Common Chemicals

Agenda

- Metals
- Organic Chemicals
  - Petroleum
  - Coal Tar
  - Chlorinated Solvents
  - PCBs
  - PFAS

What do we test for?

- Inorganics: Target Analyte List (TAL) From the EPA's Contract Laboratory Program (CLP).
- Organics Target Compound List (TCL)
  - TICs (volatiles & semi-volatiles) also defined by the CLP
- NYSDEC recently began requiring PFAS for this sampling, and lowered the detection limit for 1,4-dioxane
- What's next?

TAL

- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Magnesium
- Manganese
- Mercury
- Nickel
- Potassium
- Selenium
- Silver
- Sodium
- Thallium
- Vanadium
- Zinc
- Cyanide

Metals

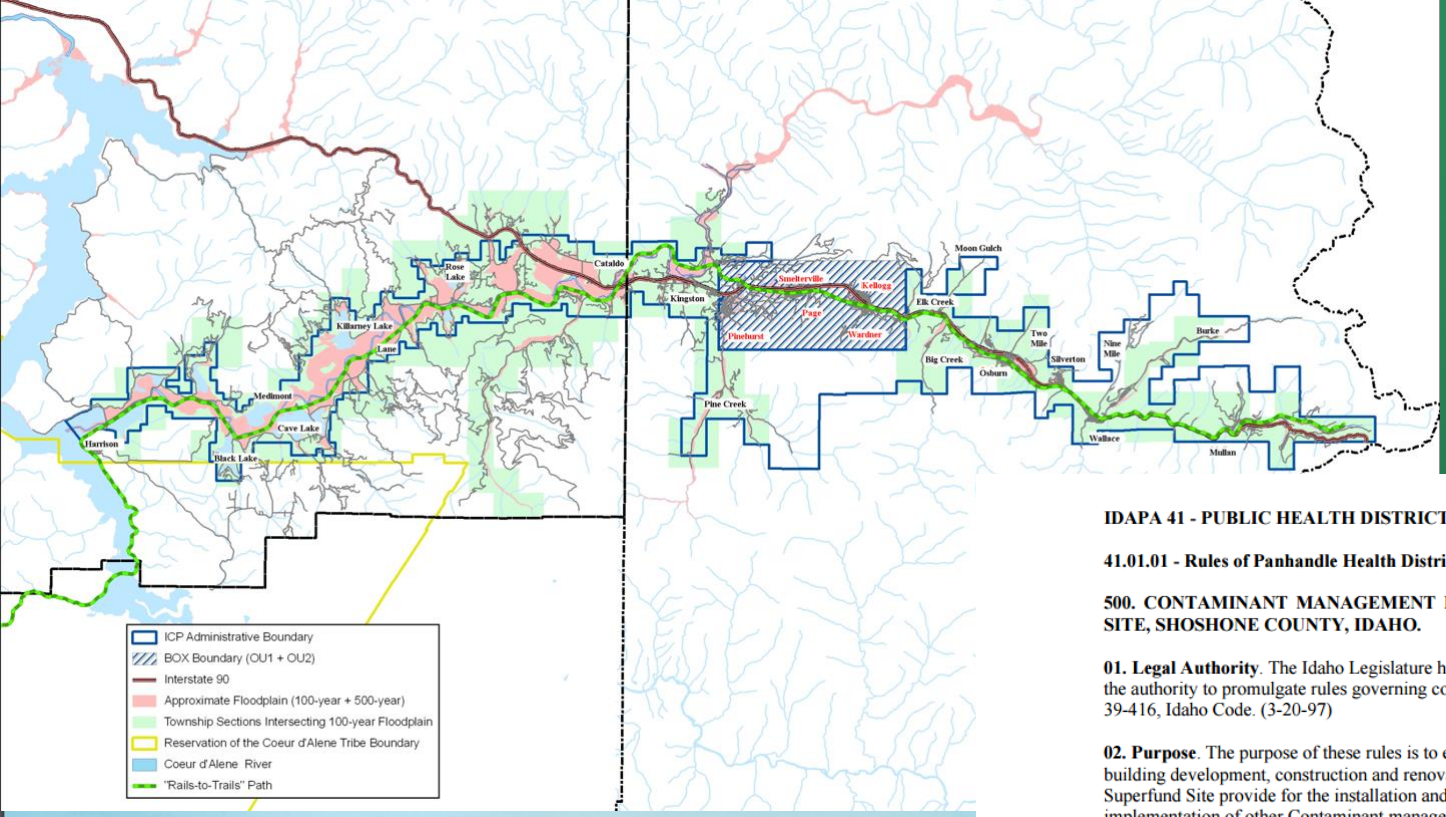
- Totals vs TCLP vs SPLP
- Most health risk criteria are based on total concentration.
- RCRA determinations are based on TCLP.
- If you want to know how it will actually leach, use SPLP.
  - "East coast" vs "west coast"

Lead

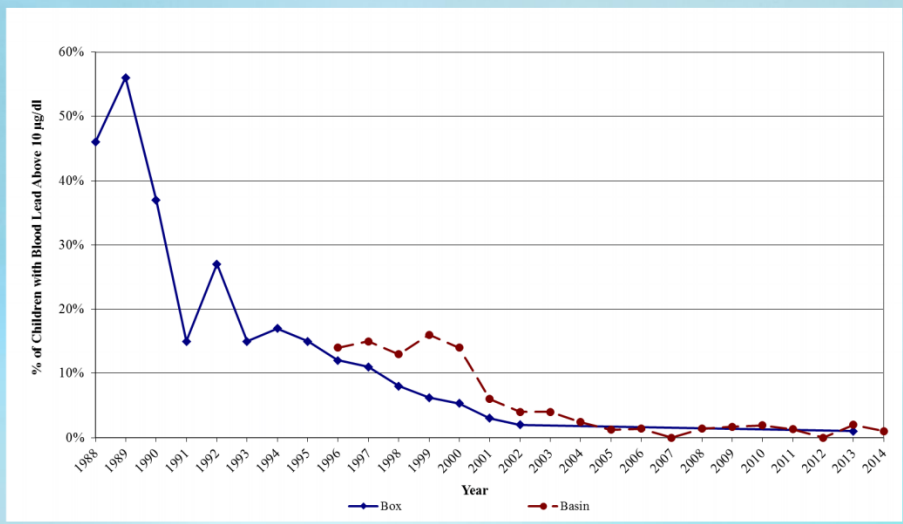
- Direct exposure is the primary concern (ingestion, inhalation).
  - No amount of lead is safe for children
- Hazardous waste with TCLP >5
- LDR restrictions: 0.75 ppm TCLP (alternative standard: 90% reduction capped at 7.5 ppm).
- Chemical stabilization will decrease TCLP.
- Relatively low solubility unless pH is low
- Consumer products (cosmetics with 50% lead by weight)

Lead Sites

- Frequently in historic fill
- Mines, smelting
- Battery recycler, CRTs
- Bunker Hill, Idaho
  - From smelting
  - Very large area
  - Public health crisis



Percent of Children with Blood Lead Levels ≥ 10 µg/dl, Box and Basin, 1988-2014



IDAPA 41 - PUBLIC HEALTH DISTRICTS

41.01.01 - Rules of Panhandle Health District 1

500. CONTAMINANT MANAGEMENT IN THE BUNKER HILL SUPERFUND SITE, SHOSHONE COUNTY, IDAHO.

01. Legal Authority. The Idaho Legislature has given the Board of Health of the District the authority to promulgate rules governing contaminant management pursuant to Section 39-416, Idaho Code. (3-20-97)

02. Purpose. The purpose of these rules is to ensure that activities involving excavations, building development, construction and renovation and grading within the Bunker Hill Superfund Site provide for the installation and maintenance of Barriers and implementation of other Contaminant management standards to preclude the migration of, and particularly, human exposure to Contaminants within the Site as necessary to protect the public health and the environment. It is imperative that redevelopment and future development proceed in a manner which minimizes the release of Contaminants into the air or water to minimize exposure to workers, Site residents and the communities. Further, it is the purpose of these rules to complement existing land use authorities and permitting processes, and to provide a screening process to determine whether proposed activities are subject to these rules. (3-20-97)

03. Written Interpretations. This agency may have written statements and standards which pertain to the interpretation of the rules of this chapter, or to the documentation of compliance with the rules of this chapter. If available, written statements and standards can be inspected and copied at cost at the Panhandle Health District Office, 114 West Riverside Avenue, Kellogg, Idaho. (3-20-97)

04. Administrative Appeals. Persons may be entitled to appeal final agency actions authorized under this chapter pursuant to IDAPA 04.11.01, "Idaho Rules of Administrative Procedure of the Attorney General." (3-20-97)

05. Definitions. The following terms shall be construed throughout these rules in a manner consistent with these definitions: (3-20-97)

a. Applicant. Any person, contractor, public utility, government or other entity that is required to apply for an ICP Permit. (3-20-97)

b. Barrier. Any physical structure, material or mechanism which breaks the pathway between contaminants and human receptors, including but not limited to walls, floors, ceilings, soil, asphalt, concrete, fences, control over access, or other structure or covering which separates contaminants from contact with people or keeps contaminants in place.

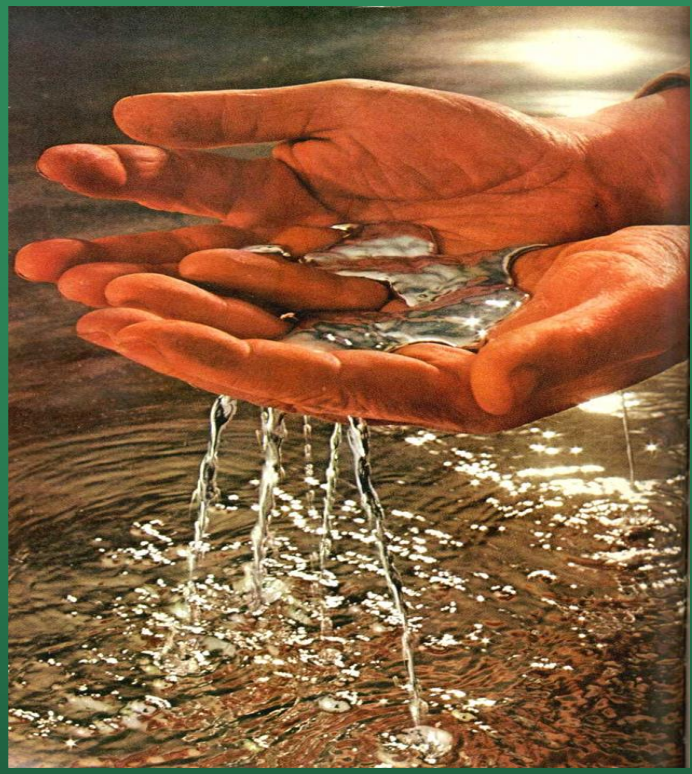
Arsenic

- Acute poison (tolerance)
- Carcinogen
- Pesticides (lead arsenate)
  - orchards
- Bangladesh
  - 20 million people
  - Wells installed to eliminate waterborne disease
- RCRA (5.0 mg/l TCLP)

Chromium

- Hexavalent vs Trivalent
- Erin Brockovich
- Chemical reduction of groundwater to treat hex chrome
- ISCO can mobilize naturally occurring chromium (appears to be transient)
- California set a 10 ppb MCL. Vacated by the courts (2017)

Mercury



- Elemental
  - Specialized response
  - Call in the experts
- RCRA
- Vapors
- Kiddie Kollege
- Cosmetics and supplements
  - Ayurvedic medicine up to 3% mercury

Metal Plating sites

- Metals
  - Cyanide
  - Chromium
  - Other metals (nickel…)
- Solvents
- Acids
- PFAS

Organic Chemicals

- EPA “Target Analyte List” (TAL)
  - Volatile organic chemicals
  - Semi-volatile organic chemicals
  - Pesticides
  - PCBs
- Emerging contaminants - PFAS

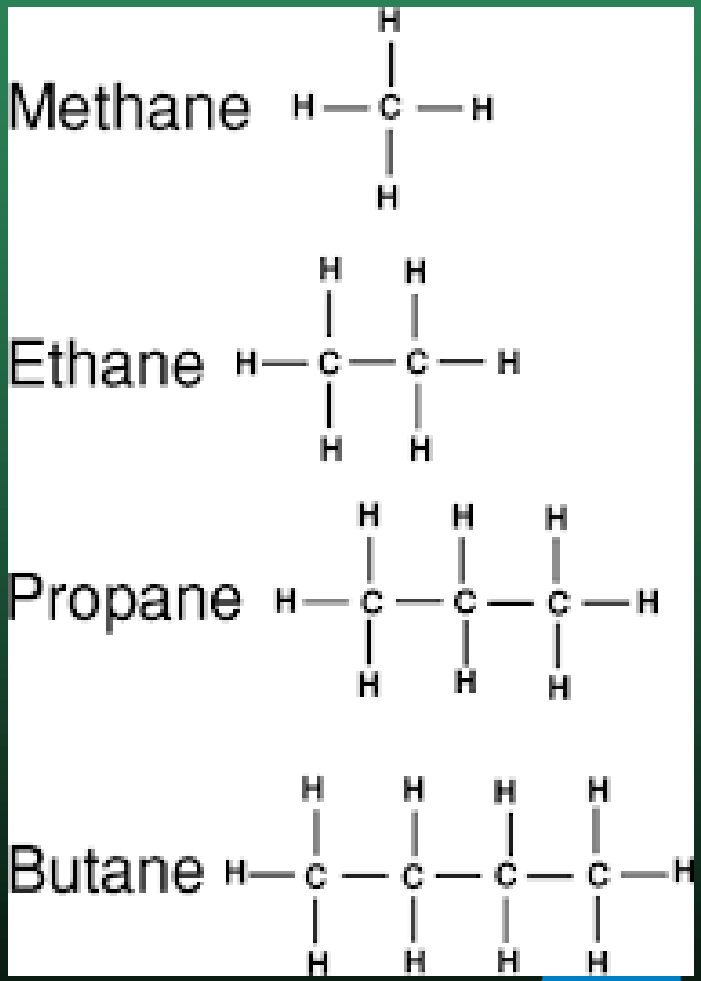
Forensic: PIANO

- Paraffins
- Isoparaffins
- Aromatics
- Naphthenes
- Olefins

Paraffins (Alkanes)

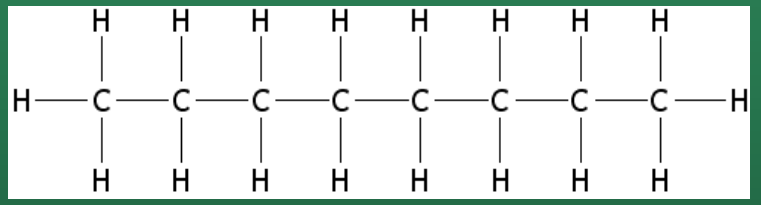
Normal paraffins have single carbon-carbon bonds and are saturated. Also sometimes called straight chain hydrocarbons.

Paraffin has a separate meaning: a flammable, whitish, translucent, waxy solid.

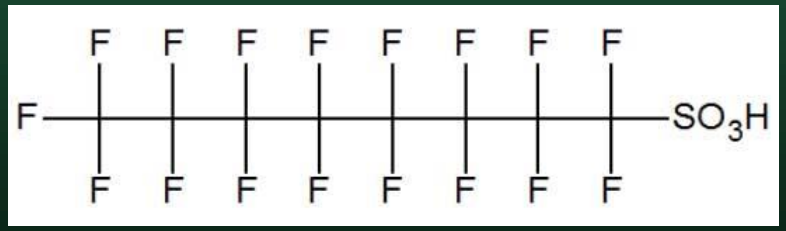


PFOS –VS- Octane

Octane

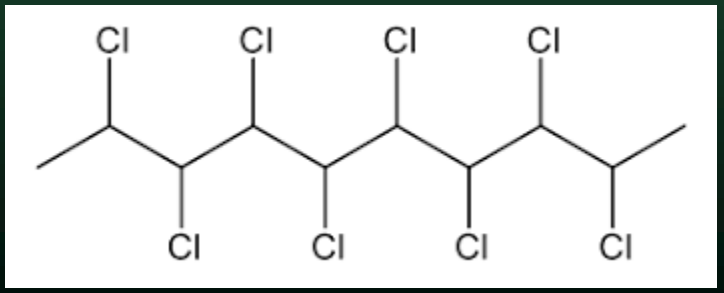


PFOS



Are there Chlorainated Alkanes?

- Referred to as chlorinated paraffins (CPs)
- Classified as persistent, expected to have a high potential for bioaccumulation.
- Classified as toxic to aquatic organisms, and carcinogenic to rats and mice.
- Long chain CPs are "possible human carcinogens" group 2B (IARC).



Octachlorodecane

Isoparaffins (branched alkanes)

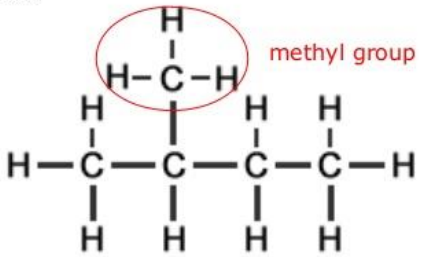
ALKANES

IUPAC naming system:

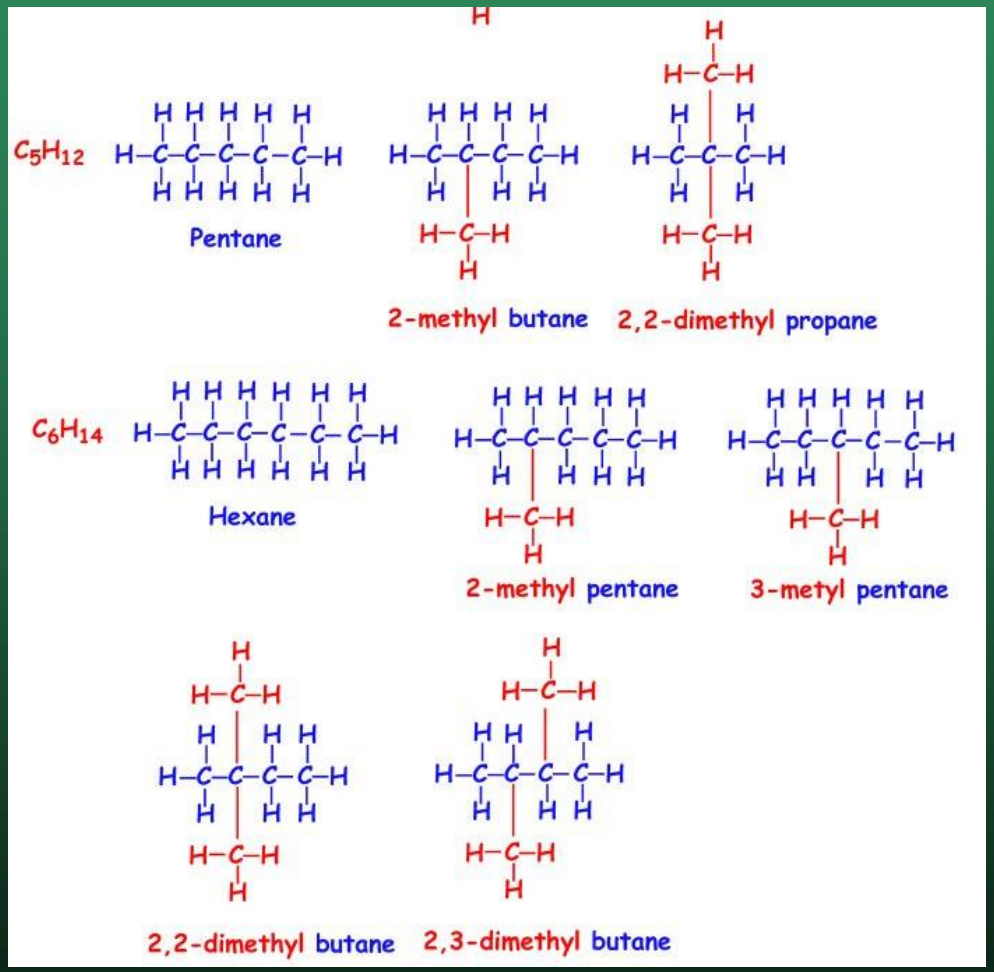
Not all alkanes are straight chains. Some alkanes have alkyl side groups (*alkyl substituents*) attached.

$-CH_3$	**methyl**
$-C_2H_5$	**ethyl**
$-C_3H_7$	**propyl**
$-C_4H_9$	**butyl**
$-C_5H_{11}$	**pentyl**
$-C_6H_{13}$	**hexyl**
$-C_7H_{15}$	**heptyl**
$-C_8H_{17}$	**octyl**

Ex:



name: methylbutane

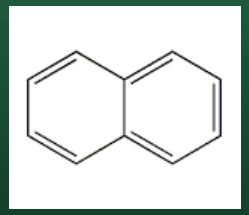


Isomers

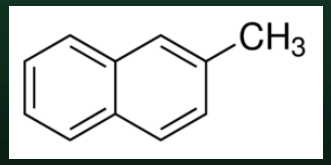
- Octane (n-octane)
- 2-Methylheptane.
- 3-Methylheptane (2 enantiomers)
- 4-Methylheptane.
- 3-Ethylhexane.
- 2,2-Dimethylhexane.
- 2,3-Dimethylhexane (2 enantiomers)
- 2,4-Dimethylhexane (2 enantiomers)

Aromatics

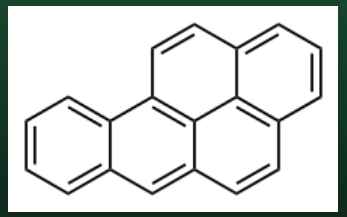
- Rings like benzene and PAHs
- Benzo(a)pyrene shown at right
- Aromatics have unsaturated rings



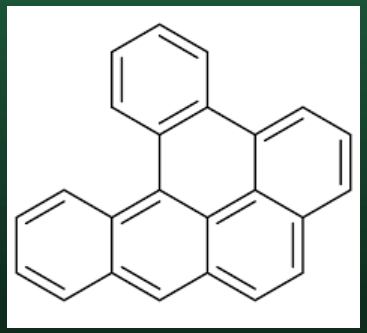
Naphthalene



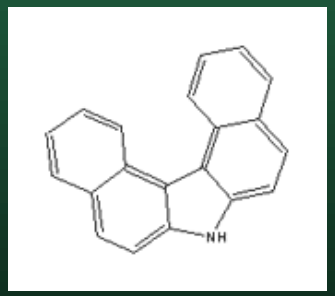
2-methylnaphthalene



Benzo(a)pyrene



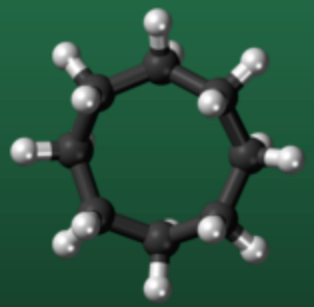
Dibenzo[a,l]pyrene



Dibenzo[a,h]pyrene

Naphthenes

- Cyclo alkanes
  - Cyclohexane
  - Cyclooctane



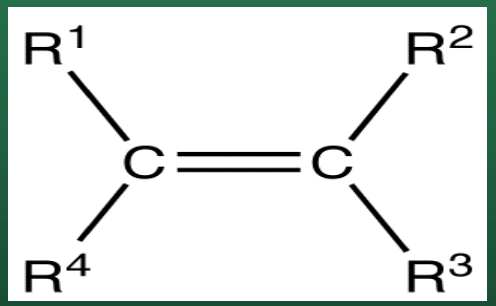
Olefins (Alkenes)

Olefins or alkenes

Double bond at the primary or alpha (α) position.

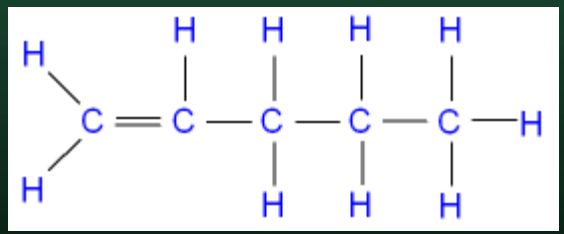
Examples:

Ethene (PCE, TCE, DCE)

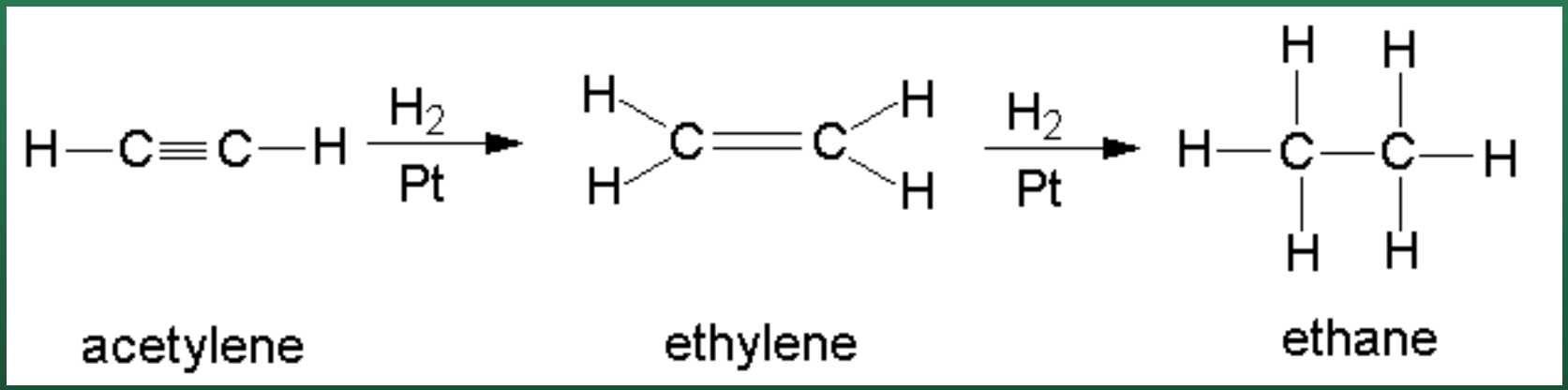


Longer chains are possible

But not common: Pentene



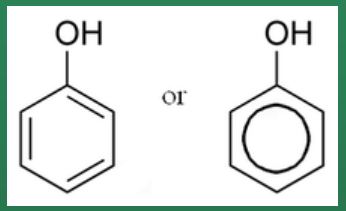
Ethene and Ethane



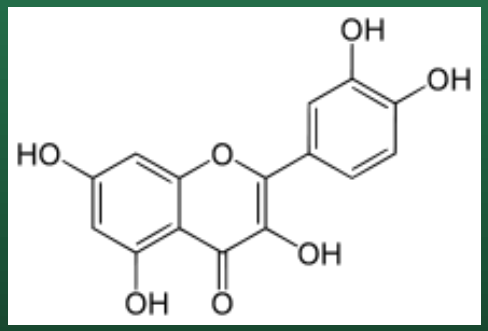
Could have a similar chain with Pentyne, Pentene, Pentane

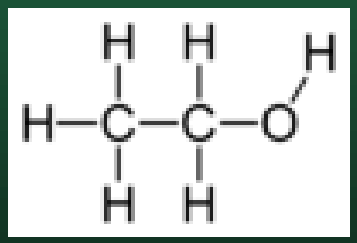
Alcohols and Phenols

Consists of a hydroxyl group (—OH) bonded directly to an aromatic hydrocarbon group.



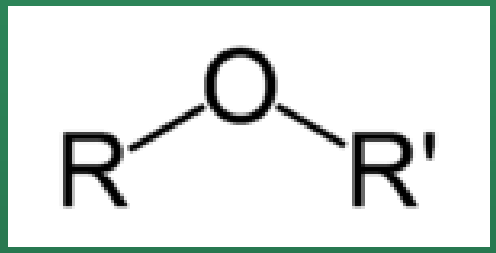
Phenol





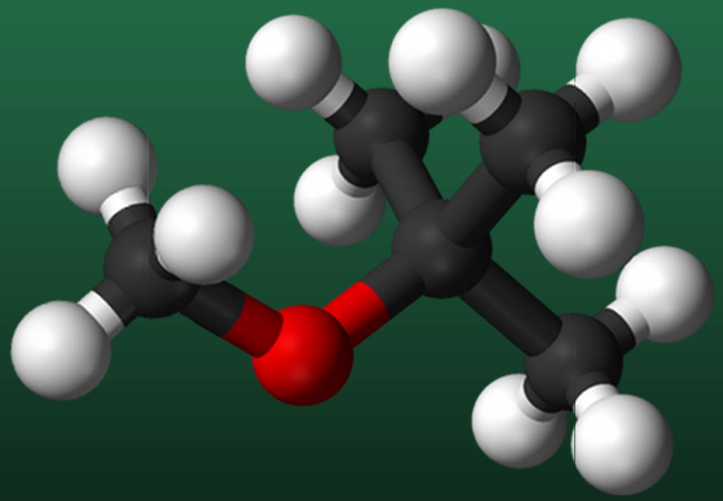
EtOH (Ethyl Alcohol)

Ethers



An organic compound that contains an ether group.

MTBE ->
1,4-dioxane
Propylene Glycol



Protection of Groundwater

- [Soil] = foc x Koc x [Water]
  - foc = fraction of organic carbon of the natural soil medium.
  - Koc = partition coefficient between water and soil media.
- DAF: Dilution-Attenuation Factor (~100)

Deep Breath

End of basic organic chemistry review

Petroleum

- Gasoline
  - More volatile chemicals
- Diesel and Kerosene
  - Lower volatile content
- Jet fuel:
  - Similar to diesel/kerosene
- #6: Has to be heated to flow.
  - Very little volatile content. (a.k.a. “Bunker Fuel”)

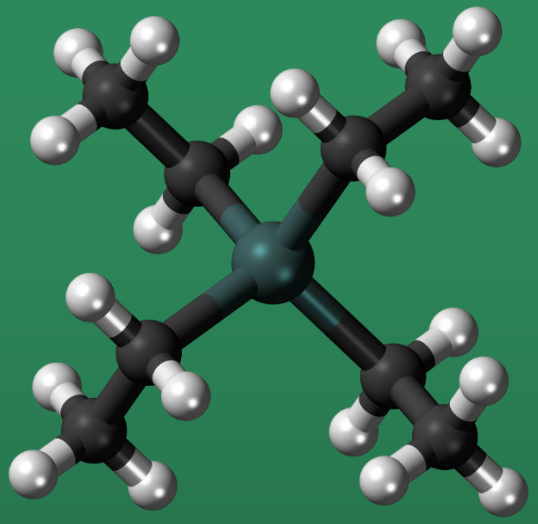
Composition of Crude Oil

Hydrocarbon	Average	Range
Alkanes (paraffins)	30%	15 to 60%
Naphthenes	49%	30 to 60%
Aromatics	15%	3 to 30%
Asphaltics	6%	remainder

SUPPLY AND DEMAND

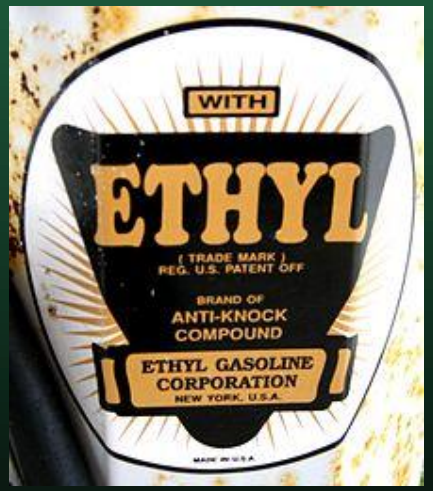
When crude oil is distilled it produces a certain % of each of the main products. Unfortunately the market demands are different to the actual supply.

Fraction	Number of carbon atoms	Approx. % from crude oil	Approx. % required
Gas	1 -4	2	4
Petrol	5 - 10	6	22
Naphtha	8 - 12	10	5
Paraffin	9 - 16	13	8
Diesel	15 - 25	19	23
Fuel Oil/residue	20 - 30	50	38



Tetraethyllead

- Invented in 1921 to improve performance
- Invented by Thomas Midgley Jr., who later came up with Freon
- Midgley possessed "an instinct for the regrettable that was almost uncanny”
- Large number of lead poisoning deaths in production facilities
- $(CH_3CH_2)_4Pb$



BTEX

- Degrade aerobically
- Volatile
- Toxicity

Coal Tar

- Coal carbonization
  - Valuable byproduct
- Water gas
  - Hot/Cold plant
  - Viscosity
  - Emulsions
- Tar handling equipment


CAUTION
CAUTION


'99 9 24

Tar –vs- petroleum

- Hump-o-gram vs spikes

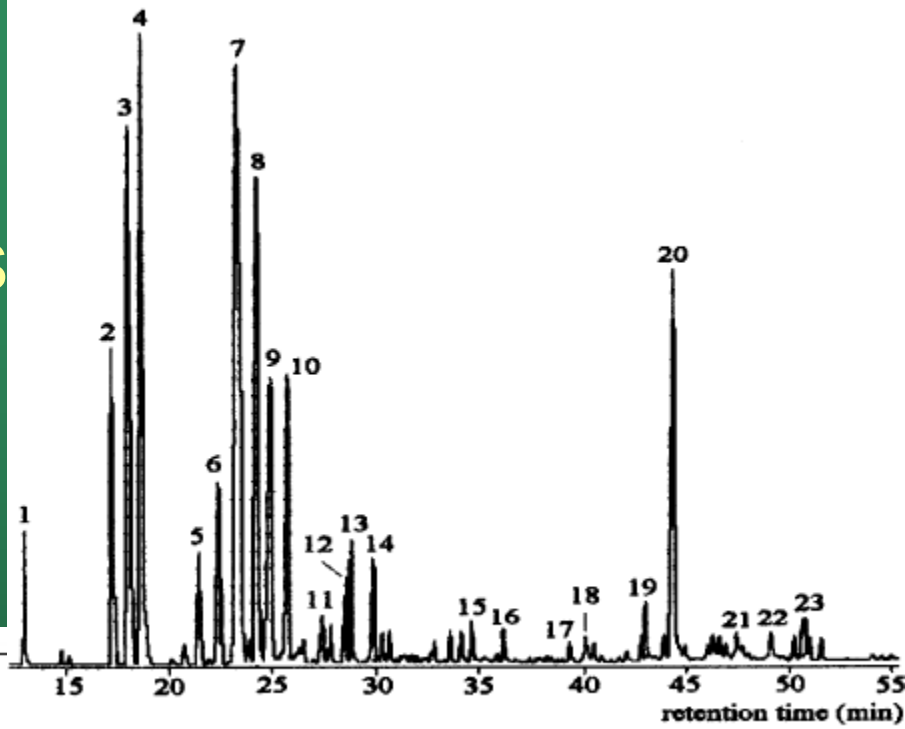


Figure 1. TIC chromatogram of the phenolic compounds in coal tar extract

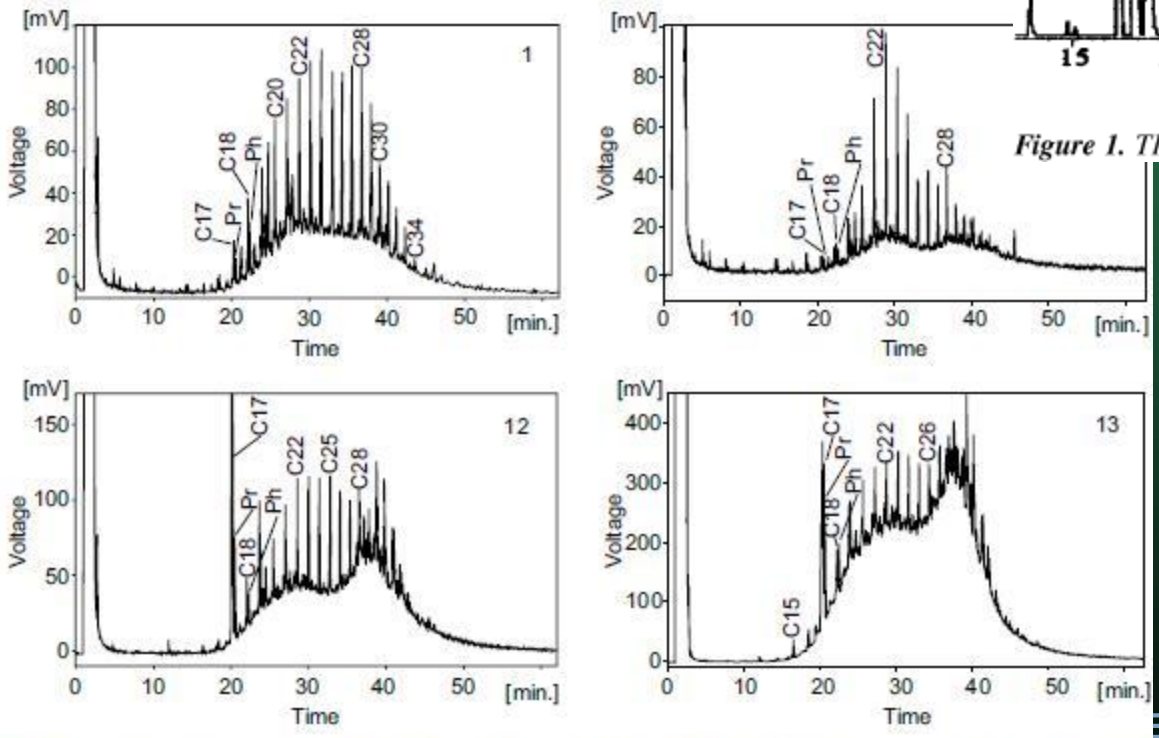


Fig. 2. Selected gas chromatograms of the aliphatic hydrocarbon fractions of sediment samples collected at Northeastern Havana Littoral

Environmental Conservation

Chlorinated Solvents

PCE, TCE

TCA

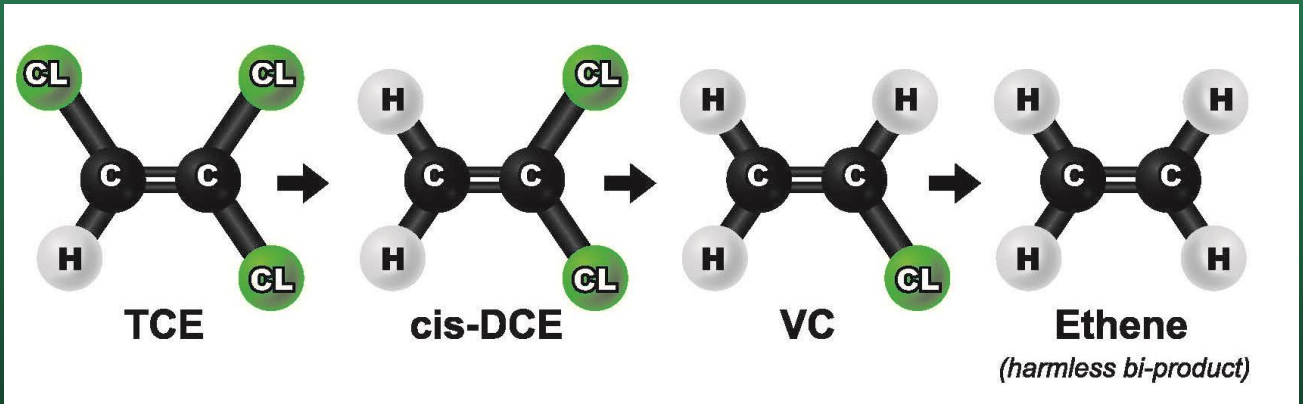
Physical properties

- Specific gravity >1 (DNAPL)
- Low vapor pressure and henry's law constant leads to soil vapor intrusion (SVI) concerns
- Penetrating ability (also gets you into clay and rock fractures)
- Do not biodegrade aerobically
- TCA is an ozone depleting substance

SVI

- EPA issued their first draft guidance in 2002. A result of a lawsuit in Colorado.
- Initial guidance assumed all vapors were coming from contaminated groundwater

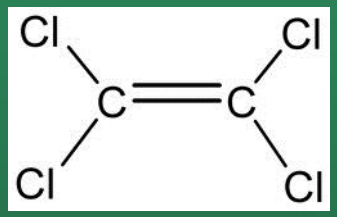
Reductive Dechlorination



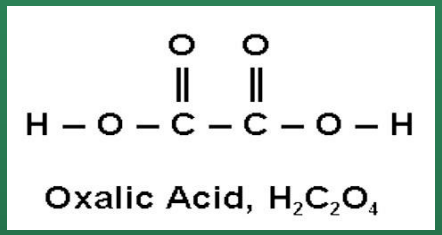
Attenuation parameters

- Dissolved oxygen (DO)
  - <0.5 mg/L for reductive dechlorination
- Oxidation-Reduction Potential
  - Has to be negative for reductive dechlorination (-200 to -300).

Chemical Oxidation

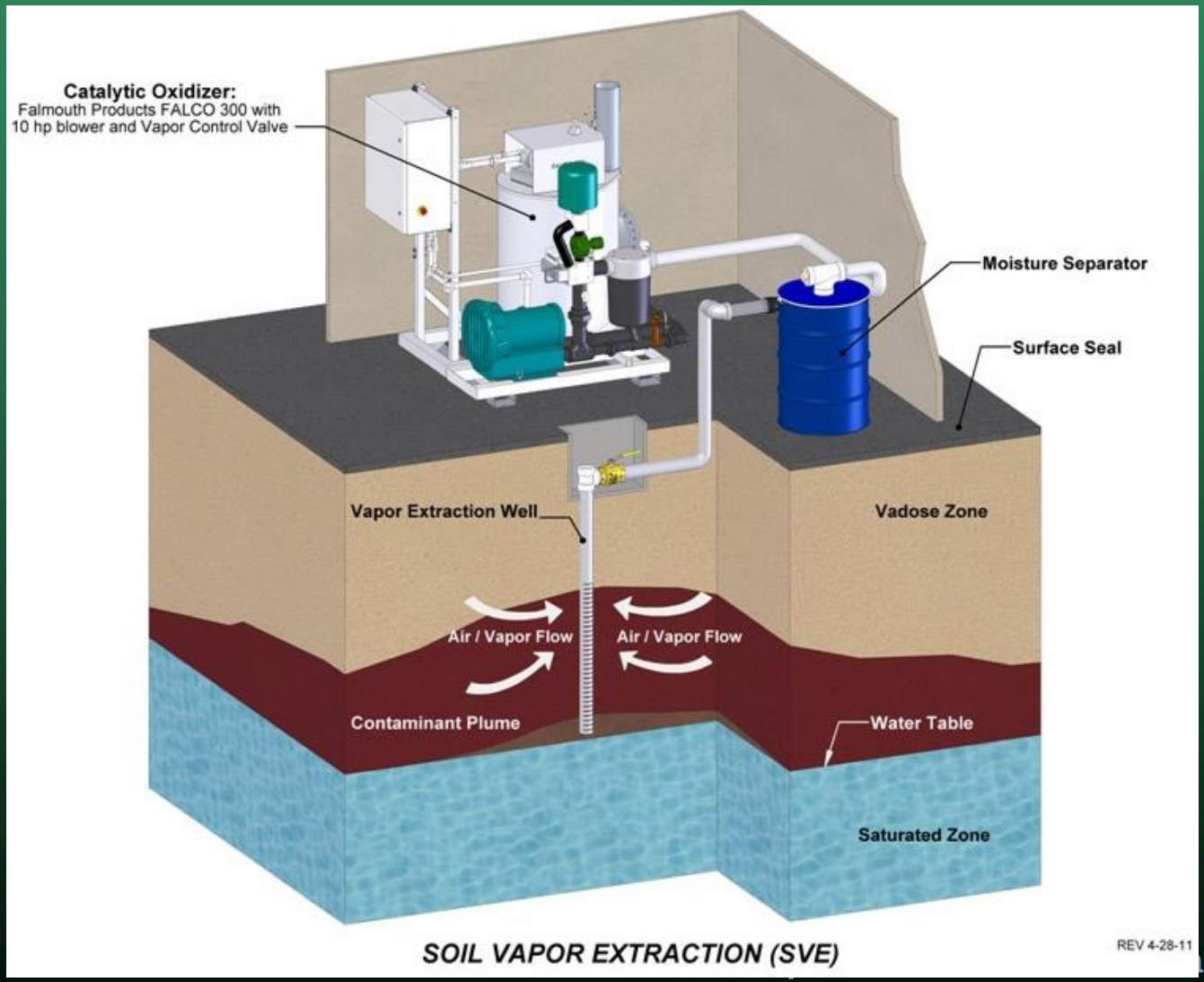


Chlorine Liberated



- Need to make contact
- An aqueous reaction

Soil Vapor Extraction



Geology Rules

None of these cool tricks work well in low-permeability soil

Matrix Diffusion

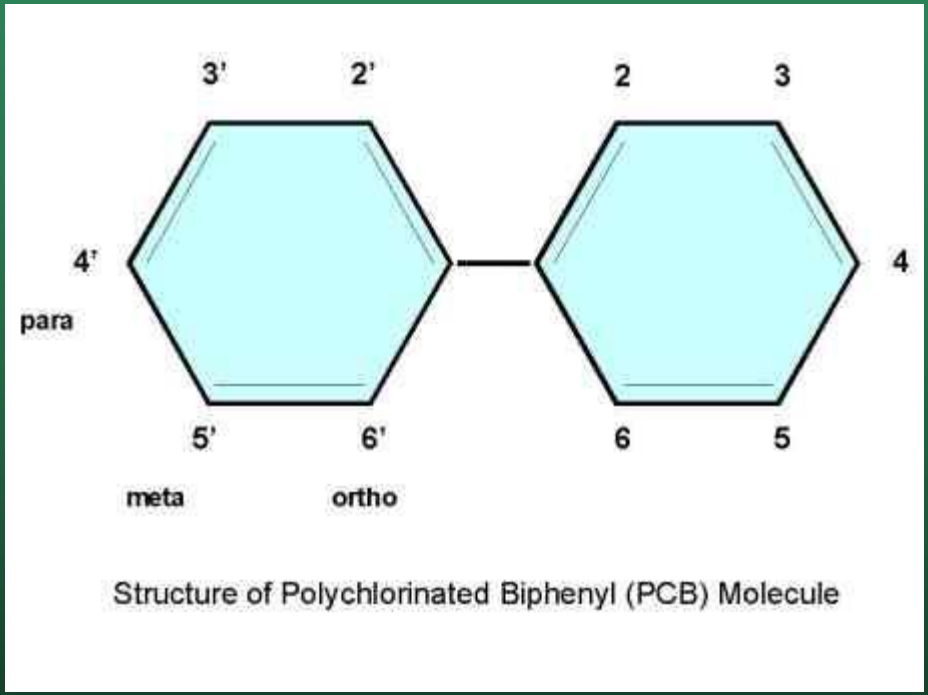
- Penetrates Clay
- Clay becomes the long-terms source.
- Most treatments can’t penetrate clay
  - Excavation, soil mixing, thermal

PCBs

Regulated under TSCA

Toxic Substances Control Act

PCB Structure



Structure of Polychlorinated Biphenyl (PCB) Molecule

- Source: USEPA

Part 1: What are PCBs?

- “Polychlorinated biphenyls”, a family of synthetic organic compounds.
- PCB mixtures (“aroclors”) were produced by distillation of chlorinated biphenyl; the exact aroclor composition could vary from batch to batch.
- Target percent chlorine by weight
- Aroclors are PCB mixtures, commonly sold in the United States.
- In most cases, the number starts with “12”, and ends with the average percentage of chlorine by weight.

Commonly Used Aroclors

- A 1221 – 21% Cl
- A 1232 – 32% Cl
- A 1242 – 42% Cl
- A 1248 – 48% Cl
- A 1254 – 54% Cl
- A 1260 – 60% Cl
- A 1016 – 41% Cl

PCB Congeners

- 209 different possible chlorinated biphenyls
  - PCB “congeners”. Not all congeners were produced
  - “congener number” (Ballschmiter and Zell 1980) “BZ number”)
  - IUPAC name
  - CAS number.
- Example, congener #40 is 2,2’,3,3’-Tetrachlorobiphenyl, CAS No. 38444-93-8.

Table 4-2. Chemical Identity of Polychlorinated Biphenyl Congeners and Homologs *(continued)*

PCB No.[a]	Structure	CAS No.[b]
34	2•;3,5	37680-68-5
35	3,3•;4	37680-69-6
36	3,3•;5	38444-87-0
37	3,4,4••	38444-90-5
38	3,4,5	53555-66-1
39	3,4•;5	38444-88-1
	Tetrachlorobiphenyl	26914-33-0
40	2,2•;3,3••	38444-93-8
41	2,2•;3,4	52663-59-9
42	2,2•;3,4••	36559-22-5
43	2,2•;3,5	70362-46-8
44	2,2•;3,5••	41464-39-5
45	2,2•;3,6	70362-45-7
46	2,2•;3,6••	41464-47-5
47	2,2•;4,4••	2437-79-8
48	2,2•;4,5	70362-47-9
49	2,2•;4,5••	41464-40-8
50	2,2•;4,6	62796-65-0
51	2,2•;4,6••	68194-04-7
52	2,2•;5,5••	35693-99-3
53	2,2•;5,6••	41464-41-9
54	2,2•;6,6••	15968-05-5
55	2,3,3•;4	74338-24-2
56	2,3,3•;4••	41464-43-1
57	2,3,3•;5	70424-67-8
58	2,3,3•;5••	41464-49-7
59	2,3,3•;6	74472-33-6
60	2,3,4,4••	33025-41-1
61	2,3,4,5	33284-53-6
62	2,3,4,6	54230-22-7
63	2,3,4•;5	74472-35-8
64	2,3,4•;6	52663-58-8
65	2,3,5,6	33284-54-7
66	2,3•;4,4••	32598-10-0
67	2,3•;4,5	73575-53-8
68	2,3•;4,5••	73575-52-7
69	2,3•;4,6	60233-24-1
70	2,3•;4•;5	32598-11-1
71	2,3•;4•;6	41464-46-4

Source: ATSDR

nservation

“Dioxin-like” Congeners

- In recent years, EPA has been increasing the focus on PCB congeners whose structure and toxicity are similar to 2,3,7,8 – tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD).
- These congeners have primarily meta and para chlorines.
- The World Health organization has established Toxic Equivalency Quotients for these congeners.

The International Programme on Chemical Safety (IPCS)

WHO IOMC UNEP

Compound	WHO 1998 TEF	WHO 2005 TEF*
chlorinated dibenzo-p-dioxins		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	**0.0003**
chlorinated dibenzofurans		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	**0.03**
2,3,4,7,8-PeCDF	0.5	**0.3**
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	**0.0003**
non-ortho substituted PCBs		
PCB 77	0.0001	0.0001
PCB 81	0.0001	**0.0003**
PCB 126	0.1	0.1
PCB 169	0.01	**0.03**
mono-ortho substituted PCBs		
105	0.0001	**0.00003**
114	0.0005	**0.00003**
118	0.0001	**0.00003**
123	0.0001	**0.00003**
156	0.0005	**0.00003**
157	0.0005	**0.00003**
167	0.00001	**0.00003**
189	0.0001	**0.00003**

* Numbers in bold indicate a change in TEF value

Reference - *Van den Berg et al*:
The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds

Source: Van Den Berg et al,

al Conservation

Hydroxylated PCBs

- More toxic than parent PCBs.
- Endocrine disruptors.
- They are not detected by conventional analysis.
- Appear to be widely distributed in the environment in research completed to date.

Regulated by TSCA as Total PCBs

- Not a delegated program: EPA
- Performance based
  - Manage waste properly
- Self-implementing
  - Notify EPA, meet criteria. Soil only.
- Risk-based
  - Need EPA approval

Uses of PCBs

- PCBs were commonly used as fire retardants, insulation, capacitor dielectric fluids, and heat transfer media, and as components of wire coatings, caulks, paints, sealants, and hydraulic fluids.

Some sites with PCBs

- Electrical Stations (capacitors and transformers)
- Wire coating / insulation plants
- Paper plants which used recycled “NCR paper”
- Capacitor and transformer manufacturing or repair facilities
- Facilities with large hydraulic presses or tools, or which use heat transfer media to warm product for transfer or use
- Paint / sealant plants

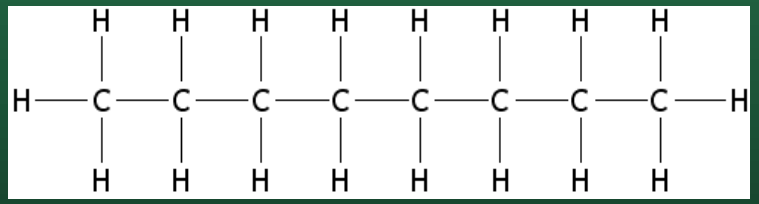
PFAS

What are they and where are they from?

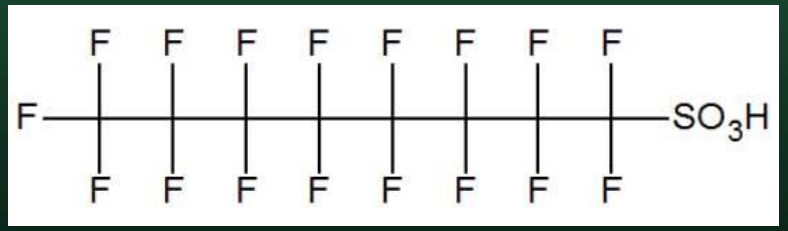
Overview

- Per and poly fluorinated alkane substances
- Alkanes with fluorine instead hydrogen
- Hundreds of different compounds

Octane



PFOS



Emerging Contaminant

- Early 2000's Washington Works plant in Parkersburg, West Virginia
  - C8 health study
- UCMR3
- EPA releases new health advisory data

Perfluorinated Compounds (PFCs)

- Remarkably stable and persistent
- Sulfonates are also bioccumulative
- Health concern at very low levels
  - Larger molecules appear to be of most concern

Polyfluorinated Alkanes

- If you have points on the chain that are not fluorinated, that is a weak spot that can be broken (“Telomers”)
- Precursors
  - Parts can break off, not get added on
  - 8:2 Fluorotelomer sulfonate
  - TOP Assay

Group	Chemical Name	Abbreviation	CAS Number
Perfluoroalkyl sulfonates	Perfluorobutanesulfonic acid	PFBS	375-73-5
	Perfluorohexanesulfonic acid	PFHxS	355-46-4
	Perfluoroheptanesulfonic acid	PFHpS	375-92-8
	Perfluorooctanessulfonic acid	PFOS	1763-23-1
	Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroalkyl carboxylates	Perfluorobutanoic acid	PFBA	375-22-4
	Perfluoropentanoic acid	PFPeA	2706-90-3
	Perfluorohexanoic acid	PFHxA	307-24-4
	Perfluoroheptanoic acid	PFHpA	375-85-9
	Perfluorooctanoic acid	PFOA	335-67-1
	Perfluorononanoic acid	PFNA	375-95-1
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluoroundecanoic acid	PFUA/PFUdA	2058-94-8
	Perfluorododecanoic acid	PFDoA	307-55-1
	Perfluorotridecanoic acid	PFTriA/PFTrDA	72629-94-8
	Perfluorotetradecanoic acid	PFTA/PFTeDA	376-06-7
Fluorinated Telomer Sulfonates	6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2
	8:2 Fluorotelomer sulfonate	8:2 FTS	39108-34-4
Perfluorooctane-sulfonamides	Perfluroroctanesulfonamide	FOSA	754-91-6
Perfluorooctane-sulfonamidoacetic acids	N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9
	N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6

PFOA - One major source:

Coated fabrics and tapes

PFOS: Perfluorooctanesulfonic acid

- Key ingredient in Scotchgard and other stain repellents.
- Stain and oil resistant papers and fabrics
- AFFF

AFFF – Aqueous Film Forming Foam

- Contains PFOS, PFHxS (Perfluorohexane sulfonic acid) and a whole host of other perfluoridated and poly-fluoridated compounds
- Used in firefighting for suppressing gasoline and similar fires
- Airports (emergencies, accidental releases and drills)
- Fire training centers
- Major traffic accidents?
  - One report of a single application creating a plume several blocks long that was still there 15 years later

Other Uses For PFAS

- Metal plating and finishing: (chrome, copper, nickel, and tin. Aluminum foil)
  - Surfactant, dispersant, wetting agent, and mist suppressing agent, fume suppresant.
  - Prevent corrosion, reduce mechanical wear, or enhance aesthetic appearance.
- Surface coating: paint, varnish, antifogging, adhesives
- Textiles: Waterproof/breathable (e.g. Goretex), and stain resistant (e.g. Scotchgard)
- Paper and cardboard packaging: waterproof and greaseproof paper.
- Cleaning products: surfactants, spot cleaners, floor polish, and dishwashing, car washes
- Plastics, resins, and rubbers (Teflon)
- Industrial use: Cement additives, product recovery, evaporation inhibitors, hydraulic oils
- Photographic industry: film, paper, and plates as dirt rejecters and friction control agents
- Electronics and semiconductor industry
- Etching: glass, plastics, fused silica, and aluminum.
- Cosmetics and personal care: emulsifiers, lubricants, or oleophobic agents.
- Pesticides: surfactant to carry pesticide (Roundup)

Q&A

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