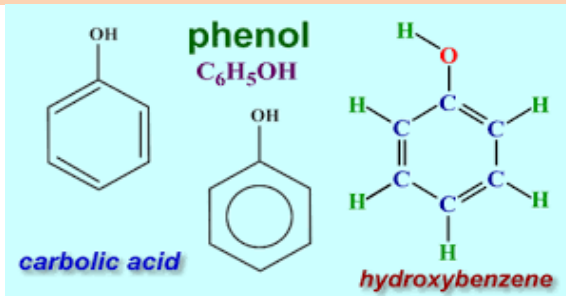


P
A
R
I
V
E
S
H

PHENOLS & PHENOLIC COMPOUNDS



CENTRAL POLLUTION CONTROL BOARD
(Ministry of Environment, Forests & Climate Change)

PariveshBhawan, East Arjun Nagar

Delhi - 110032

website: www.cpcb.nic.in

AUGUST, 2016

FOREWORD

Phenols or Phenolics are a family of organic compounds characterized by hydroxyl (-OH) group attached to an aromatic ring. Besides serving as generic name for the entire family, the term phenol (C₆H₅OH) itself is the first member commonly known as benzenol or carboic acid. All other members in the family are known as derivatives of phenol and phenolic compounds.

Phenolic compounds are common by-product of any industrial process viz. manufacture of dyes, plastics, drugs, antioxidants, paper and petroleum industries. Phenols and Phenolic compounds are widely used in household products and various industries, as intermediates during various industrial synthesis. Phenol itself is an established disinfectant in household cleaners. Phenols are used as basic material during production of plastics, explosives, drugs, Dye & Dye Intermediate Industries, commercial production of azo dyes etc.

Phenolic resins form a large part of phenol production. Phenol formaldehyde resin was one of the earliest plastic known as Bakelite, which is still in use. Many phenolic compounds occur in nature and used in manufacture of perfumes and artificial flowers because of their pleasant odour and also have wide application in food as antioxidants. Because of wide use of phenols & phenolic compounds, these are discharged alongwith the effluents from several categories of industries such as Textiles, Woolen Mills, Dye & Dye Intermediate Industries, Coke ovens, Pulp & Paper Industries, Iron & Steel Plants, Petrochemicals, Paint Industries, Oil; Drilling & Gas Extraction units; Pharmaceuticals, Coal Washeries, Refractory Industries etc. and enters various environmental matrices. Phenol and Phenolic compounds cause irritation, odour and taste problem and are toxic in higher concentration. Due to this large number of phenolic compounds are subject to regulations for air and water pollutants around the world. United States Environment Protection Agency (USEPA) has listed eleven phenolic compounds as priority pollutants. In India, the regulatory actions for phenol & phenolic compounds are contemplated under the Environment (Protection) Rules, 1986 under which several environmental standards for discharge of Phenols and Phenolic compounds in industrial effluent have already been notified.

The present issue of "Parivesh" deals with the chemistry, uses, toxicity, Environmental Implications and Environmental Regulatory Standards of Phenols & Phenolic Compounds. The issue has been diligently collated and compiled by Dr. Yogita Kharayat, Scientist 'B'; Sh. V. K. Verma, SSA; Sh. Bhupander Kumar, Scientist 'C' and Dr. C. S. Sharma, Scientist 'E'.

Hopefully, the information will be useful to all concerned.

(S. P. Singh Parihar)
IAS

Chairman

September 1, 2016

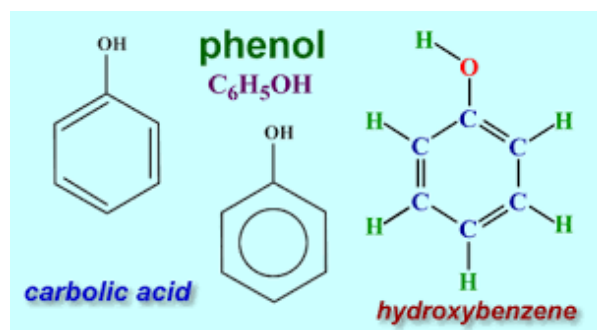
CONTENT

- 1.0 INTRODUCTION**
 - 2.0 PHENOLS AND PHENOLIC COMPOUNDS - TYPES**
 - 3.0 CHEMISTRY AND PHYSICO CHEMICAL PROPERTIES**
 - 4.0 PRODUCTION AND COMMERCIAL USES**
 - 4.1 Production**
 - 4.2 Commercial Uses**
 - 5.0 PHENOLS AND PHENOLIC COMPOUNDS IN THE ENVIRONMENT**
 - 5.1 Natural Sources**
 - 5.2 Anthropogenic Sources**
 - 6.0 DISTRIBUTION AND ENVIRONMENTAL RELEASE**
 - 7.0 EXPOSURE AND EFFECTS ON ENVIRONMENT AND HUMANS**
 - 8.0 TOXICITY OF PHENOLS AND PHENOLIC COMPOUNDS AND MECHANISM OF ACTION**
 - 9.0 MONITORING AND ANALYSIS TECHNIQUES OF PHENOLS IN ENVIRONMENTAL MATRICES**
 - 10.0 REGULATIONS AND ENVIRONMENTAL STANDARDS**
 - 10.1 International**
 - 10.2 Indian Regulations**
 - 11.0 CONTROL MEASURES FOR ABATEMENT OF IMPACT OF PHENOLS AND PHENOLIC COMPOUNDS**
 - 12.0 PROTECTION OF HUMAN HEALTH AND THE ENVIRONMENT**
- REFERENCES / FURTHER READING**

1.0 INTRODUCTION

Phenol (hydroxybenzene) is a colourless, crystalline substance of characteristic odour, soluble in water and organic solvents. Its common industrial uses including chemical – production of alkylphenols, cresols, xylenols, phenolic resins, aniline and other compounds, oil, coal processing and metallurgic. Phenol is also used in pesticides, explosives, dyes and textiles production. It is also used as a disinfectant and reagent in chemical analysis. Phenol is synthesized on an industrial scale from coal tar. Chemically, Phenol is also produced in a reaction between chlorobenzene and sodium hydroxide, toluene oxidation and synthesis from benzene and propylene.

Anthropogenic emissions of phenols in the environment are due to the activity of the chemical, pharmaceutical industries, pulp, paper and wood products sector, the mineral (non-metallic) products sector, the steel and metal products sector, and the petroleum refining and products sector. Phenol also enters into the environment through vehicle exhaust. The compounds penetrate ecosystems as the result of drainage off the municipal or industrial sewage to surface water. Moreover, the occurrence of phenols in the environment stems from the production and use of numerous pesticides, in particular phenoxy herbicides like 2,4-dichlorophenoxyacetic acid (2,4-D) or 4-chloro-2- methylphenoxyacetic acid (MCPA) and also phenolic biocides like pentachlorophenol (PCP), dinoseb pesticides. Some phenols may be formed by natural processes such as the formation of phenol and p-cresol (chlorinated phenols) during decomposition of organic matter.



Phenol (C₆H₅OH) - the simplest of the phenols

Synonyms for phenol include carbolic acid, benzo-phenol, and hydroxyl benzene. Colorless-to-white solid when pure, however, the commercial product, which contains some water, is a liquid.

Phenol is a benzene derivative and is the simplest member of the phenolic chemical. The molecule consists of a phenyl (-C₆H₅), bonded to a hydroxyl (-OH) group. Its chemical formula is C₆H₅OH. Although they share the same functional group with alcohols, where the -OH group is attached to an aliphatic carbon, the chemistry of phenols is very different from that of alcohols. Phenol is a colorless-

to-white solid when pure; however, the commercial product, which contains some water, is a liquid. Phenol is a hygroscopic, crystalline solid with characteristic acrid odor and has a sharp burning taste. The odor threshold for phenol is 0.04 parts per million (ppm), with a strong very sweet odor reported. Phenol evaporates more slowly than water, and a moderate amount can form a solution with water. Phenol can catch on fire.

It is produced on a large scale (about 7 billion kg/year) as a precursor to many materials and useful compounds. Phenol is soluble in most organic solvents, its solubility in water is limited at room temperature; above 68°C it is entirely water-soluble and is quite flammable. It has a log octanol /water partition coefficient (log K_{ow}) of 1.46. It is moderately volatile at room temperature. It is weak acid and in its ionized form, very sensitive to electrophile substitution reactions and oxidation.



Phenol Crystals



Liquid Phenol

Phenol is present in the environment due to anthropogenic activities such as wood burning, smoking, rubbish incineration and car exhausts. Phenol is present in air, especially near industrial processes. It may also occur in rain, surface water and ground water. Major uses of phenol involve its conversion to plastics or related materials. Phenols are key component for building polycarbonates, epoxies, Bakelite, nylon, detergents and a large collection of drugs, herbicides and pharmaceuticals.

Phenols and phenolic compounds are of widespread use in many industries such as polymeric resin production and oil refining, and are found in many common materials including antiseptics, medical preparations, resins, plastics, cosmetics, health aids and foods and beverages. As a result, these compounds are commonly encountered in industrial effluents and surface water.

Table 1 – Physico-Chemical Properties of Phenol	
Molecular formula	C_6H_6O
Molar mass	94.11 g mol^{-1}
Appearance	transparent crystalline solid

Density	1.07 g/cm ³
Melting point	40.5 °C, 314 K, 105 °F
Boiling point	181.7 °C, 455 K, 359 °F
Solubility in water	8.3 g/100 mL (20 °C)
Vapor Pressure	0.357 mm Hg at 20°C 2.48 mm Hg at 50°C 41.3 mm Hg at 100°C
Acidity (pK _a)	9.95 (in water) 29.1 (in acetonitrile)
Dipole moment	1.7 D
Hazards	
GHS hazard statements	H301, H311, H314, H331, H341, H373
GHS precautionary statements	P261, P280, P301+310, P305+351+338, P310
EU classification	Toxic (T), Muta. Cat. 3, Corrosive (C)
R-phrases	R23/R24/R25-R34-R48/R20/R21/R22-R68
S-phrases	(S1/2)-S24/S25-S26-S28-S36/S37/S39-S45
Flash point	79 °C
Related compounds	
Related compounds	Benzenethiol

(Source: <http://en.wikipedia.org/wiki/Phenol>)

Moreover, the occurrence of phenols in the environment stems from the production and use of numerous pesticides, in particularly phenoxyherbicides like 2, 4-dichlorophenoxyacetic acid (2,4-D) or 4-chloro, 2-methyl phenoxyacetic acid (MCPA) and also phenolic biocides like pentachlorophenol (PCP), Dioseb or diarylether pesticides. Some phenols may be formed as a result of natural processes like the formation of phenol and p-cresol during decomposition of organic matter or synthesis of chlorinated phenols by fungi and plants.

Phenol toxicity is related with two main processes – un-specified toxicity related with hydrophobicity of the individual compound and formation of free radicals. Hydrophobicity affects the solubility of phenol in a cells fractions and thus possibility of interaction of the compound with specified cell and tissue

structures. For example, the increase of hydrophobicity of chlorophenols is related to the increasing number of chlorine atoms that enhances toxicity of the individual compound. The strength of toxic influence of the compound also stems from localization of the substituent. For instance, a chlorine atom substituted in ortho position in phenol molecule decreases its toxicity and meta substitution increases toxic action of the compound. Phenols, after penetration of the cell, undergo active transformation, mainly at the participation of oxidases within cytochrome P450. Some times transformation processes lead to increase of toxicity of individual compounds by the formation of electrophilic metabolites that may bind and damage DNA or enzymes. The noxious influence of phenols and their derivatives concerns acute toxicity, histopathological changes, mutagenicity and carcinogenicity.

Phenol was one of the first compounds inscribed into The List of Priority Pollutants by the US environmental Protection Agency (US EPA). Due to their toxicity and environmental concern, some of phenols and phenolic compounds have been designated as priority pollutants by US Environmental Protection Agency (US EPA) and European Commission (EC). Priority phenols consist of a number of substituted phenolic compounds including halogenated (e.g., chlorophenol), nitrated (e.g. 2-nitrophenol), alkylated (e.g., 2,4-dimethylphenol) and ether (e.g., methoxyphenol) derivatives. The designated Priority phenols includes Phenol, 2-Chlorophenol, 2,4-Dichlorophenol, 2,4,6-Trichlorophenol, Pentachlorophenol, 2-Nitrophenol, 4-Nitrophenol, 2,4-Dinitrophenol, 2-Methyl-4,6 dinitrophenol, 2,4-Dimethylphenol, 4-Chloro-3-Methylphenol. Priority phenols are used (or produced) in several industrial processes. They are commonly used as preservatives, disinfectants, in pulp processing, in the manufacture of pesticides and other intermediates. Unfortunately, priority phenols are now common environmental pollutants found in potable water, soil / sediments and ambient air. Many priority phenols, especially the chlorophenols, are known for their toxicity, carcinogenicity, and persistence in the environment.

2.0 PHENOLS AND PHENOLIC COMPOUNDS – TYPES

The word phenol is used to refer to any compound that contains a six-membered aromatic ring, bonded directly to a hydroxyl group (-OH). Thus, phenols are a class of organic compounds of which the phenol is the simplest member. There is three terms used for phenols and their derivatives:

1. Phenol: Phenol is an organic compound known as carboxylic acid
2. Phenols: A class of chemical compounds that include phenol. These may be natural or synthetic
3. Phenolic compounds or phenolics: Any compounds derived from parent (particularly resins) derived from phenols

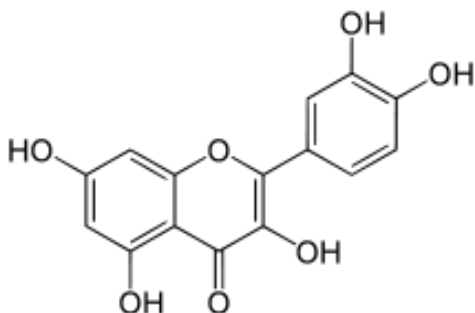
Table 2: Major Phenolic Groups and their Uses

PHENOLIC GROUPS	USES
Phenol	the parent compound, used as a disinfectant and for chemical synthesis
Bisphenol A	Bisphenols produced from ketones and phenol / cresol
BHT	(butylated hydroxytoluene) - a fat-soluble antioxidant and food additive
Capsaicin	the pungent compound of chilli peppers
Cresol	found in coal tar and creosote
Estradiol	estrogen - hormones
Eugenol	the main constituent of the essential oil of clove
Gallic acid	found in galls
Guaiacol	(2-methoxyphenol) - has a smokey flavor, and is found in roasted coffee, whisky, and smoke
4-Nonylphenol	a breakdown product of detergents and nonoxynol-9
Orthophenyl phenol	a fungicide used for waxing citrus fruits
Picric acid	(trinitrophenol) - an explosive material
Phenolphthalein	pH indicator
Polyphenol	e.g. flavonoids and tannins
Propofol	an anesthetic
Raspberry ketone	a compound with an intense raspberry smell
Serotonin/dopamine/ adrenaline/noradrenaline	natural neurotransmitters
Thymol	(2-Isopropyl-5-methyl phenol) - an antiseptic that is used in mouthwashes
Tyrosine	an amino acid
Xylenol	used in antiseptics & disinfecticides

(Source: <http://en.wikipedia.org/wiki/Phenols>)

Natural phenols, bioavailable phenols, plant phenolics, low molecular weight phenols are a class of natural organic compounds. Natural phenols are most often found in plants. They are small molecules containing one or more phenolic group. These molecules are smaller in size than polyphenols, containing less than 12 phenolic groups. They can be found in plants and are the most widely distributed class of plant secondary metabolites with several thousand different compounds identified. As they are also present in food, they may have an impact on health. Most are known to

have an antioxidant activity. The most studied natural phenols are the flavonoids, which include several thousand compounds including flavonols, flavones, flavanol (catechins), flavanones, anthocyanidins and isoflavonoids.



Quercetin: A typical flavonoid, is a natural phenol

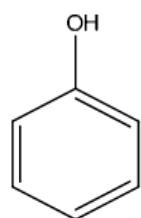
Phenolic compounds are mostly found in vascular plants (tracheophytes) i.e. Lycopodiophyta (lycophods), Pteridophyta (ferns and horsetails), Angiosperms (flowering plants or Magnoliophyta) and Gymnosperms (conifers, cycads, Ginkgo and Gnetales). In ferns, compounds such as kaempferol and its glucoside can be isolated from the methanolic extract of *Phegopteris connectilis* or kaempferol-3-O-rutinoside. Hypogallic acid, caffeic acid, paeoniflorin and pikuroside can be isolated from the freshwater fern *Salvinia molesta*. In conifers (Pinophyta), phenolics are stored in polyphenolic parenchyma cells, a tissue abundant in the phloem of all conifers. Phenolic compounds are derivatives of phenol, made of major families of secondary metabolites in plants and they represent a diverse group of compounds. These can be divided into:

- a) Non soluble compounds: e.g. Tannins, lignins and hydrocinnamic acids
- b) Soluble Phenolics: e.g. Phenolic acids, Phenyl Propanoids, Flavonoids and Quinones

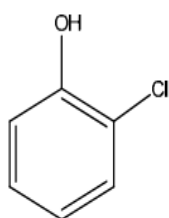
Major Phenolic Compounds in Plants

No. of carbon	Basic skeleton	No of phenol rings	Class	Examples
6	C6	1	Simple phenols, Benzoquinones	Catechol, Hydroquinone, 2,6-Dimethoxybenzoquinone
7	C6-C1	1	Phenolic acids, Phenolic aldehydes	Gallic, salicylic acids
8	C6-C2	1	Acetophenones, Tyrosine derivatives, Phenylacetic acids	3-Acetyl-6-methoxybenzaldehyde, Tyrosol, p-Hydroxyphenylacetic acid
9	C6-C3	1	Hydroxycinnamic acids, Phenylpropenes, Coumarins	Caffeic, ferulic acids, Myristicin, Eugenol, Umbelliferone, aesculetin, Bergenon, Eugenin
10	C6-C4	1	Naphthoquinones	Juglone, Plumbagin
13	C6-C1-C6	2	Xanthonoids	Mangiferin

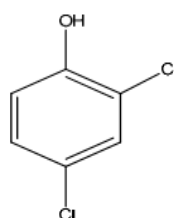
14	C6-C2-C6	2	Stilbenoids, Anthraquinones	Resveratrol, Emodin
15	C6-C3-C6	2	Chalconoids, Flavonoids, Isoflavonoids, Neoflavonoids	Quercetin, cyanidin, Genistein
18	(C6-C3)2	2	Lignans, Neolignans	Pinoresinol, Eusiderin
30	(C6-C3-C6)2	4	Biflavonoids	Amentoflavone
many	(C6-C3)n, (C6)n, (C6-C3-C6)n	n > 12	Lignins, Catechol melanins, Flavolans (Condensed tannins), Polyphenolic proteins, Polyphenols	Raspberry ellagitannin, Tannic acid



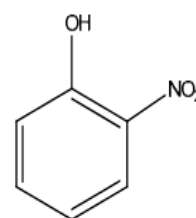
Phenol (PH)



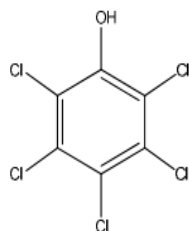
2-Chlorophenol (2-CP)



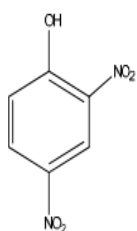
2,4-Dichlorophenol



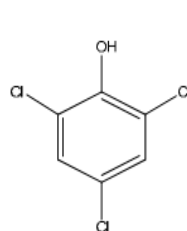
2-Nitrophenol (2NP)



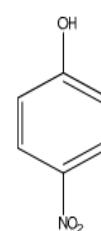
Pentachlorophenol (PCP)



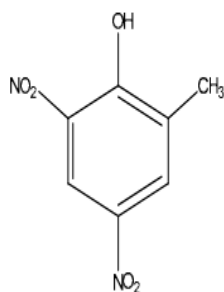
2,4-Dinitrophenol (2,4-DNP)



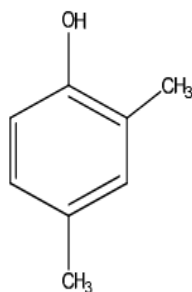
2,4,6-Trichlorophenol (TCP)



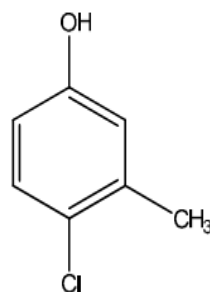
4-Nitrophenol (4NP)



4,6-Dinitroorthocresol
(4,6-DNOC)



2,4-Dimethylphenol
(2,4-DMP)



4-Chloro-3 methyl phenol
(4-C 3MP)

Fig. Eleven Priority Pollutants Phenols

Table : Chemical name of Priority Pollutants Phenols and their functional groups

Phenolic Compounds	Chemical Structural Position					
	R1	R2	R3	R4	R5	R6
USEPA Eleven Priority Pollutants Phenols						
Phenol	OH	H	H	H	H	H
2-Chloro phenol	OH	Cl	H	H	H	H
2,4-Dichloro phenol	OH	Cl	H	Cl	H	H
2,4,6-Tri chloro phenol	OH	Cl	H	Cl	H	Cl
Penta chloro phenol	OH	Cl	Cl	Cl	Cl	Cl
2-Nitro phenol	OH	NO ₂	H	H	H	H
4-Nitro phenol	OH	H	H	NO ₂	H	H
2,4-Di nitro phenol	OH	NO ₂	H	NO ₂	H	H
2-Methyl-4,6 Di nitro phenol	OH	CH ₃	H	NO ₂	H	NO ₂
2,4-Di methyl phenol	OH	CH ₃	H	CH ₃	H	H
4-Chloro-3-methylphenol	OH	H	CH ₃	Cl	H	H
Other Important Phenols						
Tetra chloro phenol (IS)	OH	H	Cl	Cl	Cl	Cl
o-Cresol	OH	CH ₃	H	H	H	H
m-Cresol	OH	H	CH ₃	H	H	H
p-Cresol	OH	H	H	CH ₃	H	H
2-Ethyl phenol	OH	C ₂ H ₅	H	H	H	H
4-Ethyl phenol	OH	H	H	C ₂ H ₅	H	H

(Source: www.esainc.com)

2.1 Chlorophenols

The chlorinated phenols comprise a group of 19 congeners, consisting of mono-, di-, tri-, tetra- and pentachlorophenol. Chlorinated phenols possess moderate volatility, enabling them to circulate between air, land, and water. Chlorophenols are the most widespread and the largest group of phenols. Chlorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. Chlorophenols are formed in the environment by chlorination of mono and polyaromatic compounds present in soil and water. The most common chlorophenols are 2-chlorophenol and 2,4-dichlorophenol, tri-chlorophenols tetra-chlorophenols and pentachlorophenols (Toxicology, 1999). Pentachlorophenol (PCP), the most commonly used and studied chlorophenol has been used as herbicide, biocide and preservative worldwide since the 1930s and as a result, extensive and prolonged contamination exists. The environmental impact increases when its many degradation products are taken into consideration. PCP and its derivatives sodium pentachlorophenate (NaPCP) and pentachlorophenyl laurate (PCPL) have been used worldwide as herbicides, biocides, pesticides and

wood preservatives since the 1930s. This extensive use has resulted in the contamination of soils, sediments and waters. PCP can degrade into as many as 30 different products depending on the experimental and environmental conditions. The main degradation products are tetrachloro-, trichloro-, and dichlorophenols (TeCP, TCP, DCP), tetrachloro-, trichloro-, and dichlorohydroquinones (TeCHQ, TCHQ, DCHQ), pentachloroanisole (PCA) and hexachlorobenzene (HCB); polychlorinated diphenylethers and polychlorinated dibenzo-p-dioxins are minor products. Chlorophenols are bioaccumulative in humans, aquatic and terrestrial organisms (Michałowicz and Duda. 2007).

A. 2,4-Dichlorophenol and trichlorophenols (2,4-DCP, 2,4,5-TCP, 2,4,6-TCP): 2,4-Dichlorophenol (2,4-DCP) and trichlorophenols (2,4,5-TCP and 2,4,6-TCP) are chlorinated phenols and are primarily used to manufacture herbicides. 2,4,5-TCP and 2,4,6-TCP are metabolites of several organochlorine chemicals, including hexachlorobenzene and hexachlorocyclohexane. Trichlorophenols are no longer intentionally manufactured, but they may be produced as byproducts of the manufacture of other chlorinated aromatic compounds. Small amounts of trichlorophenols can be produced during combustion of natural materials and from the chlorination of waste water that contains phenols. WHO's IARC (International Agency for Research on Cancer) classifies polychlorophenols (including trichlorophenols) as possibly carcinogenic to be a human carcinogen. The general population may be exposed to 2,4,6-TCP through ingestion of contaminated food or water and inhalation of contaminated air. Exposure is primarily through ingestion of contaminated water, inhalation, and skin contact.

Table 4: Applications of various Chlorophenols

Compound	Applications
2,3,4,5-Tetrachlorophenol	Fungicide
2,3,4,6-Tetrachlorophenol	Pesticide, wood preservative, slimicide for paper mills
2,4,5,6-Tetrachlorophenol	Fungicide
2,4,5-Trichlorophenol	Chemical intermediate for herbicides, insecticides, preservative for adhesives, textiles, rubber, wood, paints, in paper manufacture; cooling towers, on swimming-pool surface, veterinary medication
2,4-Dichlorophenol	In synthesis of anthelmintic bithionol sulfoxide; chemical intermediate
2,5-Dichlorophenol	Chemical intermediate for 3,6-dichloro-O-anisic acid, the herbicide
2,6-Dichlorophenol	This compound is used as a starting material for the

	manufacture of tri-chlorophenol, tetra-chlorophenols and pentachlorophenol; used as sex pheromone with pesticide control
3,5-Dichlorophenol	Known uses: used in veterinary medicine as an anthelmintic
3,4-Dichlorophenol	Chemical intermediate for 2-chloro-1,4-dihydroxyanthraquinone and 2,3,4-Trichlo
o-Chlorophenol	Component of disinfectant, soil sterilant, organic synthesis of dyes
m-Chlorophenol	Intermediate in organic synthesis and phenolformaldehyde resins, catalyst for a polymers, vet antiseptic
p-Chlorophenol	In synthesis of dyes, pharmaceuticals, solvent in refining mineral oils, intermediate for use in dental practice, bacterial agent, topical antiseptic ointment, soil sterilant

(Source: <http://onlinelibrary.wiley.com>)

B. 2,5-Dichlorophenol (2,5-DCP): 2,5-Dichlorophenol (2,5-DCP), an aromatic chemical compound, is a metabolite of paradichlorobenzene (p-DCB). It is primarily used to manufacture mothballs. 2,5-DCP replaced the more traditional naphthalene. P-dichlorobenzene is the parent compound(13). Trade names for paradichlorobenzene include *Paramoth*, *Para crystals*, and *Paracide* reflecting its widespread use as a pesticide to kill moths, molds, and mildew. p-DCB is also used as a precursor in the production of the polymer poly(p-phenylene sulfide) used in urinal deodorant blocks to deodorize restrooms and waste containers. Exposure is primarily through inhalation and skin contact.

C. Catechol and Chloro-catechol: Catechol is aromatic alcohol that has hydroxyl residues on the first and the second carbon positions. It is soluble both in water and organic solvents. On an industrial scale it is formed in a process of catalytic hydrolysis of 2-chlorophenol in high temperature. It is also formed in the result of phenol and benzoic acid hydroxylation process. Catechol and chlorocatechols are the main products of phenol and chlorophenols environmental transformation (Michałowicz and Duda. 2007).

2.2 Nitrophenol

Nitrophenols are a family of nitrated phenols with the formula $\text{HOC}_6\text{H}_4\text{NO}_2$. Three isomeric nitrophenols exist, o-Nitrophenol, m-Nitrophenol and p-Nitrophenol. Nitrophenols, particularly 2-nitrophenol and 4-nitrophenol, are formed in the reaction of phenol with nitrite ions in water. The reaction of phenol, nitrite

ions and hydroxyl radical leads to the formation of 2-nitrophenol and other nitrated compounds. Nitration of phenols substituted mainly in ortho and para position (<http://en.wikipedia.org/wiki/Nitrophenol>).

2.3 Methyl Phenol

Organic compounds having a methyl group and a hydroxyl group bound directly to a benzene ring. There are three isomeric methyl phenols with the formula $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$, differing in the relative positions of the methyl and hydroxyl groups. A mixture of the three can be obtained by distilling coal tar and is used as a germicide and antiseptic. The environmental transformation of 4-chloro-2-methylphenoxyacetic acid lead to the formation of 2-methyl phenol. The representatives of methyl phenols are cresols that form three isomers ortho-, meta- and para-cresol.

2.4 Alkyl Phenols (APs)

Alkyl phenols are phenols with one or more of the aromatic hydrogens being replaced by an alkyl group. Mixtures are called cresylic acids. More specifically, if they are recovered from coal tar, they are called tar acids. Cresols are mono-methyl derivatives of phenol. Xylenols are dimethyl derivatives. Higher alkyl phenols such as 4-tert-butylphenol, 4-iso-octylphenol, and 4-nonylphenol are used in phenolic resin production (Weber and Weber, 2010). The most commercially important alkylphenols are nonylphenol (NP) and octylphenol (OP). They exist in different forms, or “isomers”, and are used to make nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs).

APs are high production volume man-made chemicals that are reacted with ethylene oxide primarily to manufacture surfactant products called alkylphenol ethoxylates (APEs). APEs are made from and break down into alkylphenols, which are used as antioxidants in plastics and rubber products. The most common APEs are nonylphenol ethoxylates (NPEs). Alkylphenol ethoxylates (APEs) are synthetic surfactants used in some detergents and cleaning products. APES and/or other alkyphenol derivatives are also used in pesticides, lube oil, hair dyes and other hair care products, and as nonoxynol-9 in spermicides. APs and APEs have been in use for over 50 years and are important to a number of industrial processes, including pulp and paper, textiles, coatings, agricultural pesticides, lube oils and fuels, metals and plastics used in food storage. Exposure is primarily through skin contact.

4- tert octylphenol (4-t-OP) is a chemical used primarily to manufacture phenolic resins (98%), with the remainder converted into ethoxylates to produce detergent surfactants.

Nonylphenol is a toxic xenobiotic compound classified as an endocrine disrupter capable of interfering with the hormonal system of numerous organisms. Nonylphenol is used in the manufacture of antioxidants, lubricating oil additives and the production of nonylphenol ethoxylates surfactants which is

its major use (65%) (USEPA 1990). Nonylphenol ethoxylates are highly cost effective surfactants with exceptional performance and consequently used widely in industrial, institutional, commercial and household applications such as detergents, emulsifiers, wetting and dispersing agents, antistatic agents, demulsifiers and solubilisers. Due to the extensive use of nonylphenol ethoxylates, they reach sewage treatment works in substantial amounts where they are incompletely degraded to nonylphenol. Hence the major source of nonylphenol in the environment is the discharge of effluents from sewage treatment plants

2.5 Bisphenols

Bisphenol A is the most popular representative of this group, often called only "bisphenol". Bisphenol A (BPA) is the common name for 2,2-(4,4'-dihydroxydiphenyl) propane, 4,4'-isopropylidenediphenol, alternatively, 2,2'-bis(4-hydroxyphenyl) propane. Bisphenol A belongs to the phenol class of aromatic organic compounds and is a chemical compound containing two hydroxyl phenyl functional groups. It was first synthesized over 100 years ago and during the 1930's BPA was investigated as an estrogen drug and known as endocrine disruptor.

Being an important industrial chemical, Bisphenol A is primarily used as an intermediate in the production of polycarbonate (PC) plastics and epoxy resins. They are widely used in different products of daily life, including digital media (typically CDs and DVDs), electronic equipment, automobiles, construction glazing, sports safety equipment, medical devices (e.g. dental sealants), tableware, reusable bottles (e.g., baby bottles) and food storage containers. In order to protect food and drinks from direct contact with metals, epoxy resins are also used in the internal coating of food and beverage cans. Children's toys may contain BPA, being used as an additive in other types of plastic. About 95% of BPA produced in industry is used to make polycarbonate and epoxy resins, with the remaining 5% used in a variety of products. These include phenoplast resins, phenolic resins, unsaturated polyester resins, can linings, antioxidants and inhibitors for PVC manufacture and processing, ethoxylated BPA, additives for thermal paper manufacture, polyols, modified polyamide, compounding ingredient for the manufacture of car tires, flame retardants (e.g., tetrabromobisphenol A), automotive and other transportation equipment, optical media such as DVDs, electrical/electronic equipment, construction, linings inside drinking water pipes, thermal and carbonless paper coatings, foundry casting, etc. (European Union, EU, 2003). It is also found in epoxy resins used to line metal food and drink cans, as a polymer additive to polyvinyl chloride plastic (e.g. plastic cling wraps and plastic pipes), and some dental sealants. Bisphenol A is also used during the manufacture of specialty resins and flame retardants, such as tetrabromobisphenol A. The recycling code 7 on the bottom of some plastic containers, such as large water bottles used in water dispensers, often indicates that the plastic is made of polycarbonate. Human exposure of BPA includes:

- BPA can migrate from polycarbonate plastic bottles or food storage containers into foods or beverages especially once the container has been heated to high temperatures (e.g. boiling water).
- BPA can migrate from the epoxy resin inner lining of some metal food and drink cans into the food or liquid containing the food.
- BPA may also migrate from polycarbonate plastic in some clear plastic spill-proof cups and cutlery (forks, knives, and spoons) into hot or fatty foods.

2.6 Aminophenols

Aminophenol may refer to any of three isomeric chemical compounds: 2-Aminophenol, 3-Aminophenol and 4-Aminophenol with the chemical formula $C_6H_4NH_2OH$. All isomers of aminophenols and 2,4-diaminophenol are used in dyes used in colouring of hair. The presence of p-aminophenol in urine is the marker of paracetamol and aniline influence in human.

2.7 Butylhydroxytoluene and Butylhydroxyanisole

Butylhydroxytoluene (BHT) and butylhydroxyanisole (BHA) are antioxidants that are capable of scavenging reactive oxygen species and preventing their formation.

2.8 Triclosan [5-chloro-2-(2,4-dichlorophenoxy)phenol] (TRCS)

Triclosan (TRCS) is an anti-bacterial (microbicide) ingredient that can be found in a wide variety of home care products such as detergents and dish soaps, personal care products such as anti-acne cleansers, deodorants, hand soaps, cosmetics, lotions, creams, toothpastes, mouthwashes, and first aid creams. Microban is another trade name for this compound. Exposure is primarily through ingestion and skin contact. Oral exposure is primarily through consumer medical products, such as mouthwashes, throat lozenges, and toothpastes.

3.0 CHEMISTRY AND PHYSICO-CHEMICAL PROPERTIES

A phenol (or hydroxyl benzene) is a single organic compound. "Phenols" refers to the class of aromatic compounds having a hydroxyl (OH) group, as well as other substituent groups, on a six carbon benzene ring. Phenol is appreciably soluble in water, with about 8.3 g dissolving in 100 mL (0.88 M). The sodium salt of phenol, sodium phenoxide, is far more water soluble. It is slightly acidic: the phenol molecules have weak tendencies to lose the H^+ ion from the hydroxyl group, resulting in the highly water-soluble phenolate anion $C_6H_5O^-$ (also called phenoxide). Compared to aliphatic alcohols, phenol is about 1 million times more acidic, although it is still considered a weak acid. Phenol is highly reactive

toward electrophilic aromatic substitution as the oxygen atom's pi electrons donate electron density into the ring. Many groups can be appended to the ring, via halogenation, acylation, sulfonation, and other processes.

Phenol and phenolic compounds are broad-spectrum, low to intermediate type disinfectants that disrupt cell membrane and denature proteins. They are effective even in contact with organic compounds such as saliva, pus, vomit and feces and remain active and stable on the surface of fomites for long period of time.

Phenols and phenolic compounds are aromatic hydroxyl compounds classified as monohydric (e.g., phenol, cresols [methyl phenols], xylenols [dimethylphenols]), dihydric (e.g., catechols [o-dihydroxybenzenes], resorcinols [m-dihydroxybenzenes]) or polyhydric (with three or more hydroxy groups), depending on the number of hydroxyl groups attached to the aromatic benzene ring.

Monohydric phenols such as phenol, o-, m- and p-cresol and xylenols (2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5- xylene) and dihydric phenols such as the derivatives of catechol, resorcinol, and quinol (hydroquinone) all have relatively low vapour pressures (0.0053–0.67 kPa) and high water solubilities (24–840 g/l) (USEPA 1979; Verschueren 1983; Merck Index 1983).

Organic Group	Definition
Phenol	naturally occurring aromatic compound produced by some plant species
Phenolics	Chemically modified phenol-containing compounds containing halogen or other functional groups.
Bisphenol	It contain two phenol rings, such as orthophenylphenol(Lysol), trichlosan and hexachlorophene.

2-Chlorophenol is liquid at room temperature and remaining all are solids. Chlorophenols have a strong medicinal taste and odor. Chlorophenol contains one or more covalently bonded chlorine atoms. Chlorophenols are produced by electrophilic halogenation of phenol with chlorine. Most chlorophenols have a number of different isomers. Mono-chlorophenols have three isomers because there is only chlorine atom which can occupy one of three ring positions on the phenol molecule; 2-chlorophenol, for example, is the isomer that has a chlorine atom in the ortho position. Pentachlorophenol, by contrast, has only one isomer because all five available ring positions on the phenol are fully chlorinated.

Table 5: Chemical characteristics of Phenolic Compounds

Phenolic Compound	Chemical Characteristics	Nature
Phenol	<ul style="list-style-type: none"> ▪ May explode on heating above 78 °C ▪ On combustion, forms toxic fumes (carbon monoxide) Upon heating, toxic fumes are formed ▪ The solution in water is a weak acid Reacts with oxidants causing fire and explosion hazard 	corrosive
Catechols	<ul style="list-style-type: none"> • On combustion, forms acrid and irritating fumes Reacts with oxidants 	Non toxic
2-chlorophenol	<ul style="list-style-type: none"> ▪ Decomposes on heating producing toxic and corrosive fumes (hydrochloric acid, chlorine) ▪ Reacts with oxidants 	Toxic
3-chlorophenol	<ul style="list-style-type: none"> ▪ The substance decomposes on heating producing toxic and corrosive fumes (hydrochloric acid, chlorine) ▪ Reacts with oxidants 	Non toxic
4-chlorophenol	<ul style="list-style-type: none"> ▪ The substance decomposes on heating producing toxic and corrosive fumes (hydrochloric acid, chlorine) ▪ Reacts with oxidants 	Toxic
O-cresol P-cresol	<ul style="list-style-type: none"> ▪ On combustion, forms toxic fumes ▪ Reacts violently with strong oxidizing agents, causing fire and explosion hazard ▪ Easily oxidized on exposure to air 	Toxic and corrosive
M-cresol	<ul style="list-style-type: none"> ▪ The substance decomposes on burning producing toxic and irritating fumes ▪ Reacts with strong oxidants 	Toxic and corrosive
2,4-di-chloro-phenol	<ul style="list-style-type: none"> ▪ On combustion, forms corrosive gas (hydrogen chloride) ▪ Reacts violently with strong oxidants Gives off toxic fumes in a fire 	Toxic
2,5-di-chloro-phenol	<ul style="list-style-type: none"> ▪ The substance decomposes on burning producing irritating and poisonous gases ▪ Reacts with oxidants, acid chlorides, acid anhydrides 	Toxic
3,5-di-chloro-phenol	<ul style="list-style-type: none"> ▪ The substance decomposes on burning producing irritating and poisonous gases, acid chlorides, acid anhydrides 	Toxic

	<ul style="list-style-type: none"> Reacts with oxidants 	
Hydroquinone	<ul style="list-style-type: none"> Dust explosion possible if in powder or granular form, mixed with air Reacts violently with sodium hydroxide 	Toxic
Pentachlorophenol	<ul style="list-style-type: none"> The substance decomposes on heating above 200 °C, producing toxic fumes and toxic gases including hydrogen chloride, dioxines, chlorinated phenols Reacts violently with strong oxidants and water, causing fire and explosion hazard 	Toxic
2,3,5,6-tetra-chloro-phenol	<ul style="list-style-type: none"> The substance decomposes on heating and on contact with strong oxidants producing toxic and irritant vapours and fumes such as hydrogen chloride, phosgene The substance is a weak acid 	Toxic
2,3,4-tri-chloro phenol	<ul style="list-style-type: none"> The substance decomposes on heating producing carbon monoxide, hydrogen chloride Reacts with oxidants, acid anhydrides, and acid chlorides 	Non toxic
2,3,5-tri-chloro phenol	<ul style="list-style-type: none"> The substance decomposes on heating, on burning and on contact with strong oxidants producing toxic and irritant vapour and fumes (hydrogen chloride and phosgene) The substance is a weak acid Reacts with strong oxidants 	Non toxic
2,3,6-tri-chloro-phenol	<ul style="list-style-type: none"> May explode on heating The substance decomposes on heating, on contact with strong oxidants producing toxic and irritant vapours and fumes (hydrogen chloride and phosgene) The substance is a weak acid Reacts with strong oxidants 	Non toxic
2,4,5-tri-chloro-phenol	<ul style="list-style-type: none"> May explode on heating to decomposition The substance decomposes on heating and on contact with strong oxidants producing toxic and irritating fumes (chlorine, hydrochloric acid) The substance is a weak acid Reacts with strong oxidants Reacts in an alkaline medium at high temperatures producing highly toxic chlorinated dioxins 	Non toxic
2,4,6-tri-chloro-	<ul style="list-style-type: none"> On combustion, forms toxic fumes (HCl, CO) 	Non toxic

phenol	<ul style="list-style-type: none"> The substance decomposes on heating or on burning producing toxic and corrosive fumes (hydrogen chloride and chlorine) Reacts violently with strong oxidants 	
--------	---	--

Nitrophenols are a family of nitrated phenols, are produced industrially by the reaction of chlorides with sodium hydroxide at temperatures close to 200 °C. 2-Nitrophenol is a light yellow solid with a peculiar aromatic smell. 4-Nitrophenol is a colorless to light yellow solid with very little odor. 2-Nitrophenol is slightly soluble in cold water, but 4-nitrophenol is moderately soluble in cold water. Neither chemical evaporates at room temperature. These are man-made chemicals with no evidence of their formation from any natural source. The physicochemical properties of some important phenolic compounds are given in Table 6.

Table 6: Physico-chemical properties of important Phenolic Compounds

Phenolic compound	Colour/Form	Physical properties of Phenolic compounds					
		BP (°C)	MP (°C)	MW	Sol. In H ₂ O	RD (water=1)	VP (KPA)
p-tert-butylphenol	Monoclinic tablets, colourless crystals, discolour to brown on exposure to air and light	237	98	150.21	sol	0.908 @ 80 °C	1.3x10 ² Pa at 60 ⁰ C
p-Chloro-m-cresol	dimorphous crystals; needles from petroleum ether; white or slightly pink crystals	235	67	142.58	Sl sol	1.37g/cu. m	5x10 ⁻² mm Hg @20 ⁰ C
2-chloro-phenol	light amber liquid; colourless to yellow brown liquid	174.9	9.3	128.6	sl sol	1.2634	0.23
3-chloro-phenol	needles; white crystals	214	33	128.6	sl sol	1.268 @ 25°C	0.13 @ 44.2°C
4-chloro-phenol	needle like, white to straw-coloured crystals; pink crystals	220	43	128.6	sl sol	1.2238 @78°C/4°C	13 Pa
cresol, all isomers	colourless, yellowish, brownish-yellow, or pinkish liquid	191-203	11-35	108.13	50 parts	1.030-1.038 @ 25°C/25 °C	14-32Pa @ 25 °C
o-cresol-	colourless crystalline compound; white crystals/liquid	191	31	108.1	sol	1.047	33 Pa @ 25 °C
m-cresol	colourless or yellowish liquid	202	12	108.1	sl sol	1.034	20 Pa @ 25 °C
p-cresol	crystals; prisms;	201.9	35	108.13	sl sol	1.0178	15 Pa

	colourless; white crystals; crystalline mass						@ 25 °C
2,6-DI- <i>tert</i> -butyl- <i>p</i> -cresol	white crystalline solid; pale yellowish crystalline powder	265	70	220.34	insol	1.048	1.1Pa@20°C
2,4-dichlorophenol	colourless crystals; hexagonal needles from benzene; white solid	210	45	163.00	sl sol	1.383 @ 60°C/25°C	0.075 mm Hg @ 25.0°C
2,4-dimethyl phenol	crystals; needles from water; colourless needles	211.5 @ 766 mm Hg	25.4-26	122.16	sl sol	0.9650	10 mm Hg @ 92.3 °C
hydroquinone	colourless, hexagonal prisms; white crystals; monoclinic prisms (sublimation); needles from water; prisms from methanol	285-287	172	110.11	sol	1.332	0.12 Pa
2-hydroxy biphenyl	needles from petroleum ether; pinkish crystals; white, flaky crystals; colourless crystals	286	59	170.20	insol	1.213 @ 25°C/4 °C	2.7 @163 °C
Pentachlorophenol	colourless crystals (pure); dark greyish powder or flakes (crude product); solid beads or flakes; white monoclinic, crystalline solid; needle-like crystals	309-310	190-191	266.3	sl sol	1.978 @ 22°C/4°C	0.02 Pa
resorcinol	white needle-like crystals; needles from benzene; plates from water; rhombic tablets & pyramids; powder	280	111	110.11	sol	1.2717	1 mm Hg @108.4 °C
2,3,4,6-tetrachlorophenol	needles from ligroin, acetic acid; brown flakes or sublimed mass; light brown mass	150@ 15 mm Hg	70	231.89	insol	1.83 @ 25°C/4°C	1 mm Hg @100°C
2,3,5,6-tetrachlorophenol	leaf, from ligroin	288	115	231.89	sl sol	1.7	<10 Pa
2,3,6-trichlorophenol	needles from diluted alcohol, petroleum ether; colourless needles	253	58	197.44	sl sol	1.5	-
2,4,5-trichlorophenol	needles from alcohol or ligroin; gray flakes in sublimed mass; colourless needles	253	67	197.4	sl sol	1.678 @ 25°C/4°C	2.9 Pa @ 25°C

2,4,6-tri-chlorophenol	crystals from ligroin; yellow flakes; rhombic needles from acetic acid; colourless needles	246	69	197.45	800 mg/l @25°C	1.4901	133 Pa @76.5°C
------------------------	--	-----	----	--------	----------------	--------	----------------

Note: BP-Boiling Point, MP: Melting point, MW: molecular weight, Sol: Solubility, RD: Relative Density, RVD: Relative Vapour Density, VP: Vapour Pressure

Nonylphenol (NP) is a viscous liquid with a molecular weight of 220.3 g·mol⁻¹, a water solubility of 5.43 mg·L⁻¹ at 20.5°C, a vapour pressure of 4550 Pa, and a Henry's law constant of 11.02 Pa·m³·mol⁻¹.

4.0 PRODUCTION AND COMMERCIAL USES

4.1 Production

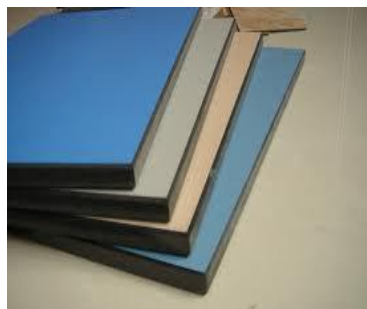
Phenol was first isolated from coal tar in the cooking of coal but the first commercial process was the sulphonation of benzene and subsequent fusion with caustic soda. There are now three synthetic methods used for production of phenol.

- The most common method for the production of phenol is from cumene (isopropyl benzene). In this method, benzene and propylene are reacted to form cumene, which is oxidized to hydroperoxide, followed by acid catalyzed cleavage to yield phenol and acetone. This is the most economic method.
- Phenol is also produced from the hydrolysis of chlorobenzene.
- The third process is based on liquid phase oxidation of toluene to benzoic acid, which is further oxidized to phenol.

Currently, nearly all world production of phenol is via cumene peroxidation, with acetone as a coproduct. Its main use is as a chemical intermediate in the manufacture of bisphenol A, phenol-formaldehyde resins, caprolactam, alkyl phenols, aniline and 2,6-xyleneol.



Silicon Resin



Phenol Board



laminated bakelite sheet

The majority of phenol is made by the cumene process. The process has three stages:

- production of cumene
- conversion of cumene to cumene hydroperoxide
- decomposition of cumene hydroperoxide

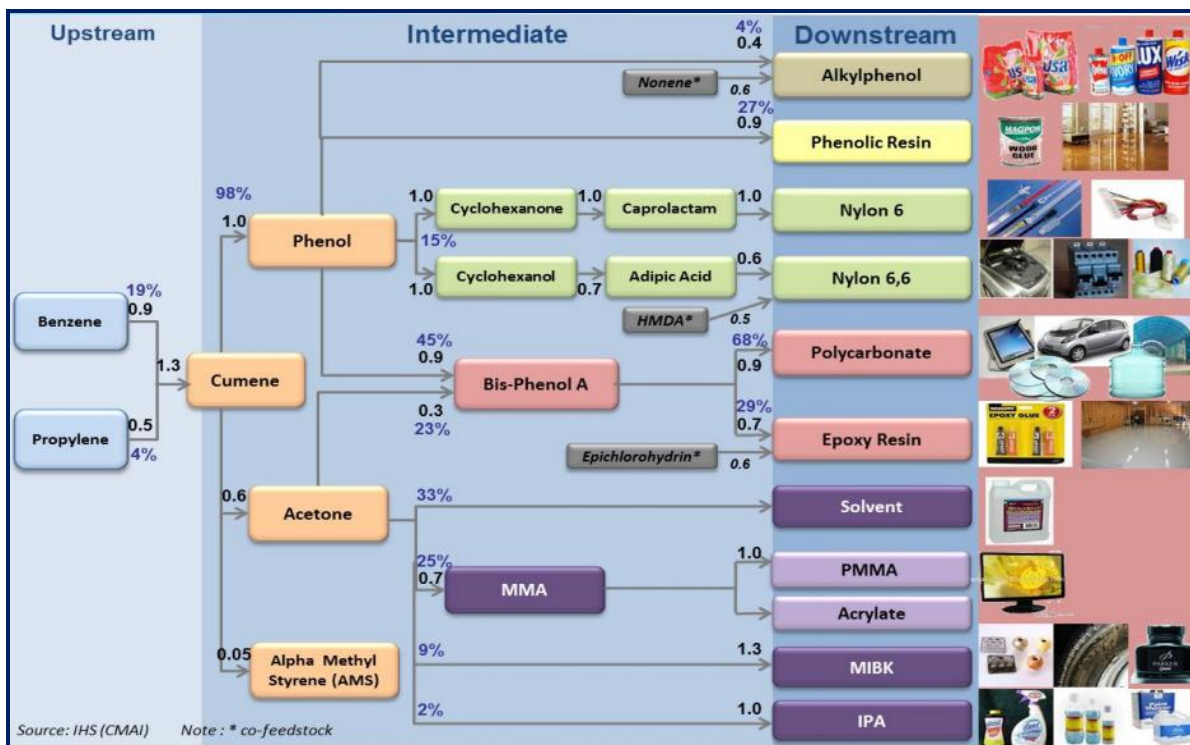
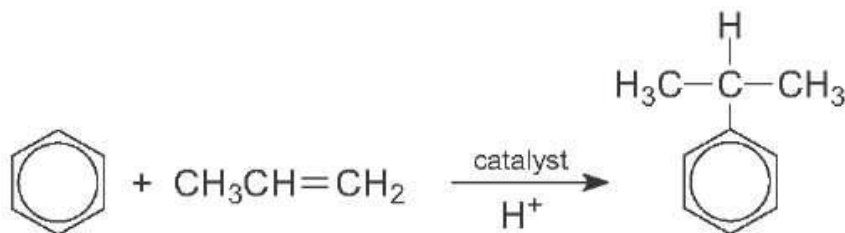


Fig. Phenol chain derivatives

A. Production of cumene

Cumene is the name often given to (1-methylethyl) benzene (isopropylbenzene). It is produced by the reaction of benzene and propene, using an acid catalyst; this is an example of a Friedel-Crafts reaction:



In one process, benzene and propene (3:1) are passed over an acid catalyst, usually a zeolite such as ZSM-5 at ca 600 K and under pressure (ca 10 atm) in a fixed bed reactor. The zeolite is more environmentally friendly than traditional acid catalysts such as aluminium chloride. The effluent is much cleaner and lower temperatures and pressures can be used. Alternatively, propene gas is liquefied under pressure (ca 30 atm) and mixed with benzene before being passed, still under pressure, through a reactor containing the solid zeolite at ca 435 K. This process is becoming more popular as it uses

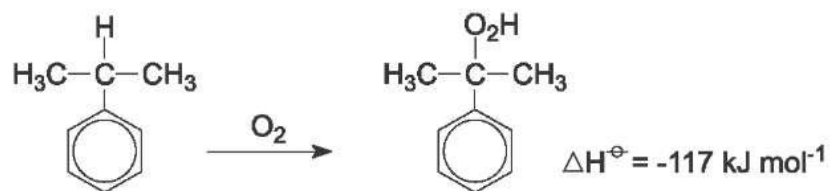
even lower temperatures and thus saves energy. In some plants, solid phosphoric acid is used as the catalyst, in place of zeolites.



Fig. Representative of Oxidation units in which cumene hydroperoxide is produced.
Source, <http://www.essentialchemicalindustry.org/chemicals/phenol.html>.

B. Conversion of cumene to cumene hydroperoxide

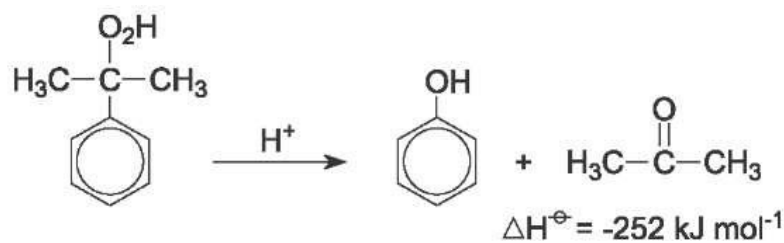
Cumene is then oxidized with air to give the hydroperoxide (Figure 3). The reaction is autocatalyzed by cumene hydroperoxide. The overall reaction can be represented as:



The reaction takes place at temperatures between 350-390 K and 1-7 atm pressure, the latter to retain the system in the liquid phase.

C. Decomposition of cumene hydroperoxide

Finally, the hydroperoxide is mixed with sulfuric acid at 313-373 K to give, after neutralisation, phenol and propanone. This reaction when carried out with small amounts of sulfuric acid (500 ppm by mass) is termed homogeneous cleavage:



The products are separated by distillation, in up to six columns. Product yield is 85-87%, based on benzene.



Fig. Representative of Distillation units to separate phenol and propanone.

Source, <http://www.essentialchemicalindustry.org/chemicals/phenol>.

4.2 Uses of phenol

The primary use of phenol is in the production of phenolic resins. It is also used in the production of caprolactam and bisphenol A, respectively. Other uses of phenol include as a slimicide, as a disinfectant, and in medicinal products such as ear and nose drops, throat lozenges, and mouthwashes.

Phenol is consumed mainly for production of bisphenol A and phenolic resins, which amounted to around 44% and 27%, respectively, of its total 2010 global consumption. Other applications for phenol include caprolactam, alkylphenols, aniline and adipic acid. The most important chemical made from phenol is bisphenol A, which is used to make the polycarbonates. Phenol is also catalytically reduced to cyclohexanol, which is used in the manufacture of polyamides. Phenol is also used to make a range of thermosetting polymers (resins). It reacts with methanol in the presence of a catalyst to form phenol-methanol resins.

Among the other uses of phenol is the production of phenylamine (aniline) needed, for example, for the manufacture of dyes. Antiseptics such as 2,4-and 2,6-dichlorophenols are also made from phenol. The following pie chart shows Country wise World consumption of phenol:

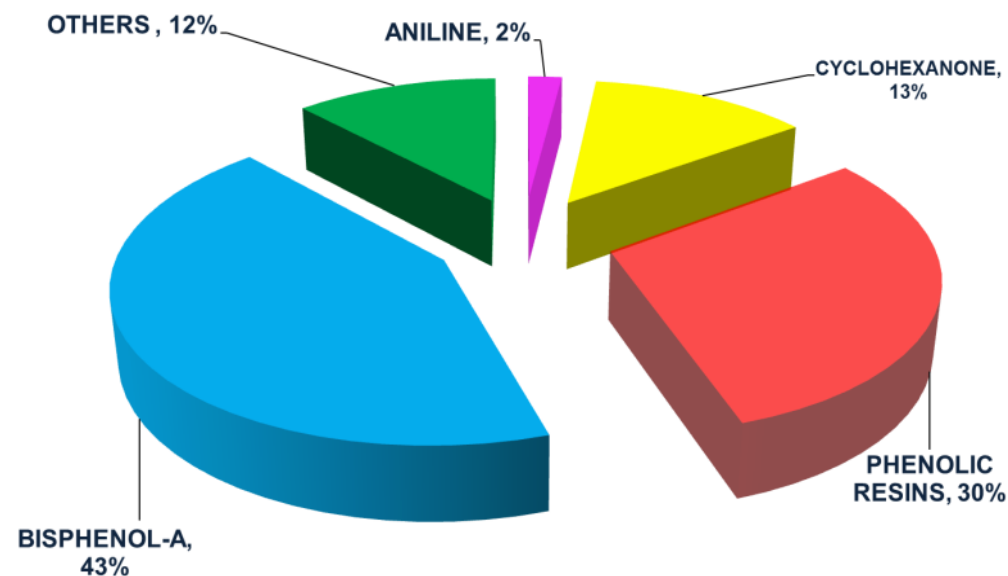
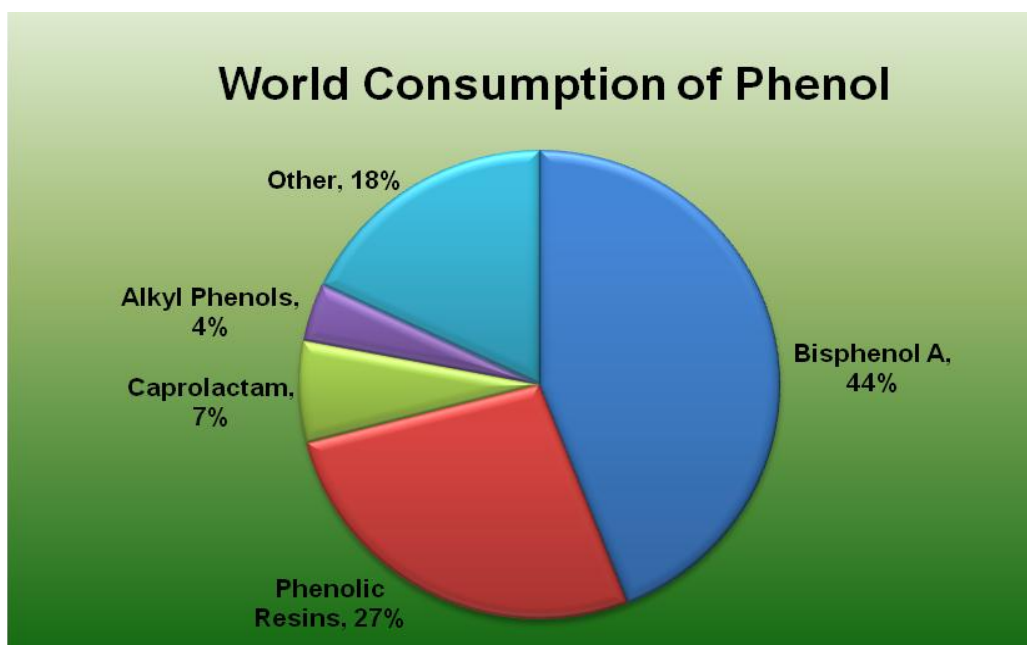


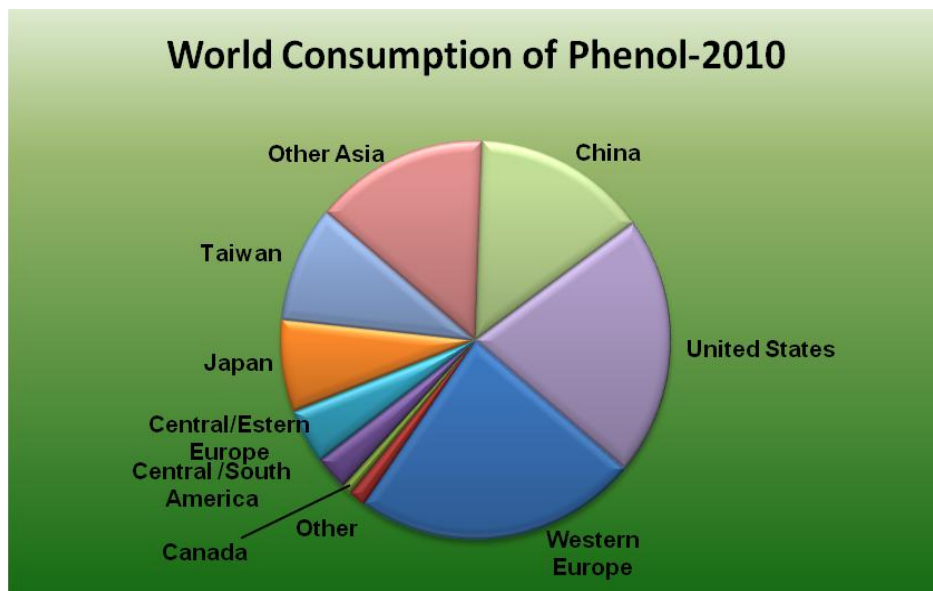
Fig. Worldwide Phenol Demand- Application wise

Since 2001, phenol demand has been growing at an average of 4-5%/year due to healthy growth for BPA driven by polycarbonate as well as epoxy resins, with the strongest growth in Asia, particularly China. However, demand was badly hit by the economic recession with the market declining in 2009. The worldwide phenol growth is expected to return to around 5% per year through to 2015. Total demand will recover from 7.9m tones in 2009 to reach 10.6m tones by 2015.



Source: <http://chemical.ihs.com/WP/Public/phenol>

Bisphenol A and phenol-formaldehyde resins are produced in all regions; production of bisphenol A is more prevalent in developed economies. Phenol consumption for caprolactam and, to a lesser degree, alkyl phenols is limited mainly to the United States and Western Europe. In the US, Western Europe and Japan, growth in phenol consumption for phenol formaldehyde resins is forecast to be slow in 2007-2012. In contrast developing regions such as Southeast Asia, Central and Eastern Europe are expected to increase consumption of PF resins to meet growing local and export markets.



Source: <http://chemical.ihs.com/CEH/PblicReports>





Fig. Various commercial uses of phenolic compounds

Global production and consumption of phenol in 2010 were almost 8.5 million metric tons. Global capacity utilization was 83% in 2010, down from 79% in 2009. Phenol consumption in 2010 is estimated to have increased by 7% from 2009; it is expected to average growth of 4.5% per year from 2010 to 2015, and 2.3% per year from 2015 to 2020. Utilization rates are expected to increase gradually, ranging from the low 80s to the high 80s range. The largest market for phenol is BPA which has been driven by the strong growth in polycarbonate resins. BPA's other main derivative is epoxy resins which are used in high performance coatings, electrical-electronic laminates, adhesives, flooring and paving applications, and composites.

The second largest outlet for phenol is phenolic resins which are largely used as durable binders and adhesives in structural wood panels and as binders in mineral wool insulation. They have a wide spectrum of uses in the automotive and construction industries including brake linings, foundry binders, insulation foams and composites.

Phenol is also used as an antiseptic, a general disinfectant, and a slimicide (chemicals that kill bacteria and fungi in slimes), in medical preparations including lotions, ointments, mouthwashes, salves. Phenol is also the active ingredient in some over-the-counter oral

anesthetics sprays used as a treatment for sore throats. Minor uses of phenol include the manufacture of paint and varnish removers, lacquers, paints, rubber, ink, illuminating gases, tanning dyes, perfumes, soaps and toys.

Indian Scenario

Phenol is a part of the Indian petrochemical industry and at present the growth in this sector is sluggish since phenol is an intermediate chemical as a result of which, the demand is dependent totally on the user-end industry. Phenol is typically prepared mainly by oxidation of Cumene. There are also several other benzene-based processes which are used in the manufacture of phenol. The production of phenol was around 62,000 tons in 1998-1999 and by 2000 it is expected to reach 70,000 tons. The price of phenol in the international market is gradually declining - in 1998 it was US\$ 700 per ton and in 2000 it came down to US\$ 390 per ton. In India, the market of phenol is around Rs. 465 crore. Due to the fall in the international price of phenol, around 39% of it was imported. In fact, imports went up in 1998-1999 to 31,000 tons from 15,000 tons the previous year. However, in recent times the demand for phenol has fallen sharply.

<http://business.mapsofindia.com/india-petroleum-industry/phenol.html>.

More than 50% of the phenol that is produced is used in the manufacture of phenolic resins. And the rest of the phenol is used in the manufacture of rubber chemicals, pharmaceuticals, and cellulose acetate explosives. The main companies producing phenol are:

1. Bengal chemicals and pharmaceuticals in Kolkata
2. Herdillia chemicals in Thane
3. HOCL in Ernakulum

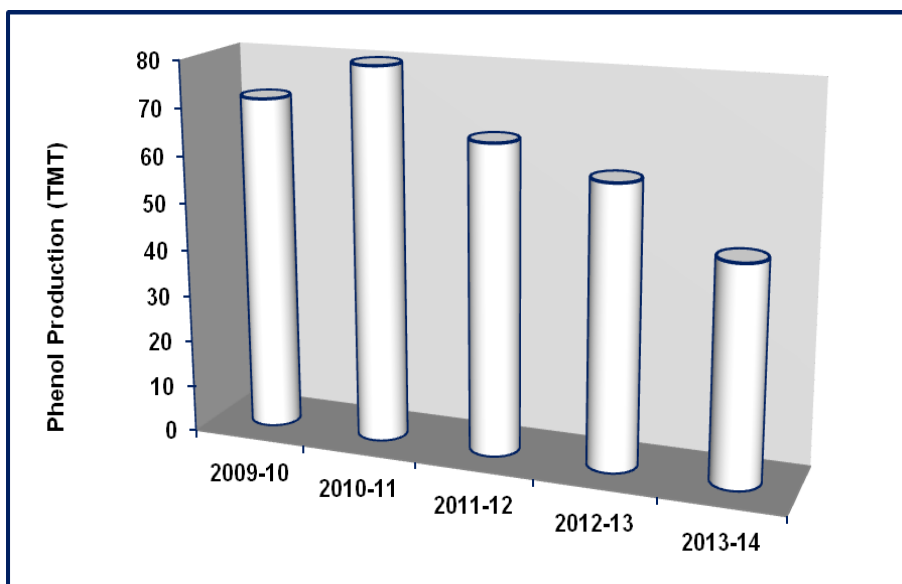


Fig. Production of Phenol in India during 2009-10 to 2013-14

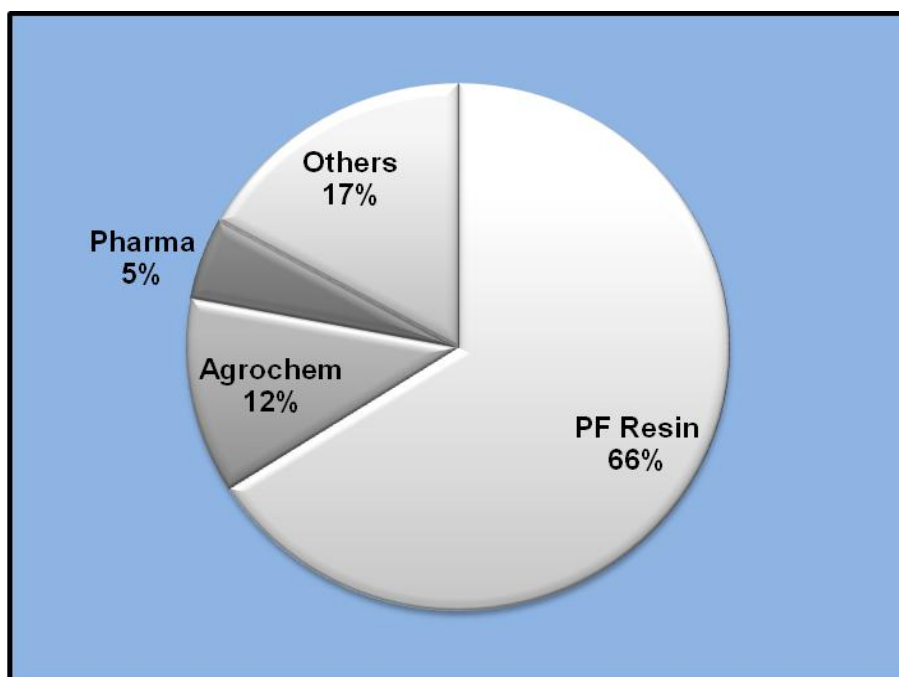
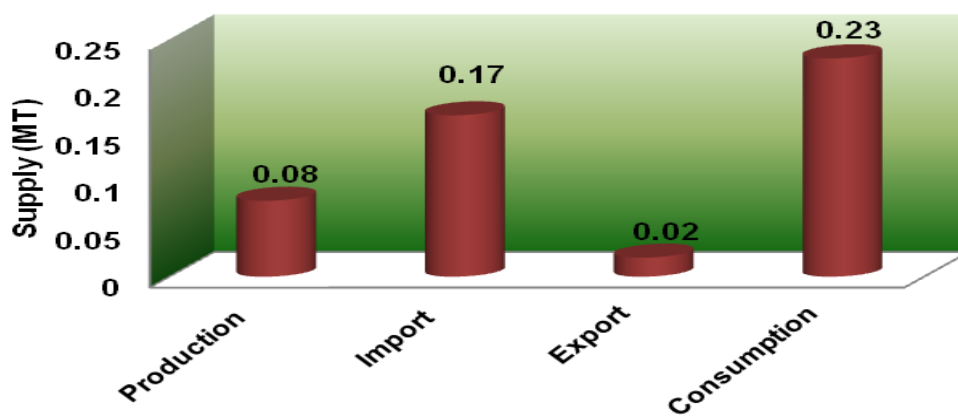


Fig. Indian Phenol Demand- Application wise







(Source-Deptt of Chemicals & Fertilizers, Government of India)

Demand and Supply of Phenol in India during 2009-10



(Source: HICI, 2010)

Table 7: Physical properties of Phenolic Resins

Phenolic compounds	Properties	Resin Appearance
Alkyl Phenolic Resins	Shoe Adhesives, Upholstery Adhesives, Automotive Adhesives	
Phenol Formaldehyde Resins	binder for friction materials, grinding wheels and moulding compositions	
Modified Phenolic Resins	Imparts excellent gloss and gives sharp prints with excellent press stability. application in Offset printing inks, high gloss gravure printing inks	
Modified Maleic Resins	used for improving the film hardness of nitrocellulose, chlorinated rubber paints and also used in sanding sealer and hammerton paints	
Ketone Formaldehyde Resins / Ketonic Resins	Improves gloss, hardness, filling, adhesive strength and durability of the final product. Its applications in the manufacture of flexographic inks, gravure inks, lamination inks, lacquers and paper coatings.	
Polyamide Resins	This resin provides excellent resistance to grease & water, and good glossy sharp prints.	

(Source: HICI, 2010)

5.0 PHENOL AND PHENOLIC COMPOUNDS IN THE ENVIRONMENT

5.1 Natural Sources

Phenol is produced by the natural degradation of organic wastes including benzene. Phenol is a major metabolite of benzene, which is found extensively in the environment (Agency for Toxic Substances and Disease Registry, 2006), therefore, phenol may be formed in the environment as a result of the natural degradation of benzene. Increased environmental levels may result from forest fires. Phenol has been detected among the volatile components from liquid manure.

Decaying vegetation and, in particular, wood produces numerous phenols because the benzene with the hydroxyl group is in a major portion of a woody substance called lignin. Lignin is removed from paper pulp made from trees and degrades to form numerous substances including phenols.

5.2 Anthropogenic Sources

5.2.1 Phenol

Phenol is the basic feedstock from which a number of commercially important materials are made, including phenolic resins, bisphenol A, caprolactam, alkyl phenols, as well as chlorophenols such as pentachlorophenol (IARC, 1989). The most important phenol emissions result from the use of phenolic resins. Phenolic resins are used as a binding material in, for example, insulation materials, chipboard and triplex, paints and casting sand foundries. Their contents vary from 2-3% for insulation material to > 50% for moulds. Emissions are approximately proportional to the concentration of free phenol, which is present as a monomer in these materials (1-5%). In addition, phenol may be released as a result of thermal decomposition of the resins. In foundries, phenol emissions develop both during the production of moulds and kernels and during founding. Other industrial activities, in which phenol may be emitted to the air, are listed below:

- ❖ Production of phenols and phenol derivatives.
- ❖ Production of caprolactam (0.02-0.05 g phenol as intermediate emitted per kg cyclohexanone produced).
- ❖ Production of cokes.
- ❖ Production of insulation materials.
- ❖ Process emissions.

Emissions to water may also result from processing. Emission gases from all material incinerators and home fires, especially wood-burning, may contain substantial quantities of phenol. Another potential source of phenol is the atmospheric degradation of benzene under the influence of light. Phenols have

been detected in smoked foods also. Phenolic compounds are often found in wastewaters from coal gasification, coke-oven batteries, refinery and petrochemical plants and other industries, such as synthetic chemicals, herbicides, pesticides, antioxidants, pulp-and-paper, photo developing chemicals, etc. (Chakraborty et al, 2010). Apart from these functions, phenolic compounds have substantial allelopathic applications in agriculture and forestry as herbicides, insecticides, and fungicides (Zhao et al., 2010).

5.2.1 Chlorophenols

Chlorophenols are also present in drinking water due to substitution of organic matter and low molecular weight compounds (present in purified water) with chlorine atoms derived from inorganic chlorine oxidants. The presence of chlorophenols in the environment is also related to the use and degradation of organic compounds like growth regulators, pesticides and, in particular, phenoxy herbicides and phenolic biocides. The biodegradation of 2,4-dichlorophenoxyacetic acid (2,4-D), 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4,5-trichloro-phenoxyacetic acid (2,4,5-T) leads to formation of both phenols (phenol, 2-chlorophenol and 2,4-dichlorophenol) and catechols (catechol and 4,6-dichloro-catechol). The other well-known phenol used pesticide is pentachlorophenol (PCP). This compound is also used to impregnate wood, textile and skin products as it has strong fungicide capacities. In the environment pentachlorophenol is usually degraded to chlorophenols of lower number of chlorine atoms. The compound may also be formed from other pesticides including hexachlorocyclohexane, hexachlorobenzene, pentachlorobenzene and pentachloronitrobenzene.

5.2.2 Catechol and Chlorocatechols

Chlorocatechols in regard to anthropogenic origin more commonly occur in polluted water. Catechol is used in a variety of applications. It is used as a reagent for photography, dyeing for, rubber, plastic production and drug synthesis. It is also used in cosmetic, dye and insecticide production. Substituted catechols, especially chlorinated and methylated Catechols are by-products in pulp and oil mills. Catechols are intermediary products from the degradation of aromatic compounds and lignin by microorganisms (Schweigert et al., 2001). These are employed in production of 4-tert-butylcatechol, the compound that inhibits the polymerization process of synthetic materials. Chlorinated derivatives of catechol are used in dichloroaniline and chlorinated biphenyls production. Catechol and chlorocatechols are the main products of phenol and chlorophenols environmental transformation.

5.2.3 Nitrophenols

The presence of nitrophenols in the environment is related both to natural processes and anthropogenic activity. Nitrophenols are formed by man during production and degradation of

pesticides like 2-buthyl-4,6-dinitrophenol (Dinoseb) and 4,6-dinitro-2-methylphenol (DNMP). Those compounds are also used as components and precursors in polymers and drug production and employed as photographic developers and preservatives. Moreover, nitrated phenols are used in dyes, solvents, plastics and explosives production and formed due to electric, electronic and metallurgic industrial activity. Mono-nitrophenols, 3-methyl-4-nitrophenol and 4-nitro-3-phenylphenol reach the environment in regards to vehicular emissions (Michalowicz and Duda, 2007).

5.2.4 Methyl Phenols

Methylphenols are contained in high concentrations (up to several grams per kilogram) in coal tar used for asphalt production and wood impregnation. The commonness of creosote usage is the reason for releasing considerable concentrations of methylphenols, in particular 4-methylphenol, to the natural environment. Chlorinated and nitrated form of o-cresol is used as a compound of herbicide and pesticide properties. It is also used for epoxy-resins, dyes and drug production. Both cresols, dimethylphenol and 2,4,6-trimethylphenol are formed during coal and gasoline combustion. The presence of p-cresol is also related to the production of sewage by the petrochemical industry. The occurrence of m-cresol in the environment is mainly related to use this compound in cosmetic, fragrance, disinfectant, explosive and pesticide production. The mixture of m-cresol and p-cresol is used in insecticide synthesis. The solution of cresols in potassium soap is known as lisle and is used in medicine as it reveals strong disinfecting activity. Cresols at concentrations normally found in the environment (Michalowicz and Duda, 2007).

5.2.5 Alkyl Phenols

Alkylphenols of low molecular weight commonly exist in rock-oil and shale oils. The sources of these compounds in particular substituted in para position are geochemical processes like methylation, butylation and alkylation that proceed in geological structures. These compounds are also produced in some technological processes. For example, nonylphenols are derived from nonylphenol ethoxylates—the surfactants produced for industrial and farming purposes. They are also used as emulsifiers, wetting agents and dispersing agents. Nonylphenol polyethoxylate are used in many sectors including textile processing, pulp and paper processing, paints, resins and oil production and steel manufacturing. Alkylphenols are also formed as a result of pesticide degradation, agriculture and industrial sewage production (Michalowicz and Duda, 2007).

5.2.6 Bisphenols

Bisphenol-A (BPA) is used for the production of special resins for coating applications in the phenolic resin area. Presently the main use for BPA is the production of polycarbonates and epoxide resins (Weber and Weber, 2010).

Bisphenols, in particular bisphenols A and F are used as the components or are formed as by-products in lubricants, epoxy-resins, rubber and other synthetic production. Brominated bisphenols like tetrachlorobisphenol in considerable concentrations are present in ashes produced during aluminium processing. The use of bisphenols in plastic packages and varnishes in internal sides of tins causes penetration of these compounds to food (Michalowicz and Duda, 2007).

5.2.7 Aminophenols

Para-aminophenol is used in oil, lubricants and as photographic developer. As *N-acetylated* form it is used as the main component of paracetamol, a drug of anti-inflammatory and analgesic capacities. 3-aminophenol is used as the marker in analysis of antibacterial drugs –sulphonamides and 2-aminophenol is used as the precursor for indols synthesis. All isomers of aminophenols and 2,4-diaminophenol are used in dyes used in colouring of hair (Michalowicz and Duda, 2007).

5.2.8 Buthylhydroxytoluene and Buthylhydroxyanisole

Buthylhydroxytoluene (BHT) and buthylhydroxyanisole (BHA) are commonly used in food-stuffs given to animals. BHT is commonly used in gasoline, lubricants, oils, waxes, synthetics, rubber, plastics and elastomers as it prevents those materials from oxidation during storage. BHT is also used in edibles – oils, vitamins, cosmetics and fragrances (Michalowicz and Duda, 2007).

6.0 DISTRIBUTION AND ENVIRONMENTAL RELEASE

Phenol is released into the air and discharged into water from both manufacturing and use. Based on its high water solubility and the fact that it has been detected in rainwater, some phenol may wash out of the atmosphere; however, it is probable that only limited amounts wash out because of the short atmospheric half-life of phenol. During the day, when photochemically produced hydroxyl radical concentrations are highest in the atmosphere, very little atmospheric transport of phenol is likely to occur.

In water, neither volatilization nor sorption to sediments and suspended particulates are expected to be important transport mechanisms. Based on its relatively high solubility in water and the relatively low vapour pressure at room temperature, phenol is expected to end up largely in the water phase upon

distribution between air and water. Consequently, transport from air to soil and water is likely. Volatilization from dry near-surface soil should be relatively rapid. Phenol exists in a partially dissociated state in water and moist soils and, therefore, its transport and reactivity may be affected by pH.

Chlorophenols enter into the environment while they are being made or used as pesticides. Most of the chlorophenols released into the environment go into the water, with very little entering the air. The compounds that are most likely go into the air are mono- and di-chlorophenols, because they are the most volatile. Once in the air, sunlight helps destroy these compounds and rain washes them out of the air. Chlorophenols stick to soil and to sediment at the bottom of lakes, rivers, or streams, however low level of chlorophenols in water, soil or sediment are broken down by microorganisms and are removed from the environment within a few days or weeks.

6.1 Air

Phenol is mainly release to the atmosphere from domestic manufacturing and processing facilities. During manufacturing, phenol is released primarily to the atmosphere from storage tank vents and during transport loading. Other major sources of release to the atmosphere are residential wood burning and automobile exhaust. Volatilization from environmental waters and soils has been shown to be a slow process and is not expected to be a significant source of atmospheric phenol. Phenol is released into the atmosphere from industrial combustion processes, it is also found in cigarette smoke and in plastics.

Phenol may react in air with hydroxyl and NO_3 radicals, and undergo other photochemical reactions to form dihydroxy-benzenes, nitrophenols, and ring cleavage products. Phenols generally react in sunlit natural water via reaction with photochemically produced hydroxyl and peroxy radicals; typical half-lives were reported to be 100 and 19.2 h, respectively. Higher levels of phenol in air may be expected for urban areas, mainly due to traffic emissions.

The gas-phase reaction of phenol with photochemically produced hydroxyl radicals is probably a major removal mechanism in the atmosphere. An estimated half-life for phenol for this reaction is 0.61 days. The reaction of phenol with nitrate radicals during the night may constitute a significant removal process. This is based on a rate constant of 3.8×10^{-12} $\text{cm}^3/\text{molecule second}$ for this reaction, corresponding to a half-life of 15 minutes at an atmospheric concentration of 2×10^8 nitrate radicals per cm^3 (Atkinson et al. 1987). The reaction of phenol with nitrate radicals present in the atmosphere during smog episodes may decrease the half-life of phenol in polluted atmospheres. The above data indicate that phenol has a short half-life in the atmosphere, probably <1 day. Phenol does not absorb light in the region of 290–330 nm, therefore, it should not photo-degrade directly in the atmosphere.

6.2 Water

The most common anthropogenic sources of phenol in natural water include coal tar and waste water from manufacturing industries such as resins, plastics, fibers, adhesives, iron, steel, aluminum, leather, rubber, and effluents from synthetic fuel manufacturing. Phenol is also released from paper pulp mills and wood treatment facilities.

Other releases of phenol result from commercial use of phenol and phenol-containing products, including slimicides, general disinfectants and medicinal preparations such as throat lozenges, mouthwashes, gargles, and antiseptic lotions.



Pulp and Paper Industries

Two natural sources of phenol in aquatic media are animal wastes and decomposition of organic wastes. As a metabolite of benzene, phenol may be released from publicly owned treatment works (POTWs) and sewage overflows. Phenols may occur in domestic and industrial wastewaters, natural waters and potable water supplies. Chlorination of these waters may produce odorous and objectionable tasting chlorophenols.

Phenol has been detected in surface waters, rainwater, sediments, drinking water, groundwater, industrial effluents, urban runoff, and at hazardous waste sites. Background levels of phenol from relatively pristine sites can be as high as 1 ppb for unpolluted groundwater and have been reported to range from 0.01 to 1 ppb in unpolluted rivers.



Common Effluent Treatment Plants

The presence of phenol in drinking water probably results from using contaminated surface water or groundwater as a source. Its presence in groundwater is probably the result of release to soil, often industrial releases or leachate from waste dumps, and the subsequent leaching of phenol through the soil to the groundwater.



Pharmaceutical Industry



Coal Washeries

6.3 Soil/Sediment

Phenol may be released to the soil during its manufacturing process, when spills occur during loading and transport, and when it leaches from hazardous waste sites and landfills. Generally, data on concentrations of phenol found in soil at sites other than hazardous waste sites are lacking. This may be due in part to a rapid rate of biodegradation and leaching. Phenol can be expected to be found in soils that receive continuous or consistent releases from a point source. Phenol that leaches through soil to groundwater spends at least some time in that soil as it travels to the groundwater. Phenol has been found in groundwater, mainly at or near hazardous waste sites.

Table 8: Phenol in Environment

• Environment Matrix	Time period
Air	Phenols released in ambient air are quickly broken down in the air, usually within 1–2 days.
Water	Phenol discharged into water may persist in water for a week or more.
Soil	Phenols released to soil may be broken down by bacteria or other microorganisms.

(Source: ATSDR, 2008)

Very few data concerning the presence of phenol in soils were found. Phenol generally does not adsorb very strongly to soils and tends to leach rapidly through soil, which may account for the lack of monitoring data, since any phenol released to soils is likely to leach to groundwater. Moreover, phenol is readily degraded in the environment, which is expected to attenuate its levels in soil. Phenol can be found in air and water after release from the manufacture, use, and disposal of products containing phenol. Phenol in soil is likely to move to groundwater.

7.0 EXPOSURE AND EFFECTS ON ENVIRONMENT AND HUMANS

The main source of exposure to phenol is at manufacturing and hazardous waste sites; therefore, people living near landfills, hazardous waste sites, or plants manufacturing phenol are the most likely populations to be exposed. Other possible direct exposure may occur through use of consumer products containing phenol. Phenol is present in a number of consumer products that are swallowed, rubbed on, or applied to various parts of the body. These include throat lozenges, mouthwashes, gargles, and antiseptic lotions. Phenol has been found in drinking water, tobacco smoke, air, and certain foods, including smoked summer sausage, fried chicken, mountain cheese, and some species of fish.

Populations residing near phenol spills, waste disposal sites, or landfill sites may be at risk for higher exposure to phenol than other populations. If phenol is present at a waste site near homes that have wells as a source of water, it is possible that the well water could be contaminated. If phenol is spilled at a waste site, it is possible for a person, such as a child playing in dirt containing phenol, to have skin contact or to swallow soil or water contaminated with phenol. Skin contact with phenol or swallowing products containing phenol may lead to increased exposure. This type of exposure is expected to occur infrequently and generally occurs over a short time period.

At the workplace, exposure to phenol can occur from breathing contaminated air. However, skin contact with phenol during its manufacture and use is considered the major route of exposure in the workplace. Total exposure at the workplace is potentially higher than in non-workplace settings.

Phenol is a product of combustion of coal, wood, and municipal solid waste; therefore, residents near coal and petroleum fueled facilities as well as residents near municipal waste incinerators may have increased exposure to phenol. Phenol is also a product of auto exhaust, and therefore, areas of high traffic likely contain increased levels of phenol.

Table 9: Exposure pathways of Phenol in the Environmental Matrixes

Environmental Matrix	Exposure Pathway
Air	The primary way we can be exposed to phenol is by breathing air containing it. Releases of phenol into the air occur from Industries using or manufacturing phenol, automobile exhaust, cigarette smoke, and wood burning.
Water and soil	Phenol has been detected in surface waters, rainwater, sediments, drinking water, groundwater, industrial and urban runoff, and at hazardous waste sites. Phenol in soil is likely to move to groundwater.
Work Environment	Workers in the following industries may be exposed to phenol: petroleum industry ,manufacture of nylon, epoxy resins and olycarbonates, herbicides, wood preservatives, hydraulic fluids, heavy-duty surfactants, lube-oil additives, tank linings and coatings, and intermediates for plasticizers and other specialty chemicals Exposure occurs through breathing and dermal contact with contaminated air or by skin contact with products containing phenol.
Food	Low levels of phenol have been found in foods such as smoked summer sausage, smoked pork belly, mountain cheese, fried bacon, fried chicken, and black fermented tea.
Consumer products	Dermal contact can occur through the use of general disinfectants and ointments containing phenol. Ingestion can occur through the use of products such as throat lozenges or sore throat sprays that contain phenol.

(Source: ATSDR, 2008)

7.1 Air

Ambient air levels of phenol extensively monitored in the highly industrialized and urbanized region. Phenol is rapidly removed from air; half is removed in less than 1 day. No data are available for background levels of phenol in air, away from emission sources. They are expected to be low (< 1 ng phenol/m³).

Urban phenol concentrations have been reported for Osaka, Japan (1-4 µg phenol/m³) Nagoya, Japan (0.2-8 µg phenol/m³ with an average of 1.7 µg phenol/m³), Paris, France (0.7-8 µg phenol/m³), and Portland, USA (0.22 to 0.42 µg phenol/m³).

Environmental Matrix	Environmental Levels
Air	Median concentration of 0.03 ppb in 7 samples from urban/suburban U.S. air
Sediment and Soil	Range from 0.07 to 0.7 mg/kg in a small percentage of U.S. sediment samples; data from 2006
Water	Up to 1 ppb in unpolluted groundwater and 0.01–1 ppb in unpolluted rivers; data from 1985. Range of 2–56 ppb in waterways in Chicago, IL; data from 2006.

7.2 Water

Phenol is readily biodegradable in natural water, provided the concentration is not high enough to cause significant inhibition through microbial toxicity. Complete removal of phenol in river water has been reported after 2 days at 20 °C and after 4 days at 4°C. The degradation of phenol is somewhat slower in salt water, and a half-life of 9 days has been reported in an estuarine river (EPA 1979b). Rapid degradation of phenol also has been reported in various sewage and water treatment processes. Removal in aerobic activated sludge reactors is frequently >90% with a retention time of 8 hours. Utilization of phenols is also very high in anaerobic reactors, although acclimation periods are longer and degradation usually takes about 2 weeks. One method of phenol breakdown is accomplished by the bacterium *Pseudomonas sp.* CF600, which uses a set of enzymes encoded by the plasmid *dmp* operon. The use of sequence batch reactors (SBR) in treating sludge contaminated with phenolic compounds has proven effective in breaking down the compounds biologically with no evidence of phenol volatility. Lower concentrations as high as 800 mg/L can be broken down to <0.5 mg/L with a 1-day retention time. The alga *Ochromonas danica* has also been shown to degrade phenol. When grown in the dark with 0.1–1 mM phenol as the sole carbon source, phenol was removed within 3 days. Because of the rapid rate of biodegradation, groundwater is generally free of phenol even though it is highly mobile in soil. However, monitoring data in Section 6.4.2 contain groundwater concentrations in areas of large phenol releases.

It was observed that phenol can be rapidly and virtually completely degraded under both natural water and sewage treatment plant conditions. In some situations, the concentration of phenol may be too high or the populations of microorganisms may not be present in sufficient concentration for significant biodegradation to occur.

7.3 Soil / Sediments

Phenol biodegrades in soil may takes place under both aerobic and anaerobic soil conditions. The half-life of phenol in soil is generally <5 days, but acidic soils and some surface soils may have half-lives of up to 23 days. Some Plants have capability to metabolize phenol readily. Phenol has been reported in sediments at levels as high as 608 ppm dry weight; however, it is not known whether the location of the site where this concentration was reported is at or near a point source of release, such as a hazardous waste dump. The moderately low soil sorption partition coefficient (1.21–1.96) suggests that sorption to sediment is not an important transport process. There is very little sorption of phenol onto aquifer materials, suggesting that phenol sorption to sediments may also be minimal. Based on the soil adsorption coefficient, phenol is expected to leach to groundwater; however, the rate of phenol biodegradation in the soil may be so rapid, except in cases of large releases such as spills or continuous releases such as leaching from landfill sites, that the probability of groundwater contamination may be low. Phenol has been detected in groundwater as a result of leaching through soil from a spill of phenol, from landfill sites, and from hazardous waste sites. The sorption coefficient for phenol by soils increases with increasing soil organic matter which may indicate that soil organic matter may be the primary phenol sorbent in soil.

7.4 Marine Environment

Phenols may occur naturally in aquatic environments from the decomposition of aquatic vegetation. The major anthropogenic sources are industrial effluents and domestic sewage. Most natural sources release only trace amounts of phenolic substances to water. Phenol concentrations in surface waters are generally <2 $\mu\text{g}\times\text{L}^{-1}$ (Environment Canada 1998a).

Most of the information concerning the aquatic fate of mono- and dihydric phenols refers to the compound phenol. Photo-oxidation, oxidation, and microbial degradation are expected to be the major fate processes of phenols in the aquatic environment. Phenol is not expected to dissociate in the environment at pH <9 based on its high pKa (10.02), Phenol may exist in a partially dissociated state in water. Coordination with dissolved or suspended di- and trivalent metal cations can markedly increase ionization, leading to enhanced solubility (USEPA 1979).

The most important sub lethal acute effects observed in freshwater species after phenol exposure were a reduced heart rate and damage to the epithelium of gills (with loss of function), liver, kidneys, intestines and blood vessels. One study reported the occurrence of severe seizures, mediated by the central nervous system, in *Salmo gairdneri* after exposure to sub lethal phenol concentrations. In invertebrates, growth inhibition was usually observed. Most toxicity studies concentrated on lethal effects. Death was usually preceded by immobility, loss of equilibrium, paralysis and respiratory

distress. In acute toxicity studies on some marine organisms (crustaceans, worms, snails and fish), the LC50 values ranged from 8.8-330 mg phenol/litre. In general, the sensitivities of marine and freshwater organisms for phenol were similar.

Most long-term studies with freshwater species have concerned growth, reproduction and/or mortality; A few long-term studies with freshwater fish have been designed to detect sublethal effects of phenol exposure. Increased proteolysis as a result of stress, mild kidney damage, and an inhibitory effect on the development and maturation of the ovary, secondary to a liver dysfunction, were some of the effects reported. At a sublethal phenol concentration, activities of some enzymes appeared to be decreased in the brain, liver and muscle tissue of *Sarotherodon mossambicus*; this effect was independent of salinity.

7.5 Human Fluid / Tissues

Phenol is present in a number of consumer products which are swallowed, rubbed on, or added to various parts of the body. These include ointments, ear and nose drops, cold sore lotions, mouthwashes, gargles, toothache drops, analgesic rubs, throat lozenges, and antiseptic lotions. Phenol has been found in drinking water, air, automobile exhaust, tobacco smoke, marijuana smoke, and certain foods including smoked summer sausage, fried chicken, mountain cheese, and some species of fish. Phenol has not been reported in soil except at hazardous waste sites; this is probably due to the fact that phenol does not remain in soil for very long, rather than the fact that it never occurs there. Exposure to phenol at the workplace may occur through breathing contaminated air or through skin contact with phenol when it is made and used. Exposures may be higher than outside the workplace.

In addition to workplace exposures, other possible exposures include breathing contaminated air, tobacco smoking or environmental tobacco smoke exposure, drinking water from contaminated surface or groundwater supplies, swallowing products containing phenol, and coming into contact with contaminated water and products containing phenol when bathing or putting lotions on the skin. The use of medical products and other consumer products that contain phenol usually accounts for much more of your total exposure to phenol than releases in the workplace and outdoors. These exposures, however, may not occur often and are usually over short periods of time. Phenol can enter the body through the skin and lungs. The skin may take in as much as one-half the phenol that enters the body when a person is exposed to phenol in air. Although a person may be exposed to air contaminated with phenol at a waste site, most spilled phenol will stay in soil or water rather than evaporate into air. Studies in humans and animals show that most phenol that enters the body through the skin, by breathing contaminated air, or eating food, drinking water, or taking products that contain phenol leaves the body in the urine within 24 hours.

When chlorophenols are accidentally ingested, almost all of the compounds quickly enter the body. Chlorophenols also rapidly enter the body through the skin. Little is known about how much of the chlorophenols enter the body if one breathes air containing them. The monochlorophenols do not stay inside the body very long. They are changed to less harmful products, and excreted within 24 hours. The other chlorophenols (dichlorophenol, trichlorophenols, tetrachlorophenols), might stay within the body for several days.

Table 10: Pathways of Human Exposure

Routes	Process
Oral	Phenol is readily absorbed from the gastrointestinal tract (WHO, 1994).
Inhalation	Phenol is readily absorbed from the lungs (Allen, 1991)
Dermal	When spilt on the skin, intact or abraded, it is rapidly absorbed and may lead to systemic poisoning (Brooks & Riviere, 1996).
Eye	Phenol is absorbed through the mucous membranes of the eye (WHO, 1994).
Parenteral	Therapeutic use: phenol can be administered by intrathecal injection to relieve pain and spasticity (Geller, 1997), and has been used as a sclerosing agent.

Phenol is readily absorbed by the inhalation, oral, and dermal routes. The portal-of-entry metabolism for the inhalation and oral routes appears to be extensive and involves sulfate and glucuronide conjugation and, to a lesser extent, oxidation. The primary oxidative metabolites include hydroquinone and catechol, which are also substrates for conjugation. Secondary products of hydroquinone or catechol metabolism, including benzoquinone and trihydroxybenzene, can also be formed. Once absorbed, phenol is widely distributed in the body, although the levels in the lung, liver, and kidney are often reported as being higher than in other tissues (on a per-gram-tissue basis). Elimination from the body is rapid, primarily as sulfate and glucuronide conjugates in the urine, regardless of the route of administration. Phenol does not appear to accumulate significantly in the body.

The type and number of glycosylation are the main factors that affect the absorption of phenolic compounds. They are primarily absorbed in the stomach and in the gastrointestinal (GI) tract. Bioavailability is affected by the fat and protein content, by the type of glucoside and by the aglycones occurring in the phenolic compound. The maximum concentration in the plasma is generally reached within 15-30 minutes after consumption. The half time disappearance for the same phenolic aglycones proceeds in the order galactose > glucose > arabinose, whether in the case of the same sugar moiety, the order followed is trihydroxy > dihydroxy > methoxy > dimethoxy > trimethoxy phenol. Generally the bioavailability is very low, less than 1% of the quantity consumed.

8.0 TOXICITY OF PHENOL AND PHENOLIC COMPOUNDS AND MECHANISM OF ACTION

Phenol toxicity is related with two main processes – unspecified toxicity related with hydrophobicity of the individual compound and formation of free radicals. Hydrophobicity affects the solubility of phenol in a cell fractions and thus possibility of interaction of the compound with specified cell and tissue structures. For example, the increase of hydrophobicity of chlorophenols is related to the increasing number of chlorine atoms that enhances toxicity of the individual compound.

Toxic influence of organic compounds depends on many factors. Penetration of phenol to organisms is related with diffusion of the compound across a cell membrane. The factor that strongly affects diffusion is hydrophobicity of the individual compound. The increase of hydrophobicity affects the more effective penetration of a cell membrane by phenol and thus enhances the toxicity of xenobiotics. When comparing toxic effects of phenols one cannot omit such important parameters as pKa (Where Ka is the compound dissociation constant) and log P (where P is the octanol-water partition coefficient of the undissociated acids). The increase of hydrophobicity and the value of logP and the decrease of pKa value result in more effective membrane penetration by xenobiotics and, thus, enhance their toxicity.

The essential factor that determines phenol toxicity is the reactivity of the compound with a cell's biomolecules and is related with easiness of donation of free electrons by phenol from oxidized substrate. One-electron reactions in cells are usually catalyzed by oxidative enzymes like peroxidases present in liver, lungs and other organs, prostaglandins and myeloperoxidases contained in bone marrow. The effect of their action is the formation of phenoxy radicals and intermediate metabolites-semiquinones and quinone methides that interact with biomolecules in the cell. In these reactions reactive oxygen species like superoxide radicals or hydrogen peroxide also are formed. The effect of these forms on specified cell structures depends on phenol reactivity. Phenols that exert higher reactivity quickly undergo radical reactions and provoke lipid peroxidation of a cell's membrane. The forms of lower activity penetrate internal spaces of the cell and damage membranes of endoplasmatic reticulum, mitochondria and nucleus and also their components like enzymes and nucleic acids. Interaction of phenols (nitrophenols, nitrocatechols and pentachlorophenol) or its radical metabolites with mitochondrion also leads to coupling between oxidative phosphorylation and electron transport in respiratory chain.

Toxic influence of phenols is also related to the kind of substrate that comes into reaction, also its localization in cell and phase of cell proliferation. An important factor is also tissue type (cell) exposed to phenol activity. For example, diffusion of phenol to hepatocytes leads to its conjugation with glucuronides, sulphates, aminoacids and other substrates that protect cells from electrophilic metabolite

influences. Most phenols including phenol, chlorophenols, nitrophenols and aminophenols are characterized by toxic activity. Toxic influence is also exerted by catechol, chlorocatechols, methylphenols and other phenolic Compounds.

8.1 Acute Toxicity

Phenol irritates skin and causes its necrosis, it damages kidneys, liver, muscle and eyes. Damage to skin is caused by its coagulation related to reaction to phenol with aminoacids contained in keratin of epidermis and collagen in inner skin. In a dose of 1 g phenol may be lethal for an adult man, but individual tolerance for this compound can be high. Acute poison with phenol is characterized by dryness in throat and mouth, dark-coloured urine and strong irritation of mucous membranes. Chronic administration of phenol by animals leads to pathological changes in skin, esophagus, lungs, liver, kidneys and also urogenital tract. Described changes are mainly induced by lipid peroxidation that is responsible for damage and finally degradation of a cell's membrane. Chronic exposure of workers to phenol vapours causes anorexia, lost of body weight, weakness, headache and muscles pain. Phenol is mainly accumulated in brain, kidneys, liver and muscles. Catechol is also considered a strong toxin. Doses of 50 to 500 mg/kg of body weight usually cause death. The toxic effects by different phenolic compounds are shown in table 11.

Table 11: Toxic effects of Various Phenolic Compounds in Human beings

Phenolic compound	Toxic Effects
Phenol	<p>Acute effects:</p> <ul style="list-style-type: none"> ➤ Irregular breathing, muscle weakness and tremors, loss of coordination, convulsions, coma, and respiratory arrest ➤ Central Nervous System disorders, Myocardial depression ➤ Burning effect, whitening and erosion of the skin ➤ Renal damage and salivation, eye irritation, conjunctival swelling, corneal whitening and blindness. <p>Chronic effects:</p> <ul style="list-style-type: none"> ➤ Anorexia, dermal rash, dysphasia, vomiting, weakness, weightlessness, muscle pain, hepatic tenderness and nervous disorder , paralysis, cancer and genetofibre striation, Gastrointestinal irritation ➤ Central Nervous Systems (CNS), kidney, liver, respiratory, and cardiovascular effects, cardiac arrhythmias
Chlorophenols	Acute effect:

	<p>Burning pain in mouth and throat, white necrotic lesions in mouth, esophagus and stomach, vomiting, headache, irregular pulse, decrease of temperature and muscle weakness, convulsions and death.</p> <p>Chronic Effect:</p> <p>Hypotension, fall of body temperature, weakness and abdominal pain, damage to lungs, liver, kidneys, skin and digestive tract.</p>
Nitrophenols	<p>Irritation to eyes, skin, and respiratory tract, Causes cyanosis, confusion, and unconsciousness When ingested, it causes abdominal pain and vomiting. Circulatory and cardiac failure caused death</p>
Methylphenols	<p>burning pain in mouth and throat, abdominal pain, headache, weak irregular pulse, hypotension, fall of body temperature, stentorous breathing, dark colored urine, shock, paralysis of nervous system, coma and death</p>
Aminophenol	<p>Skin and eye irritation, eczemas, asthma and anoxia.</p>
Buthylhydroxytoluene/ buthylhydroxyanisole	<p>cause damage of adrenal gland and increase brain and liver weight</p>
Catechols	<p>DNA damage in the form of oxidative damage or DNA arylation; protein damage by sulphhydryl arylation or oxidation; and interference with electron transport in energy transducing compounds</p>
Bisphenols	<p>heart disease, diabetes and liver abnormalities in adults as well as brain and hormone development problems in fetuses and young children</p>

8.2 Mutagenicity

Phenol also inhibited synthesis and replication of DNA in Hela cells. Moreover, phenol stopped reparation of DNA in diploid human fibroblasts. Hydroquinone (1.4-dihydroxyphenol) induced damages of chromosomes in human lymphocytes, increasing deletion ratio in 7th chromosome, which may lead to leukemia development. Catechol and hydroquinone induced morphological changes in cells of hamster embryos. Catechol and hydroquinone inhibited ribonucleotide reductase activity (the enzyme that participates in DNA synthesis) and thus stopped activation and proliferation of T lymphocytes. Those compounds also inhibited the proliferation cycle of lymphocytes in G1 phase. Catechol in the presence

of NADPH and Cu^{2+} was able to modify guanine and thymine residues and induce gene mutations and chromosome aberrations. Catechol and hydroquinone damaged chromatids and induced incorrect DNA synthesis. The similar changes were provoked by pyrogallol, which induced the strongest (among hydroxybenzenes) chromosome aberrations. Pyrogallol and hydroquinone expressed their toxicity by forming a reactive oxygen species that included a hydroxy radical that caused deprotonation of the substrates and thus degraded deoxyribose. Semiquinone and quinone radicals are involved in damage of DNA structure by some xenobiotics. Chromosome aberrations and other structural changes within chromosomes were also induced by pentachlorophenol. Nitrophenols and nitrated aminophenols are also shown to have a mutagenic influence. In the test with the use of *Salmonella typhimurium* mutagenic activity was observed for 2,3-dinitrophenol, 2,5-dinitrophenol, 3,4-dinitrophenol, 2,4,6-trinitrophenol and 2-nitro-5-aminophenol. In another experiment performed on *Salmonella typhimurium* and *Escherichia coli*, mutagenic activity was noted for bisphenol F. This compound induced the increase of frequency of sister chromatid exchange and decreased the number of micronucleus in human lymphocytes. 4-aminophenol is capable of interacting with genetic material at the presence of Fe^{3+} and thus damages DNA contained in mouse and human lymphocytes. Some BHA and BHT metabolites also reveal genotoxic capacity toward DNA. Tert-butylhydroquinone (TBHQ) is formed in cells from butylhydroxyanisole in oxidative demethylation reaction and reveals genotoxic, cytotoxic, clastogenic and mutagenic capacities. 2,5-di-tert-butylhydroquinone (DTBHQ) is formed from 2,5-di-tert-butylhydroxyanisole (DTBHA), the compound that contaminates commercial preparations of BHA. In performed experiment both DTBHQ and DTBHA unplaited DNA helix by cleavage of single and double hydrogen bonds. TBHQ revealed stronger activity – 92.5% of DNA structure was damaged. BHT metabolism is related with hydroxylation of alkyl substituents, and also with oxidation of aromatic ring. In the experiment some butylhydroxyanisole metabolites like 2,6-ditertbutyl-4-hydroxyl-4-methyl-2-cyclohexadienone (BH T-OOH) and 2,6-ditertbutyl-4-benzoquinone (BH T-quinone) caused damage to DNA in the presence of Cu^{2+} by cleavage of hydrogen bonds.

These compounds also induced characteristics of apoptosis endonucleosomal DNA fragmentation. The mechanism of action of both metabolites was different: BH T-OOH indirectly damaged genetic material and BH T-quinone interacted by the formation of hydrogen peroxide.

8.3 Carcinogenicity

Mixture of chlorophenols or sodium salts of these compounds is probably carcinogenic for animals. People exposed to chlorophenols influence fall ill with of tumours, sarcoma and lung cancer. An admissible daily dose of individual chlorophenol that may be taken by a man that does not induce carcinogenic changes is $5\mu\text{g}/\text{kg}$ of body weight for 2-chlorophenol, and $3\mu\text{g}/\text{kg}$ of body weight for 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol. Catechol also reveals carcinogenic

activity. The U.S. Environmental Protection Agency classified this compound as a carcinogen and the World Health Organization classified catechol in 2B group as a compound of possible carcinogenicity. Para-cresol was classified as probable carcinogenic for human and 2,4-dimethylphenol was considered as the compound responsible for carcinogenic influence. Chronic exposure of skin rats to 2,4-dimethylphenol caused the formation of skin tumours (31% towards control).

Application of 3% dimethyl-benzanthracene caused the formation of skin tumours (50% towards control) and 18% of skin cancer. These changes were induced by o-quinones, in particular quinones methide that revealed high toxicity and additionally generated reactive oxygen species. Occupational exposure of workers to phenoxyherbicides is related to an increase of death incidents. The observed increase of mortality was linked to morbidity on cancer of respiratory system, lymphoma and myocardial ischaemia. The positive correlation was also noted between non-Hodgkins lymphoma appearance among children and documented frequency of using pesticides and their effect on the organism of birth child. The investigations of 10,000 workers employed in vinyl chloride production factories revealed that they suffered from liver and lung cancer. Chlorophenols are the main by-products that are formed during vinyl chloride production.

The exposure of people to chlorophenol influence appears also in factories that produce chloro-organic pesticides, mainly phenolic biocides. The main compound that is formed in this process is pentachlorophenol that was classified by the U.S. EPA as a probable carcinogen. The workers that are employed in pesticides production suffer from non- Hodgkins lymphoma and sarcoma. Carcinogenic properties are also characteristic for 4-methylcatechol and 4-methoxyphenol that are responsible for skin cancer and epithelium cancer development.

The cancer development in people exposed to phenols is related with microsomal activation of cytochrome P450. The oxidation reactions lead to conversion of some xenobiotics to electrophilic forms that actively interact with a cell's structures. For example, pentachlorophenol activation leads to the formation of tetrachloro-1,4-benzoquinone and tetrachloro-1,2-benzoquinone by intermediate steps with formation of respective semiquinone radicals. Formation of the above-mentioned compounds is also related to liver cancer development in mice. The essential is that cancer development is also correlated with the level (strength) of microsomal activation of cytochrome P450 of hepatocytes. Much lower activation of this cytochrome by PCP in rats does not lead to cancer development in spite of the identical pentachlorophenol metabolism in this species.

8.4 Other Toxic Effects of Phenols

4-octylphenol and 4-nonylphenol induce immunotoxicity by inhibition of lymphocytes proliferation. The second compound revealed stronger toxic activity and induced this process even in a concentration of 1

$\mu\text{M}/\text{kg}$ of body weight. Administration of 4-nonylpheno to rats in doses of 125-375 mg/kg of body weight caused changes in the activity of the immunological system. Phenols also affect the function of the hormonal system. Some phenols are capable of disturbing sexual hormones function, which finally may lead to sterility of animals and humans. The examples are alkylphenols, bisphenol A, 2,4-dichlorophenol and pentachlorophenol.

Alkylphenols imitates a ring A in E2 estrogens and thus reveal estrogenic activity. Bisphenol A cause protein expressions in TM4 cells in mice, which play a key role in spermatogenesis. It was noted that viability of cells decreased 10 to 70% after exposure to doses of 50-250 $\mu\text{M}/\text{kg}$ of body weight over 16 hours. Bisphenol A may induce infertility in mice. Phenols also modulate the activity of ion channels in the nervous system. It was noted that simple phenols and in particular trichlorophenols, triiodophenols and butylphenol may block ion channels in a micromolar concentrations range. The conclusion of investigation was that phenol and hydrophobic residues – alkyl chains or additional phenyl rings substituted in third, fourth and fifth positions are responsible for the above-described kind of toxic activity. Some phenols like phenol and p-cresole may be formed from non-toxic compounds like tyrosine in digestive tract of mammals, including humans. P-cresol is also a marker of organism exposure to toluene. This compound in the presence of hydrogen peroxide caused DNA adducts formation in HL -60 cells. Researchers revealed that DNA damages were induced by a metabolite of 4-methylphenol – quinone methide of p-cresol (PCQM) that also may be used as biomarker of organism exposure to toluene influence. Damages caused by aminophenols are related to fast oxidation of these compounds in physiological conditions to benzosemiquinoimines that are finally transformed to p-benzoquinoimines. The second metabolite generates a superoxide radical that in a dismutation reaction forms hydrogen peroxide converted in the presence of Fe^{3+} to a highly reactive oxygen form –hydroxyl radical.

In an experiment damage of epithelium cells of colon was induced by catechol and p-aminophenol. As the authors suggest, the above process may lead to chronic inflammation of large intestine. The investigations led by Bukowska, Duchnowicz and co-workers have revealed numerous toxic effects caused by phenols on human erythrocytes. The authors observed lipid peroxidation in erythrocytes incubated with 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4-dimethylphenol, and 3-(dimethylamino)phenol. Chlorophenols and catechol decreased human membrane erythrocytes acetylcholinesterase activity. Chlorophenol and dimethylphenol changed ATPase activity and membrane fluidity and also damaged membrane proteins. All investigated phenols oxidized haemoglobin, and the highest activity was revealed by 3-(dimethylamino-) phenol, catechol and 2,4-dimethylphenol (2,4-DMP). 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichloro phenol (2,4,5-TCP) and catechol decreased the activity of catalase. Moreover, catechol decreased superoxide dismutase activity. In the presence of 2,4-DMP and

2,4,5-TCP, a decrease in the amount of ATP that coincided with a simultaneous increase in ADP and AMP content was observed, which in the consequence caused a decrease of the energy charge of erythrocytes. The changes in the above parameters provoked haemolysis of the cells. The level of haemolysis was the highest in the presence of catechol and the lowest in the presence of phenol. In the light of obtained results the most toxic compounds towards erythrocytes were 3-(dimethylamino-) phenol and catechol.

9.0 MONITORING AND ANALYSIS TECHNIQUES OF PHENOLS IN ENVIRONMENTAL MATRIXES

Many of the analytical methods used for environmental samples. These methods are approved by federal agencies and organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH). US EPA Method 604 describes a gas chromatography (GC) method for determining phenols, using mass spectrometry (MS) or flame ionization detection (FID). However, many phenol-containing samples can poison GC columns. Liquid chromatography, combined with automated sample pretreatment, can be used to determine all 11 phenolic compounds listed in Method 604 with detection limits equivalent to GC-MS and superior to GC-FID.

9.1 Environmental Monitoring

The accuracy and sensitivity of phenol determination in environmental samples depends on sample pre-concentration and pretreatment and the analytical method employed. The recovery of phenol from air and water by the various pre-concentration methods is usually low for samples containing low levels of phenol. The two pre-concentration methods commonly used for phenols in water are adsorption on XAD resin and adsorption on carbon. Both can give low recoveries. Solvent extraction at acidic pH with subsequent solvent concentration also gives unsatisfactory recovery for phenol. Even during carefully controlled conditions, phenol losses of up to 60% may occur during solvent evaporation. The *in situ* acetylation with subsequent solvent extraction is probably one of the most promising methods.

Capillary columns may provide the best method for the separation of phenols prior to their quantification (Eichelberger et al. 1983; Shafer et al. 1981; Sithole et al. 1986). Of the various methods available for detection, the two commonly used methods that are most sensitive are mass spectrometry and flame ionization detection. Although electron capture detectors provide good sensitivities for higher chlorinesubstituted phenols, they are poor for phenol itself. The best method for the quantification of phenol may be mass spectrometric detection in the selected ion mode, but the loss of qualitative information may be significant.

High Performance Liquid Chromatography with UV detection is the method of choice for determination of 11 priority pollutant phenols. Central Pollution Control Board has standardized and validated a quick and easy methodology for determination of Phenols and Phenolic compounds in water and wastewater by HPLC equipped with Ultra Violet- Diode Array Detector (UV-DAD).



Fig. High Performance Liquid Chromatography

Table 12: Analytical Methods for Determining Phenol in Environmental Samples

Sample matrix	Preparation method	Analytical method	Reference
Ambient Air			
Air	Sample collected on a solid sorbent tube, desorbed using methanol	GC-FID	NIOSH 1994b
Air	Sample collected on a thermal desorption tube	GC-MS	NIOSH 1996
Occupational	Sample collected with a thermal	GC-MS	NIOSH 1994

air	desorption tube using a sorbent capable of capturing a C ₆ organic compound		
Source Emission			
Total particulate matter in cigarette smoke	Extract particulate matter with NaOH, buffer to pH 4.6	HPLC-fluorescence spectrophotometer	Tomkins et al. 1984
Industrial emission, auto exhaust, and tobacco smoke	Sample collected in NaOH bubbler and derivatized to <i>p</i> -nitrobenzene-diazonium tetrafluoroborate	HPLC-UV	Kuwata et al 1980
Water and Wastewater			
Drinking water, waste water, and natural water	Direct distillation of solventcleaned sample (if necessary) at acidic pH, react with 4-amino-antipyrine and potassium ferricyanide at pH 8,extract in chloroform	Spectrophotometer	APHA/AWWA/WPCF 1985
Water	Direct distillation or distillation of solvent-cleaned sample at acidic pH, react with 4-amino antipyrine and potassium ferricyanide at pH 10 or extract colored complex in chloroform	Spectrophotometric (ASTM Method D-1783)	ASTM 1978
Drinking Water	1-L sample is extracted using a solid phase extraction cartridge	GC-MS (Method 528)	EPA 2000a
Water	1-L sample acidified and extracted with methylene chloride	GC-FID (Method 604)	EPA 2001a
Water and Wastewater	Acidified sample extract with solvent, concentrated or derivatized to zentafluorobenzylbromide product	GC-FID; GC-ECD (for derivatized EPA Method 604)	EPA 1982
Water	The sample is extracted at pH 12–13, then at pH <2 with methylene chloride using continuous extraction techniques; the extract is dried over sodium sulfate and concentrated to a volume of 1 mL	GC-MS (Method 1625)	EPA 2001b
Aqueous samples	Samples extracted and cleaned up (according to sample matrix) and the solvent appropriately exchanged; the phenols are then determined with or without derivatization	GC-MS (Method 8041A)	EPA 2000b

Water	Water samples filtered using glass fiber filters; samples extracted using SPE cartridges	GC-MS (Method 01433-01)	USGS 2002
Groundwater	Solvent extraction in acidic pH, extract concentrated	GC-MS (EPA-CLP Method)	EPA 1987
Groundwater	Solvent extraction, column chromatographic cleanup, concentration of extract	GC-MS (EPA Method 8250A)	EPA 1994b
Groundwater	Solvent extraction, column chromatographic cleanup, concentration of extract	HRGC-MS (EPA Method 8270B)	EPA1994c
Soil and Sediment			
Soil, sediment	Sample mixed with anhydrous powdered Na ₂ SO ₄ , solvent extracted ultrasonically, extract subjected to GPC if necessary, extract concentrated	GC-MS (EPA-CLP Method)	EPA 1987
Sediment	Homogenized sample solvent extracted at acidic pH, fractionated by GPC and fractions concentrated	HRGC-MS	Lopez-Avila et al. 1983
Bottom sediment	Wet sediment samples dried and compounds extracted using dichloromethane	GC-MS (Method 0- 5130-95)	USGS 1995
Soil, sludge, or solid waste	Extracted by soxlet or sonication, extract subjected to column chromatographic cleanup and concentrated	GC-MS (EPA Method 8250A)	EPA1994b
Soil, sludge, or solid waste	Extracted soxlet or sonication, extract subjected to column chromatographic cleanup, concentrated	HRGC-MS (EPA Method 8270C)	EPA1994c
Soil, air, water,	Soxlet extraction with acetone/hexane	GC-MS (Method 8270D)	EPA 1998

9.2 Biological Materials

Phenol is expected to be present in blood and urine in its free acid and conjugated forms (glucuronide and sulfate). The average urinary phenol concentration in unexposed individuals is 9.5±3.6 mg/L when corrected to a standard specific gravity of 1.024. In exposed individuals, the urinary phenol level may vary from 10 to 200 mg/L. The two common methods for quantifying conjugated phenol are chemical and enzymatic hydrolysis of the conjugate to the free phenol form. The chemical method uses acidic hydrolysis. Both the nature of the acid (sulfuric versus perchloric) and the temperature should be controlled carefully to obtain a quantitative yield and to avoid thermal decomposition of other phenolic

or related compounds that may interfere with phenol quantification. The best available method appears to be specific enzyme hydrolysis or hydrolysis at ambient temperature with sulfuric acid. Enzymatic hydrolysis with an extract of *Helix pomatia* has also been used to liberate phenol from its conjugates. High-performance liquid chromatographic separation with electrochemical detection may provide the best sensitivity for phenol quantification in biological samples. The use of gas chromatography with a flame ionization detector may be a more versatile method, if other non-ionic pollutants must be quantified. The level of phenol detected in blood or urine may not accurately reflect actual phenol exposure because phenol may also appear as a metabolite of benzene or other drugs. It has been shown that under certain acidic conditions used for the hydrolysis of conjugated phenols, acetyl salicylic acid (aspirin) may produce phenol and yield spuriously higher values for phenol in blood and urine. For occupational exposure, it is recommended that urine samples be collected at the end of an 8-hour work shift (ACGIH 2001). Small amounts of thymol can be used as a preservative, and the urine can be stored for 4 days if refrigerated, or at least 3 months if frozen.

10.0 REGULATIONS AND ENVIRONMENTAL STANDARDS

A number of phenols are subject to regulation as air and water pollutants around the world. In the US, eleven phenols are listed as priority pollutants by the EPA, five phenols are regulated as hazardous pollutants under the Clean Air Act, and pentachlorophenol is regulated under the National Primary Drinking Water Regulation.

10.1 International

Phenol is regulated by the Clean Water Effluent Guidelines for the following industrial point sources: electroplating, organic chemicals, steam electric, asbestos, timber products processing, metal finishing, paving and roofing, paint formulating, ink formulating, gum and wood, carbon black, metal molding and casting, aluminum forming, and electrical and electronic components; see the electronic Code of Federal Regulations for a complete listing (NARA 2006).

EPA regulates phenol under the Clean Water Act (CWA) and the Clean Air Act (CAA) and has designated it as a hazardous substance and a hazardous air pollutant (HAP) (EPA 2006b, 2006c). Phenol is on the list of chemicals appearing in "Toxic Chemicals Subject to Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986" (EPA 2006j) and has been assigned a reportable quantity (RQ) limit of 1,000 pounds (EPA 2006h). The RQ represents the amount of a designated hazardous substance which, when released to the environment, must be reported to the appropriate authority. Phenol is also considered to be an extremely hazardous substance (EPA 2006i).

EPA (IRIS 2006) derived an oral reference dose (RfD) of 0.3 mg/kg/day for phenol based on a BMDL of 93 mg/kg/day for decreased maternal weight gain observed in Sprague-Dawley rats dosed with phenol during gestation (York 1997).

The IARC classification for phenol is Group 3, not classifiable with regard to its carcinogenicity to humans (IARC 2004). The EPA cancer classification for phenol is D, not classifiable as to human carcinogenicity (IRIS 2006). The National Toxicology Program has not classified phenol for human carcinogenicity (NTP 2005). The American Conference of Governmental Industrial Hygienists (ACGIH) has classified phenol as an A4 carcinogen (not classifiable as a human carcinogen) (ACGIH 2005).

OSHA has required employers of workers who are occupationally exposed to phenol to institute engineering controls and work practices to reduce and maintain employee exposure at or below permissible exposure limits (PELs) (OSHA 2005a). The employer must use engineering and work practice controls to reduce exposures to or below an 8-hour time-weighted average (TWA) of 5 ppm for phenol (OSHA 2005a). ACGIH (2005) and NIOSH (2005) also recommend a TWA exposure limit of 5 ppm for occupational exposure.

International and national regulations and guidelines pertinent to human exposure to phenol are summarized in Tables below.

REGULATIONS AND INTERNATIONAL GUIDELINES APPLICABLE TO PHENOL

International Guidelines

Agency	Description	Information	Reference
IARC	Carcinogenicity classification	Group 3a	IARC 2004
WHO	Air quality guidelines	No data	WHO 2000
	Drinking water quality guidelines	No data	WHO 2004

National Regulations and Guidelines

Agency	Description	Information	Reference
AIR			
ACGIH	TLV (8-hour TWA) ^b	5 ppm	ACGIH 2005
EPA	AEGL-1 ^{c,d}		EPA 2006a
	10 minutes	19 ppm	
	30 minutes	19 ppm	
	60 minutes	15 ppm	
	4 hours	9.5 ppm	
	8 hours	6.3 ppm	
	AEGL-2 ^{c,d}		
	10 minutes	29 ppm	
	30 minutes	29 ppm	
	60 minutes	23 ppm	
4 hours	15 ppm		

	8 hours Hazardous air pollutant	12 ppm Yes	EPA 2006d 42 USC 7412
NIOSH	REL (10-hour TWA)e Ceiling limit (15-minute TWA) IDLH	5 ppm 15.6 ppm 250 ppm	NIOSH 2005 (National Institute for Occupational Safety and Health)
OSHA (Occupational Safety and Health Administration)	PEL (8-hour TWA) for general industry PEL (8-hour TWA) for construction industry PEL (8-hour TWA) for shipyard industry	5 ppm 5 ppm 5 ppm	OSHA 2005c 29 CFR 1910.1000 OSHA 2005b 29 CFR 1926.55, OSHA 2005a FR 915.1000
WATER			
EPA (Environmental Protection Agency)	Designated as a hazardous substances in accordance with Section 311(b)(2)(A) of the Clean Water Act Designated as a toxic pollutant in accordance with Section 307(a)(1) of the Federal Water Pollution Control Act Drinking water standards and health advisories 1-day health advisory for a 10- kg child 10-day health advisory for a 10-kg child DWEL Lifetime National primary drinking water standards Reportable quantities of hazardous substances designated pursuant to Section 311 of the Clean Water Act Toxics criteria for those states not complying with Clean Water Act Section 303(c)(2)(B) for human health (10-6 risk for carcinogens) for consumption of: Water + organism Organism only Water quality criteria for human health consumption of: Water + organism Organism only	 6 mg/L 6 mg/L 11 mg/L 2 mg/L No data 1,000 pounds 21 mg/L 4,600 mg/L 21 mg/L 1,700 mg/L	EPA 2006b 40 CFR 116.4 EPA 2006c 40 CFR 401.15 EPA 2004 EPA 2003 EPA 2006g 40 CFR 117.3 EPA 2006m 40 CFR 131.36 EPA 2006f
FOOD			
EPA	Exemptions from the requirement of a tolerance as an inert ingredient (as a solvent) when used pre-harvest Exemptions from the requirement of a	Yes Yes	EPA 2006k 40 CFR 180.920 EPA 2006l

	tolerance as an inert ingredients (as a solvent) when applied to animals		40 CFR 180.930 (Environmental Protection Agency)
FDA	Bottled drinking water Included on the "Everything Added to Foods in the United States" List	0.001 mg/L Yes	FDA 2005 FDA 2006 (Food and Drug Administration)
OTHER			
ACGIH	Carcinogenicity classification Biological exposure indices (end of shift) for total phenol in urine	A4 ⁹ 250 mg/g creatinine	ACGIH 2005 (American Conference of Governmental Industrial Hygienists)
CPSC	Substance named in the Federal Caustic Poison Act; phenol and any preparation containing phenol in a concentration	≤5%	CPSC 2005 (Consumer Product Safety Commission)
EPA (Environmental Protection Agency)	Carcinogenicity classification Oral slope factor Inhalation unit risk RfC RfD Identification and listing of hazardous waste; hazardous waste number Superfund, emergency planning, and community right-to-know Designated CERCLA hazardous Substance Reportable quantity Effective date of toxic chemical release reporting Extremely hazardous substances and their threshold planning quantities	Group D ^h NA NA NA 0.3 mg/kg/day U188 Yes 1,000 pounds 01/01/87 500/10,000 pounds	IRIS 2006 (Integrated Risk Information System) IRIS 2006e 40 CFR 261, Appendix VIII EPA 2006h 40 CFR 302.4 EPA 2006j 40 CFR 372.65 EPA 2006i 40 CFR 355, Appendix A
NTP	Carcinogenicity classification	No data	NTP 2005

Note: AEGL = Acute Exposure Guideline Level; CERCLA = Comprehensive Environmental Response, Compensation, and Liability Act; CFR = Code of Federal Regulations; DWEL = drinking water equivalent level; IARC = International Agency for Research on Cancer; IDLH = immediately dangerous to life or health; NTP = National Toxicology Program; PEL = permissible exposure limit; REL = recommended exposure limit;

RfC = inhalation reference concentration; RfD = oral reference dose; TLV = threshold limit values; TWA = time-weighted average; USC = United States Code;

Human health water quality criteria are numeric values that protect human health from the harmful effects of pollutants in surface water. Under section 304(a) of the Clean Water Act, water quality criteria are based solely on data and scientific judgments about the relationship between pollutant

concentrations and environmental and human health effects; economic or social impacts do not influence criteria recommendations. The following table presents the updated final criteria values and the reference doses used to derive the respective criteria values:

Table 13: Updated Draft Criteria for Phenol

Phenol	Current criteria	Updated draft criteria
IRIS RfD	0.60 mg/(kg ^{-d}) (published 2/90).	0.30 mg/(kg ^{-d}) (published 9/02) (http://www.epa.gov/ncea/iris/subst/0088.htm)
Water + Organisms	20,700 µg/l	10,400 µg/l
Organisms Only	1,700,000 µg/l	857,000 µg/l

Some regulations and recommendations for phenol include the following:

Drinking water

EPA	IS:10500
6 mg/L for up to 10 days lifetime exposure to 2 mg/L phenol in drinking water	0.001 mg/l

Workplace air

OSHA	NIOSH
5 parts per million (ppm) phenols in air To protect workers during 8-hour work shift.	Workroom air to be limited to 5 ppm over a 10-hour work shift.

Table 14: Soil quality guidelines for phenol (mg·kg⁻¹) (Canadian Environmental Quality Guidelines, Canadian Council of Ministers of the Environment, 1999)

Guidelines	Land use			
	Agricultural	Residential / parkland	Commercial	Industrial
SQG _{HH}	3.8	3.8	3.8	3.8
SQG _E	20	20	128	128
Interim soil quality criterion (CCME 1991)	0.1	1	10	10

Notes: SQG_E = soil quality guideline for environmental health; SQG_{HH} = soil quality guideline for human health

Table 15: Water quality guidelines for the protection of aquatic life (Environment Canada 2001):

Phenolic Compound	Guideline value (µg·L ⁻¹)	
	Fresh Water	Marine
Mono- and Dihydric phenols	4.0	NRG*

Nonylphenol and its ethoxylates	1.0*	0.7*†
---------------------------------	------	-------

NRG: No recommended guideline; * Expressed on a TEQ basis using NP TEFs; † Interim guideline.

Some of the Regulatory Environmental Standards for different types of industries for phenolic compounds under Environmental (Protection) Rules, 1986 are mentioned in the table given in Table 16.

**Table 16: Indian Industrial Standards for Phenolic Compounds
[Environmental (Protection) Rules, 1986]**

Industry	Parameter	Regulatory Environmental Standards (mg/l)
Cotton textile industry (Composite and Processing)	Phenolic compounds (as C ₄ H ₂ OH)	5.0
Composite Woolen mills	Phenolic compounds (as C ₆ H ₅ OH)	5.0
Dye and Dye Intermediate Industries	Phenolic compounds (as C ₆ H ₅ OH)	1.0
Coke Ovens	Phenolic compounds (as C ₆ H ₅ OH)	5.0
Integrated Iron and Steel Plants Coke Oven (effluent)	Phenol	1.0
Petrochemicals (Basic and Intermediate)	Phenol	5.0
Pesticide Manufacturing and Formulation Industries	Phenolic compounds (as C ₆ H ₅ OH)	1.0
Paint Industries Wastewater discharge	Phenolic compounds (as C ₆ H ₅ OH)	1.0
CETP	A. Primary treatment Phenolic compounds as C ₆ H ₅ OH) B. Treated effluent quality Phenolic compounds as C ₆ H ₅ OH)	5.0 1.0 (ISW) 5.0 (MCW)
Organic Chemicals Manufacturing Industries	Phenolic compounds as C ₆ H ₅ OH)	5.0
Oil drilling and Gas Extraction Industries	Phenolic compounds as C ₆ H ₅ OH)	1.2
Pharmaceuticals (Manufacturing and Formulation Industries)	Phenolic compounds as C ₆ H ₅ OH)	1.0
Coal Washeries	Phenolic compounds as C ₆ H ₅ OH)	1.0
Textile Industries	Phenolic compounds as C ₆ H ₅ OH)	1.0
Refractory Industries	Phenolic compounds	1.0(ISW)

	as C ₆ H ₅ OH)	5.0 (PS)
Cashew Seed Processing Industries	Phenolic compounds as C ₆ H ₅ OH)	1.0(ISW) 5.0 (PS)

ISW: Inland surface water; MCW: Marine Coastal Water; PS: Public Sewer

11.0 CONTROL MEASURES FOR ABATEMENT OF IMPACT OF PHENOLS AND PHENOLIC COMPOUNDS

11.1 Personal hygiene procedures

If phenol contacts the skin, workers should immediately wash the affected areas with soap and water. Clothing contaminated with phenol should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of phenol, particularly its potential for causing irritation and tissue corrosion. A worker who handles phenol should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, applying cosmetics, or taking medication. Workers should not eat, drink, use tobacco products, apply cosmetics, or take medication in areas where phenol or a solution containing phenol is handled, processed, or stored.

11.2 Storage

Phenol should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's Hazard Communication Standard [29 CFR 1910.1200]. Containers of phenol should be protected from physical damage and ignition sources, and should be stored separately from strong oxidizers (especially calcium hypochlorite), acids, and halogens.

11.3 Spills and leaks

In the event of a spill or leak involving phenol, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Use non-sparking tools.
5. Water spray may be used to reduce vapors.
6. For small dry spills, use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area.

7. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
8. For large liquid spills, build dikes far ahead of the spill to contain the phenol for later reclamation or disposal.

11.4 Specific Preventative Measures

Phenol should be kept in a tightly closed container, in a cool, dry place, away from heat, flame and oxidizing agents. It is light sensitive and should be kept in the dark (WHO, 1994). Protective clothing should be appropriate to the amount and form of the phenol being handled. It should be handled wearing an approved respirator; viton, butyl rubber or neoprene gloves (not nitrile or PVA gloves), safety goggles and other protective clothing. Safety showers and polyethylene glycol 300 should be near where phenol is being handled (Allen, 1991).

11.5 Other

Phenol is not likely to persist in air, soil or sewage, sea or surface water. It readily reacts photochemically, is rapidly biodegraded aerobically to mainly carbon dioxide, and anaerobic biodegradation occurs also at a slower rate. Low removal rates of phenol in ground water and soil may occur e.g. following spills, with subsequent inhibition of the microbial populations. Phenol is toxic to aquatic organisms: the lowest EC₅₀ for water organisms is estimated to be 3.1mg/L. The lowest chronic NOEC is estimated to be 0.2 (g/L).

12.0 PROTECTION OF HUMAN HEALTH AND THE ENVIRONMENT

In United State of America, federal government develops regulations and recommendations to protect public health. Regulations can be enforced by law. Federal agencies that develop regulations for toxic substances include the Environmental Protection Agency (EPA), the Occupational Safety and Health Administration (OSHA), and the Food and Drug Administration (FDA). Recommendations provide valuable guidelines to protect public health but cannot be enforced by law. Federal organizations that develop recommendations for toxic substances include the Agency for Toxic Substances and Disease Registry (ATSDR) and the National Institute for Occupational Safety and Health (NIOSH).

Types of hazard/exposure	Acute hazards/symptoms	Prevention
Fire	Combustible	No open flames. No contact with strong oxidants.
Explosion	Above 79°C explosive vapour/air mixtures may be formed.	Above 79°C use a closed system, ventilation.
Exposure		Avoid all contact

Inhalation	Sore throat. Burning sensation. Cough. Dizziness. Headache. Nausea. Vomiting. Shortness of breath. Laboured breathing. Unconsciousness. Symptoms may be delayed (see Notes).	Avoid inhalation of fine dust and mist. Ventilation, local exhaust, or breathing protection.
Skin	Easily Absorbed. Serious skin burns. Numbness. Convulsion. Collapse. Coma. Death.	Protective gloves. Protective clothing.
Eyes	Pain. Redness. Permanent loss of vision. Severe deep burns.	Face shield, or eye protection in combination with breathing protection.
Ingestion	Corrosive. Abdominal pain. Convulsions. Diarrhoea. Shock or collapse. Sore throat. Smoky, greenish-dark urine.	Do not eat, drink, or smoke during work. Wash hands before eating.

Regulations and recommendations can be expressed in not-to-exceed levels in air, water, soil, or food that are usually based on levels that affect animals, then they are adjusted to help protect people. Sometimes these not-to-exceed levels differ among federal organizations because of different exposure times (an 8-hour workday or a 24-hour day), the use of different animal studies, or other factors. Recommendations and regulations are also periodically updated as more information becomes available. For the most current information, check with the federal agency or organization that provides it. Some regulations and recommendations for chlorophenols include the following:

The EPA recommends that drinking water concentrations of 2-chlorophenol should not be more than 0.04 part per million (ppm), and concentrations of 2,4-dichlorophenol should not be more than 0.02 ppm; these are levels that can be tasted. In order for chlorophenols to be lower than levels that can be tasted, the EPA recommends levels of 0.1 part per billion (ppb; the amount of chlorophenols per billion parts of water) for monochlorophenols, 0.3 ppb for 2,4- dichlorophenols, and 1 ppb for 2,4,5-trichlorophenol and 2,3,4,6-tetrachlorophenol.

12.1 Pollution Prevention during Phenol Use

Pollution prevention means using source reduction techniques in managing waste problems and, as a second preference, environmentally sound recycling. The benefits of practicing pollution prevention include reduced operating costs, improved worker safety, reduced compliance costs, increased productivity, increased environmental protection, reduced exposure to future liability costs, continual improvement, resource conservation and enhanced public image.

12.2 Pollution Prevention from Phenol in Industries

Pollution prevention in a manufacturing setting generally means material substitution, process improvement, and product change or redesign. Often, pollution prevention practice involves applying one or more of these strategies in tandem.

- Process Improvement means to improve the operational process thereby reducing or eliminating the need for phenol usage. This includes, for example, increasing the operating efficiency of an equipment or a process, good maintenance programs, and training to reduce the risk of waste generation. A chemical manufacturer produces phenol and phenol derivatives. By upgrading the packing in two phenol-stripping columns, it was able to reduce wastewater generation by four million gallons a year. In the extractive distillation column, the packing was replaced with graphite trays. This modification decreased the amount of phenol in the wastewater by 147,000 pounds a year.
- Material Substitution is to use a different material or materials that are less toxic or non-toxic. This may include the use of a phenol-free raw material or different equipment that does not require phenol.
- Product Change or Redesign has the potential to eliminate the phenol usage altogether from the manufacturing process, especially where phenol becomes incorporated into the product.

The manufacturing process for traditional fiber glass insulation products utilizes a thermosetting phenol-formaldehyde based resin or binder. Glass fibers will not stick together by themselves. To hold the glass fibers together an adhesive (called a binder) is sprayed on the fibers. After curing in an oven, the binder holds the fibers together to keep their shape and overall form. This results in corresponding releases of ammonia, formaldehyde and phenol.

Recently, a line of insulation products that utilizes a new acrylic-based binder has been introduced. The acrylic binder used in this new fiberglass holds the fibers together just like the phenol-formaldehyde resin used in conventional fiberglass. It is a thermo-setting resin and heat is used to cure the binder same as with the traditional process.

Another new product is produced by fusing two different types of glass together. This results in a naturally curly fiber. The glass fibers inter-twine and lock themselves together. The binder is eliminated from the manufacturing process of this new product.

This new product also has some additional benefits, according to the manufacturer. The fibers are more resilient, stronger, and less prone to breakage, so fewer fiber particles will get into the air or into the

installer's skin. The company describes the material as non-itchy. Further, because the new product is more springy than conventional fiberglass and made without binders, rolls can be packed much more tightly. Rolls of this new product rated at R-25 are just 13.8 inches in diameter, compared with rolls of conventional fiberglass that are 27.6 inches in diameter. This means that shipping is considerably more efficient.

12.3 Systematic Approaches to Pollution Prevention

A systematic approach to pollution prevention establishes and maintains a systematic management plan designed to continually identify and reduce environmental impacts through pollution prevention. Many facilities are incorporating pollution prevention into their quality programmes or environmental management systems.

A producer of phenol and phenol derivative chemicals was generating phenol-containing wastewater from its bisphenol A (BPA) plant. The possibility of recovering phenol from this process water was investigated. The sources of the water streams from the BPA plant were studied for flow, phenol concentration, and variability. The principle source of water was from the hydrochloric acid (HCl) recovery process. It was found to have a wide variability in phenol concentration due the operational and mechanical instabilities of the HCl recovery column.

The facility studied distillation, adsorption and liquid-liquid extraction as possible phenol recovery technologies. Distillation was determined to be infeasible as the distillate phenol stream would be too high in water content to be returned directly to any on-site processes. The facility further considered concentrating the recovered phenol using membrane technology. This technology was found to be untried in this service and extremely expensive. Adsorption processes using either a resin or activated carbon were studied. While these were potentially feasible, they were rejected due to operational concerns and high capital and operating costs.

Liquid-liquid extraction using cumene with a caustic wash to recover the extracted phenol was investigated thoroughly in the laboratory and in a pilot operation. This scheme proved to be effective in removing phenol. But there were major drawbacks. The recovered phenol contained caustic which could not be returned to the BPA process. The recovered material could contain chlorides from the BPA process which would make returning it to another process of the facility objectionable. In addition, the presence of chlorides required more expensive construction materials. These concerns made the liquid-liquid extraction marginally attractive.

The facility undertook further study and investigation of the BPA process and the process water streams it generates. The wide variability in the phenol concentration was found to be due to

operational problems and mechanical instabilities of the HCl recovery column. This portion of the process was targeted for improvements. It was determined that improvements could be made to reduce the phenol concentration of the BPA process water to approximately the same level as any add-on recovery system. This would reduce the causes of phenol concentration variability and be much less costly to install than any add-on system.

REFERENCES / FURTHER READING

1. Canadian Council of Ministers of the Environment. [1999]. Canadian water quality guidelines for the protection of aquatic life: Phenols — Mono- and dihydric phenols. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
2. U.S. Environmental Protection Agency (US EPA). [2002]. Toxicological Review of Phenol. Integrated Risk Information System (IRIS). Washington D.C.
3. Agency for Toxic Substances and Disease Registry (ATSDR). [2006]. Toxicological Profile for Phenol, U.S. Department Of Health And Human Services, Public Health Service.
4. Agency for Toxic Substances and Disease Registry and (ATSDR). [2001]. "ToxFAQs for pentachlorophenol. <http://www.atsdr.cdc.gov/tfacts51.html>.
5. European Union (EU). [2003]. European Union Risk Assessment Report. Bisphenol A, CAS No: 80-05-7. Institute for Health and Consumer Protection, European Chemicals Bureau, European Commission Joint Research Centre, 3 rd Priority List. Luxembourg: Office for Official Publications of the European Communities.
6. Phenol. <http://www.essentialchemicalindustry.org/chemicals/phenol.html>
7. Breast Cancer & The Environment Research Centers Early Life Exposure to Phenols and Breast Cancer Risk in Later Years Fact Sheet On Phenols, 11/07/07
8. Toxicological Profile for Chlorophenols. [1999]. U.S. Department Of Health And Human Services, Public Health Service Agency for Toxic Substances and Disease Registry.
9. Michałowicz and Duda. [2007]. Phenols – Sources and Toxicityj(Review), Polish J. of Environ. Stud., 16(3), 347-362.
10. Santana C. M et al., [2009]. Methodologies for the Extraction of Phenolic Compounds from Environmental Samples: New Approaches. Molecules 14, 298-320.


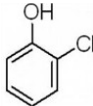

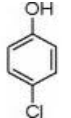

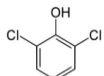
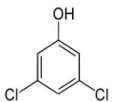
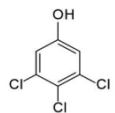
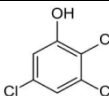
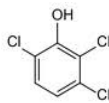
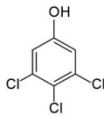
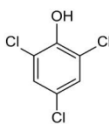
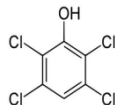
11. International Agency for Research on Cancer (IARC). [1989]. "Phenol," In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans, *World Health Organization*, 47:263-287.
12. NTP-CERHR Report on the Reproductive and Developmental Toxicity of Bisphenol A, http://cerhr.niehs.nih.gov/chemicals/bisphenol/BPA_Interim_DraftRpt.pdf.
13. vom Saal FS, Hughes C. [2005]. An extensive new literature concerning low-dose effects of bisphenol A shows the need for a new risk assessment, *Environ Health Perspect* 113:926-933.
14. The list of priority substances in the field of water policy and amending directive, Council directive 2455/2001/ECC. Official Journal L331, November 20, 2001, 1-5.
15. Martínez-Uruñuela, A.; Rodríguez, I.; Cela, R.; González-Sáiz, J.M.; Pizarro, C. [2005]. Development of a solid-phase extraction method for the simultaneous determination of chloroanisoles and chlorophenols in red wine using gas chromatography–tandem mass spectrometry. *Anal. Chim. Acta*, 549, 117-123.
16. Weber M. and M. Weber. Phenols. L. Pilato (ed.), *Phenolic Resins: A Century of Progress*, Springer-Verlag Berlin Heidelberg 2010.
17. Plants and Projects; ICB Chemical Profile, [2010]. INSIGHT: Acetone price falls plague phenol producer margins, ICIS news; 6th ICIS World Phenol-Acetone Conference, Berlin, Germany.
18. Allen R, Ed. [1991]. *Chemical Safety data Sheets, Volume 4b: Toxic Chemicals (m-z)*. Royal Society of Chemistry, Cambridge. Printed by Staples Printers Rochester Ltd, Kent.
19. WHO [1994]. IPCS Environmental Health Criteria for Phenol (161) First draft prepared by Ms G.K. Montizan. Published by WHO. Printed in Finland.
20. European Commission, [2002]. European Union Draft Risk Assessment Report: Phenol. CAS No: 108-95-2. EINECS No. 203-632-7. Draft of 12 November 2002. Luxembourg: Office of Official Publications of the European Communities.
21. World Health Organization (WHO), [1994]. *Environmental Health Criteria 161: Phenol*. Geneva: WHO. <http://www.who.int/ipcs/publications/ehc/en/>.
22. International Programme on Chemical Safety (IPCS), [1999]. *Poisons Information Monograph (PIM) 412: Phenol*. Geneva: IPCS. Available from: <http://www.inchem.org/documents/pims/chemical/pim412.htm>.

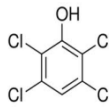
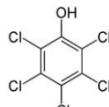
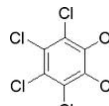
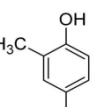
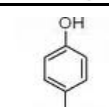
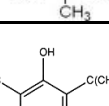
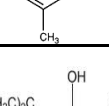
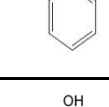
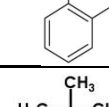
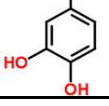
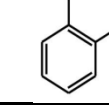
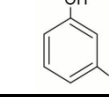
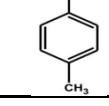
23. Chakraborty S., T. Bhattacharya, T.N. Patel and K.K. Tiwari, [2010]. Biodegradation of phenol by native microorganisms isolated from coke processing wastewater. *Journal of Environmental Biology*, 31 293-296.
24. Agency for Toxic Substances and Disease Registry (ATSDR). [1992]. Toxicological profile for nitrophenols. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. <http://www.atsdr.cdc.gov/toxprofiles/tp50.pdf>.
25. Santana, C.M.; Ferrera, Z.S.; Padrón, M.E.T.; Rodríguez, J.J.S. [2009]. Methodologies for the extraction of phenolic compounds from environmental samples: New Approaches. *Molecules*, 14, 298-320.
26. Agency for Toxic Substances and Disease Registry (ATSDR). [2008]. Toxicological profile for Phenol. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
27. National Pollutant Inventory - Phenol Fact Sheet, 2007.
28. Hand Book of Indian Chemical Industry, [2010]. Prepared by FICCI, Tata Strategic Management Group and Roland Berger Strategy Consultant
29. ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
30. ACGIH [1994]. 1994-1995 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
31. NFPA [1986]. Fire protection guide on hazardous materials. 9th ed. Quincy, MA: National Fire Protection Association.
32. NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.
33. NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.
34. NIOSH [1991]. Registry of toxic effects of chemical substances: Phenol. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

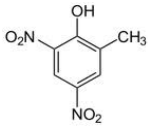
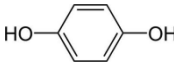
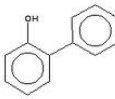

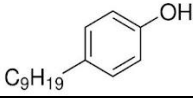
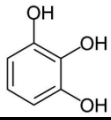
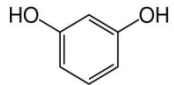
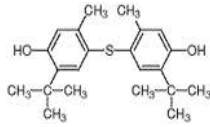
35. NIOSH [1992]. Recommendations for occupational safety and health: Compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.
36. NIOSH [1994a]. NIOSH pocket guide to chemical hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-116.
37. NIOSH [1994b]. NIOSH manual of analytical methods. 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
38. OSHA [1994]. Computerized information system. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration.
39. Handbook of Indian Chemical Industry. [2010]. Prepared by FICCI, Tata Strategic management Group and Ronald Berger Strategy Consultants.
40. Phenol (HSG 88, EHC 161) Published by WHO, Geneva, 1994.
41. Nina Schweigert, Alexander J.B. Zehnder and Rik I.L. Eggen. [2001]. Chemical Properties of Catechols and Their Molecular Modes of Toxic action in cells, from Microorganism to mammals- Mini review. Environmental Microbiology, 3(2), 81-91.
42. Atkinson R, Darnall KR, Lloyd AC, Winer AM, & Pitts JN Jr. [1979]. Kinetics and mechanisms of the reactions of the hydroxyl radical with organic compounds in the gas phase. Adv in Photochem, 11: 375.
43. www.bcerc.org/COTCpubs/BCERC.FactSheet_Phenols.pdf

APPENDIX

Phenols & Phenolic Compounds : Chemical Identification

CHEMICAL NAME	SYNONYMS	CAS-NUMBER	CHEMICAL STRUCTURE
PHENOL	Benzenol; Carboic acid; Hydroxybenzene; Monohydroxybenzene; Monophenol; Oxybenzene; Phenic acid; Phenol alcohol; Phenyl hydrate; Phenyl hydroxide; Phenylic acid; Phenylic alcohol	108-95-2	
<i>o</i> -CHLORO PHENOL	2-Chlorophenol	95-57-8	
<i>m</i> -CHLORO PHENOL	3-Chlorophenol	108-43-0	
<i>p</i> -CHLORO PHENOL	4-Chlorophenol	106-48-9	
2,4-DI CHLORO PHENOL	2,4-DCP; 2,4-Dichlorohydroxybenzene	120-83-2	
2,5-DICHLORO PHENOL		583-78-8	
3,5-DICHLORO PHENOL		591-35-5	
2,3,4-TRI CHLORO PHENOL		15950-66-0	
2,3,5-TRI CHLORO PHENOL		933-78-8	
2,3,6-TRI CHLORO PHENOL		933-75-5	
2,4,5-TRI CHLORO PHENOL	Collunosol; Dowcide 2; Dowicide 2; Dowicide B; Nurelle; Preventol I	95-95-4	
2,4,6-TRI CHLORO PHENOL		88-06-2	
2,3,5,6-TETRA CHLORO PHENOL		935-95-5	

2,4,5,6-TETRA CHLORO PHENOL	Dowicide 6; TCP; 2,3,4,6-Tetrachlorophenol	58-90-2	
PENTA CHLORO PHENOL	Dowicide 7; Dow pentachlorophenol DP-2 antimicrobial; Durotox; EP 30; 1-Hydroxypentachlorobenzene; Lauxtol; Lauxtol A; Liroprem	87-86-5	
PENTA CHLORO PHENOL, SODIUM SALT	Pentachlorophenate sodium; Penta chlorophenoxy sodium; Pentaphenate; Sodium pentachlorophenate; Sodium pentachlorophenol;	131-52-2	
2,4-DIMETHYL PHENOL	4,6-Dimethylphenol; 1-Hydroxy-2,4-Dimethylbenzene; <i>m</i> -Xylenol; 2,4-Xylenol	105-67-9	
<i>p</i>-tert-BUTYL PHENOL	4- <i>tert</i> -Butylphenol; 4-(1,1-Dimethylethyl)phenol; 1-Hydroxy-4- <i>tert</i> -butylbenzene; Phenol, 4-(1,1-Dimethylethyl)-; PTBP	98-54-4	
2,6-DI-<i>tert</i>-BUTYL -<i>p</i>-CRESOL	2,6-Bis(1,1-dimethylethyl)-4-methyl phenol; Butylated hydroxytoluene; Butyl hydroxyl toluene; DBMP; DBPC; 2,6-Di- <i>tert</i> -butyl-1-hydroxy-4-methylbenzene; 3,5-Di- <i>tert</i> -butyl-4-hydroxy toluene; 2,6-Di- <i>tert</i> -butyl- <i>p</i> -methylphenol; 2,6-Di- <i>tert</i> -butyl-4-methyl phenol; 4-Hydroxy-3,5-di- <i>tert</i> -butyltoluene	128-37-0	
2,6-DI-<i>tert</i>-BUTYL PHENOL	2,6-Bis(<i>tert</i> -butyl)phenol	128-39-2	
CATECHOL	<i>o</i> -Benzenediol; 1,2-Benzenediol; Catechol; <i>o</i> -Di hydroxybenzene; 1,2-Dihydroxybenzene; <i>o</i> -Di oxybenzene; <i>o</i> -Diphenol; <i>o</i> -Hydroquinone; <i>o</i> -Hydroxy phenol; 2-Hydroxyphenol; <i>o</i> -Phenylenediol]	120-80-9	
4-<i>tert</i>-BUTYL PYRO CATECHOL	1,2-Benzenediol, 4-(1,1-Dimethylethyl)-; 4- <i>tert</i> -butyl-1,2-benzenediol; 4- <i>tert</i> -Butylcatechol; <i>p</i> - <i>tert</i> -Butylpyrocatechol; 4- <i>tert</i> -Butylpyrocatechol	98-29-3	
<i>o</i>-CRESOL	2-Cresol; <i>o</i> -Cresylic acid; 1-Hydroxy-2-ethyl benzene; <i>o</i> -Hydroxytoluene; 2-Hydroxytoluene; <i>o</i> -Methylphenol; 2-Methylphenol; <i>o</i> -Methyl phenylol; <i>o</i> -Oxytoluene; Phenol UN2076	95-48-7	
<i>m</i>-CRESOL	3-Cresol; <i>m</i> -Cresylic acid; 1-Hydroxy- 3-methylbenzene; <i>m</i> -Hydroxytoluene; 3-Hydroxy toluene; <i>m</i> -Methylphenol; 3-Methylphenol UN2076	108-39-4	
<i>p</i>-CRESOL	4-Cresol; <i>p</i> -Cresylic acid; 1-Hydroxy-4-methylbenzene; <i>p</i> -Hydroxytoluene; 4-Hydroxytoluene; <i>p</i> -Methylhydroxybenzene; 1-Methyl-4-hydroxybenzene; <i>p</i> -Methylphenol; 4-Methylphenol UN2076	106-44-5	
<i>p</i>-CHLORO-<i>m</i>-CRESOL	4-Chlor- <i>m</i> -cresol; Chlorocresol; <i>p</i> -Chlorocresol; 6-Chloro- <i>m</i> -cresol; 2-Chloro-hydroxytoluene	59-50-7	

DINITRO-<i>o</i>-CRESOL	Dinitrocresol; 2,4-Dinitro- <i>o</i> -cresol; 4,6-Dinitro- <i>o</i> -cresol; Dinitroendroxal; 3,5-Dinitro-2-hydroxytoluene; Dinitrol; Dinitromethyl cyclohexyltriolenol; 2,4-Dinitro-6-methylphenol; DNOC; 2-Methyl-4,6-dinitrophenol; Nitrador UN1598	534-52-1	
HYDRO QUINONE	<i>p</i> -Benzenediol; 1,4-Benzenediol; Benzohydroquinone; Benzoquinol; Dihydroxybenzene; <i>p</i> -Dihydroxybenzene; 1,4-Dihydroxybenzene; <i>p</i> -dioxobenzene; <i>p</i> -Dioxybenzene; <i>p</i> -Hydroquinone UN2662	123-31-9	
2-HYDROXY BIPHENYL	<i>o</i> -Biphenylol; 2-Biphenylol; <i>o</i> -Diphenylol; <i>o</i> -Hydroxydiphenyl; 2-Hydroxydiphenyl; Orthohydroxydiphenyl	90-43-7	
4-METHOXY PHENOL	Hydroquinone monomethyl ether; <i>p</i> -Methoxyphenol; 4-Methoxyphenol; MME; Monomethyl ether hydroquinone	150-76-5	
NONYL PHENOL, ALL ISOMERS	Hydroxyl no. 253	25154-52-3	
PYROGALLOL	Benzene, 1,2,3-trihydroxy-; 1,2,3-Benzenetriol; Fouramine Brown AP; Fouramine PG; Fouramine 85; Pyrogallol; 1,2,3-Trihydroxybenzene	87-66-1	
RESORCINOL	<i>m</i> -Benzenediol; 1,3-Benzenediol; <i>m</i> -Dihydroxybenzene; 1,3-Dihydroxybenzene; <i>m</i> -Dioxybenzene; <i>m</i> -Hydroquinone; 3-Hydroxycyclohexadien-1-one; <i>m</i> -Hydroxyphenol; 3-Hydroxyphenol; Phenol, <i>m</i> -hydroxy- UN2876	108-46-3	
4,4'-THIOBIS (6-<i>tert</i>-BUTYL-<i>m</i>-CRESOL)	Bis(3- <i>tert</i> -butyl-4-hydroxy-6-methylphenyl) sulphide; Bis(4-hydroxy-5- <i>tert</i> -butyl-2-methylphenyl) sulphide; 4,4'-Thiobis(6- <i>tert</i> -butyl- <i>m</i> -cresol)	96-69-5	
XYLENOL	Dimethylphenol; Phenol, dimethyl- UN2261	1300-71-6	