



Review

Sources and transformations of chlorophenols in the natural environment

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Abstract

The present review updates our knowledge about chlorophenols, their chemical reactions and transformations in the natural environment, as well as factors affecting kinetics and mechanisms of these processes. Effects of pH of the environment and structure of molecules (also the number of chlorine atoms and their position in the molecule) on the behaviour of these compounds in the natural environment are also discussed. In addition, ways of propagation of chlorophenols in the natural environment are presented and discussed on the background of their physical and chemical properties, which influence the propagation rate in the ecosystems.

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1. Sources of chlorophenols

Chlorophenols are synthetic organic compounds, obtained on large, industrial and commercial scales by chlorinating phenol or hydrolysing chlorobenzenes. Chlorophenols also arise as an intermediate product at some stages of 2,3-dichlorophenoxyacetate acid production (Kent and James, 1983), or during wood pulp bleaching. Kringstad and Lindström (1984) describe in detail the formation of chlorophenols in the wood pulp bleaching process.

A lot of studies concerning surface water, including ocean water, showed the presence of chlorophenols in these waters in concentrations even to 10 ng/l (Grimvall, 1995; Asplund and

Grimvall, 1991; Grimvall et al., 1994). In this case, probably natural reactions of humic acid chlorination are the main source of chlorophenol formation (Gribble, 1995). Laboratory investigations carried out by Hodin et al. (1991) showed that 2,4,6-trichlorophenol had been formed after addition of chloroperoxidase, hydrogen peroxide and potassium chloride to the fungi *Culduriomyces fumugo*. Chloroperoxidase catalyzes the chlorination of aromatic structures, such as phenols and humic material. Hoekstra et al. (1999) also indicated natural processes occurring in soils as a source of chlorophenol formation. These authors, basing on examination of the samples drawn from humic soil layer of a Douglas fir forest and the same samples spiked with Na³⁷Cl solution, stated that after 1 year of incubation the samples con-

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tained larger amounts of 4-chlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol and 2,4,5-trichlorophenol. They detected the presence of the ^{37}Cl isotope in particles of determined compounds. Moreover, Ando et al. (1970) reported the de novo synthesis of 2,4-dichlorophenol by a soil fungus of the group of *Penicillium*.

Only eight of chlorophenols (monochlorophenols, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,5-tetrachlorophenol, 2,3,4,6-tetrachlorophenol pentachlorophenol) have been used by the industry. Chlorophenols, pentachlorophenol (PCP) and tetrachlorophenols in particular, have been used as plant protecting chemicals. Mixtures of chlorophenols, due to their fungicidal and bactericidal properties, were used as wood and leather impregnants (Kringstad and Lindström, 1984; Oikari et al., 1985). Chlorophenols with one chlorine atom have been used in production of plant protecting agents or as antiseptics. Chlorophenols may also be formed as by-products during disinfection of drinking water by chlorinating, production of paper, coking process or distillation of wood (Paasivirta et al., 1985; Oikari et al., 1985; Öberg et al., 1989). Viau et al. (1984) confirmed the presence of 2,4,6-trichlorophenol in gases emitted from a municipal incinerator. Taylor and Dellinger (1999) described in detail the mechanism of PCP formation during a coal pyrolysis.

Other sources of chlorophenols in the environment are processes of biodegradation of pesticides and herbicides. Microbial degradation of herbicides, especially of 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and pesticides, yields numerous chlorophenols as intermediate metabolites of their decomposition.

In the whole world, because of their adverse environmental effects, applications of this group compounds to plant protection were significantly limited, if not left out entirely in some cases. Presently, limitations are imposed on both use and production of chlorophenols in many countries.

2. Chlorophenols in the natural environment

Investigations into the state of the environmental pollution, carried out across the world, confirm the

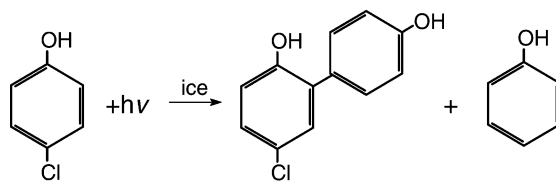


Fig. 1. Photodegradation of 3-chlorophenol in ice (Klan et al., 2001).

presence of chlorophenols in many ecosystems: surface and ground waters, bottom sediments, atmospheric air and soils (Xie et al., 1986; Paasivirta et al., 1985; Sinkkonen and Paasivirta, 2000). Under some circumstances chloroderivatives of phenol may become substrates for the formation of polychlorinated biphenyls and dioxins (Choudhry and Hutzinger, 1982; Vollmuth et al., 1994; Connell, 1997; Tuppurainen et al., 2000; Klan et al., 2001). Results of the study carried out by Wagner et al. (1990) showed an enzymatic oxidation of 2,4,5-trichlorophenol in the presence of hydrogen peroxide and a culture filtrate of the soil fungus *Phanerochaete chrysosporium*. Studies of Svenson et al. (1989), Öberg et al. (1990) and Öberg and Rappe (1992) also reported an enzymatic conversion of chlorophenols in the presence of horseradish peroxidase enzyme and other peroxidases. Moreover, Hoekstra et al. (1999) proposed a possible formation mechanism of dioxins congeners mediated by peroxidases occurring in soils. Öberg and Rappe (1992) also stated the formation of dioxins in the sewage sludge marked by ^{13}C -PCP.

In 1997, Connell (1997) noticed that polychlorinated dibenzodioxins and dibenzofuranes (PCDD/F) were emitted from combustion of wood soaked with PCP. In 1994, Vollmuth et al. proposed a photochemical mechanism explaining the formation of dioxins during irradiation of water solutions containing PCP with UV rays.

Klan et al. (2001) showed that hydroxychlorobiphenyl and phenol might be formed by irradiating 3-chlorophenol present in ice with UV light. A scheme of the reaction is presented in Fig. 1.

In the aquatic environment, chlorophenols exist as dissociated, non-dissociated or adsorbed onto suspended matter. The forms of occurrence of

chlorophenols depend on pH of the environment, as well as on physical and chemical properties of the particular compounds.

2.1. Water

Examinations of Canadian surface waters demonstrate significant qualitative and quantitative variations in concentration of chlorophenols in lakes and rivers. Concentrations of chlorophenols in water reservoirs, depending on a kind of the reservoir, were from 2 to 2000 ng/l. In surface waters of the province of Alberta, Sithole and Williams (1986) confirmed the presence of 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. Concentrations of monochlorophenol and dichlorophenol were below 10 ng/l, concentration of 2,4,6-trichlorophenol was 40 ng/l. In some samples concentration of 2,4,6-trichlorophenol reached 3 µg/l (Alberta Environment, 1985). Canadian drinking water was contaminated too, 20% of the samples contained PCP. Apart from this, chlorophenols most often identified in drinking water were: 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol.

Albanis and Danis (1999) found 2,4-dichlorophenol and PCP in bottom sediments from Thermaikos gulf (Greece) and from the river Loudias. Czaplicka (2001) found 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol in bottom sediments from the dam reservoir Dzierżno Duże (Poland). Concentrations of these chlorophenols in Dzierżno Duże were differentiated, depended on a sampling site, and varied between 0.01 and 3.41 ng/g for 4-chloro-3-methylphenol, between 0.01 and 0.62 ng/g for 2,4,6-trichlorophenol, and were close to 0.02 ng/g for 2,4-dichlorophenol.

In 1978, in water taken from the Dutch part of the Rhine, the presence of 2,4,6-trichlorophenol and 2,4,5-trichlorophenol was confirmed (Buikema et al., 1979). Their concentrations were between 0.04 and 0.63 µg/l. Determinations of a level of contamination of the river Fraser (Carey et al., 1988) showed the presence of trichlorophenols and tetrachlorophenols in samples taken. Their concentrations varied from 0.07 to 0.17 µg/l for trichlo-

rophenols and from 0.05 to 0.16 µg/m³ for tetrachlorophenols.

During realisation of the 3-year program of phenols, content oriented monitoring of water quality of the river Pio (Italy), Davi and Gnudi (1999) did not find chlorophenols in the river despite evidenced the presence of some phenols. However, the presence of these other phenols suggests probable occurrence of chlorophenols in the water. Such a result was possibly due to the low detection limit of the analytical method used (1 µg/l).

2.2. Air

In ambient air, chlorophenols are present as vapours coming from production-related activities and manufacturing of some—other than chlorophenols—end-use products, combustion of wastes, coal or wood (Cautreels et al., 1977; Viau et al., 1984; Paasivirta et al., 1985; Oikari et al., 1985; Wark et al., 1998; Öberg et al., 1989; Annual Report, 1997). In general, the level of concentration of chlorophenols in ambient air is an effect of local emission sources. Within the frame of the Air Toxins ‘Hot Spots’ program, released by the US Environmental Protection Agency (EPA) for the California area (Annual Report, 1997), the total emission of these compounds was estimated at 118 kg/year. Results of measurements of PCP concentrations in ambient air in a vicinity of a wood impregnation plant, presented by Schroeder and Lane (1988), showed that these concentrations varied from a few to 500 mg/m³. The report of the Agency for Toxic Substances and Disease Registry (1998) announces the presence of PCP in samples of air taken in mountains in the La Paz region (Bolivia) at 5200 m above the sea level. Concentrations of this compound were from 0.25 to 0.93 ng/m³. Significantly higher concentrations were found in samples of air from urbanized areas. For instance, ambient air in Antwerp comprised from 5.7 to 7.8 ng/m³ of PCP (Cautreels et al., 1977), and in Canadian cities it was 1 µg/m³ (Wark et al., 1998).

2.3. Soil

Chlorophenols in soil may originate from technological processes, biodegradation of herbicides

and pesticides, and from atmospheric deposition. In 1995, Danis and Albanis (1996), carried out examinations of arable grounds in the environs of Thessaloniki and Ionnina (Greece). In the region of Thessaloniki they found 2,4-dichlorophenol and PCP in amounts of 0.12 and 0.24 ng/g, respectively. In the region of Ionnina, in a vicinity of a wood impregnation factory, they identified 2,3,4,6-tetrachlorophenol and PCP in soils. Amounts of these compounds in samples changed with depth of the layer they were taken from. The highest contents have been determined in samples taken at the depth of 30 m and they were 8 and 53.3 ng/g for 2,3,4,6-tetrachlorophenol and PCP, respectively. An examination of topsoil samples collected from three Finnish sawmill environments carried out by Knuutinen et al. (1990) showed the total chlorophenol contents in determined samples to be varied from 260 to 480 mg/g (dry wt.). The authors also detected chlorophenol metabolites in examined samples, i.e. dihydroxybenzenes and traces of chlorinated anisoles. The problem of contamination of soils with chlorophenols is especially important for countries where great amounts of plant protecting agents and fungicides have been used (for instance, Canada, Finland and Sweden). In these countries, in the 1960s and 1970s, chlorophenols were commonly used as wood preserving agents at sawmills (Valo et al., 1984).

As far as soils are concerned, an especially important phenomenon is the transport of contaminants. The transport of chlorophenols in soil is affected by many factors: their solubility in water, pH of the soil, total precipitation, content of organic matter, graininess and permeability of the soil, biological processes occurring in the soil, evaporation rate, etc. Influence of some of these factors on behaviour of chlorophenols in the natural environment is more precisely described in the sections characterizing their transformation.

The facts presented above show that chlorophenols are present in all types of the natural environment. The concentration levels in ambient air, water and soil vary significantly and to a great degree depend on industrialization rate of the region and on local sources of emission. Contamination of the natural environment with chloro-

phenols is an important ecological problem in countries where wood preserving and plant protecting agents, comprising chlorophenols, have been in common use.

3. Physical and chemical properties of chlorophenols

Chlorophenols consist of the benzene ring, –OH group and atoms of chlorine. Together with the 19 main compounds, chloroderivatives of methyl- and ethyl-phenols are also considered as chlorophenols. The whole group of chlorophenols comprises tens of compounds, significantly differing from each other with their molecular structure, and consequently with their physical and chemical properties. The physical and chemical properties of selected chlorophenols are presented in Table 1. All chlorophenols, except one, i.e. 2-chlorophenol, are solids, with their melting points between 33 and 191 °C. In general, these compounds dissolve weakly in water, but well in organic solvents. Their water solubility decreases with increasing number of chlorine atoms in a molecule. They are weakly acidic—their acidity is slightly lower than that of phenols. In reactions with alkaline metals (sodium, potassium) in the aquatic environment, they yield salts highly soluble in water.

The fate and transport of a chemical compound in the natural environment strictly depend on the value of the dissociation constant (K_a) and the partition coefficient (K_{OW}) in the octanol–water system. The dissociation constant depends on the structure of a compound molecule—among other things on the number of chlorine atoms in the molecule. In the case of chlorophenols, the dissociation constant of a compound increases (i.e. its $pK_a = -\log K_a$ decreases), with the increasing number of chlorine atoms in a molecule. Depending on the value of pK_a , chlorophenols dissociate totally or partially. Their octanol–water partition coefficients (K_{OW}) strongly increase with the number of chlorine atoms and the water solubility (hydrophilicity) inversely decreases. Also, the degree of dissociation of chlorophenols increases (indicated as descending pK_a values) with increasing number of chlorine atoms.

Table 1
Physical–chemical properties of chlorophenols

No.	Compound	Formula	Molecular weight	Boiling point (°C)	Melting point (°C)	Solubility g/l ^a	pKa	Log <i>K</i> _{o/w}
1	2-Chlorophenol	C ₆ H ₅ ClO	128.56	174.9	9.3	28	8.3–8.6	2.12–2.17
2	3-Chlorophenol	C ₆ H ₅ ClO	128.56	214	33–34	26	8.8–9.1	2.48–2.50
3	4-Chlorophenol	C ₆ H ₅ ClO	128.56	217–219	42–44	27	9.1–9.4	2.35–2.44
4	2,3-Dichlorophenol	C ₆ H ₄ Cl ₂ O	163.00	206	57–58	na	6.4–7.8	3.15–3.19
5	2,4-Dichlorophenol	C ₆ H ₄ Cl ₂ O	163.00	210	45	4.50	7.5–8.1	2.75–3.30
6	2,5-Dichlorophenol	C ₆ H ₄ Cl ₂ O	163.00	211	58–59	na	6.4–7.5	3.20–3.24
7	2,6-Dichlorophenol	C ₆ H ₄ Cl ₂ O	163.00	219	68	na	6.7–7.8	2.57–2.86
8	3,4-Dichlorophenol	C ₆ H ₄ Cl ₂ O	163.00	253–254	65–68	na	7.4–8.7	3.13–3.44
9	3,5-Dichlorophenol	C ₆ H ₄ Cl ₂ O	163.00	233	68	na	6.9–8.3	2.57–3.56
10	2,3,4-Trichlorophenol	C ₆ H ₃ Cl ₃ O	197.45	Sublimes	77–84	0.22	6.5–7.7	3.49–4.07
11	2,3,5-Trichlorophenol	C ₆ H ₃ Cl ₃ O	197.45	248–255	57–62	0.22	6.8–7.4	3.84–4.56
12	2,3,6-Trichlorophenol	C ₆ H ₃ Cl ₃ O	197.45	246	58	na	6.0–7.1	3.88
13	2,4,5-Trichlorophenol	C ₆ H ₃ Cl ₃ O	197.45	Sublimes	67–70	0.948	7.0–7.7	3.72–4.10
14	2,4,6-Trichlorophenol	C ₆ H ₃ Cl ₃ O	197.45	243–249	69	0.434	6.0–7.4	3.60–4.05
15	3,4,5-Trichlorophenol	C ₆ H ₃ Cl ₃ O	197.45	271–277	101	na	7.7–7.8	4.01–4.39
16	2,3,4,5-Tetrachlorophenol	C ₆ H ₂ Cl ₄ O	231.89	Sublimes	116–117	0.166	6.2–7.0	4.21–5.16
17	2,3,4,6-Tetrachlorophenol	C ₆ H ₂ Cl ₄ O	231.89	150	70	0.183	5.3–6.6	4.10–4.81
18	2,3,5,6-Tetrachlorophenol	C ₆ H ₂ Cl ₄ O	231.89	188	114–116	0.100	5.2–5.5	3.88–4.92
19	PCP	C ₆ Cl ₅ OH	266.34	300	190	0.014	4.7–4.9	5.01–5.86

na, not available.

^a Solubility g/l at 20 °C.

4. Toxicity of chlorophenols

Toxicity is the property of a chemical substance defined as its ability to adversely affect biological systems. It is usually related to the time and degree of exposure, chemical dose and the properties of the biological system involved.

Toxicity of chlorophenols depends on the degree of chlorination and the position of chlorine atoms relative to the hydroxyl group. Toxicity of chlorophenols decreases with the number of chlorine substituents.

Higher immunity to microbial degradation was observed for chlorophenols with chlorine atoms at positions 3- or 3,5-, relative to the hydroxyl group, than for their isomers with chlorine atoms at the positions 2- or 2,6- (Liu et al., 1982; Saito et al., 1991). It was also observed that chlorophenols with the chlorine atom at the position 2- are less toxic than other chlorophenols. Toxicity of chlorophenols increases if chlorines are substituted at the 3-, 4- and 5- positions. This regularity may account for higher toxicity of 3,4,5-trichlorophenol compared to other chlorophenols. In contrast, low-

ering of toxic properties is due to simultaneous occurrence of chlorine atoms substituted at the positions 2- and 6- or only at the position 2-. This proposition may be confirmed by comparing toxicity of 2,6-dichlorophenol and 3,5-dichlorophenol. Works by Salkinoja-Salonen et al. (1981) and Saito et al. (1991) demonstrate that 2,6-dichlorophenol is less toxic than 3,5-dichlorophenol. These facts may suggest that PCP is more toxic than other chlorophenols. Investigations by Liu et al. (1982) and Saito et al. (1991) showed, however, that it was in fact less toxic than 3,4,5-trichlorophenol. This relative lowering of the PCP toxicity is accounted for by chlorine atoms substituted at the positions 2- and 6-.

It was also noticed that carcinogenicity of chlorophenols was affected by pH and the presence of some other compounds accompanying them in the environment (Boutwell and Bosch, 1959; Exon, 1984). In their works, Boutwell and Bosch (1959) show that the presence of 9,10-dimethyl-1,2-benzanthracene in samples comprising 2-chlorophenol and 2,4-dichlorophenol enhances carcinogenicity of these two compounds. It should also be

acknowledged that a metabolism of some chlorophenols in human body may yield substances more toxic than chlorophenols themselves. For instance, tetrachloro-*p*-hydroquinone arises as a result of the metabolism of 2,3,5,6-tetrachlorophenol (WHO, 1998).

Investigations carried out by Haimi et al. (1992) and Mackay and Shui (1997) confirmed that chlorophenols can bio-accumulate. For instance, bio-accumulation coefficients (BCF) for 2,4-dichlorophenol are: 1.00 for trout, 1.53 for gold fish and 2.41 for algae. Higher BCF are found for PCP (ATSDR, 1994), and they are: 1000 for gold fish, 324 for mussels and 78 for oysters.

5. Effects on human health

The effects of the human exposure to any hazardous substance depend on exposure dose, duration, personal traits and habits and interactions with other chemicals present.

Possible routes of human exposure to chlorophenols are inhalation, ingestion, eye and dermal contact. The number of chlorine atoms in a molecule affects symptoms of intoxication: immediate exposure to lower chlorinated phenols (one or two chlorines in a molecule) causes convulsions, while higher chlorinated phenols cause oxidative phosphorylation. DeMarini et al. (1990) and Zeljezic and Garaj-Vrhovac (2001) suggest that exposure to these compounds elevates risk for occurrence of chromosomal aberrations.

Hattula and Knuutinen (1985) presented results of their study on chlorophenol mutagenicity in mammalian cell assay (Chinese hamster cells V-79). Investigations were carried out using two methods. A cell mediated mutagenesis assay was used as a direct method without metabolising cell and a cell-mediated assay with irradiated fibroblasts and hepatocytes was studied. In the case of direct method *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine was used as a positive control, 7,8-dimethylbenz(*a*)anthracene was used in the cell-mediated method. Obtained results indicated mutagenic properties of 2,4,6-trichlorophenol, 3,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol, under conditions of the carried out experiment.

Experiments on carcinogenicity of particular chlorophenols, carried out on rats by Exon and Koller (1983), showed that contact with PCP and 2,4,6-trichlorophenol caused a rise in the cancer morbidity in these rodents. In the 2-year experiment on a group of 60 male rats, Chhabra et al. (1999) were feeding these animals with 1000 ppm of PCP in food for the first 52 weeks, and with control food for the rest of the 2-year period. After these 2 years of the experiment, they observed malignant mesothelioma, originating from tunica vaginalis, in nine, and nasal squamous cell carcinomas in five animals.

5.1. Cohort studies

In countries where great amounts of phenoxy herbicides and chlorophenols have been used, investigations into the carcinogenic effects of exposure to these compounds are now being statistically examined. Cohort studies on workers exposed to phenoxy herbicides and chlorophenols in a Dutch chemical factory (Hooiveld et al., 1998) showed elevated levels of relative risks for total mortality, cancer mortality, respiratory cancer, non-Hodgkin's lymphoma and ischemic heart diseases in male workers. Heacock et al. (2000) examined existence of relationship between occupational exposure of British Columbia sawmill workers (to chlorophenols and their dioxin contaminants) and childhood cancer in their offspring. The results provided little evidence to support the relationship. Mikoczy et al. (1996) studied a cohort of workers employed in Swedish leather tanneries. They found no associations between exposure to chlorophenols and soft tissue sarcomas. Flesch-Janys et al. (1995) in their retrospective cohort study on the relation between mortality and exposure to polychlorinated dibenzo-*p*-dioxins and furans showed a strong positive effect of exposure to these compounds on mortality from cancer or ischemic heart diseases among workers of a chemical plant in Hamburg. The plant produced phenoxy herbicides, chlorophenols and insecticides contaminated with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and other higher chlorinated dioxins (HCD) and furans. Kogevinas et al. (1997) and Vena et al. (1998) presented retrospectively a linkage between

cancer mortality and occupational exposure to phenoxy herbicides, chlorophenols and dioxins. Kogevinas et al. (1997) examined 21 863 cases of deaths from cancer of workers exposed to these compounds in the period from 1939 to 1992 in 12 countries. They were especially interested in mortality from the soft tissue sarcomas, malignant neoplasms, non-Hodgkin's lymphoma and lung cancer. The analysis of data showed that the risk for neoplasms, sarcomas and lymphomas was increasing with time since the first exposure. In workers exposed to phenoxy herbicides mortality from neoplasms, non-Hodgkin's lymphoma and lung cancer was close to the expected value. The Poisson regression analysis showed higher risk for neoplasms in workers exposed to TCDD or HCD, if compared with workers exposed to phenoxy herbicides and chlorophenols only. They also found that exposure to herbicides contaminated with TCDD and HCD may slightly increase overall cancer risk, as well as risk for specific cancers. Hoppin et al. (1998) analysed data from the Selected Cancers Study, a population-based case-control study, which included 295 males soft tissue sarcoma. Chlorophenol exposure was assigned using intensity and a confidence estimate. Seventeen percent of the jobs rated involved wood preservation, while 82% involved cutting oils. Obtained results suggest that chlorophenol exposure independent of phenoxy herbicides may increase the risk of soft tissue sarcoma.

Taking under consideration results of many years of investigations, the World Health Organization (WHO, 1989, 1986) qualified some of the chlorophenols, i.e. 2,4,6-trichlorophenol, 2,4,5-trichlorophenol and PCP, as compounds suspected of having carcinogenic properties. The International Agency for Research on Cancers (IARC) (Kalliokoski and Kauppinen, 1990) classified five chlorophenols—PCP, 2,3,4,6-tetrachlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol and 2,4-dichlorophenol—as belonging to the 2B group of possible human carcinogens. US EPA has classified 2-chlorophenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol and PCP as priority pollutants in the aquatic medium (EPA, 1999). The Human Health Assessment Group in EPA's Office of Health and Environmental Assess-

ment (EPA, 1988), on the basis of examination of 2,4,5-trichlorophenol's possible oncogenicity, classified this compound as belonging to the D group of compounds considered to be non classifiable as to human carcinogenicity.

The maximum admissible concentrations (MACs) in drinking water were set up for the most harmful compounds by the WHO. These MAC values are: 300 $\mu\text{g}/\text{l}$ for 2,4,6-trichlorophenol, 10 $\mu\text{g}/\text{l}$ for 2-chlorophenol, 9 $\mu\text{g}/\text{l}$ for PCP and 40 $\mu\text{g}/\text{l}$ for 2,4-dichlorophenol (WHO, 1998). Governmental agencies for environmental protection defined permissible concentrations of chlorophenols in drinking water, and in some cases for ground water, to be enforced in particular countries.

6. Transformations of chlorophenols in the natural environment

In the natural environment, chlorophenols decay—they are biodegraded, degraded in photochemical reactions and physically transformed by evaporating or adsorbing. Often, these processes are accompanied by oxidation and hydrolysis. All the mentioned processes carry on in all types of the natural environment at various efficiencies and rates. The running time of these transformations varies from several days to several months. The end products of decomposition processes of chlorophenols in the environment are CO_2 , H_2O and Cl . In the course of photochemical reactions caused by UV-Vis irradiation, and also as the effect of biodegradation, chlorophenols are partially or, in some cases, totally decomposed. Both, photo- and biodegradation processes are the objects of investigations were conducted worldwide.

6.1. Photodegradation

The photochemical processes comprise, among other reactions, photodissociation, photosubstitution, photooxidation and photoreduction. Most often, photodegradation of substances in the environment is a resultant of all the processes listed above, and its rate and efficiency depend on many factors. The factors of the greatest importance to the photochemical processes are the maximum

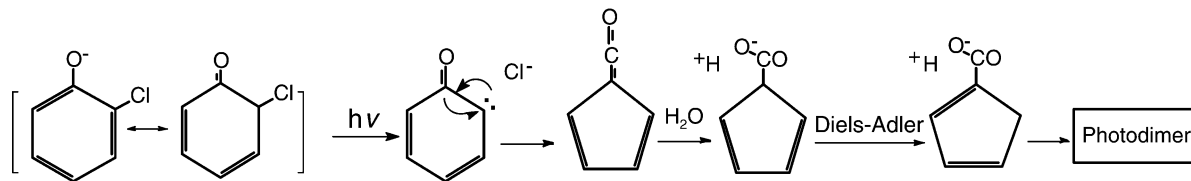


Fig. 2. Mechanism of photodegradation of anionic form of 2-chlorophenol (Boule et al., 1982).

light absorption of a compound undergoing the process, wavelength of the radiation, time of exposure and the state of the reaction environment. The photodegradation processes occur mainly in the air and aquatic environments. Investigations into mechanism and kinetics of the photodegradation of chlorophenols in ambient air, conducted by Bunce and Nakai (1989), revealed a simultaneous occurrence of both the immediate photolysis and the hydroxyl radical attack. Nevertheless, the authors point out that in the case of mono-, di- and trichlorophenols the efficiency of the photolytic degradation is considerably lower than that of the radical reaction.

Photodegradation in water may be either an effect of the direct photolysis of chlorophenol or the reaction of chlorophenol with both the oxygen singlet and the peroxy radicals created by sunlight (Wong and Crosby, 1978; Ononye et al., 1986; Kawaguchi, 1992a; Nakagawa and Shimokawa, 2002). In an aquatic environment, photodegradation occurs only in the surface layer. Results of investigation by Kawaguchi (1992a) show that the half-time of 2-chlorophenol decomposition depends on a season of a year. In general, the degradation is faster in summer than in winter. For instance, the half-life of 2,4-dichlorophenol is 0.8 h in summer and 3 h in winter.

In the aquatic environment, a mechanism of the photodegradation process of chlorophenols, proposed by Boule et al. (1982, 1984), follows the scheme: the C–Cl bond cleavage occurs at the first stage of the reaction, and next—the C–OH bond is formed. Boule et al. (1982) found that as a result of oxygen and hydroxyl radicals effect on the position 2- in 2-chlorophenol, irradiated with 254-nm light, the unstable product—1,2-benzosemiquinone—was detected. Next, depending on the

form of 2-chlorophenol, pyrocatechol or cyclopentadienic acid dimers are formed as a final product. Pyrocatechol is a product of the photodegradation of non-dissociated molecules. The photodegradation of anionic forms leads to the formation of dimers of cyclopentadienic acid according to the Diels–Alder reaction. A by-product of the reaction is hydrochloric acid. The proposed mechanism of the reaction is presented in Fig. 2. UV irradiation of 3-chlorophenol, independently of the form of its occurrence, leads to the formation of resorcinol as a final product.

The photodegradation of dichlorophenols, trichlorophenols and tetrachlorophenols runs in a slightly different way. Boule et al. (1984) stated that during irradiation of solution of 2,4-dichlorophenol with 254-nm light chloroquinone and isomers of chlorocyclopentadiene acid were formed. Crosby and Tutass (1966) proposed the following decomposition pathway of 2,4-dichlorophenol: 4-chloro-1,2-benzenediol, 1,2,4-benzenetriol, hydroxybenzoquinone, polymeric humic acids.

Boule et al. (1982), Kawaguchi (1992a,b) and Tratnyek and Holgné (1991) demonstrated that the photodegradation rate of chlorophenols depends on a form of occurrence of the compound (as non-dissociated or as anionic phenolates), pH of the reaction environment, structure of the compound (especially of a position of the chlorine atom relative to the hydroxyl group). The chlorine atom at the 4- and 6- positions is photo-labile while at positions 3- and 5- is not photoreactive (Kochany and Bolton, 1991). Therefore, depending on the molecule structure, the rate and yield of a process vary considerably.

Other important reactions occurring in the aquatic environment in the presence of light are the processes of photomineralization, photooxidation

and photocatalytic degradation. Investigations into mechanisms and kinetics of the photomineralization and photooxidation of organic chloroderivatives, including chlorophenols, in the presence of TiO_2 , ozone, H_2O_2 and Fenton reagent are presented in the literature (Mills and Hoffmann, 1993; Tseng and Huang, 1994; Trapido et al., 1997; Kokorin et al., 1998; Kwon et al., 1999; Robert et al., 2000). The results obtained by Panadiyan et al. (2002) showed that in the presence of TiO_2 , monochlorophenols dehalogenated faster than polysubstituted phenols. Doong et al. (2000) confirmed influence of pH of the environment on the photodegradation rate of mono- and dichlorophenols in the presence of TiO_2 . They stated that in an acidic environment, the degradation of 4-chlorophenol was faster than that of 2-chlorophenol and 2,4-dichlorophenol, while in the basic environment 2,4-dichlorophenol was decomposed first.

6.2. Sorption

The sorption of chlorophenols plays an important role in the propagation of these compounds in the natural environment (Boyd, 1982; Viau et al., 1984; Paasivirta et al., 1985; Brusseau and Rao, 1991; Peuravuori et al., 2002). Viau et al. (1984) and Paasivirta et al. (1985) showed that fly ashes and dusts emitted to the atmosphere from processes of combustion of wastes, wood and oils, comprised polysubstituted chlorophenols. Particulates of dust are removed from the air by rains and transported to waters and soil.

In the water environment, the properties of chlorophenols are favourable to their accumulation, especially in bottom sediments and on suspended matter (Boyd, 1982; Schellenberg et al., 1984; Peuravuori et al., 2002). The sorption of chlorophenols is a function of their coefficients of partition between the water and the solid phase, sediments or suspended particulates. Detailed investigations by Xie et al. (1986) into distribution of chlorophenols in the marine environment confirmed that the sorption of chlorophenols was dependent not only on their lipophilicity, but that it was also strongly influenced by the pH of ambient water. The accumulation of chlorophenols in sediment depends on the percentage and nature

of the organic matter. These results show the significance of the effect of the pH of solution, number of chlorine atoms in a molecule, and the presence of other compounds in the solution on the sorption of chlorophenols. Works by Bhandari et al. (1996) brought to wider attention the ability of chlorophenols to form covalent bonds, resulting from biologically or chemically catalysed reactions with organic matter of soil. Results of batch studies on sorption in aqueous CaCl_2 solutions, carried out by Lee et al. (1990) to determine influence of solvent and sorbent on distribution of PCP in octanol–water and soil–water solution, show increasing sorption of ions of PCP^- with increasing ionic strength of the solvent. The value of octanol–water partition coefficient suggests that the formation and partitioning of PCP^- are influenced by the cationic species. From investigations of non-equilibrium sorption, conducted by Lee et al. (1991) and Brusseau and Rao (1991), it is known that sorption and transport of chlorophenols in soils depends on the degree of solute ionisation ($\text{pH}-\text{p}K_a$), solubility enhancement (co-solvent effect) and on the formation of pairs of ions (electrolyte effect). The transport velocity depends on a value of octanol–water partition coefficients, equilibrium sorption coefficients and on a form of the compound occurrence: dissociated or non-dissociated (Drever, 1997). The ionised forms were noticed to be more susceptible to leaching than non-dissociated forms. DiVincenzo and Sparks (1997) show that the kinetics of PCP sorption in soils is affected by this compound concentration as well. PCP undergoes process of leaching to groundwater in sandy soils and in soils where the biodegradation is not rapid. Examinations of sorption of PCP, performed by Tam et al. (1999), showed an effect of such organic structures as benzoic acid, lactic acid and catechol on kinetics of adsorption of this compound in soils. A dissolved humic matter also has an essential influence on the release of the bound PCP from the solid sediment. In the case of lake sedimentary, Paaso et al. (2002) showed that the increase of the dissolved humic matter concentration affected the equilibrium partitioning of PCP between the solid sediment matter and dissolved humic matter. However, obtained results suggest that the structural

dissimilarity of these sorbents do not play such strong roles in the binding affinity of PCP.

6.2.1. Hysteresis in the sorption and desorption

Desorption is a process inseparably connected with sorption. Desorption of organic contaminants in soils includes a relatively fast initial release of the sorbate followed by a prolonged and increasingly slower desorption, suggesting the possibility that a fraction of the solute may remain bound or sequestered within the soil matrix. The sorption–desorption phenomenon for organic compounds in soils was quantitatively described by Huang et al. (1997) as the hysteresis index (HI) expressed by the Eq. (1):

$$HI = \frac{q_e^d - q_e^a}{q_e^a} |T, C_e| \quad (1)$$

where: q_e^a and q_e^d are solid-phase solute concentrations for the adsorption and desorption experiments, respectively; and T and C_e specify conditions of constants temperature and residual aqueous phase concentration.

Weber et al. (Weber and Huang, 1996; Huang et al., 1998; Weber et al., 1998) presented, in their many papers, a hysteresis in the sorption and desorption of hydrophobic organic contaminants. Xu and Bhandari (2000) showed the influence of peroxidase on the sorption–desorption phenomena and the binding of phenol mixtures in soils. Results obtained by these authors show that the addition of enzymes causes the increased adsorption of phenol and dichlorophenol, and lead much more than desorption hysteresis. These studies obtained values of HI ($C_e = 10 \mu\text{M}$) for dichlorophenol. In the conditions of the experiment, 5.31 and 0.07 amounted in the case of the sample with the addition of horseradish peroxidase enzyme and without enzyme, respectively. An addition of the enzymes also causes a dramatic enhancement in contaminant binding.

DiVincenzo and Sparks (1997), basing on kinetic studies of sorption and desorption of PCP, paid attention to artifacts observed during carried out investigations. They suggest that one of the causes of unreal hysteresis is the initiating desorption before sorption equilibrium is reached. They also

observed the influence of PCP concentration in soils on sorption and desorption kinetics.

6.3. Biodegradation

Biological transformation and degradation are the two main processes for removal of chlorophenols from the water–soil environment. Significance of these processes for years has been forcing numerous detailed investigations into mechanisms and kinetics of biodegradation of chlorophenols in waters, bottom sediments and grounds. The investigations have been conducted equally for aerobic and anaerobic conditions, with the use of various bacterial cultures (Liu and Pacepavicius, 1990; Palm et al., 1991; Anmenante et al., 1992; Lacorte and Barcelo, 1994). In aerobic conditions majority of chlorophenols are resistant to biodegradation because chlorine atoms interfere with the action of many oxygenase enzymes, which normally initiate the degradation of aromatic rings (Copley, 1997). In numerous works Chang et al. (Chang et al., 1993, 1995d,a,b; Chang and Yuan, 1996) and Häggblom et al. (Häggblom et al., 1989, 1993; Häggblom, 1990) describe the degradation process of chlorophenols in aerobic and anaerobic conditions. Strains of *Norcadia*, *Pseudomonas*, *Bacillus* and *Mycobacterium Coeliacum* were used in experiments in aerobic conditions (Uotila et al., 1992; Fulthorpe and Allen, 1995). The investigation showed that 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 3-methyl-4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2-chlorophenol and PCP were biodegraded in aerobic conditions (Ahel et al., 1994). Among them 2,4-dichlorophenol, 2,6-dichlorophenol and 2-chlorophenol may be biodegraded in anaerobic conditions as well, but generally, their biodegradation is slower and occurs under strictly defined conditions. For instance, 2-chlorophenol is biodegraded in anaerobic conditions only with an aquifer material from an actively methanogenic site. 2,4,5-Trichlorophenol is not biodegradable in anaerobic conditions and in sterile soils. Behaviour of 2,4-dichlorophenol differs considerably: this compound is biodegraded in aerobic and anaerobic conditions, equally in soil and water. It should be acknowledged that the proposed schemes of the transformations are valid

Table 2
Aerobic and anaerobic biodegradation of chlorophenols by PCP adapted bacteria (Liu and Pacepavicius, 1990)

Compounds	Lag time (h)	
	Aerobic	Anaerobic
2-Chlorophenol	25	250
4-Chlorophenol	25	51
2,4,5-Trichlorophenol	300	nd
2,4,6-Trichlorophenol	0	300
2,3,4,5-Tetrachlorophenol	50	500
2,3,5,6-Tetrachlorophenol	nd	nd

nd, not degraded after 700 h of incubation.

under particular conditions of the experiments. The lag time to degradation of selected chlorophenols in aerobic and anaerobic conditions using a PCP-degrading bacterial culture is presented in Table 2.

Becker et al. (1999) proposed pathways for 2-chlorophenol biotransformation in the anaerobic sediment slurry reactors. One of them consists of the reductive dehalogenation of the chlorophenol to phenol followed by carboxylation of phenol to 4-hydroxybenzoate and subsequent dehydroxylation to benzoate. In the other possible reaction, 2-chlorophenol is para-carboxylated to produce 3-chloro-4-hydroxybenzoate, which is subsequently dehydroxylated to 3-chlorobenzoate.

PCP exhibits the different behaviour—its bio degradation is faster in anaerobic than in aerobic conditions. Results of experiments by D'Angelo and Reddy (2000) show that in aerobic conditions, the biotransformation of PCP yields small amounts of pentachloroanisole at the beginning, and more than 75% of pentachloroanisole decays in samples during first 30 days. The authors have not found any correlation between soil properties and the transformation rate in the conditions of the experiment. In anaerobic conditions, dechlorination of PCP led to the formation of a mixture of tetra-, tri- and dichlorophenols. In this case, the transformation rate was correlated with measurements of electron donor supply and microbial biomass. Addition of protein-based electron donors enhanced reductive dechlorination in soil low in organic matter and microbial biomass.

For majority of chlorophenols there are proposed pathways of transformations leading to the removal

of chlorine atoms (dechlorination). Reddy et al. (1998) proposed the pathway for degradation of 2,4,6-trichlorophenol by *Phanerochaete chrysosporium*, Louie et al. (2002) examined transformations of this compound in the presence of *Ralstonia eutropha* JMP143. Metabolites identified from the *Phanerochaete chrysosporium* degradation of 2,4,6-trichlorophenol and pathway are given in Fig. 3.

In experiments on biodegradation of chlorophenols in soil and water, described in the literature, the most often used subject of investigation is PCP. Examinations of the mechanism of biodegradation processes of PCP in the presence of cultures of *Rhodococcus* (Apajalahti and Salkinoja-Salonen, 1986; Häggblom et al., 1989), *Mycobacterium* (Uotila et al., 1992), *Flavobacterium* (Xun et al., 1992) showed that in the conditions of the experiments, this compound is totally mineralized. Simultaneously, inorganic chlorine and CO₂ (aerobic conditions) or methane (anaerobic conditions) are formed. Dechlorination pathway of chlorophenols in contaminated sediment, proposed by Masunaga et al. (1996), is presented in Fig. 4. Authors of the cited papers paid special attention to pH of the environment. The pH equal to 8.0 was optimal to cultures of *Rhodococcus*, and the best results in the biodegradation for *Flavobacterium* were achieved at the pH value 8.5. It was also noticed that in an acidic environment the bacterial metabolism was slower than that at higher pHs.

Chang et al. (1995c) described the degradation of 2,4,6-trichlorophenol and PCP in the presence of 2,4-dichlorophenol and 3,4-dichlorophenol in anaerobic conditions. They showed that dechlorination rates of 2,4,6-tetrachlorophenol and PCP were higher in the presence of dichlorophenols. The authors point out the effect of conditions of the experiment on the course of the process. Namely, they show that the dechlorination of 2,4,6-tetrachlorophenol and PCP is influenced not only by the presence of dichlorophenols, but also by pH, temperature, structure of the molecule and the presence of other substances.

Masunaga et al. (1996) confirmed an effect of the number of atoms in a molecule of the compound on the biodegradation process rate. The

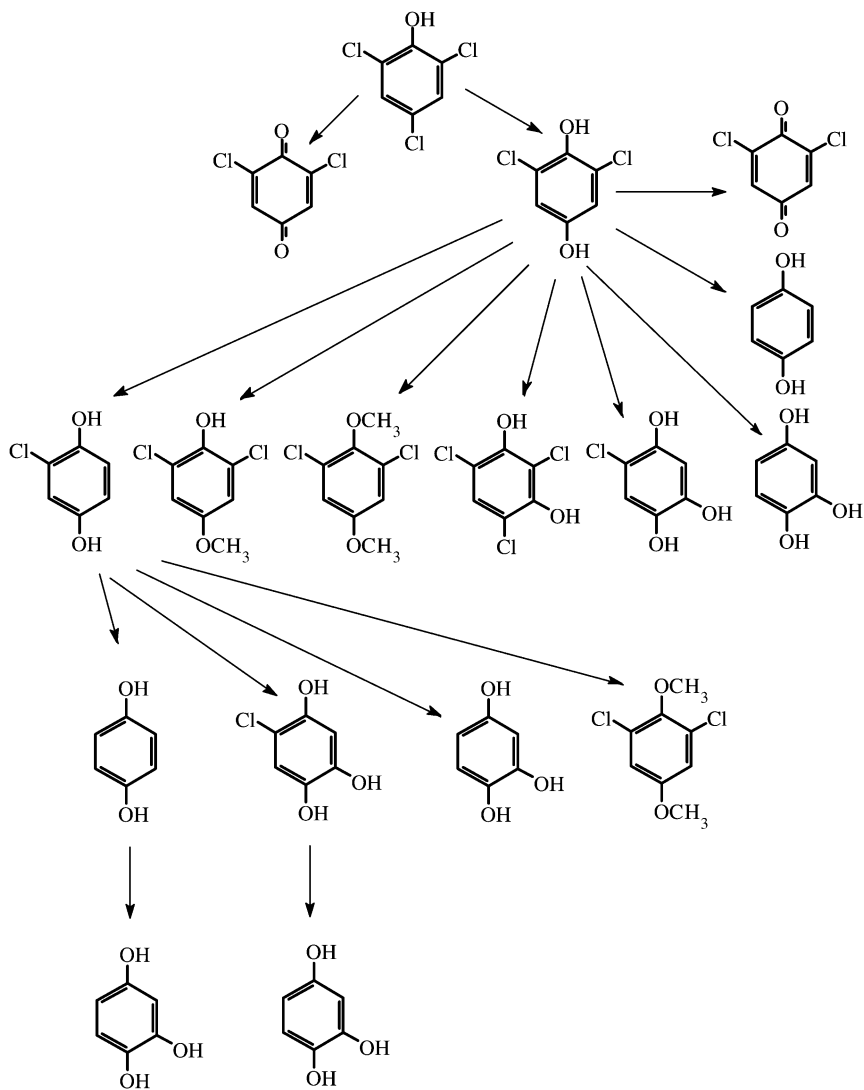


Fig. 3. Metabolites identified from the *P. cryosporium* degradation of 2,4,6-trichlorophenol (Reddy et al., 1998).

investigations showed that a greater number of atoms in a molecule slowed down the degradation process. Liu and Pacepavicius (1990) showed that the position of a chlorine atom in the molecule affected the process rate. Chlorophenols with chlorine atoms at the positions 2-, 4- and 6- are biodegraded faster than compounds comprising chlorine atoms at the 3- or 5- positions. Other factors affecting biodegradation of chlorophenols are: availability of organic carbon, soil humidity

and soil permeability (clay content) (Park et al., 2000). With increasing humidity and decreasing permeability the process rate grows. The biodegradation rate depends also on the aeration, moisture and cation exchange capacity that is conducive to microbial growth. Field investigations carried out by Palm et al. (1991) in sawmill environments showed presence in soils of the methylation products of chlorophenols, such as 2,3,4,6-tetrachloroanisole and pentachloroanisole.

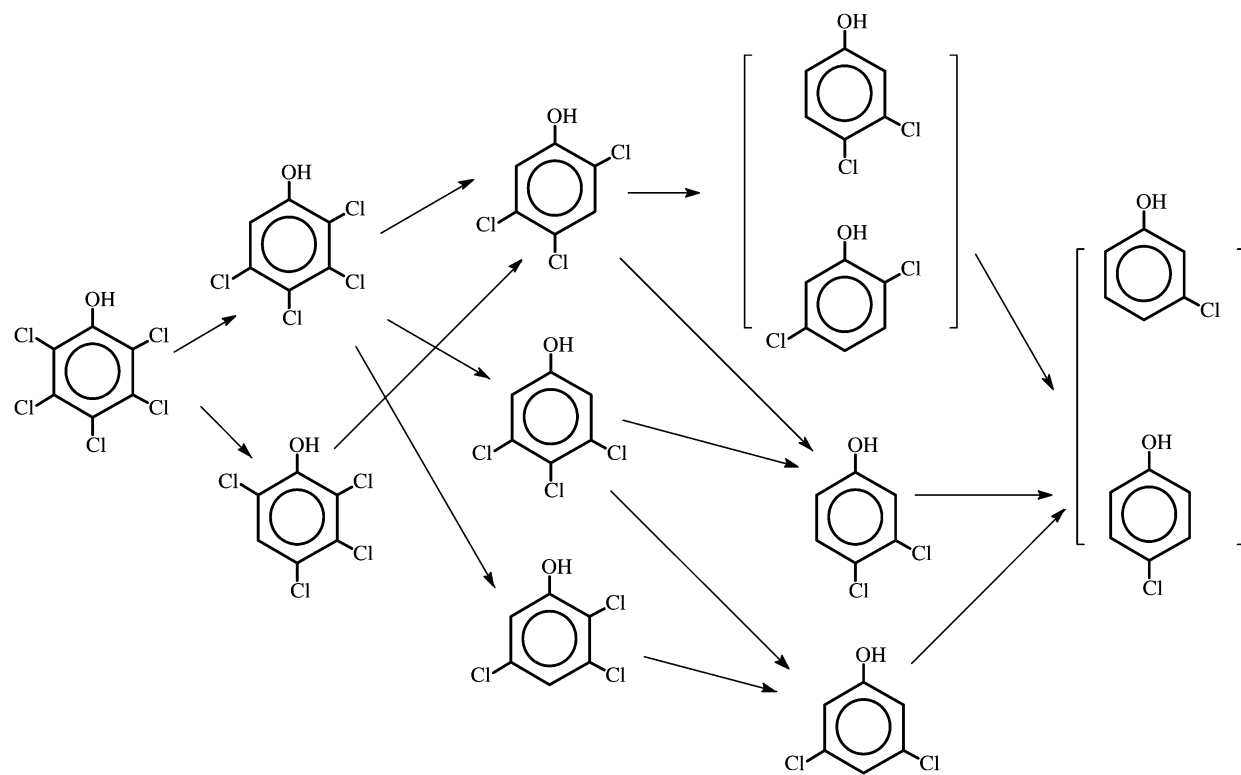


Fig. 4. Dechlorination pathway of PCP in contaminated sediment (Masunaga et al., 1996).

Kuo and Sharak Genthner (1996) noticed an effect of heavy metal ions on processes of biotransformation and biodegradation of chlorophenol. They examined an influence of cadmium, chromium, mercury and copper additions on the biodegradation rate for 2-chlorophenol in anaerobic bacterial consortia. In most considered cases, dehalogenation, aromatic degradation and methanogenesis showed different sensitivities to the added ions of heavy metals. Obtained results indicate that the presence of heavy metals can affect the outcome of anaerobic biotransformation.

6.4. Oxidation and evaporation

The immediate oxidation process utilizing the atmospheric oxygen dissolved in the water does not play an important role in the environmental degradation of chlorophenols. Chlorophenols comprising the greater number of chlorine atoms in a molecule are usually immune to oxidation processes in ambient temperature. The advanced oxidation processes, occurring under the effect of the hydroxyl radicals, are much more important. Tratnyek and Holgné (1991), Boncz et al. (1997) and Goi et al. (2001) described the kinetics and mechanism of this process.

The oxidation rate depends on the concentration of the compound in the environment and on the temperature. An increase of the temperature yields an increase in the rate of the reaction. Chlorophenols may also undergo reactions of auto-oxidation and catalysis, especially on surfaces comprising of clay and silica. These reactions are usually catalysed by ions of metal.

Another process affecting the behaviour of compounds from this group in the natural environment is evaporation. The evaporation rate from water solutions depends strictly on the vapour pressure and water solubility (Henry's law constant). In laboratory conditions, investigations into the evaporation of chlorophenols were conducted by Chiou et al. (1980) and Piwoni et al. (1989). They showed that the evaporative processes play insignificant role in the removal of chlorophenols from the water environment. Nevertheless, Drever (1997) observed occurrence of this process in the natural environment during rapid mixing of waters.

The evaporation of chlorophenols may occur also from shallow surface waters, when an ambient temperature is above 20 °C.

7. Conclusions

The real environmental threat caused by chlorophenols is due to anthropogenic inputs from industrial wastes, degradation processes of chlorinated pesticides and their use as wood preservatives. The chlorophenols are noxious substances for human health. The toxic effects of chlorophenols are directly dependent on the degree of chlorination and on the position of chlorine atom. Oral exposure to chlorophenol-contaminated food and water is the main route of the human population exposure to these compounds. An understanding of the behaviour of chlorophenols in the environment necessitates comprehending the processes that influence their fate and transport in air, soil and groundwater.

Not only the pH, oxygen content, presence of other organic and inorganic substances and temperature, but also the structure of the compound molecule—including the number of chlorine atoms and their position in the molecule—affect the behaviour of chlorophenols in the natural environment. Most of the works cited here put emphasis on the effect of these factors on behaviour of these compounds in the environment.

In the environment, the most important degradation processes of chlorophenols are photodegradation and biodegradation. These processes cannot be considered simply as separate unitary transformations. For instance, in the natural conditions, the photodegradation processes comprise the photolysis, photomineralization and photooxidation. The biodegradation depends, among other things, on sorption, biosorption and bioremediation processes in soil. It should be noted that many of the results presented in this paper were received as results of investigations conducted under conditions simulated in a laboratory. In the natural environment many other important conditions, characteristic of a specific ecosystem, affect kinetics and mechanisms of the considered processes, especially the presence of other organic and inor-

ganic compounds acting as inhibitors or catalytic agents in the reactions.

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