

Issue #3: Chlorinated solvents: air and water pollution

- Chlorinated alkanes: CH₂Cl₂; CHCl₃; CCl₄; ClCH₂CH₂Cl; CH₃CCl₃ (MC) ← methyl chloroform
 - Chlorinated alkenes: Cl₂C=CHCl (TCE); Cl₂C=CCl₂ (PCE or PERC) ← perchloroethylene ("perc")
- (Italics = Montreal Protocol substance)

→ inc. dry cleaning

Text p294

- Major uses of MC, TCE, PER as degreasing solvents
- Atmospheric concern is stratospheric ozone depletion:
 - $k_{OH} 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ or less for the alkanes
 - $k_{OH} 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ or less for the alkenes
- Recall that banning MC has already led to a decrease in atmospheric concentration (my page 58)
- Terrestrial concern is ground water contamination especially by TCE and PER (~70% of all contaminated sites): refer back to Ch. 8: permeable reactive barriers (my page 150)
- Concern of drinking water contamination, especially by TCE, which is a rodent carcinogen

see my p 73 re. rate consts. in context of tropospheric rxns

Halogenated Solvents Industry Alliance

For an industry perspective on TCE (1995), see:

http://www.hsia.org/white_papers/trichloro.htm
/paper.html

CH₂Cl₂
MC
PCE
TCE

For a perspective from the US National Institutes of Environmental Health Sciences (1996), see:

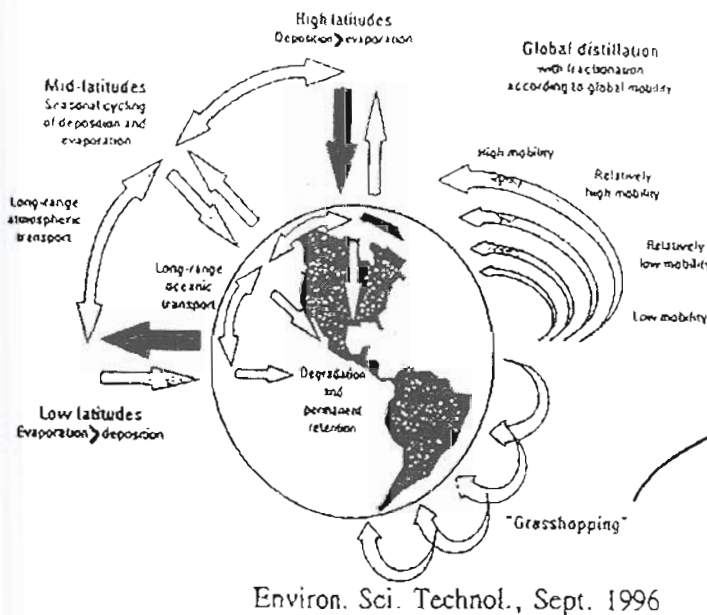
<http://ehp.niehs.nih.gov/roc/ninth/rahc/trichloroethylene.pdf>

TCE → "reasonably anticipated to be a human carcinogen ..."

Issue #4: Long range transport of organochlorines: Persistent organic pollutants (POPs)

Environment Canada's *Toxic Substances Management Policy*: persistent if $t_{1/2}$ in the atmosphere > 2 days. Ancillary criterion: "evidence of atmospheric transport to remote regions such as the arctic"

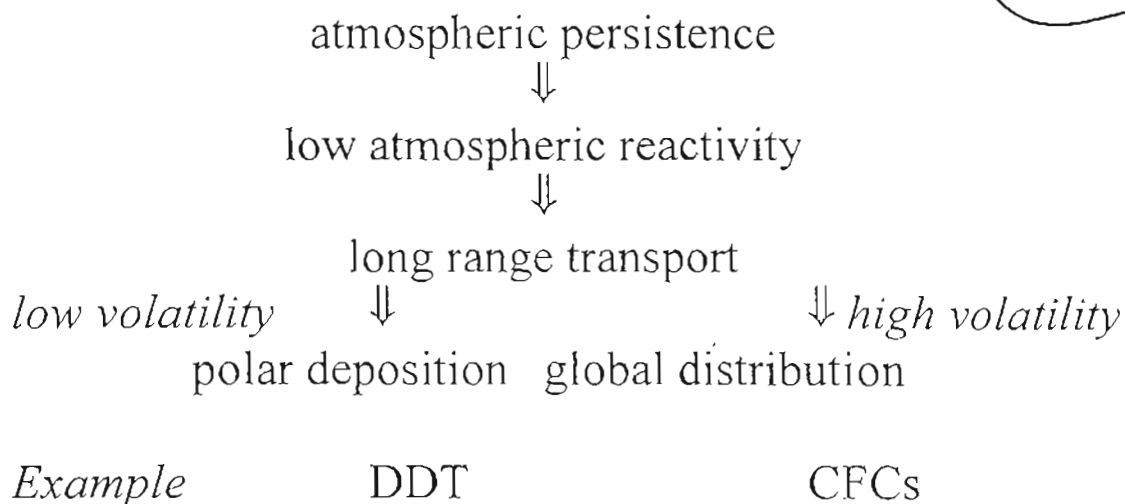
- low chemical and metabolic reactivity
- often associated with halogenated compounds
- able to distribute globally if even slightly volatile
- accumulate in the polar regions if they have low vapour pressure: "global distillation"



Canadian concern: Native Canadians and wildlife in the Arctic.

Hence different POP composition in different latitudes

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Properties of POPs as a function of vapour pressure

<i>Vapour pressure, Pa</i> *	<i>Mobility</i>	<i>Properties</i>	<i>Examples</i>
log p < -4	very low	deposition or retention close to the source	PCBs > 8 Cl PAH > 4 rings
log p -4 to -2	low	accumulation in mid-latitudes	PCBs 4-8 Cl 4 ring PAH
log p -2 to 0	high	accumulation in polar regions	PCBs 1-4 Cl 3 ring PAH HCH; DDT
log p > 0	very high	no deposition	chloroaliphatic solvents; CFCs 1-2 ring aromatics

Source: Wania and Mackay, 1996

* $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$
 $1 \text{ Pa} \approx 1 \times 10^{-5} \text{ atm}$

U.N.'s POP "Dirty Dozen" and status 160

<u>POP</u>	<u>US</u>	<u>Canada</u>	<u>UK</u>	<u>Mexico</u>	<u>China</u>	<u>India</u>	<u>Use</u>
DDT	X	X	X	R	R	R	Mosquitoes
Aldrin	X	X	X	X	OK	OK	Termites
Dieldrin	X	X	X	X	OK	R	Crops
Endrin	X	X	X	X	OK	X	Rodents
Chlordane	R	X	X	OK	R	OK	Termites
Heptachlor	R	X	X	X	OK	OK	Soil insects
Hexachlorobenzene	X	X	X				Fungicide
Mirex	X	X	X	R	R		Ants, Termites
Toxaphene	X	X	X	X	OK	X	Ticks, mites
PCBs*	X	R	R	OK			Many uses
Dioxins*	BP	BP	BP	BP	BP	BP	
Furans*	BP	BP	BP	BP	BP	BP	

- * = not pesticides.
- X = banned
- R = severely restricted use
- OK = not restricted
- BP = by-product (not manufactured; traces in other commodities).

Polybrominated diphenyl ethers (PBDEs): an emerging environmental problem

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- widely used as flame retardants
- flame retardants are used in:
 - soft furnishings and bedding
 - childrens' sleepware
 - automobiles and aircraft
 - TV sets and computer housings

on heating release Br[•] which react with free radicals in combustion → non radicals & quench fire.

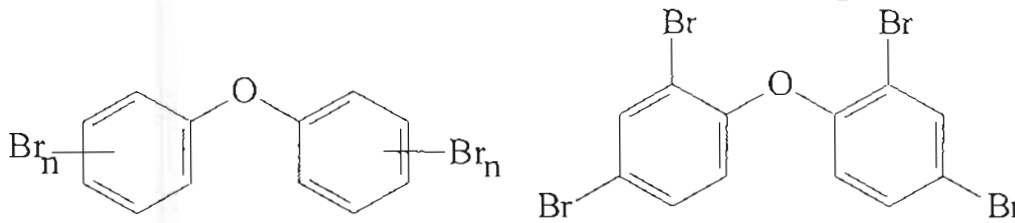
current production > 67,000 tonnes per year; toxicity largely unknown*

long range transport - have been detected in the Arctic

- found to bioconcentrate in:
 - human milk
 - seal and whale blubber

Concn. rose sharply in 90s

} i.e. persistent, lipophilic. Have been found in sewage sludge



Br atoms can occupy any of the 10 positions

⇒ 209 possible congeners

(solids at normal temps)

Left: generic PBDE structure

Right: a major component of the "penta" BDE mixture

As of May 2001, the European Union agreed to phase out the use of polybrominated diphenyl ethers as flame retardants because of their increasing environmental contamination

* Toxicity decreases as # Br atoms increases (decabromo DE is the least toxic)

PBDEs with > 6 Br atoms probably do not bioaccumulate.

The 4 & 5-dibromo ones are the most distributed in the environment; they are the most bioaccumulative; most toxic

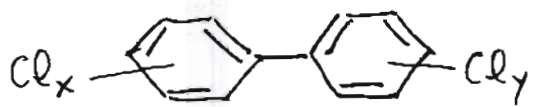
Issue #5: Toxic organochlorine aromatic compounds

Emphasis on polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins (PCDDs or "dioxins")

DDT ^{myp. 154} (structure earlier) a 1940s/1950s insecticide

- effective against malaria mosquitos; cheap, readily applied
- synthesis = Friedel-Crafts alkylation of chlorobenzene (2 mol) with chloral hydrate $\text{Cl}_3\text{C}-\text{CH}=\text{O}$ ($\text{Cl}_3\text{C}-\text{CH}(\text{OH})_2$)
- discovered to be persistent in the terrestrial environment, 1960s, and to be ubiquitous in biota, 1960s
- an emphasis in Rachel Carson's book *Silent Spring* (reduced fecundity of birds): biomagnification
- banned in developed countries 1969-1970; still in use in India for mosquito control: disease control vs environmental impact
- residues still found in Canadian biota, despite declines; reason is long range atmospheric transport
- technical product is mainly *p,p'*-DDT, but also contains *o,p'*- and *o,o'*- isomers: *o,p'*-DDT considered to be weakly estrogenic

p,p' can undergo metabolic/photochemical degradation to give DDE (dichloro-diphenyl-ethylene). DDT and DDE hence often occur together.



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Polychlorinated Biphenyls (PCBs)

Section 9.5 (txt p300)

different isomers
diff. # of Cl's

- Produced ~1930-1970 by chlorination of biphenyl: complex mixtures: final North American ban 1976
- Production in North America was in the range 10^3 to 10^5 tonnes/year \rightarrow total 10^6 tonnes worldwide
- Original usage was for dielectric fluids in transformers and capacitors "closed uses": excellent electrical and thermal insulators; very unreactive chemically
- Later uses were "open uses": plasticizers, de-inkers, golf ball interiors, carbonless copy paper
- In theory 209 possible **congeners**
- Commonest tradename in North America = Aroclor (Monsanto): four digit code Aroclor 1254 \equiv 12 carbons (biphenyl) and 54% by weight chlorine \rightarrow average composition approx $C_{12}H_5Cl_5$

for recycling newspaper

Why are PCBs still a problem?

- Principal environmental problem was improper disposal (landfilling) \rightarrow leaching into ground water; volatilization to the atmosphere
- Very unreactive chemically \rightarrow persistent
- Once something escapes into the environment, you cannot get it back!
- Discovered in wildlife 1966 (Jensen, Sweden) and soon found to be ubiquitous
- Highly lipophilic ($\log K_{ow} > 5$): bioaccumulate: found together with DDT, PBDEs, dioxins
- Notably found in Great Lakes fish

See Table 9.3 (txt p304) for biomagnification.

(interestingly this Table looks like the one on p 154 of my notes ascribed to DDT..... hmmm!!)

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Analysis

- GC-MS after separation from more polar contaminants by conventional extraction and chromatography: large number of congeners + PCDD/PCDFs makes analysis very challenging

↑ dioxins (later) ↑ furans

Can analyse to better than ppq level

1 ppq = 1 pg L⁻¹

(1 in 10¹⁵)

Environment Canada Regulations

- PCBs may not be manufactured or used
- 1 kg allowed for research purposes
- High strength PCB wastes: > 5000 ppm; "not a PCB" at < 50 ppm (i.e. do not follow regulations) / filtered
- Transformers may be drained and refilled but no new PCB added

- Gradual phase-out of PCB fluids in transformers → replacement with high boiling mineral oils

Are PCBs toxic? — complicated 'cos of all the congeners which have different toxicities

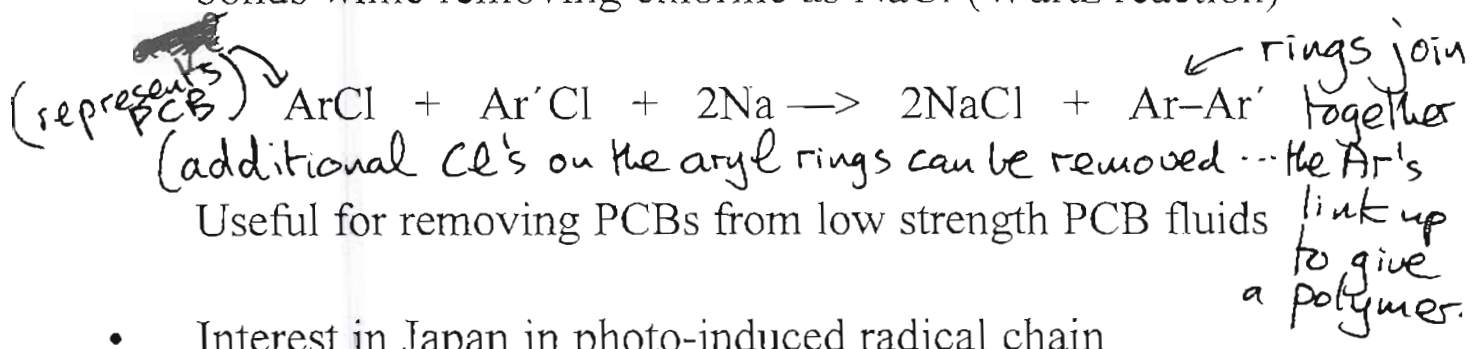
- Acute toxicity very low: LD₅₀ values ~ 1 g/kg
- "Coplanar" congeners (no *ortho* Cl atoms) have dioxin-like toxicity: see later → i.e. subst'd in 3, 4, 5 positions in each ring
- Act as "inducers" of Phase I metabolizing enzymes
- Ingestion leads to "chloracne": "Yusho disease", Japan 1968 from eating ^{PCB} contaminated rice oil: toxicity most likely from traces of oxidized material: PCDFs (polychlorinated dibenzofurans)
- Much controversy over possible developmental effects, including lowered IQ

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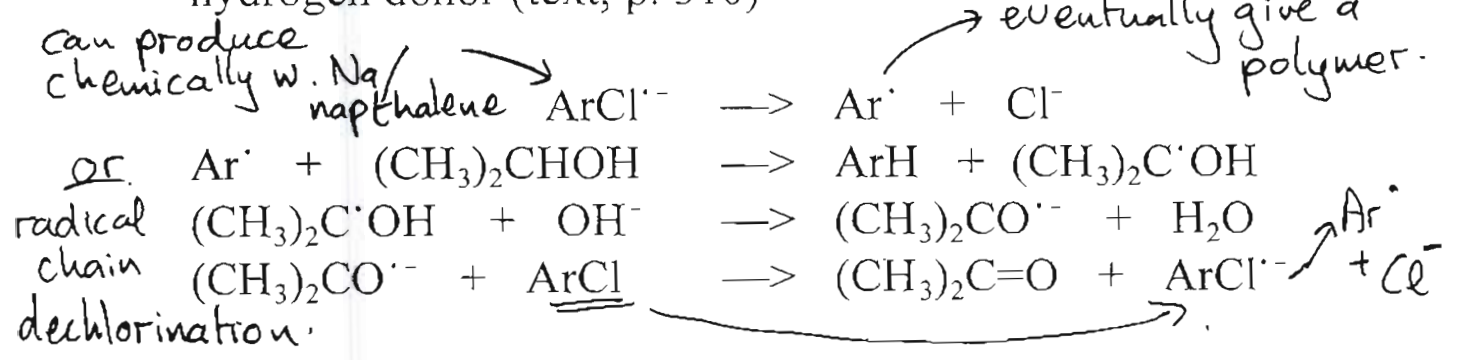
Destruction of PCBs

- Incineration = high temperature combustion (with a large xs of fuel oil)
 - public opposition to incinerators: NO_x and formation of traces of dioxins, especially in the range 700-1000°C: successful combustion T > 1000°C and contact time > 2 s
 - Dioxin formation is generally ~ 10⁻¹⁰%
 - Requirement is "six nines" destruction = 99.9999%
 - Storage vs transport: both have problems (St. Basile-grand) ← Aug. 1988, PCB storage fire
 - Combination with cement manufacture: PCBs provide a (poor) fuel source + Cl⁻ required for high-chloride cement: source of controversy

- Reaction with active metals (usually Na): forms C-C bonds while removing chlorine as NaCl (Wurtz reaction)



- Interest in Japan in photo-induced radical chain chemistry involving NaOH/isopropyl alcohol as a hydrogen donor (text, p. 310)



Alterations in PCB congener distributions

- Grasshopper effect depletes the more volatile congeners close to the source
- Microbial action, though slow, consumes less chlorinated congeners preferentially
- Consequence: analysis at a remote site or at a "historical" site does not give a signature of the original source

PCB-contaminated sites

- Soil: generally excavate and either incinerate or transport to secure landfill
- Sediment: problem of the Hudson River, NY state and emissions of Aroclor 1242 from the GE plant there
 - "natural attenuation"?
 - dredge and resuspend the sediments?

analysis shows different congener patterns than those in the original Aroclor 1242.

Microorganisms seem to have degradation effects

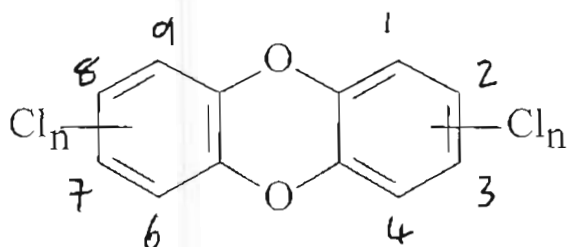
-- perhaps, over time, they'll degrade all the PCBs! ?

"Dioxins"

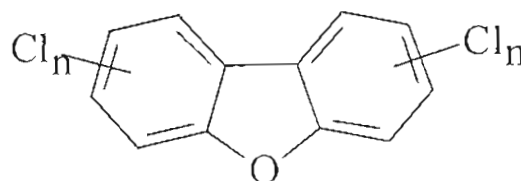
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- Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)

(generally colourless solids)



PCDD structure



PCDF structure

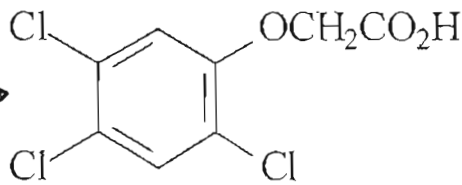
- "Dioxin" is used both as a general term for PCDDs and specifically for the highly toxic congener 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) } this one gets all the press
- Unlike PCBs, PCDDs and PCDFs have never been intentionally manufactured: they are trace byproducts in other commodities
- 75 PCDD congeners: 135 PCDFs: the 2,3,7,8-positions must all be substituted for high toxicity: example of a structure-activity relationship (see section 9.6.2)
- TCDD has been the most thoroughly studied

Historical background

- Introduction of the herbicide 2,4,5-T (1948)

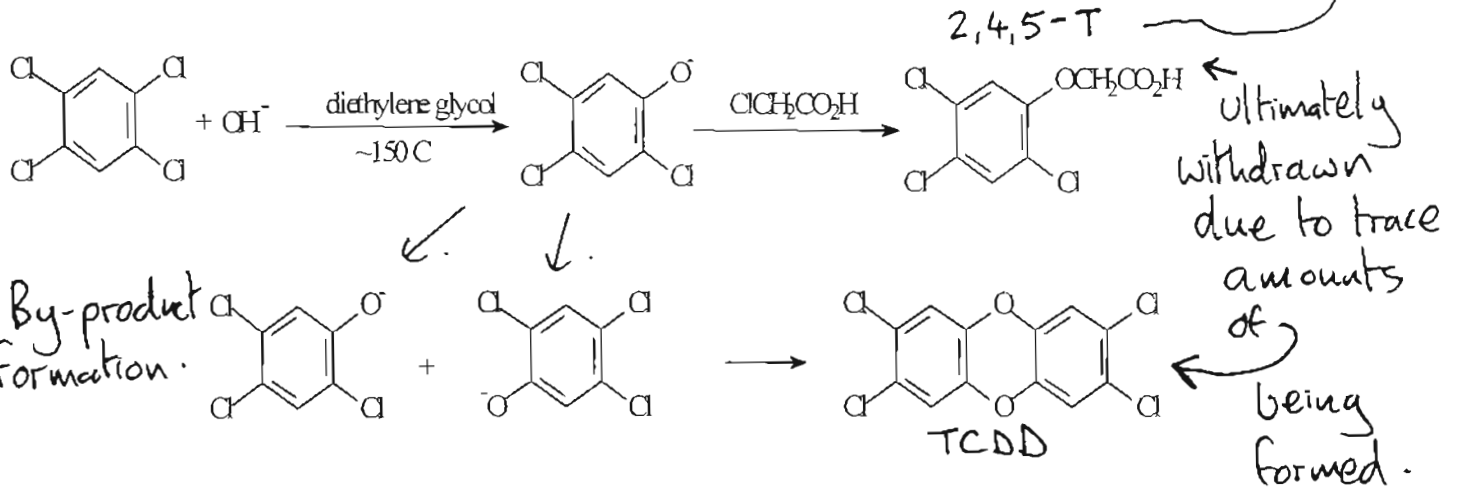
2,4,5-trichlorophenol

used to make →



2,4,5-trichloro-phenoxyacetic acid

- Explosions at chlorophenol manufacturing facilities (1949, Monsanto; 1953 Boehringer-Ingelheim) led to chloracne among exposed workers
- Identification of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) as the acnigenic agent (1957): ppm contaminant



- Pulmonary chick edema (1957): "toxic fat syndrome" traced (1973) to the presence of 2,3,7,8-TCDD in recycled fat: February 1999: almost identical episode in Belgium led to removal of all eggs and chickens from Belgian food supply

containers contained
33 ppm of TCDD

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1970s:

Sprayed
on roads
and
horse
arenas

- Spraying of "still bottoms" from 2,4,5-T manufacture in Verona, MO led to deaths among horses and eventually to the closure of the town of Times Beach, MO
- Defoliant spraying of Agent Orange (mixture of 2,4-D and 2,4,5-T, containing ~ 2 ppm of TCDD) in Vietnam war claimed to be associated with various diseases among military personnel
- Underbrush spraying of Alsea Basin forest lands (Oregon) with 2,4,5,-T claimed to be associated with human miscarriages and birth defects
- Explosion at 2,4,5-trichlorophenol plant at Seveso, Italy (1976) —> substantial exposure of the "civilian" population: blood TCDD levels correlate with severity of chloracne
- Evidence that "dioxins" are formed in numerous pyrolytic processes, including municipal and hospital waste incinerators
- Combustion reactions involve "de novo" synthesis, and afford principally the most highly chlorinated congeners (octa, hepta, hexa)
- Concentrations in soils, tissues etc rarely reach 1 ppb; pptr and ppq values are common

1 in 10¹² 1 in 10¹⁵
↑ 1 second every 320 centuries