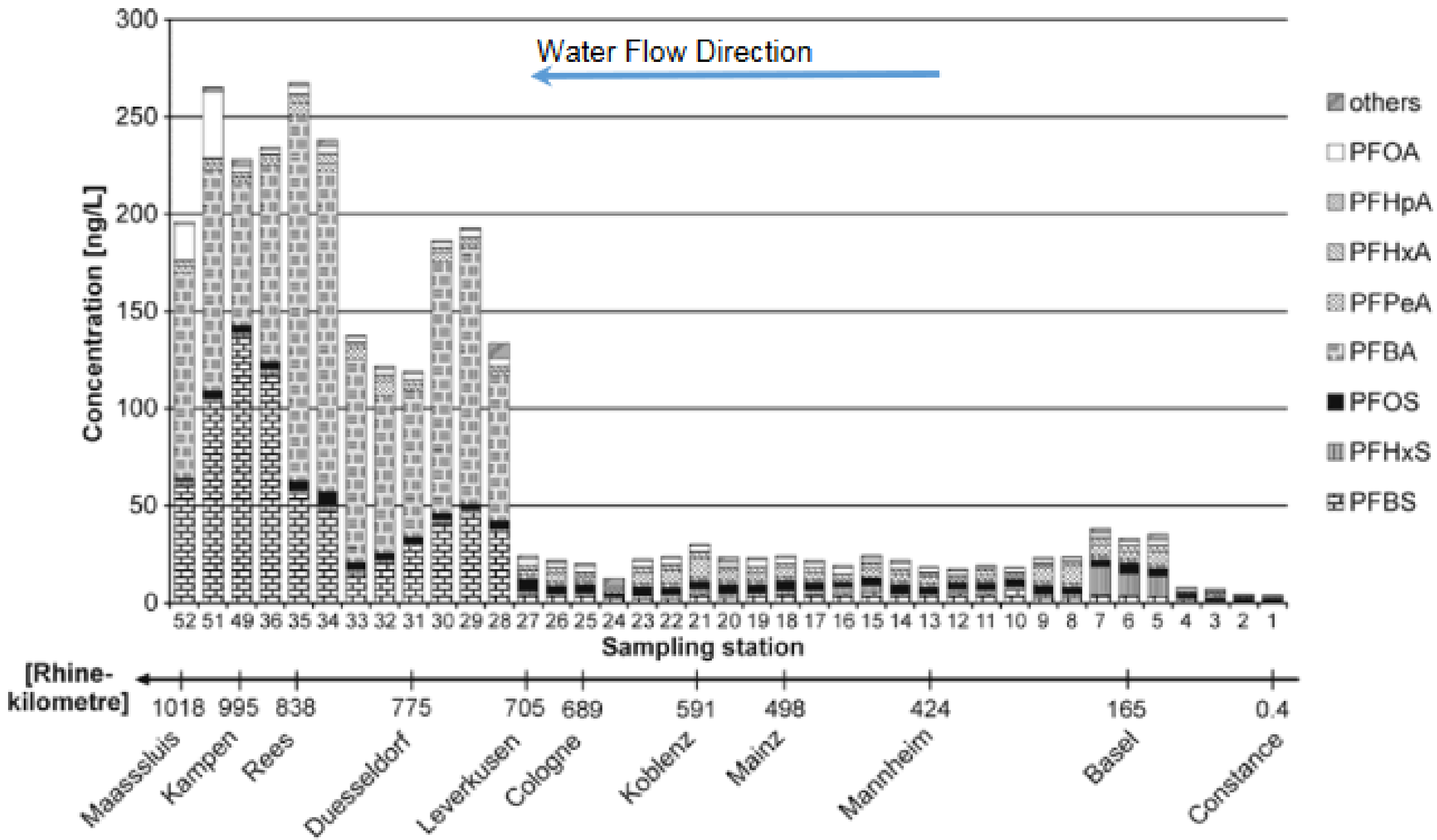
Precursors forming stable end-products e.g., perfluorinated carbonic acids (PFCAs) and perflurionated sulfonic acids (PFSAs)



Wang et al. 2009 Chemosphere 75 1089–1096

"New" contaminants: Per-, polyfluoroalkyl subst. (PFAS)

Figure 6.1: PFAS concentration profile in surface water along the River Rhine (Moeller et al., 2010)



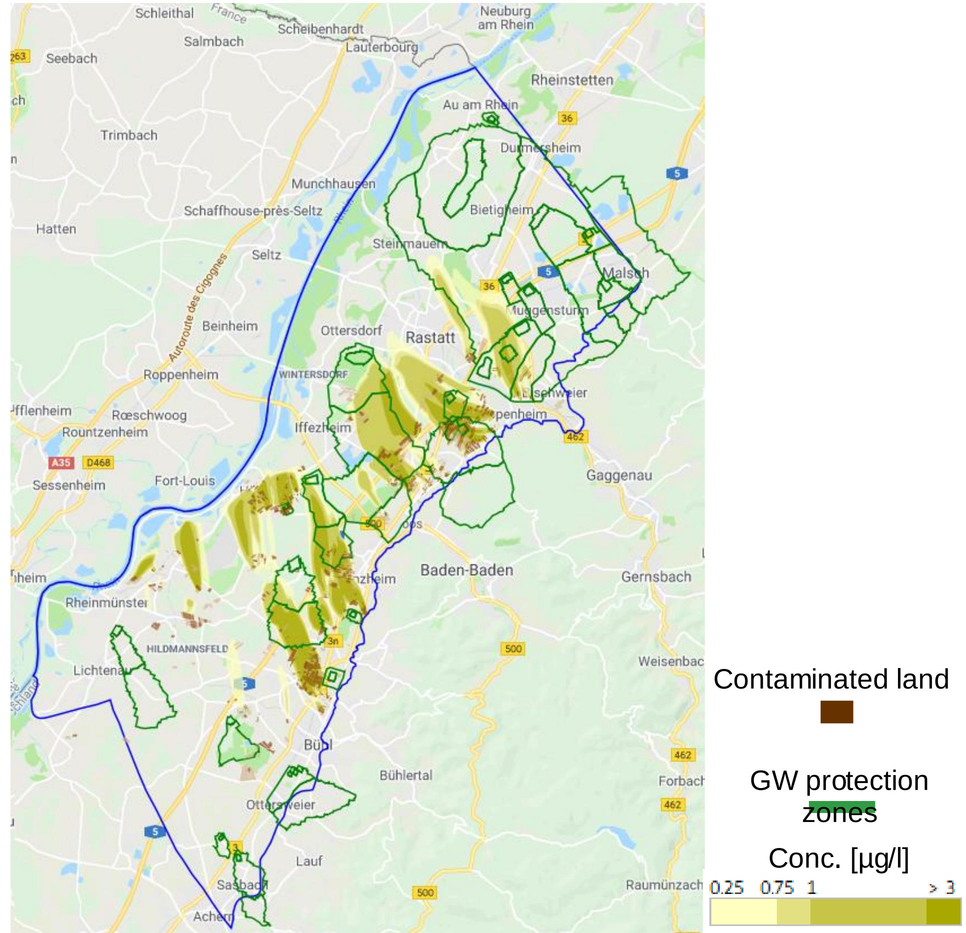
Flux: ca. 30 kg / day

"New" contaminants: Per-, polyfluoroalkyl subst. (PFAS)

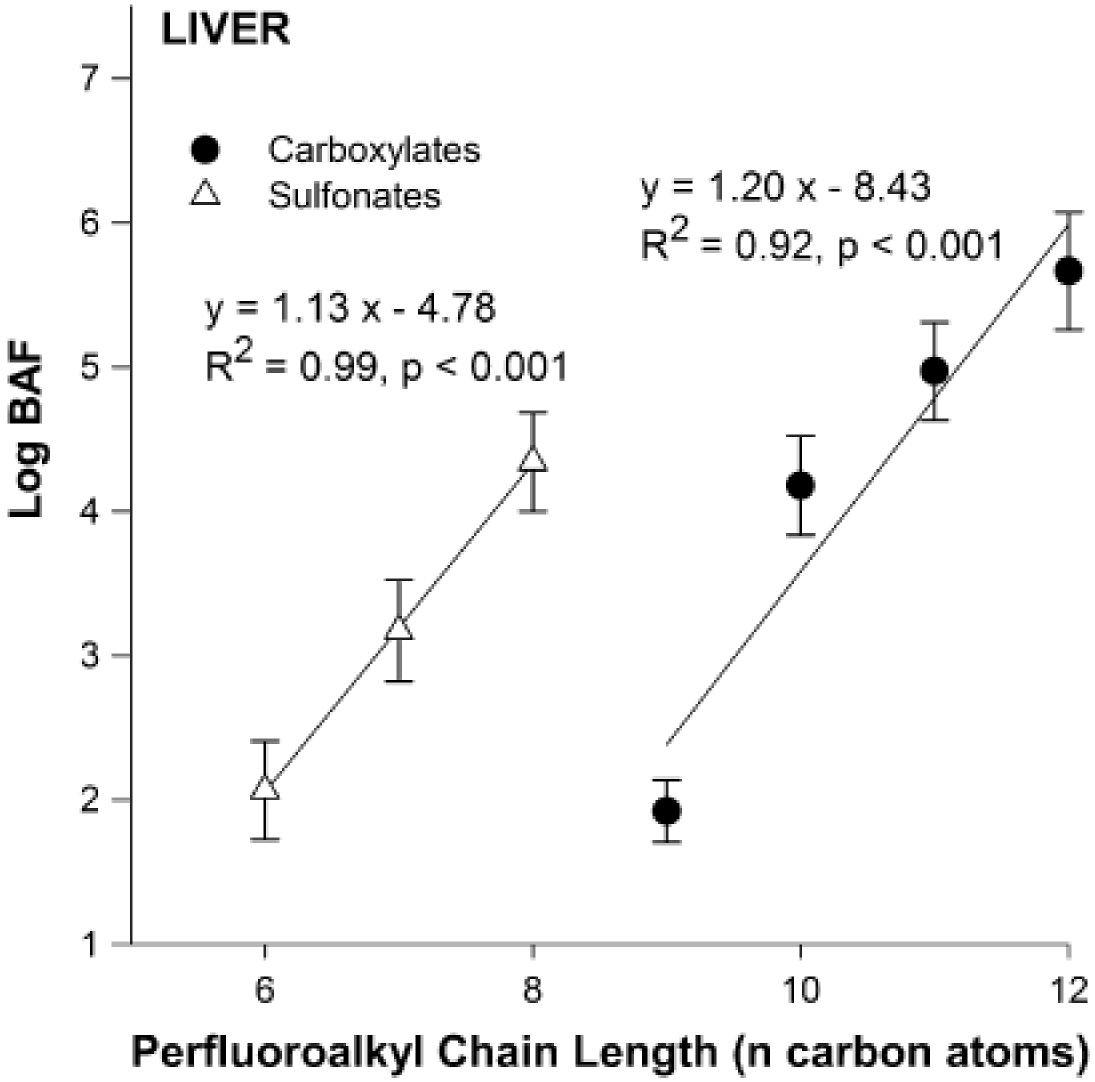
Agricultural Cases

- In Baden-Wuerttemberg approx. 600 Ha of agricultural land contaminated with compost containing PFAS (paper sludge)

"Terrafarm"



“New” contaminants: Per-, polyfluoroalkyl subst. (PFAS)



Labadie, P., Chevreuil, M. (2011): Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environmental Pollution, 159, 391-397

Environmentally Significant Phys.-chem. Properties of Organic Pollutants

1. **Volatility:** Boiling Point, vapor pressure; saturation concentration in air (soil air)

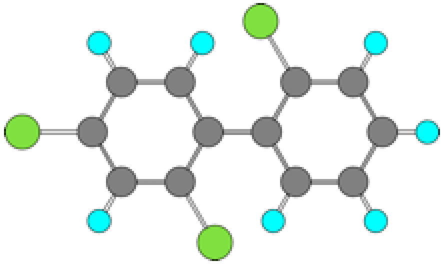
2. **Solubility** in surface water, groundwater, seepage water: Dependency on dissolved organic carbon, colloidal/suspended particles, cosolvents, surfactants, ionic strength, etc.

3. **Mobility:** Density, viscosity, wetting properties of non-aqueous phase liquids (NAPL); diffusion of dissolved and vapor phase compounds; sorption/retardation.

4. **Persistence:** Hydrolysis, photo-, biodegradation, bioavailability

5. **Accumulation:** Hydrophobicity, lipophily, sorption (octanol/water-partitioning coefficient: K_{ow})

Example: PCB-accumulation in environmental compartments



PCB concentrations [mg/kg] in the North Sea

- Sea water: 0.000002
- sediments: 0.01
- plankton: 10
- fish: 19
- birds: 110
- mammals: 160

Accumulation / bioconcentration factors

- sediments: 5 000
- mammals: 1 000 000