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Aquatic Pollution by Phenolic Compounds

a review

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Phenolic compounds

1. Occurrence and behaviour in the environment

A wide variety of phenolic substances, ranging from amino acids to precursors of lignin and flavonoids and bromophenols, are found as natural constituents in plants and other living organisms. Derived directly from these natural sources or from their decay products a number of phenolic compounds are found in surface water in the order of some micrograms per liter. (Degens, E.T., Renter, J.H., and Shaw, K.N.F., Geochim. et Cosmoch. Acta 28, 45 (1964)).

In polluted water the presence of phenols is generally caused by discharges from gas works (e.g. spent en crude gas liquors, cokeoven effluents: (Dierichs, A., Die Entphenolung von Industrielabwässern und -ölen nach dem Phenolsolvanverfahren, Chemikerreitung (1942), 289), but many chemical waste liquors are also liable to contain phenols.

Experiments on the persistence of phenols and cresols in polluted and unpolluted river water have shown that the gradual disappearance of the phenols is due largely to the biochemical action of micro-organisms. (Ettinger, M.B., and Ruchhoft, C.C., Removal of phenol and cresols from natural waters, Ind. Engin. Chem. 41, 1422-7 (1949)).

Breakdown is , in general, more rapid at 20°C than at 4°C.

As a result the concentration of phenol in the river Rhine at Lobith varies between 5 micrograms per liter in summer to 150 µg/l in winter (average value : 37 µg/l).

2. Human toxicity

Human toxicity studies are mostly restricted to the effects of pentachloro-phenol (Bergner, H., Constantinides, P., and Martin, J.H., Industrial Pentachlorophenol Poisoning in Winnipeg, Can. Med. Assoc. J. 92, 448 (1965)).

Mammalian systems have been used to test the toxicity of a number of chlorophenols in an attempt to extrapolate the human toxic potential of these compounds (Table I).

Table I : Median lethal doses (LD50) of various chlorophenols after a single oral administration.

Phenol compound	Animal	LD50 (mg/Kg body weight)
p-chloro	rat	500
o-chloro	blue fox	440
o-chloro	mice	670
2,4-dichloro	rat (male)	3600
2,4-dichloro	rat (female)	4500
2,4-dichloro	mice	1630
2,4,5-tichloro	rat (male)	2830
2,4,5-tichloro	rat (female)	2460
2,4,5-tichloro	rat	2960
pentachloro	rat (male)	205
pentachloro	rat (female)	135

These data indicates a sharp decrease in toxicity going from the mono to di-chlorinated phenols and then a progressive increase in toxicity with greater chlorination.

3. Toxicity to aquatic organisms

3.1. Fish toxicity

Acute toxicity of pure phenol varies between 0.08 mg/l in 30 min. to minnows, and 56.0 mg/l in 96 hours to mosquito fish (Gambusia Affenis). Mitrovic c.s. found a 48-hours LC50 of 7,4 mg/l to trout; they noted that exposure to 6,5 mg/l caused damage to epithelical cells in 2 hours, and extensive damage to reproductive systems in 7 days. (Metrovic, U.U., Brown, V.M., Shurban, D.G. and Berryman, M.H., Some pathological effects of sub-acute and acute poisoning of rainbow trout by phenol in hard water, Water Res. 2, 249-254 (1968)).

The response of individual fish to phenol not only varies widely but also involves the elapse of a long time interval between overturning and death, for example, the survival time of Crucian carp ranged from 21 to 171 hours in 25 mg/l of phenol, and from 3 to 148 hours in 50 mg/l of phenol containing water (Lukanenko, V.I., Fish Toxicology, Moskva, Ird. Pishchevaia promichlennost (1967)).
Taking into account the reliable figures for median lethal concentrations for periods between 6 and 96 hours, the range is between 4 and 56 mg/l, the most frequent values for adult fish in well-aerated fresh water being 9-25 mg/l of phenol.

Lethal concentrations of xylenols, cresols and phenols are usually within a two-fold range, but differences are not consistent between authors. Comparable data on the acute toxicity of phenol, the three isomers of cresol and of xylenols are given by Albersmayer and Erichtsen for several species over a range of temperatures of 13 to 19°C (see table II) (Albersmayer, W. und Erichsen, L. von, Untersuchungen zur Wirkung von Teerbestandteilen in Abwässern. Mitteillungen I-VII. Z. Fisch 8, 29-66 (1959)).
Pickering and Henderson give the 96-h LC50 of o-cresol for goldfisch as 17 to 31 mg/l at 25°C. A mixture of xylenols used by them was intermediate between phenol and o-cresol in its toxicity to goldfisch, fathead minnow, and the guppy. (Pickering, P.H. and Henderson, C., Acute toxicity of some important petrochemicals to fish, J. Water, Poll. Contr. Fed. 38, 1419-29 (1966)).

Table II: Approximate 24-h LC50 of phenols to fish (mg/l) (from Albersmayer and Erichsen, 1959).

Phenolic compound	LC50(fish)	LC50(Salmonid embryos
phenol	20	5
o-cresol	20	2
m-cresol	20	7
p-cresol	15	4
1,3,4,-xylenol	20	28
1,4,5,-xylenol	10	2
1,2,4,-xylenol	15	4
1,3,5,-xylenol	50	50
pentachlorophenol	0,1[a)]	

a) Matida, Y, Kimura, S., Yokote, M., Kumada, H. and Tanaka, H., V Some Effects of Sodium Pentachlorophenate to Freshwater Fishes, Bull. Freshwater Fish Res. Lab. Tokyo, 20, 127 (1970).

Somepolyhydric phenols, including hydroquinone, 8-oxyquinolin, and naphthols were reported more toxic than phenol (0,1-4,0 mg/l) by Sollmann and Bandt (Sollmann, T., Correlation of the aquarium goldfish toxicity of some phenols, quinones, and other benzene derivatives with their inhibition of the auto-oxidative reactions J. Gen. Physiol 32, 671-679 (1949) (Bandt, H.J., Phenolabwässer und Abwasserphenole, ihre Entstehung, Schadwirkung und abwassertechnische Behandlung. Eine monographische Studie. Wiss. Abhandl 33 Berlin, Academia-Verlag, 1958, 36 p.).

3.2. Toxicity data on invertebrates and algae

Generally it has been found that bacteria, algae, protozoa, crustacea and mollusca are more resistant thant fish to phenols (e.g. Bandt,(1958) and Albersmayer and Erichsen, (1959). However, the cladoceran, Daphnia sp. appears to be somewhat more sensitive than most invertebrates. Toxicity of phenols to D. magna at 18°C has been measured by Kopperman e.a. in 1974 (Kopperman, H.L., Carlson, R.M., and Caple, R., Aqueous chlorination and ozonisation studies 1. Structure-toxicity correlations of phenolic compounds to Chem. Biol. Interactions 9, 245-251 (1974)

Table III: Toxicity of phenols to Daphnia magna (LC50-96-h) (Kopperman et al.)

Phenol compound	LC50(mg/l)
phenol	12
o-cresol	16
p-cresol	21
1,3,2-Xylenol	10
o-Methoxy	26
m-Methoxy	41
p-Nitro	8,3
o-chloro	7,4
p-chloro	4,8
p-bromo	6,0
2,4-Dinitro	4,7
2,4-Dichloro	2,6
2,4,6-Tribromo	1,3
p-Phenyl	3,7

With a mixture of cresols, as with phenol, there is some evidence that immature organisms are more sensitive than adults; the 48-h LC50 value for immature Asellus militaris and Gammarus fasciatus were 33 and 8,6 mg/l respectively and the corresponding values for the adults were 2 to 3 times higher (Emery, R.M., The comparative acute toxicity of cresol to two benthic crustaceous, Water Res. 4, 485-491 (1970).

4. Taste and odour

4.1. Public water supplies

Phenols affect municipal water systems where trace concentrations of phenolic compounds affect the organoleptic properties of the drinking water (see table IV).

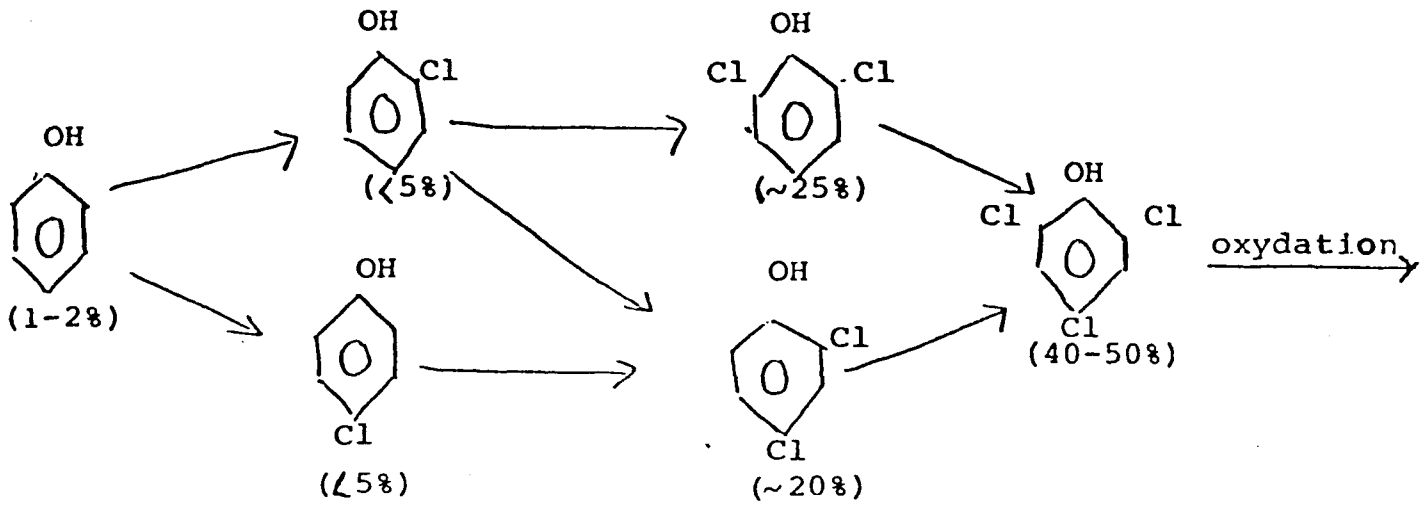
Table IV: Taste and odour threshold concentrations of phenolic compounds (from: Rosen, et.al., 1962 and Burttschell, et.al., 1959)

Phenolic compound	Taste (µg/l)	Odour (µg/l)
phenol	>1000	4200
o-cresol		260
m-cresol		250
p-cresol		55
o-chloro	4	2
p-chloro	>1000	250
2,4-dichloro	8	2
2,6-dichloro	2	3
2,4,6-trichloro	>1000	>1000

(Rosen, A.A., Peter, J.B., and Middleton, F.M., Odour thresholds of mixed organic chemicals, J. Water. Poll. Contr. Fed. 34, 7-14 (1962); Burttschell, R.H., Rosen, A.A., Middleton, F.M. and Ettinger, M.B., Chlorine derivatives of phenol causing taste and odour, J. Am. Water Works Ass. 51, 205-214 (1959)).
If phenolic compounds are present in waters that are chlorinated for desinfection, chlorophenols may be formed. The Kinetics of this reaction are such that chlorophenols may not appear until the water has been distributed from the treatment plant (Lee, G.F.,

and Morris, J.C., Kinetics of chlorination of phenol-chlorophenolic tastes and odours, Int. J. Air Water Poll., 6, 419-431 (1962)) Both Aly and Barnhart have demonstrated that chlorination of phenols and cresols in aqueous solution can occur under conditions similar to those used for desinfection (Aly, O.M., Separation of Phenols in Water by Thin-Layer Chromatography, Water Res. 2, 587 (1968))(BArnhart, E.L., Campbell, G.R., The Effect of Chlorination on Selected Organic Chemicals, Governmental Printing Office, (12020 EXG 603/72), Washington, D.C.)). The chlorination of phenol proceeds by the stepwise substitution of the 2,4 and 6 positions of the aromatic ring, according to the reaction scheme presented in fig. 1. The compounds found to have the strongest organoleptic properties were o-chlorophenol, 2,4-dichlorophenol and 2,6-dichlorophenol (see Table IV).

Figure 1.: Course of Chlorination of 20 mg/l Phenol solution reacted with 40 mg/l chlorine at pH 8. The parenthesized figures refer to the approximate amount present after 18 hours (from Burtschell, et.al. (1959)).



The rates of chlorination of phenol in the neutral pH range are of similar magnitude to those of the chlorophenols. Maximum rates of chlorination occurs in the pH 7-9 range. At pH = 9 dichlorophenols are chlorinated about 10 to 20 times slower than the monochlorophenols. Therefore, the chlorination of phenol in the alkaline pH-range, e.g. pH = 9 or greater, will result in the

building-up of the odorous dichlorophenols. While at pH 7-8, dichlorophenols are chlorinated at the same or at a greater rate than phenol or the monochlorophenols (lee, et.al. 1962). A large excess of free chlorine in the water insures a rapid chlorination of phenol to the odourless 2,4,6-trichlorophenol or oxidation products.

4.2 Aquatic life

Phenolic compounds can taint the flesh of fish and other edible aquatic organisms at concentrations of the offending material lower than those recognized as being harmful to an animal. In tests with o-chlorophenol Boetius reported that eels and oysters were able to concentrate the substance in their bodies.
At concentrations of 0,1-1 ppb eels and oysters required up to resp. 4 and 11 days exposure before impairment of flavour was detected. (Boetius, J., Foul Taste of Fish and Oysters caused by Chlorophenols, Medd. Dan. Fish. Havundes (N.S.) 1 (4), 1-8 (1954)) Short-term exposure of fish to 25 mg/l phenol or for up to four days at 2,5 mg/l did not impair the flavour of the flesh, while 10 mg/l cresol induced only a slight taint. Phenolic compounds associated with fish tainting problems are given in Table V. By comparison of Table V with the Tables II and III it can be seen that the taste of fish in most polluted situation is adversely affected by phenolics before acute toxic effects are observed. (Ebeling, C., Versuche über die Wirkung phenolhaltiger Abwässer in Zusammenhang mit Rheinuntersuchungen auf der Strecke von Mainz bis Emmerich in der Jahren 1935-1937, Vom Wasser 14, 81-91 (1940)) (Krishnaswami, S.K. and E.E. Kupchanko, Relationship between odour of petroleum refinery waste water and occurrence of "oily" taste-flavour in rainbow trout (Salmo gairdneri), J. Water Poll. Contr. Fed. 41 189-196 (1969)) (Albersmayer and Erichsen, (1959)).

4.3 Technical aspects

Super-chlorination of water followed by dechlorination has great merit in terms of elimination of "chlorophenolic" tastes and odours in water supplies by producing the odourless, 2,4,6-trichlorophenol or oxidation products.

The breakpoint chlorination of water, as usually practiced, may not necessary render the water free from "Chlorophenolic" tastes and odours because of the slow (24-60 hr) reaction between aqueous chlorine and phenol at low concentrations of each. Free residual chlorine present in the water supply after breakpoint chlorination could still react with phenolic compounds in the water to form malodorous waters in the distribution system (Lee et. al., (1962)). Ammonia is chlorinated several orders of magnitude faster than phenol; therefore, little or no chlorophenol is formed initially when a phenol-containing water is chlorinated in the presence of excess ammonia. However, later on the slow reactions between chloramines and phenol may still produce chlorophenols, particulary in dead ends of the distribution system.

5. Recommendation

In view of the wide range of concentration of phenolics which produce toxic effects in fish and the generally lower levels which taint fish flesh, it is recommended that taste and odour criteria be used to determine suitability of waste receiving waters to support usable fish populations.
Concentrations of phenolic compounds safe to fish should be lower than 0,1 mg/l at any time or place in order to protect the most sensitive fish species to toxic effects.
Concentrations of phenolic compounds of the tables IV and V are recommended as guidelines in determining what concentration of phenolic compounds in water may cause tainting of the flesh of fish or other aquatic organisms.

In the case of the very toxic pentachlorophenol and related biocides a maximum concentration of 0,0001 mg/l is recommended in order to protect aquatic life.

Table V : Concentrations of phenolic compounds in water that can cause tainting of the flesh of the fish and other aquatic organisms (from : Water Quality Criteria, E.P.A., Washington 1972, p. 148).

Phenolic compound	Threshold level in water (µg/l)
phenol	1.000 - 10.000
o-cresol	400
m-cresol	200
p-cresol	120
o-sec, butyl	300
p-tert. butyl	30
o-chloro	0,1 - 15
m-chloro	60 a)
p-chloro	10 - 60
2,3-dichloro	84
2,4-dichloro	1 - 5
2,5-dichloro	23
2,6-dichloro	35
2-methyl-4-chloro	75
2-methyl-6-chloro	3
2,4,6-trichloro	3 - 50
o-phenyl	1000
phenols in polluted rivers	20 - 100 a)
naphthol	500
2-naphthol	300
xylenols	1000 - 5000 a)

a) E. Schulze, Zur geschmacklichen Beeinflussung von Fischen durch Phenolhaltige Abwässer, Int. Revue ges. Hydrobiol. 46, 81-90 (1961).