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Origin/Formation

Dioxins are formed as a by-product of the combustion of carbon compounds with chlorine and/or bromine in the temperature range between about 300 and 600° C. Oxygen deficiency and the presence of copper salts are conducive to their formation.

Dioxins have always been present in the environment; for example, they are known to be formed during thunderstorms and when forest areas are cleared by fire. Entrainment into the environment has been enhanced by flue gas emissions and by combustion and production residues.

The concept

Dioxin is used as a generic identifier for polychlorinated dibenzodioxins (I) and polychlorinated dibenzofuranes (II). These chemically similar compounds also have similar toxic properties. They exhibit the following structural formulae:

(1)

(11)

(I) is known in 75 and (II) is known in 135 different compounds.

The best-known variety, and the one which has been most extensively studied, is 2,3,7,8-TCDD (tetrachlorodibenzodioxin/n,m = 2) which achieved notoriety after an accidental discharge from a herbicide factory in Seveso, Italy, in 1976.

TCDD

Occurrence in nature

Compounds containing a dioxin ring system are widely encountered in nature, e.g. in higher plants/brown algae. Having permeated the environment, they are now to be found in the soil, water, air and all life forms.

Economic significance

Dioxins themselves are of no economic significance. They occur as by-products of chemical synthesis and production processes.

Economic significance accrues, however, to substances from which dioxins can be formed at elevated temperature, such as polychlorinated biphenyls (PCB, used as liquid insulators in transformers), chlorinated hydrocarbons and special plastics used, for example, in fire control applications (e.g. flame-retardant cable materials or Askarel/Clophen).

Hazard potential and effects

Effects on human beings

Dioxins can enter the body by inhalation, resorption through the skin or via the food chain. The latter is the most significant path, the main source of dioxins in the diet being animal fats. Dioxins exhibit a high bioaccumulation potential and are ingested via the digestive tract. Animal fats enhance this process. The dioxins accumulate in the liver, in fatty and cutaneous tissue and in the muscles. The dwell time (half life) is about one month in rats, about 8 years in humans. Decomposition, e.g. in the liver, gives rise to reactive intermediate products which may themselves be toxic. The main hazard potential lies in their long-term effects.

Cancerogenous effects have been demonstrated in experiments with animals; however, epidemiological studies have up to now failed to verify such effects in humans. Exposure to large doses is known to cause chloracne.

Ecological impact

Dioxin exhibits only low mobility in soil; its half life – in the absence of light – is several years. Photochemical breakdown takes about 8 days in the atmosphere and in the near-surface soil, between 21 and 118 hours in water.

Brevi bacteria, which are widespread in the environment, are capable of decomposing the dioxins.

Toxicity

The in all 210 compounds differ widely in terms of their toxicity. But because all these compounds can occur in parallel, limits are expressed as toxicity equivalents (TE) based on the dioxin with the highest toxicity (TCDD). In the industrialised nations, the average daily dioxin intake is about 0.1 ng (1 nanogram = 10^{-9} g) TE/person ($\triangleq 1.5$ pg TE/kg body weight in the case of a person weighing 75 kg). From this we can calculate an average concentration of 30 ppt (parts per trillion) TE in the fatty tissue. The first slight effects can be expected if this concentration is exceeded by a factor of 80 to 100. In infants, the daily dioxin intake via their mothers' milk is significantly higher, being on average around 80-90 pg (1 picogramm = 10^{-12} g) TE/kg body weight per day.

Limits

There is not yet any clear consensus as to limits and acceptable exposures. The dose identified as the no observed effect level (NOEL) in animal experiments is 1 ng/kg body weight per day.

On the international scene, various countries and organizations have specified diverse acceptable daily intakes (ADI):

USA (EPA)

Germany

UK

1—10 pg TE/kg body weight/day

UK

1 pg TE/kg body weight/day

Sweden

5 pg TE/kg body weight/day

Netherlands

4 pg TE/kg body weight/day

WHO

1—10 pg TE/kg body weight/day

Germany specifies a soil concentration limit of 1,000 ng/kg for populated areas and 10,000 ng/kg for unpopulated areas.

Analysis

Analysis for dioxins is relatively expensive and time-consuming. The procedure involves building up the dioxin concentration to a measurable level (as a rule by means of chromatographic methods) and then performing the analysis by means of gas chromatography. The whole procedure takes about 4 days; in Germany a single analysis nowadays costs about DM 2,000. It takes several analyses to obtain a reliable reading of the level of contamination in an enclosed area (about 5 analyses for an average room in a house).

Disposal

Contamination with dioxin is generally the result of a fire. The contaminated materials may be in solid or liquid form, e.g. contaminated fire-fighting water, effluent or seepage. Solid materials can be decontaminated and/or disposed of by high-temperature treatment (>1200° C). In this case it is important to ensure an adequate oxygen supply. If suitable plant technology is available (catalytic combustion or thermal post-conditioning), lower temperatures (>800° C) may be sufficient.

Effluents and seepage water may be detoxified either by microbacteria or by means of ozone in an alkaline medium.

Preventive measures

Dioxin emissions can be kept within allowable limits by controlling the reactions taking place in combustion processes (>800° C), ensuring a moderate oxygen surplus, use of flue gas separators, thermal post-conditioning, and/or catalytic combustion. Plants employing potentially dioxin-producing processes should be regularly monitored for dioxin emissions even during normal operation. The long-term aim should be to substitute input substances that could give rise to dioxin in the production process.

Tips for the underwriter

The formation of dioxin is to be expected in:

industries operating the following facilities:

- o spent oil reprocessing
- paper manufacture (in conjunction with chlorine bleaching agents)
- o plastics manufacturing (due to elevated temperatures)
- o metals disposal/scrap-metal smelting
- o aluminium smelting

fires involving:

- refrigerating facilities (refrigerant agents)
- o transformers (Askarel)
- o cables
- o spent oil
- o scrap metal with plastic parts or linings
- o computer scrap
- o special-purpose plastics (e.g. fire-resistant plastics)
- c refuse incineration facilities (exhaust gases and slag)
- o filter dusts/fly ash

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