

Review Article

NEW CHLOROBENZENE PESTICIDES, THEIR IMPACTS ON ENVIRONMENT AND FOOD QUALITY

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This review article summarizes details of new chlorobenzenes pesticides reported in the form of 127 publications in the journals of international repute. The review describes their chemical and physical constants such as molecular formula, relative molecular mass, physical state, melting point, boiling point, vapor pressure, aqueous solubility, vapor density, Henry's law constant (KPa m³/mole), and soil sorption (K_{oc}). It reports the impacts of these pesticides on environment and quality of food. The review discusses their characteristics such as transport and distribution, biodegradation, bioaccumulation, transformation etc. in different atmospheric matrices such as terrestrial fate, aquatic fate, environmental levels, and LD₅₀. Thus it is very useful and informative for the readers and researchers who are working in the area of abatement, monitoring and control of environmental pollution, plant protection, national policies, marketing, public health, food quality monitoring etc.

Keywords: Chlorobenzenes, Environment, Food, Pesticides, Uses, Hazards

INTRODUCTION

Despite many efforts to develop non-chemical methods of crop protection, none of the alternatives have been found in order to avoid chemical-crop protection. Therefore, there is general consensus about the use of chemical pesticides in the foreseeable future. It has been realized that the environmental pollution in turn food contamination can be minimized by selecting suitable chemicals which are less hazardous and are applied at low concentration. Recently, some new pesticides have been developed which are biodegradable, high mammalian safety, low residual life, compatible with non-target organisms and allied traits. It is an appreciable approach.

The old chemicals which are persistent in the environment in turn in foodstuffs and are toxic to non-target organisms need to be phased out. Among the organochlorine pesticides, DDT, BHC, dieldrin, and lindane appear to be widely distributed. Approximately 50% of all pesticide residues detected in food are organochlorines, and 60% of these are found primarily in animal products. Their residues have been found to be carcinogenic and mutagenic so their use in many countries is restricted or banned.

In the year 2011 some new chemical pesticides have been included (1). Amongst new pesticides some chlorobenzenes such as (a) 1,2,3-trichlorobenzene (1,2,3-TCB); (b) 1,2,4-

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trichlorobenzene (1,2,4-TCB); (c) 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB); (d) 1,2,3,5-tetrachlorobenzene (1,2,3,5-TeCB); and (e) 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB) are also included. Therefore, it was decided to discuss their properties and their impacts on environment and food quality in brief.

NATURE OF CHLOROBENZENES

The chlorobenzenes derivatives, C₆H_(6-x)Cl_x, form a group of stable, colorless, pleasant smelling compounds. Chlorine can be substituted for six hydrogen atoms on the benzene ring, forming twelve different chlorinated compounds namely; (i) monochlorobenzene; (ii) ortho-dichloro-benzene; (iii) meta-dichlorobenzene; (iv) para-dichlorobenzene; (v) 1,2,3-TCB; (vi) 1,2,4-TCB, (vii) 1,3,5-trichlorobenzene; (viii) 1,2,3,4-TeCB; (ix) 1,3,4,5-tetrachlorobenzene (1,3,4,5-TeCB); (x) 1,2,4,5-TeCB; (xi) pentachlorobenzene; and (xii) hexachlorobenzene (Tables 1 and 2).

1,2,3-TRICHLOROBENZENE

It is a synthetic chemical that is also known as allyltrichloride, glyceroltrichlorohydrin, and trichlorohydrin (Table 1). It is colorless, heavy liquid with a sweet but strong odour. It evaporates very quickly and small amounts dissolve in water. It is mainly used to make other chemicals. Some

of it also used as an industrial high boiling solvent, dielectric fluid, coolant in electrical installation, glass tempering, dye carrier, transformer oils, lubricants, paint and varnish remover, heat transfer fluid, and cleaning and degreasing agent (Table 2). It is also used as insecticide and fungicide. Historically, 1,2,3-TCB was used as termite control agent but it is not currently used for that purpose (US Environmental Protection Agency, 1981; and Optick Richard, 1993). Its oral rat LD 50 is 1,830 mg/kg and hazard class is 6.1. 1,2,3-TCB is moderately irritating to skin. Its vapors are said to be irritating to the eyes and respiratory tract. It is irritating to eyes and mucous membranes.

1,2,3-TCB is prepared by the chlorination reaction of benzene in the liquid phase in the presence of iron (III) chloride. It is obtained from the chlorination of appropriate chlorobenzene isomers in presence of Lewis acid catalyst. 1,2,3-TCB is formed in minor quantities in the production of monochlorobenzene and dichlorobenzene. However it becomes the primary product if the chlorine input is increased to about 3 moles of chlorine per mole of benzene. It is also obtained on the dehydrohalogenation of 1,2,3,4,5,6-hexachlorocyclohexane. It is obtained (13-30%) by reacting hexachlorocyclohexane with aqueous alkali or alkaline earth solutions, ammonia, or other catalysts in the temperature range 90-250 °C.

Table 1: Synonyms and Trade Names of New Chlorobenzene Pesticides

| Pesticide | Synonyms |
|--|--|
| (a) 1, 2, 3-TCB | 1, 2, 3-Trichlorobenzene; 1, 2, 3-Trichlorobenzol; 1, 2, 6-Trichlorobenzene; Vic-Trichlorobenzene. |
| (b) 1, 2, 4-TCB | 1, 2, 4-Trichlorobenzene; as-Trichlorobenzene; 1, 2, 4-Trichlorobenzonol. |
| (c) 1, 2, 3, 4-TeCB | 1, 2, 3, 4-Tetrachlorobenzene; Tetrachlorobenzene Oekanol, 250. |
| (d) 1, 2, 3, 5-TeCB | 1, 2, 3, 5-Tetrachlorobenzene; 1, 2, 3, 5-Tetrachloro-benzene. |
| (e) 1, 2, 4, 5-TeCB | 1, 2, 4, 5- Tetrachlorobenzene; s-Tetrachlorobenzene; Benzene Tetrachloride, Ethenyltrichloride. |
| Note: As = Unsymmetrical, s = Symmetrical; (US Environmental Protection Agency, 1977; 1984; and Sax and Lewis (1989). | |

Table 2: Properties of New Chlorobenzene Pesticides

| Pesticides | 1, 2, 3-TCB | 1, 2, 4-TCB | 1, 2, 3, 4-TeCB | 1, 2, 3, 5-TeCB | 1, 2, 4, 5-TeCB |
|---|---|---|---|---|---|
| Molecular formula | C ₆ H ₃ Cl ₃ | C ₆ H ₃ Cl ₃ | C ₆ H ₂ Cl ₄ | C ₆ H ₂ Cl ₄ | C ₆ H ₂ Cl ₃ |
| Relative molecular | | | | | |
| Mass | 181.5 | 181.5 | 215.9 | 215.9 | 215.9 |
| Physical state | White flakes | Colorless Liquid | White to off-white crystals | White crystals | Colorless crystals |
| Melting point (°C) | 53.5 | 17.0 | 47.5 | 54.5 | 139.5 |
| Boiling point (°C) | 218.5 | 213.5 | 254.0 | 246.0 | 243.6 |
| Vapor Pressure at 25 °C(pa) | 17.3 | 0.29 | 5.2 | 9.8 | 0.72 |
| Density (g/ml at20°/4°C) | 1.69 | 1.46 | 1.73 | na | na |
| Aqueous | 12.2 | 31 | 12.1 | 2,81 | 2.16 |
| Solubility at 25 °C(mg/L) | | | | | |
| Vapor density (air = 1) | 6.26 | 6.26 | na | na | na |
| Henry's law | 0.306 | 0.439 | 0.261 | 0.593 | 0.261 |
| Constant KPa m ³ /mole | | | | | |
| Log octanol/water (Kow) | 4.04 | 3.98 | 4.55 | 4.65 | 4.51 |
| Soil sorption (Koc) | 3,680 | 2,670 | na | 8,560 | 6,990 |
| Note: Na = not available; (Handbook of Environmental Fate and Exposure Data for Organic Chemicals, 1990; Reid et al., 1977; Windholz, 1984; Weast, 1978; and Kirk-Othmer1980). | | | | | |

Several analytical methods have been used for the analysis of 1,2,3-TCB. It can be determined most conveniently by wide-bore open-tubular capillary column gas chromatography using both single column/single detector and dual column/dual detectors. This method has been described for the determination of 1,2,3-TCB in extracts prepared from environmental samples and RCRA water at ppb concentration (Method, 8121).

Impacts on Environment and Food Quality

Florida Spectrum

The release of 1,2,3-TCB will occur through its manufacture and use as an industrial chemical, chemical intermediate, dielectric fluid, heat transfer medium, and chemical solvent. If released to the soil, 1,2,3-TCB should display

limited mobility, and it would be expected to adsorb to the organic matter of soil and not readily leach into groundwater. Examples of its presence in groundwater have been demonstrated, and thus 1,2,3-TCB can be considered to be mobile under certain conditions. 1,2,3-TCB can slowly degrade in soil. If released to the water, 1,2,3-TCB should adsorb onto the sediment and particulate matter, and should bioconcentrate in aquatic organisms. Hydrolysis will not occur, and biodegradation should not be an important fate process. Volatilization from the water to the air should be rapid. If 1,2,3-TCB is released to the atmosphere, direct photolytic degradation is possible, but not expected to be important. The estimated vapor phase half-life for the reaction

with photochemically produced hydroxy radicals is on the order of a few months. Exposure to 1,2,3-trichlorobenzene will mainly be due to occupational exposure during its production, use as an intermediate, and through the use of commercial products in which it is contained. Exposure to the general public should be through the ingestion of contaminated water or aquatic organisms, or through inhalation near industrial areas where it is in use.

Terrestrial Fate

The experimentally determined values for K_{oc} , 589, and for the log octanol/water partition coefficient, 4.05, suggest that 1,2,3-TCB should have a low mobility in soil). The field determined K_{oc} values for lake and river sediment, 5,012 and 1,259 respectively, suggest that adsorption to surface water sediment will be an important fate process. 1,2,3-TCB has been shown to slowly degrade in soil. Laboratory studies on the mineralization of radiolabeled 1,2,3-trichlorobenzene (50 ug/g soil) gave an average degradation rate of 0.36 nmol/day per 20 g of soil (Nixon sandy loam).

Aquatic Fate

If released into water, 1,2,3-trichlorobenzene would be expected to adsorb onto the sediment and particulate matter, and to bioconcentrate in aquatic organisms. This compound should not readily biodegrade in water, will not hydrolyze (est half-life 4.9 year), and should not undergo degradation by direct photolysis. Volatilization into the atmosphere should be rapid. With the experimentally determined Henry's Law Constant of 1.25×10^{-3} atm-cu m/mol, the half-life of 1,2,3-TCB in a model river 1 m deep, flowing at 1 m/sec, and a wind velocity of 3 m/s, can be estimated at 4.9 h. Reported down flux of 1,2,3-TCB to sediment, 20 g/day which represents 1%

of the daily loading from the Niagara river.

Atmospheric Fate

If 1,2,3-TCB is released to the atmosphere it will be subject to reaction with photochemically produced hydroxy radicals with an estimated vapor phase half-life of 55 days (1, SRC). It will not be expected to be subject to appreciable direct photolysis.

Drinking Water

1,2,3-Trichlorobenzene was detected in municipal discharge in Catawba Creek, NC at a concn of between 21-46 ug/L. Detected at a level of approximately 0.1 ug/L in chlorinated drinking water samples from two out of ten Canadian water treatment plants, detection limit <0.1 ug/L. Drinking water samples from Niagara Falls, NY collected during April 11, 1979 and April 18, 1979 contained 1,2,3-trichloro-benzene at a concentration of 0.38 and 0.26 ug/L, respectively. April-Nov. 1980, drinking water samples from three cities in the Lake Ontario vicinity, mean concn 0.1 ng/L.

Surface Water

1,2,3-Trichlorobenzene has been detected in water from Lake Ontario, Lake Erie, Lake Huron, and Lake Superior watersheds. Sept 1981 to March 1983, Niagara river water, concn range 0.70-15 ng/L, mean concn 2.7 ng/L, median concn 2.3 ng/L. April-Nov 1980, Lake Ontario, five sites, concn range 0.1-0.2 ng/L, mean concn 0.1 ng/L; Lake Huron, five sites, not detected, detection limit approx 0.1 ng/L; and Grand River, ten sites, max. concn 0.7 ng/L, mean concn 0.1 ng/L. Detected in Niagara River (1982) at Niagara-on-the-Lake 2.3 ng/L average concn over five weeks. Little change in concn as a function of depth was observed. Qualitatively identified in Narragansett Bay, RI. Water collected in the vicinity of an industrial outfall in the Calacasieu River estuary,

LA - 12 ng/L(14). Water samples collected Aug 1983 to July 1984 in the southern North Sea, 108 samples, concn range 0.1-25 ng/L, mean concn 1.4 ng/L, median concn 0.7 ng/L(7). Water samples collected from the Rhine River during Nov 1983, one sample, 6 ng/L(7).

Groundwater

1,2,3-Trichlorobenzene was found in two of nineteen wells two years after a PCB/TCB spill of transformer fluid near Kingston, TN (1973), in concn of 0.18 and 0.097 ug/l . (vii) EFFL: Identified in effluent gas from a coal-fired power plant at a concn of 3.9 ng/cu m. 2.7 ug/L found in an effluent sample collected on Sept. 18, 1980 from a community septic tank serving 97 homes in Tacoma, WA . April-Nov. 1980, wastewater effluents from four activated sludge wastewater treatment plants, two discharging into Lake Ontario and two discharging into the Grand River, concn range 2-3 ng/L, mean concn 2 ng/L. Of 250 ug/L of 1,2,3-TCB initially in a pilot plant two stage aerated effluent treatment facility, approximately 65% remained in the effluent of the first stage, and approximately 80% remained in the effluent of the second stage.

1, 2, 4-TRICHLOROBENZENE

It is a synthetic colorless liquid or white solid with a sharp chlorobenzene odor. Major applications of 1, 2, 4-TCB include its use as a solvent in chemical manufacturing, dyes and intermediates. It is also used as dielectric fluid , synthetic transformer oil, lubricant, heat-transfer medium, insecticide, herbicide, degreasing agent, septic tank and drain cleaner, wood preservative and as an ingredient in abrasive formulations. It is also used as a comonomer with p-dichlorobenzene in the production of arylene sulfide polymers. It is stable, insoluble in water, incompatible with

strong oxidizing agents and combustible. It is skin, eye and respiratory irritant. It alters liver enzymes and hepatic porphyria. Chronic dermal contact with 1, 2, 4-TCB can cause dermatitis in human. It causes cancer in mice but not in rats on giving in diet. DNA synthesis study on 1,2,4-TCB shows that it does not induce in vitro DNA repair at concentrations up to 1% (V/V). Other studies with up to seven strains of Salmonella typhimurium were negative for mutation with or without metabolic activation (14). Its acute oral and acute dermal rat LD 50 is 756 mg/kg and more than 5 mg/kg respectively.

The most common process by which 1,2,4-TCB is formed is the catalytic chlorination of o- and p-dichlorobenzene at 20 °C to 30 °C in the presence of ferric chloride. The reaction is allowed to proceed until a density of 1.4 g/mL at 15 °C is obtained and then the acid is neutralized and the products are fractionally distilled to yield 1,2,4- and 1,2,3-isomers (US Environmental Protection Agency, 1977). Ultra trace determination of 1,2,4-TCB in waste water has been made by using Purge and trap-gas chromatography coupled to different detectors: flame ionization (FID), electron capture (ECD), and multiple ion detector-mass spectrometry (MID-MS). Other chromatographic techniques such as HPLC have also been used. But MID-MS is the latest technique.

Impacts on Environment and Food Quality

1,2,4-TCB has been measured in the air of Los Angeles. Its concentration has been found to be from 0.007 to 275 ppb in the drinking water supplies of US cities (8). It is bioaccumulator and is persistent in the environment. 1,2,3-TCB adsorbs to soils with 1-2% organic matter, as predicted by its Koc (Table 2), but leaching into ground water can occur from deep soils. It slowly evaporates into the atmosphere from surface

water and, to a lesser extent, from soils (US Air Force, 1989). 1,2,3-TCB reacts with hydroxyl radicals with an estimated half-life of approximately 18.8 days. It is slowly biodegrade in soils. Half-lives of 1,2,3-TCB in water range from 1 day in rivers to 10 days in lakes and 100 days in ground waters. Its half-life of volatilization is 11 to 22 days for aerated seawaters. 1,2,3-TCB is expected to bioaccumulate in aquatic organisms. Metabolism of 1,2,3-TCB is mediated by oxidation to form chlorophenols which are conjugated to glutathione, glucuronic acid or sulfate. Chronic dermal contact with 1,2,3-TCB can cause dermatitis in humans.

During LD50 studies, rats and mice had symptoms of depressed activity at lower doses and extensor convulsions at lethal doses. No mortality was observed in rats exposed by inhalation to 418 ppm 1, 2, 3-TBC for 4 h; however, clinical signs included lacrimation, salivation, pink ears, labored breathing, and discoordination.

EPA results of aquatic toxicity testing on 1,2,3-TCB show that it is highly toxic to aquatic organisms. It adversely affects survival, growth, and reproduction in mysid shrimp. The 48-h LC50 for Salmon gairdneri (rainbow trout) is 1.95 mg/L. Based on the bioconcentration factor in fish (182-3,200), 1,2,3-TCB also has potential to bioconcentrate in the tissues of aquatic organisms (IPCS, 1991).

1,2,3,4-TETRACHLORO-BENZENE

It is a synthetic solid in the form of white or off-white crystals. It is used industrially mainly as an intermediate in the production of fungicides, herbicides, defoliant, insecticides and in the formulation of dielectric fluids for transformers. It is also used as solvent. It is very unreactive and

insoluble in water. 1,2,3, 4-TeCB is incompatible with strong oxidizing and reducing agents. It is also incompatible with many amines, nitrides, azo/diazo compounds, alkali metals, and epoxides. Its rat LD50 (oral) is 1,167 mg/kg. 1,2,3,4-TeCB is harmful if ingested or inhaled. Its severe overexposure can result in injury or death. It is irritating to eyes and skin on contact. Its inhalation causes irritation of the lungs and respiratory system. Inflammation of the eye due to 1,2,3,4-TeCB is characterized by redness, watering, and itching. Skin inflammation due to 1,2,3,4-TeCB is characterized by itching, scaling, reddening, or, occasionally, blistering.

1,2,3,4-TeCB is prepared by the addition of chlorine to trichlorobenzenes in the presence of aluminium catalyst. The wide-bore open tubular, capillary column gas chromatography is applied for analyzing 1,2,3,4-TeCB. It is determined at low concentration in tissues and sediments by using gas chromatography/electron capture detection.

Impacts on Environment and Food Quality

The principle sources of environmental contaminations by 1,2,3,4-TeCB are likely spillage of the dielectric fluids, and long-range transborder transport and deposition. Losses associated with use as industrial reagent, residues in the final product and via industrial effluents and landfill leachates are also expected.

Although chlorobenzenes have previously been considered to be entirely anthropogenic, there is now some evidence that some congeners can be produced naturally by both biotic and abiotic processes (e.g., 1,2,3,4-TeCB is found naturally in the Mississippi salt marsh needle rush).

1,2,3,4-TeCB has been found in various water courses in Canada, primarily in the Great Lakes

basin. when it present above detection limits concentration have been reported to range from <0.00001 to 0.126 ug/L. Levels near the upper part of the range are usually near known sites of contamination the St. Clair and Niagara Rivers. Elevated levels, some above the ranges previously noted, have been reported in industrial effluents in Ontario and Nova Scotia.

Levels of 1, 2, 3, 4-TeCB in invertebrates and fish ranged from <0.01 to 26.8 ug/kg (w/w). The values in the upper part of the range are for organism collected near sites in the Great Lakes basin known to be contaminated.

In the aquatic environment, 1,2,3,4-TeCb is found mostly in organic phases (organisms, sediments) or associated with suspended/dissolved organic material rather than dissolved in the water phase (k_{ow} log octanol-water partition 4.5), with half-lives of 4.2-14 months in the water and 1.1-3.4 years in the sediments (Mackay *et al.*, 1992).

1,2,3,5-TETRACHLOROBENZENE

It is a synthetic simple aromatic halogenated organic compound which is available in the form of white crystals or off-white solid. It is very unreactive, incompatible with strong oxidizing and reducing agents and is also incompatible with many amines, nitrides, azo/diazo compounds, alkali metals, and epoxides. 1,2,3,5-TeCB may react with oxidizers. It is insoluble in water. Its acute oral rat LD₅₀ is 2,297 mg/kg. It is used in the synthesis of medicines and pesticide intermediate. It may cause irritation on contact. It is required to wear a NIOSH-approved half face respirator equipped with an organic vapor/acid gas cartridge (specific for organic vapors, HCl, acid gas and SO₂) with a dust /mist filter. Rats fed 1,2,3,5-TeCB at 500 ppm showed a significance increase in aminopyrinedemethylase

activity 1,2,3,5-TeCB is synthesized by 1,2,3-trichlorobenzene and chlorine under aluminum amalgam. Gas chromatography-capillary column technique based on the dual-column/ dual-detector approach involves the use of two 30 m x 0.5 mm ID fused-silica open-tubular columns of different polarities, thus different selectivity towards the target compounds. The columns are connected to an injection tee and two identical detectors. When compared to the packed columns, the mega bore fused-silica open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis.

Impacts on Environment and Food Quality

Histological changes in the tissues produced by the administration of the 1,2,3,5-TeCB were mild even at the highest dose levels. The metabolism of three tetrachlorobenzene isomers (TeCB) was investigated in the squirrel monkey. The animals were administered orally 6 single doses of ¹⁴C-labeled 1,2,3,4-, 1,2,4,5-, or 1,2,3,5-tetrachlorobenzene over a 3-wk period at levels ranging from 50 to 100 mg/kg body weight (bw) and kept in individual metabolism cages to collect urine and feces for radio assay. Approximately 38% (1,2,3,4-TeCB), 36% (1,2,3,5-TeCB), and 18% (1,2,4,5-TeCB) of the doses were excreted respectively in the feces 48 h post administration. In monkeys dosed with 1,2,3,4-TeCB, unchanged compound accounted for 50% of the fecal radioactivity; its fecal metabolites were identified as 1,2,4,5-tetrachlorophenol (TeCP, 22%), N-acetyl-S-(2,3,4,5-tetrachlorophenyl) cysteine (18%), 2,3,4,5-tetrachlorophenyl sulfinic acid (3%), 2,3,4-trichlorophenyl methyl sulfide (0.6%), and 2,3,4,5-tetrachlorophenyl methyl sulfide (0.2%). As was the case with 1,2,3,4-TeCB, unchanged compound accounted for more than

50% of the fecal radioactivity found in the monkeys dosed with 1,2,3,5-TeCB. The fecal metabolites of 1,2,3,5-TeCB consisted of 2,3,4,5-TeCP (2%), 2,3,4,6-TeCP (14%), 2,3,5,6-TeCP (9%), and 2,3,5,6-tetrachlorophenyl sulfinic acid (15%). No metabolites were detected in the feces of monkeys dosed with 1,2,4,5-TeCB. While the fecal route represented the major route of excretion for 1,2,3,4-TeCB, the other two isomers were eliminated exclusively in the feces. The above data in the squirrel monkey are different from those obtained with the rat and the rabbit, and demonstrate the different metabolic pathways for the isomers (Schwartz *et al.*, 1987).

The acute, lethal potency of the 1,2,3,4-, 1,2,4,5- and 1,2,3,5-tetrachlorobenzene isomers was compared in the terrestrial and aquatic oligochaetes *Eisenia andrei* and *Tubifex tubifex*. 1, 2,4,5-TeCB was neither lethal, nor produced any perceptible adverse effects, at lipid normalized concentrations predicted to be lethal according to the well-established critical body residue concept. If a narcotic is defined as a substance capable of inducing narcosis, rather than a substance displaying certain physical or chemical properties (e.g., $\log K_{ow}$), then we do not believe these findings challenge the critical body residue because by the former definition, 1,2,4,5-tetrachlorobenzene is not a narcotic (Christopher *et al.*, 2011).

TCB are industrial chemicals which have been used as intermediates for chemical synthesis and for electrical insulation. Recently TCB residues have been found in Great Lakes fish. The present study was designed to determine the sub chronic toxicity of these compounds. Groups of 15 male and 15 female rats were fed diets containing 0, 0.5, 5.0, 50 or 500 ppm of each of 1,2,3,4-, 1,2, 3, 5- and 1, 2, 4, 5-TCB for 13 weeks. Rats fed 500

ppm 1, 2, 4, 5-TCB exhibited significant increases in liver and kidney weight. 1,2,4,5-TCB at the highest dose level caused a significant increase in serum cholesterol levels. Hepatic microsomal aminopyrinedemethylase and aniline hydroxylase activities were induced by this compound at 50 and 500 ppm in the males, and 500 ppm in the females. Moderate to severe histological changes occurred in the liver and kidney of rats fed the three TCB isomers but the 1, 2, 4, 5-isomer caused the most severe lesions. 1, 2, 4, 5-TCB accumulated in fat and liver in a dose-dependent manner. Results indicate that 1, 2, 4, 5-TCB is the most toxic isomer of the three and accumulates in liver and fat in a dose-dependent manner (Chu *et al.*, 1984).

1,2,4,5-TETRACHLORO BENZENE

It is a synthetic substance available in the form of colorless crystals or white flaky or chunky solid. It is odorless, and insoluble in water (<0.1 g/100 mL at 21 °C). It is stable, combustible, incompatible with strong oxidizing agents, and reacts explosively with alkaline methanol solutions. Its acute oral rat LD50 is 1,500 mg/kg. 1, 2, 4, 5-TeCB is used as an intermediate or building block to make herbicides, insecticides, and defoliant. It is also used to prepare other chemicals such as 2,4,5-trichlorophenol and 2,4,5-trichlorophenoxyacetic acid.

1,2,4,5-TeCB can enter in lungs by breathing contaminated air. It can enter body by eating contaminated foodstuffs and can be absorbed through skin on contact with the substance. It is released in the environment during synthesis, packaging, storage and usage. It enters in seafood from contaminated water. Its exposure can irritate or bother eyes and skin. It can affect respiratory system in turn affect ability to breathe

and the mucous membranes. Laboratory experiments show that the animals exposed to 1,2,4,5-TeCB experienced lesions, or changes to the liver and kidney.

It is prepared by the controlled chlorination of dichlorobenzenes in presence of a suitable catalyst. Accelerated solvent extraction combined with sorptive enrichment and gas chromatography/mass spectrometry has been used for the determination of 1,2,4,5-TeCB in strawberries (Wennrich *et al.*, 2001). Residues of 1,2,4,5-TeCB in river sediments have been determined by using GC-FID (Stan and Kirsh, 1995).

Impacts on Environment and Food Quality

Thurston *et al.* (1996) have developed several tests using an automated respirometer in which fishes have been exposed to 1,2,4,5-TeCB. The principal animal has been the rainbow trout (*oncorhynchus mykiss*) and some other fish species to compare the results. They have proposed a simple predictive model to describe the rates of uptake and depuration of xenobiotics as a function of oxygen uptake rate and chemical properties of 1,2,4,5-TeCB (24). Jaffe and Hites have analyzed non-migratory fish from the mouths of tributaries to Lake Ontario and from the Niagara River and its tributaries for anthropogenic organic compounds by methane enhanced, negative ion, gas chromatography/mass spectrometry. The results indicate that non-migratory fish accumulate a variety of chlorinated pesticides such as 1,2,4,5-TeCB (Jaffe and Hites, 1986).

COMPARATIVE STUDY OF IMPACTS ON ENVIRONMENT

Transport and Distribution

The physicochemical properties of chlorobenzenes under study suggest that chlorobenzenes

(Table 2) released to the environment are likely to be volatilized to the atmosphere. The Henry's law constants measured for chlorobenzenes suggest that they are readily volatilized, especially from aquatic systems with long residence times, such as large lakes and oceans (TenHulscher *et al.*, 1992). However, chlorobenzenes released to water may be adsorbed onto sediment, if it is rich in organic matter. Volatilization from soil is also likely, although, depending on the characteristics of the soil, there may be sorption to soil.

The majority of chlorobenzenes added to soil, as either sewage sludge or spiked samples, were volatilized, with biodegradation and abiotic degradation insignificant compared with the amount volatilized (Wang and Jones, 1994a). Volatilizations occurred by two step first-order processes, with rates of volatilization during an initial step, followed by a second, much slower step, which was presumably controlled by the rate of desorption of the compound from soil. Half-lives for loss of chlorobenzenes ranged from 13.0 to 219 days for sewage sludge applications and from 10.6 to 103 days for spiked samples. Half-life increased with increasing chlorination and were also in sludge amended soil than in the spiked samples.

The adsorption of 1,2,4-TCB to soil was found to decrease with increasing soil depth (Njoroge *et al.*, 1998). These depth-related changes were attributed to changes in composition, texture, and accessibility of the soil organic matter. At deeper levels, extractable organic matter was increasingly dominated by fulvic acids. The higher fulvic-humic acid ratio in deep soil reflects an increasing hydrophilicity of the soil organic matter. Abundance of iron oxide and size of clay particles also increase with depth.

Sorption of chlorobenzenes is also affected by soil moisture, with reduced sorption to wet soil (Chiou and Shoup, 1985; and Hibaund *et al.*, 1993). Adsorption of 1,2,4-TCB to soil was reduced following the addition of sodium dodecyl sulphate (DiVincenzoJp and Dentel, 1996). Desorption occurred only when the sodium dodecyl sulphate concentration exceeded the critical micelle concentration. Single-step batch tests showed that the desorption of chlorobenzenes from sediments was slow with less than 0.5% of 1,2,4,5-TeCB desorbed within 62 days. Desorption of 1,2,4-TCB was significantly higher than that of other compounds, 3% desorbed within 62 days (Gess and Pavlostathis, 1997).

Adsorption of 1,2,4,5-TeCB on sandy aquifer solids took up to hundreds of days to reach equilibrium (33). Distribution coefficients were greatest in the size fraction with the largest grains. Mean (\pm SD) suspended sediments/water partition coefficients ($\log K_{oc}$) for chlorobenzenes measured in Ise Bay, Japan, were 3.61 ± 0.39 for 1,2,3-TCB, 3.86 ± 0.40 for 1,2,4-TCB, 3.55 ± 0.47 for 1,3,5-TCB, 4.39 ± 0.33 for 1,2,3,4-TeCB and 3.94 ± 0.33 for 1,2,3,5-TeCB and 1,2,4,5-TeCB both (Masunaga *et al.*, 1991b). Concentration of chlorobenzenes in water and adsorbed onto suspended sediment were compared. None of the chlorobenzenes gave a clear adsorbed level distribution pattern, and the correlation between the soluble and adsorbed chlorobenzenes was weak.

The fate of 1,2,4-TCB in wastewater applied soil was examined in a microcosm experiment (Piwoni *et al.*, 1986). Initial concentration of 1,2,4-TCB was 0.72 μ mole/L. Volatility of 1,2,4-TCB was not measured but it was assumed to be approximately 89%, as $>0.7\%$ of the original

concentration remained in the effluent. Octanol/air partition coefficients (\log_{oa}) measured for chlorobenzenes at 25 °C were 5.19 for 1,2,3-TCB, 5.64 for 1,2,3,4-TeCB and 5.63 for 1,2,4,5-TeCB (Harner and Mackay, 1995). Octano/air partition coefficient determined partitioning from the atmosphere to vegetation, soils, and possibly aerosols. Microcosm experiments suggested that 1,2-DCB in soil was not taken up by grass roots, although some foliar adsorption of dichlorobenzene volatilized from soil was reported (Wilson and Meharg, 1999). A root concentration factor of 19 L/kg has been reported for 1,2,4-TCB (Dietz and Schnoor, 2001). From these data, it cannot be assumed that tri and/or trichlorinated benzenes have the potential to be taken up.

TRANSFORMATION

Abiotic Degradation

Removal of chlorobenzenes from the atmosphere will primarily via reactions with hydroxyl radicals to produce nitrochlorobenzene, chlorophenol, and aliphatic dicarbonyl products, which are further removed by photolysis or reactions with hydroxyl radicals. Photolysis and reactions with ozone or nitrate radicals are of negligible importance (Grosbeak, 1991). Rate constants for reactions with hydroxyl radicals (in cm^3/s per molecule) were calculated to be 6.0×10^{-13} for 1,2,3-TCB, and 5.65×10^{-13} for 1,2,4-TCB (40-43). Assuming 24-h average hydroxyl radical and ozone concentrations of 1×10^6 and 7.2×10^{11} molecules/ cm^3 , troposphere half-lives for 1,2,4-TCB reacting with hydroxyl radicals were calculated to be 26.7 days (Klöpffer *et al.*, 1988). 1,2,4-TCB in the atmosphere may be degraded via direct photolysis, although this route of degradation is minor, due to the poor spectral

overlap between the solar spectrum and the adsorption spectrum of 1,2,4-TCB. The maximum photolysis rate for 1,2,4-TCB in summer at midday under clear skies was 0.03% per hour (Bunce *et al.*, 1989).

Chlorobenzenes in aqueous solutions may undergo photochemical reductive dechlorination. The rate of photo degradation increased in the presence of surfactants. In addition to the main reductive pathway of photodechlorination, minor pathways, including photochlorination, photohydrolysis, and photoisomerization, also occurred. 1,2,3,5-TeCB was photolysed to 1,2,4-TCB or 1,3,5-TCB in the presence of an acetone sensitizer (Choudhry and Hutzinger, 1984). Photochemical reactions in the absence of a sensitizer transformed tetrachlorobenzenes into other isomers and also produced some chlorobenzenes with greater chlorination than the original tetrachlorobenzene compound. The rate constant for reaction of 1,2,4-TCB with hydroxyl radicals in an acidic solution was $6.0 \pm 0.3 \times 10^9$ per mol/L per s (Gallard and De Laat, 2001). 1,4-DCB in aqueous solution was photo degraded to 4-chlorophenol, hydroquinone, hydroxybenzoquinone, and 2,5-dichlorophenol. The formation of 2,5-dichlorophenol demonstrates hydroxylation without dechlorination. The half-lives for photolytic degradation of 1,2,4-TCB in surface water, simulating summer conditions at 40° latitude, was 450 years (Dulin *et al.*, 1986).

Biodegradation

Chlorobenzenes in various substrates, including soil, sediment, and sewage sludge, can be degraded by microorganisms. The major mechanism of aerobic degradations via oxidative dechlorination, usually initiated by dioxygenative hydroxylation, leading to the formation of hydroxylated aromatic compounds (mainly

catechols), which undergo ring fission and subsequent mineralization to carbon dioxide and water. The less chlorinated benzenes are more readily degraded than the higher chlorinated ones (IPCS, 1991a). Biodegradation under anaerobic condition has also been reported, although this occurs at a slower rate than aerobic biodegradation. Chlorobenzene-degrading bacteria isolated from aerobic environments include *Burkholderia* (previously known as *Pseudomonas*) species (Pettigrew *et al.*, 1991; Sander *et al.*, 1991; Van der Meer *et al.*, 1991; Van der Meer *et al.*, 1994; Beil *et al.*, 1997; and Meckenstock *et al.*, 1998), *Alcaligenes* species (De Bont *et al.*, 1986; and Schraa *et al.*, 1986), *Escherichia hermanii* (Kiernicka *et al.*, 1999), *Nitrosomonas europaea* (Keener and Arp, 1994), *Mycobacterium vaccae*, and *Rhodococcus* species (Fairlee *et al.*, 1997). The degradative abilities of these bacteria vary, with some organisms exhibiting a lag or adaptation period prior to degradation. Some can degrade several chlorobenzenes (Brunsbach and Reineke, 1994), whereas others are compound-specific (Brunsbach and Reineke, 1994; Reineke and Knackmuss, 1984; and Reineke and Knackmuss, 1984). For some, degradation occurs only in the presence of other sources of carbon and energy, whereas others are able to use chlorobenzenes as their sole carbon and energy source (Van der Meer *et al.*, 1987). Genetic analysis has shown that these bacteria contain a novel combination of previously existing genes—genes for aromatic ring dioxygenase and dihydrodiol dehydrogenase—and other genes for a chlorocatechol oxidative pathway. Degradation is also dependent upon the initial chlorinated benzene concentrations. Degradation will occur only if the initial concentration is below the toxic threshold. 1,2,4-

TCB were degraded by bacteria isolated from solids sampled from pristine aquifers (Optick Richard, 1993). Degradation followed first-order rate constants, with V_{max} values of 0.38-2.71 ng/g per hour for 1,2,4-TCB. A consortium of bacteria isolated from Rhine sediment was able to degrade 1,2,3,4-TeCB, 1,2,3,5-TeCB, 1,2,4,5-TeCB, and 1,2,3-TCB via reductive dechlorination in the presence of lactate, glucose, ethanol, or isopropanol as the electron donor (Holliger *et al.*, 1992). PeCB was degraded to 1,3,5-TCB, while 1,2,3,4-TeCB and 1,2,4,5-TeCB were degraded to 1,2,4-TCB. Chlorobenzenes that were not dechlorinated during the 4-week incubation included 1,2,4-TCB, 1,3,5-TCB, and all isomers of dichlorobenzene. Other studies have reported complete mineralization of some higher chlorinated compounds. Two *Pseudomonas* strains isolated from the soil of an industrial waste deposit were able to mineralize various chlorobenzenes, including MCB, all three dichlorobenzenes, 1,2,4-TCB, and 1,2,4,5-TeCB. 1,2,4-TCB and 1,2,4,5-TeCB were degraded via dioxygenation of the aromatic ring, producing 3,4,6-trichlorocatechol. Subsequent *orthocleavage*, catalysed by a Type II catechol 1,2 dioxygenase, produced 2,3,5 trichloromuconate, which was degraded via the tricarboxylic acid pathway (Sander *et al.*, 1991).

Bartholomew and Pfaender (1983) calculated degradation rates for MCB and 1,2,4-TCB at different sites of a river system during different seasons. Rates of degradation of MCB and 1,2,4-TCB were reported to decrease over the freshwater to estuarine to marine gradient. V_{max} values for MCB degradation during May and September were 13-14 ng/L per h for fresh water, 4.9-10 ng/L per h for estuarine water, and <1-1.7

ng/L per h for marine water. V_{max} values were <1 ng/L per h at all three sites in February. The corresponding values for degradation of 1,2,4-TCB in May and July were <1-7.5 ng/L per h for fresh water, <1-7.9 ng/L per h for estuarine water, and <1-2.3 ng/L per h for marine water.

In controlled lysimeter experiments, 80% of 1,2,4,5-TeCB in soils and liquid cultures was mineralized by the bacterial strains *Isphingomonas* sp. strains HH69 and RW1 and *Pseudomonas* sp. strain PS14 within a few days (Figge *et al.*, 1993). Degradation was not increased in the presence of additional energy sources such as peptone, triolein, and glucose. Degradation did not occur in acidic soils (pH<4).

Anaerobic degradation of chlorobenzenes has been reported in river sediment (Masunaga *et al.*, 1996a; and Susarla *et al.*, 1996). Dechlorination occurred without a lag period, with half-lives ranging from 17 to 433 days. The main pathway for PeCB dechlorination was via 1,2,4,5-TeCB, 1,2,4-TCB, 1,4-DCB, and MCB was also observed. MCB was stable under anaerobic conditions. The preferences for dechlorination were two adjacent chlorine atoms, followed by one chlorine on an adjacent carbon, followed by no chlorine on the adjacent carbon. Other studies have reported similar anaerobic biodegradation (Beurskens *et al.*, 1991; Ramanand *et al.*, 1993; and Susarla *et al.*, 1997). Nowak *et al.* (1996) reported anaerobic degradation of all chlorobenzenes, including MCB, to benzene

In anaerobic sewage sludge, PeCB was dechlorinated to 1,2,3,4-TeCB and 1,2,3,5-TeCB, which were degraded to 1,2,4-TCB, 1,2,3-TCB, and 1,3,5-TCB, and then 1,2-DCB and 1,3-DCB (Yuan *et al.*, 1999). Sequential dechlorination occurred within a substrate concentration range

of 2-50 mg/L, but was slower at concentrations greater than 50 mg/L. Dechlorination rates were highest under methanogenic conditions (0.30 mg/L per day), with slower rates under sulfate-reducing (0.12 mg/L per day) and denitrifying conditions (0.08 mg/L per day). The rate of dechlorination of 1,2,3-TCB by anaerobic sediment ranged from 15 to 35 pmol/ml wet sediment per day (Yonezawa *et al.*, 1994).

1,2,3,5-TeCB and 1,3,5-TCB were resistant to degradation by soil slurry microorganisms that could degrade PeCB, 1,2,3,4-TeCB, and 1,2,4-TCB (Ramanand *et al.*, 1993).

BIOACCUMULATION

The bioaccumulation of chlorobenzenes by aquatic organisms is determined by their relative water and lipidsolubility (thus reflecting the octanol/water partition coefficients) and the number of chlorine substitutions. Uptake from water increases with increasing chlorination (Könemann and Van Leeuwen, 1980; Oliver and Niimi, 1983; Sabljic, 1987; Koelmans and Jimenez, 1994; and Wang *et al.*, 1997) and with increasing temperature (Sabljic, 1987).

Mean bioconcentration factors (BCFs) (dry weight) for phytoplankton increased from 4700 for 1,2,3-TCB at 4.5°C to 26000 for pentachlorobenzene (PeCB) at 38.6°C (56). Wang *et al.* (1997) found significant differences in the accumulation of chlorobenzenes by different marine algal species, with BCFs (dry weight) ranging from 600 to 3000 for 1, 2, 3, 4-TeCB and from 1000 to 6000 for PeCB. BCFs for a variety of fish species ranged from 7000 to 24 000 (lipid weight) for 1,2,4-TCB, with a positive correlation between bioaccumulation and lipid content (Geyer *et al.*, 1985). Galassi and Calamari (Galassi and Calamari, 1983) found BCFs (lipid weight)

ranging from 4000 to 22 000 in rainbow trout, with newly hatched fish accumulating 2-4 times the amount found in eyed eggs or young fish (alevins). Qiao *et al.* (2000) report that gill uptake of 1,2,4-TCB and PeCB could account for 98% of the body burden. Uptake of trichlorobenzenes, tetrachlorobenzenes, and PeCB was significantly reduced by the presence of suspended particles (Schrap and Opperhuizen, 1990). The rate of elimination of chlorobenzenes decreases with increasing chlorination (Melancon and Lech, 1985; and De Boer *et al.*, 1994). Sijm and Van der Linde (1995) calculated elimination rate constants and predicted elimination half-lives for 1,2,3-TCB to be 40 days in small fish, such as guppies (*Poecilia reticulata*), and >5 years in larger and/or fatty fish.

The coefficient of adsorption onto sediment influences the uptake into terrestrial plants and sediment-living aquatic invertebrates; the degree of chlorination is also correlated with uptake (Knezovich and Harrison, 1988; and IPCS, 1991a). Under non-equilibrium conditions, BCFs for chironomid midge larvae exposed to sediment bound chlorobenzenes were 29, and 225 for 1,2-DCB, and 1,2,4-TCB, respectively. BCFs were best correlated with the concentrations of the chlorobenzenes in the interstitial water (Knezovich and Harrison, 1988). The tri- and tetrachlorinated benzenes may be taken up by plants, as indicated by the root concentration factor of 19 litres/kg reported for 1,2,4-TCB (Dietz and Schnoor, 2001).

However, the prediction of BCFs is more difficult for terrestrial plants than for aquatic organisms because of the complex nature of the root soil interface combined with gaseous uptake by aerial parts (Scheunert *et al.*, 1994 and 96) compared the uptake of chlorobenzenes by plants from the soil and via the air in closed,

aerated laboratory systems. A negative correlation was demonstrated between the BCF and the soil adsorption coefficient (based on soil organic matter content) for the uptake into the roots of barley. The adsorption of chloro-benzenes onto soil organic matter increased with increasing chlorination. However, expression of uptake in barley roots in relation to the soil interstitial water concentration of the chloro-benzenes produced a positive correlation between the BCF and the octanol/water partition coefficients. Higher chlorinated chlorobenzenes, therefore, are most readily taken up by the plant roots when they are available in soil interstitial water. This will occur particularly in sandy soils with low organic matter content. In a later study, Topp *et al.* (1989) found that after growth in soil containing 2 µg each of 1,2,4-TCB and PeCB per kg dry weight, harvested barley grain contained 73 and 82 µg/plant, respectively. The concentrations in the dry grain were 0.05 and 0.06 mg/kg for 1,2,4-TCB and PeCB, respectively.

In further studies on soybeans (*Glycine max*), linear correlations were found between equilibrium tissue/water coefficients, the octanol/water partition coefficient, and measured lipid content (Tam *et al.*, 1996). The bioconcentration of chlorobenzenes into excised soybean (*Glycine max*) roots increased exponentially with increasing octanol/water partition coefficient (99). Wang and Jones (1994a) concluded that the total amount of chloro-benzenes taken up by carrots grown in sewage sludge-amended and spiked soils was low (<1%) compared with other loss pathways from the soil, principally volatilization.

Belfroid *et al.* (1994) calculated BCFs for earthworms (*Eisenia andrei*) of 104 and 156 for 1,2,3,4-TeCB and PeCB in soil; BCFs based on interstitial water were 67,000 and 307,000,

respectively, and were found to be similar to BCFs found for worms exposed in water alone (Belfroid *et al.*, 1993). BCFs for earthworms exposed via water show a clear increase in uptake of chlorobenzenes with increasing chlorination, and steady-state concentrations are reached within 5 days (Belfroid and Sijm, 1998). Elimination rate constants reveal that chlorobenzene loss decreases with increasing chlorination. A monophasic elimination curve was observed in water, whereas biphasic elimination was found in the presence of soil (Belfroid *et al.*, 1993); elimination rates in soil experiments were significantly increased by the addition of organic matter (Belfroid and Sijm, 1998). Feeding studies have revealed that earthworms can also take up chlorobenzenes via food. In studies with field contaminated soil, steady-state concentrations in worms were much lower than in laboratory studies, suggesting decreased bioavailability of chlorobenzenes (Belfroid *et al.*, 1995).

ENVIRONMENTAL LEVELS

Chlorobenzene (MCB, dichlorobenzenes, and trichlorobenzenes) concentrations have previously been reported in ambient air, with mean concentrations in the order of 0.1 µg/m³ and maximum levels of up to 100 µg/m³ at hazardous waste sites (IPCS, 1991a). A low proportion of particulate bound chlorobenzenes was also reported in air sampled from the Bering and Chukchi seas in 1993 (Strachan *et al.*, 2001). Mean gas-phase concentrations for the Bering Sea were 1.1, 4.0, and 6.6 pg/m³ for 1,2,3-TCB, 1,2,3,4-TeCB, and PeCB, respectively, and for the Chukchi Sea, 2.8, 10, and 14 pg/m³, respectively. Mean chlorobenzene concentrations at four sites throughout Michigan, USA (1992-1994), ranged from 22 to 30 pg/m³ for 1,2,4,5-TeCB, from 40 to

53 pg/m³ for 1,2,3,4-TeCB, and from 35 to 69 pg/m³ for PeCB (Hermanson *et al.*, 1997). Annual mean concentrations for southern Ontario, Canada (1988-1989), were >5.3 pg/m³ for 1,2,3,4-TeCB and >8.0 pg/m³ for PeCB (Hoff *et al.*, 1992). Higher concentrations have been reported in close proximity to pollution sources. A concentration of 5 µg/m³ for tri and tetrachloro-benzenes was found within 200 m of an Electro-industrial plant in Slovenia (Jan *et al.*, 1994). Chlorobenzenes have also been detected in rainwater, their presence presumably being due to transfer from the ambient air. Concentrations of all three dichlorobenzene isomers and 1,2,4-TCB in rainwater were less than 10 ng/L at selected sites in Oregon and California, USA (Pankow *et al.*, 1983). Chlorobenzene concentrations in US wastewater have been reported to range from 11 to 6400 µg/L for MCB, from 10 to 860 µg/L for dichlorobenzenes, and from 12 to 607 µg/L for trichlorobenzenes (IPCS, 1991a).

Concentrations of chlorobenzenes in surface waters are generally in the ng/L to µg/L range, with maximum concentrations up to 0.2 mg/L in areas close to industrial sources (IPCS, 1991a). Mean concentrations of dissolved chlorobenzenes in the Bering and Chukchi seas ranged from 3 to 10 pg/L for 1, 2, 3-TCB, from 15 to 36 pg/L for 1, 2, 3, 4-TeCB, and from 9 to 36 pg/L for PeCB (Strachan *et al.*, 2001). Higher chloro-benzene levels have been detected in coastal waters and estuaries, with Dutch coastal waters containing mean concentrations ranging from 9 to 117 ng/L for dichlorobenzenes and from 0.7 to 1.6 ng/L for trichlorobenzenes (Van de Meent *et al.*, 1986). Waters of the Scheldt estuary (The Netherlands) contained chlorobenzene concentrations ranging from <25 to 320 ng/L for trichlorobenzenes (Van Zoest and Van Eck, 1991). Mean chlorobenzene

concentrations in the Forth Estuary, United Kingdom, during 1987 from 4 to 5,500 ng/L for trichlorobenzenes. The predominant isomers detected were 1,2,3- and 1,2,4-TCB, and these were found near industrial effluent discharges (Rogers *et al.*, 1989). Further studies in 1990 revealed 1,2,3- and 1,2,4-TCB concentrations ranging up to 51 and 84 ng/L, respectively (Harper *et al.*, 1992). The highest chlorobenzene concentrations in surface waters have been reported for river waters in heavily populated and/or industrialized areas. Mean concentrations in the river Besos, Spain, were 260 ng/L for MCB, 600 ng/litre for 1,4-DCB, 5,000 ng/L for 1,2-DCB and 1,3-DCB, 1,100 ng/L for 1,2,3-TCB, and 8,100 ng/L for 1,2,4-TCB (Gomez Belinchon *et al.*, 1991). Elder *et al.* (1981) reported trichlorobenzene concentrations (isomer not specified) ranging from 0.1 to 8 µg/L in water from Niagara Falls, New York, USA. Corresponding concentrations of tetrachlorobenzene ranged from 0.1 to 200 µg/L. Concentrations in water sampled from the rivers and estuary of Osaka (a major urban area of Japan) ranged from 0.16 to 0.35 µg/L for 1,2,4-TCB, and from 0.18 to 0.30 µg/L for 1,2,3-TCB (Yamamoto *et al.*, 1997).

Mean chlorobenzene concentrations in sediment from the Bering and Chukchi seas ranged from 0.02 to 0.41 µg/kg for 1,2,3-TCB and from 0.08 to 0.87 µg/kg for 1,2,3,4-TeCB (105). Mean concentrations in coastal sediments from Ise Bay, Japan, were 4.8 µg/kg for 1,2,4-TCB, 2.3 µg/kg for 1,2-DCB, 1.9 µg/kg for 1,3-DCB, and <0.15 µg/kg for 1,3,5-TCB, tetrachlorobenzenes, and PeCB (Masunaga *et al.*, 1991b; and Lee and Fang, 1997) reported mean values for the Tsenwen estuary, Taiwan, of 3.2 µg/kg for 1,2-DCB,

20.7 µg/kg for 11.2 µg/kg for 1,2,4-TCB. Sediment samples from the river Elbe, Germany, ranged from 30 to 740 µg/kg dry weight from 1 to 115 µg/kg for trichlorobenzenes (1,2,3- and 1,2,4-TCB), (Götz *et al.*, 1993) whereas samples from the river Rhine contained concentrations ranging from <10 to 20 µg/kg for trichloro-benzenes, and (Alberti, 1983).

Chlorobenzene levels in uncontaminated soils are generally less than 0.4 mg/kg for dichlorobenzene congeners and less than 0.1 mg/kg for other chlorobenzene congeners (Wang *et al.*, 1995). Multiple applications of sewage sludge can increase the chlorobenzene content in sludge-amended soil compared with control soils. However, Wang *et al.* (1995) found that most chlorobenzenes disappear rapidly on cessation of sludge application, with around 10% remaining 30 years later. They found that 1,4-DCB levels increased significantly in United Kingdom soils during the 1960s to a maximum mean value in 1967 of 10 mg/kg in control soils and 16.6 mg/kg in sludge-amended soils. Analysis of subsoil from a former pesticide factory in Germany showed that tetrachlorobenzenes and PeCB were dominant in the upper soil layers (up to 1.9 m), accounting for 80% of chlorobenzenes, with 1,2,3,4-TeCB and PeCB accounting for 44% and 24%, respectively. At depths between 1.9 and 5.5 m, trichlorobenzenes were more dominant, accounting for 60%, with 1,2,4-TCB accounting for 37% (123). Total chlorobenzene concentrations ranged from 1.5 to 18,400 mg/kg.

Mean chlorobenzene concentrations in bivalves from US coastal waters ranged from <0.25 to 28.2 µg/kg dry weight for 1, 2, 4, 5-TeCB, and from <0.25 to 10 µg/kg for 1, 2, 3, 4-TeCB,

(Gebauer and Weseloh, 1993). Waterfowl from Lake Ontario, Canada, contained mean chlorobenzene concentrations ranging from 0.3 to 1.7 µg/kg wet weight for 1,2,3,4-TeCB and from 0.65 to 33.4 µg/kg for 1,2,4,5-TeCB (Muir *et al.*, 1992). Mean concentrations in Arctic marine mammal blubber ranged from 1 to 9.7 µg/kg wet weight for 1, 2, 3, 4-TeCB (126).

IMPACTS ON FOOD QUALITY

Most pesticides escape natural degradation processes and persist in most foodstuffs including animal tissues. Various surveys have indicated that amongst several food groups including meat, dairy products, fruits, vegetables, dried foods, most processed foods and many other house hold staples, the most persistently and highly contaminated foodstuffs are animal products, followed by leafy vegetables and garden fruits (Fan and Jackson, 1989). Among the pesticides, DDT, BHC, dieldrin, and lindane appear to be widely distributed. Approximately 50% of all pesticide residues detected in food are organochlorines, and 60% of these are found primarily in animal products. It is reported that the propensity of animal tissues to store pesticides, particularly in fat, may be characteristic, irrespective of the amount ingested in food.

To predict the pesticide residues in foodstuffs, knowledge of the physical and chemical properties of the pesticide under study is essential. The physical and chemical properties of new chlorobenzene pesticides are summarized in Table 2.

The use of pesticides must be regulated in such a manner that the intake of a pesticide residue does not exceed the Acceptable Daily Intake (ADI). However, ADI value for new

pesticides under consideration is not available. The responsibility of enforcing the Maximum Residue Limit (MRL) lies with state government.

Table 2 shows that new chlorobenzene pesticides are colorless and odorless. Their log octanol/water partition coefficients (K_{ow}) are with in 3.98 and 4.65, those for other are higher such as DDT, DDE, and dieldrin are 6.307-6.914, 6.956 and 6.200, respectively. The new chlorobenzene pesticides have low molecular weight (usually less than 216) than those of the DDT, dieldrin, and lindane are 354.49, 380.91, and 290.83, respectively.

New chlorobenzene pesticides possess low acute toxicity for mammals and birds, high toxicity for aquatic environment with prolonged use. New chlorobenzene pesticides can persist several months in soil, whereas the persistence of DDT, BHC etc. is usually below 60 days. Due to such persistence, new chlorobenzene pesticides can contaminate food because they are directly applied on crops or through contaminated water used for irrigation of cultures. Maximum Residue Levels (MRLs) of pesticide are regulated by international and national organisms. MRLs are defined for a determined pesticide in a particular food in agreement with its toxicity and daily uptake. MRLs for urea pesticides have been established for a few foods; disperse and scarce regulations are set by the different countries according to their own interests in specific crops. A more simple regulation for drinking water has been set—the European Union Legislation established in the 98/83 EC Directive on quality of water for human consumption a maximum admissible concentration of 0.1 $\mu\text{g/L}$ for each individual pesticide and 0.5 $\mu\text{g/L}$ for the sum of pesticides.

Unfortunately, very little information is available on the uses and abuses of new chlorobenzene pesticides. Therefore, more work is required to accept their use in crop protection.

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