CH3041 Tutorial 9 Answers
Pesticides, Toxic Aromatics & Heavy Metals

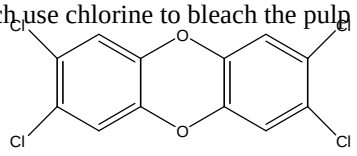
1. DDT was used in a widespread manner in the period immediately preceding and subsequent to WWII. Explain why the use of DDT was finally banned and why the replacements for DDT such as Fenthion (an organophosphate) have been successful.

DDT (p-$ClC_6H_4)_2CHCCl_3$) is a typical organochlorine pesticide molecule which is non-polar, quite unreactive, has a high K_{OW} value, low rate of biodegradation, low water solubility and low vapour pressure. This means that when sprayed in the environment DDT persists and is moved in both the gas phase and liquid phase to regions remote from the site of application. Because DDT is lipophilic and hydrophobic it is easily incorporated into biomass where it concentrates in the fatty tissue of organisms or is stored in sediments in waterways for slow release. Due to the long half life and non-polar nature of the organochlorine it is not readily excreted and the material bioaccumulates in an organism which has ingested the material. The metabolite DDE is even more stable and the Total DDT is found and analysed for in each organism. At each trophic level there is an increase in the concentration of Total DDT found in the organism which is referred to as biomagnification (each higher trophic level organism preys on many lower trophic level organisms, the sum of the Total DDT in all the lower trophic level organisms which have been consumed by one high trophic level organism is concentrated into this organism). The BioConcentration Factor for DDT is around 10^5 (water level to a higher predator such as falcons). The high levels obtained in the body of top level organisms interferes with their reproductive functioning and causes increased mortality. For this reason although they are relatively non-toxic to humans and are good insecticides (interfere with the CNS Na/K pump mechanism). Insects also gained an appreciable resistance to most OCs. The phase out of DDT was in large part due to the fast that insects developed resistance to DDT itself by developing that appropriate biochemistry to rapidly metabolise DDT into the low toxicity DDE, this rendered the insecticide inactive and so farmers moved onto new OC insecticides and then OPs such as Fenthion.

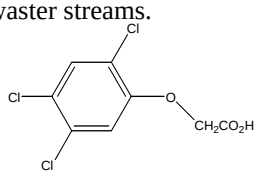
Fenthion3-methyl-4-methylthiophenyl dimethyl phosphorothionate is in the chemical group of organophosphate pesticides. It is a sulphonate ester compound with moderately low mammalian toxicity. These compounds readily biodegrade in the environment. The organophosphates are quite polar molecules and will absorb readily on soils and sediments. Combined with the ready biodegradation (high chemical reactivity) they do not enter the food chain. They are exceedingly effective acetylcholinesterase inhibitors for insects. Most cases of organophosphate poisoning result from skin absorption due to inadequate protection during preparation or use, if the instructions on use are obeyed there should be no problems. Ingestion of the product can lead to poisoning. Chronic animal studies have shown no evidence of carcinogenic or teratogenic potential. Fenthion is moderately toxic via the oral route, with reported oral LD50 values of 180 to 298 mg/kg in rats. A highly cumulative effect of fenthion was also observed, it has no mutagenic activity on rats
Fenthion is a contact and stomach organophosphate insecticide used against many sucking, biting pests, especially fruit flies, stem borers, mosquitoes, and Eurygaster cereal bugs. In mosquitoes, it is toxic to both the adult and immature forms (larvae).
Fenthion is of moderate persistence in soil, with an average field half-life of 34 days under most conditions. In one study of its persistence in water, 50% of applied fenthion remained in river water 2 weeks later, while 10% remained after 4 weeks

2. Dioxins and PAHs are important organic environmental pollutants.
   - Using examples discuss how these chemicals get into the environment and why they have similar toxicological effects.

The class of chemicals called dioxins are formed by the addition of oxygen to chlorinated aromatics in the synthesis of chlorinated chemicals such as 2,4,5-T. In the case of 2,4,5-T dioxins are formed as a side reaction which results from the coupling of two phenoxide ions formed from the phenol starting material. In general the reaction of two chloro-substituted benzene rings in the presence of chlorine and oxygen under high temperature forms a series of substituted dioxin molecules. Dioxins are also formed during incineration when organochlorine materials are being combusted eg. municipal incinerators + PVC plastics. Pulp plants which use chlorine to bleach the pulp produce dioxins in the waster streams.

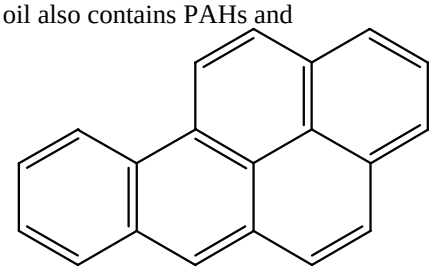


2,3,7,8-tetrachlorodibenzodioxin



2,4,5-T

Polyaromatic hydrocarbons (PAHs) are fused polyaromatic molecules which are formed during high temperature pyrolysis and in particular with the incomplete combustion that occurs in forest fires, volcanic eruptions, diesel engines, cigarettes, barbeques and in coal-fires. They form either by pyrosynthesis from smaller hydrocarbon fragments or by pyrolysis of larger hydrocarbons. Crude oil also contains PAHs and

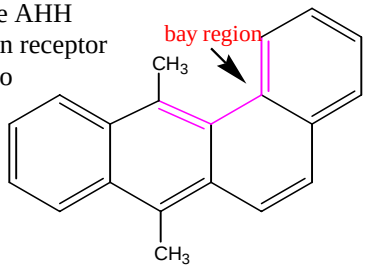


benzo[a]pyrene

The dioxins and PAHs have a low volatility but they are frequently input into the atmosphere and coat on aerosol particles which aids their dispersal. which aids in their dispersal.

Both classes of compound have multiple aromatic rings and act as mutagenic compounds which are also often carcinogens and teratogens. As mutagenic compounds the act on the cellular DNA. PAHs need to be activated to form an active epoxide and so they show chronic toxicity whereas the dioxins are active as they stand and show acute toxicity.

The structure-activity relationship for TCDD relates the property of binding to the AHH receptor as being linked to the parameters size, lipophilicity, planarity. The dioxin receptor is the Aryl Hydrogen Hydrogenase receptor an intracellular protein which binds to planar molecules (1.4 x 0.68 x 0.4nm) then migrates to the DNA receptor sites → mRNA which generates a toxic response.



For the PAHs a SAR relates the presence of a "bay region" which is adjacent to where the epoxide forms which then reacts with DNA.

Both then produce changes in DNA replication, hence are mutagens.

3. During the 1950s and 60s the Pacific Gas &Electricity used water containing chromium 6, Cr(VI), to cool pipes at their Compressor Station in Hinkley, CA. The tainted water was then discharged into local groundwater supplies and used by local residents. The discharged chromium 6 in the groundwater attained levels approaching 24 ppm in the wells which were sampled while the recommended drinking water limit in the US is 5 ppb.
    - How would you approach testing for such a toxicant.
    - What effects would you expect to see from the introduction of such elevated levels of Cr(VI) in a water supply?
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Chromium (VI) is an inorganic ion and this would be expected to be form octahedral coordination complexes in water with water molecules occupying many of the coordination sites.
The groundwater will need to be sampled from wells. Testing for such a toxicant from these wells would involve getting the water into deactivated sampling jars (acid treated glass) using a peristaltic pump and teflon tubing. The water samples would then be tested using either AA or ICP-MS if the levels were low.

The effects of elevated levels of Cr(VI) in drinking water would be the formation of cancers as Cr(VI) has been shown to be a potent carcinogen.

4. Lead has an ancient history as a poison. Discuss the relative magnitudes of the **natural** and **anthropogenic inputs** of lead into the environment and what effects lead has on humans who intake significant quantities of the element.

Lead is found in the crust at 12ppm and in the oceans at 0.03ppb. Pb is therefore a trace and the main ore is PbS. Pb metal is produced in smelters at around 33.2×10^6 t y^{-1} with the natural environment mobilising around 12×10^3 t y^{-1}. This toxic heavy metal is therefore has a significant anthropogenic perturbation.
Lead is mainly used in *lead-acid storage batteries* and the lead alkyl compounds used in *leaded petrol*. The $Pb(ethyl)_4$ was extensively used as a anti-knock agent in car engines so they could use low quality petrol and yet run at high compression ratios. The lead has dispersed all over the globe as 75% was dispersed as a Pb aerosol. 94% of the Pb found in the air is from man activities. When leaded petrol is eventually phased out then the quantity of lead being introduced to the environment will decline markedly.

Lead in particular Pb(II) is a *cumulative poison*. 90% is retained (bioaccumulates) in the bones from where it can be remobilised, the t½ is 90 y in adults. Metallothionen is a small cystein rich protein which binds Pb, strongly (M^{n+}-S bonds) to detoxify the system. Once the nominal daily input is exceed then it accumulates in the body as the metallothionen capacity is exceeded.
Daily Inputs (mg) : food 100, water 50 air 15 Pb binds strongly to AAs, Hb, RNA, DNA...
Toxic effects : impaired blood synthesis, brain damage, hypertension.
The typical soft tissue levels are around the same levels that haem synthesis interferrence occurs - 100mg Pb kg^{-1}. The Pb is stored in the bones in sites where calcium usually occurs which means there is a long half life for mobilisation ($t_{1/2}$ 20 years).