

# **Phenol & Derivatives - REACH-Consortium**

## **Qualitative Environmental Exposure Assessment**

### **PHENOL**

**CAS No: 108-95-2**

**EINECS No: 203-632-7**

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# 1. Environmental Exposure

## 1.1 General discussion

Phenol is released from a number of human-made sources. The primary sources of environmental phenol are automobile exhaust (direct emission and photochemical degradation of benzene), human and animal metabolism and different combustion processes. From industrial sources, it enters the environment from production and processing operations. Releases also occur due to the waste water from cooking plants and low-temperature carbonisation plants using hard coal and brown coal, from refineries, from pulp manufacture and landfill leachate (EC, 2006).

The purpose of this chapter is to reflect qualitatively the exposure situation in the EU that results from industrial sources of phenol production and processing. The diffuse emissions by automobile exhaust, human and animal metabolism and different combustion processes are higher than the industrial emissions.

In the appendix predefined environmental exposure scenarios are attached to this document. These enable downstream users of phenol to check and reflect their specific exposure situation in regard to surface-water and soil release and to determine their conditions for a safe use as well as their acceptable use volumes. Reference is given to an according tool, that is enclosed in the registration dossier as an attached document (ECT\_Phenol\_19Jul2010.xls) and may be downloaded from the P&D REACH Consortium-website or the web-site of the consortium members.

## 1.2 Production

The production capacity installed worldwide is more than nine million tonnes a year, compared to a total demand of more than eight million tonnes a year (CEFIC 2008; draft). The estimated production capacity in Europe reaches nearly about one third of the worldwide Production (CEFIC 2008; draft).

For 2008, the CMAI Capacity Database reports the total supply to be approx. 8 Mio tonnes worldwide and 2.3 Mio tonnes in Western Europe (CMAI, 2010). Most of the companies, where phenol is only processed on site, buy phenol from production companies in the EU.

Today the oxidation of cumene (Hock process) is by far the dominant synthetic route to phenol with a production rate of more than  $6.7 \times 10^6$  t/a of phenol and about  $4.1 \times 10^6$  t/a of the coproduct acetone. It is the most competitive process, supported by the demand for acetone. As the demand for phenol may increase more strongly in the future, there is still a commercial interest in finding new, coproduct-free routes to phenol, for example, the direct oxidation of benzene to phenol. The oxidation of toluene with benzoic acid as intermediate product is used for phenol production with an annual production of about 300 000 t. About 300 000 t of phenol is still recovered from coal tar. Since ca. 1995 the direct oxidation of benzene to phenol with nitrous oxide has been developed by Solutia but has still not been commercialized. Classic synthetic routes such as the benzene sulfonation process and hydrolysis of chlorobenzene with caustic soda no longer have any economic importance. (Ullmann's Encyclopedia of Industrial Chemistry, 2005).

Based on the best available techniques reference document, the optimised biological treatment of wastewater employing adapted microbial inocula ensures, that phenol is removed in WWTPs of production plants by up to 99.9 % (CEFIC 2008; draft). Consequently, release from production is expected to be low.

### 1.3 Uses

The major uses of phenol are the production of bisphenol-A, which accounts for 42 % of consumption, phenolic resins (28 %) and caprolactam (24 %). About 16 % are used for the manufacture of alkyl phenols, aniline and others. (CEFIC 2008; draft).

For 2008 the CMAI Capacity Database allocates the total supply of phenol to the main industrial sectors of use as follows (CMAI, 2010):

Demand	World	Western Europe
	[approx. percent of supply]	
Bisphenol A	45	37
Phenolic resin	28	19
Nylon-KA Oil	13	22
Others	14	13

The overall growth in demand of phenol is expected to be about 5 % per year in the long run. It is driven substantially by the increase of the bisphenol.-A production at rates of eight percent and higher. Whereas the other uses are estimated to grow moderately at 1-3 % per year (CEFIC 2008; draft).

As phenol is used to a great extent as an intermediate, release from these uses are expected to be regularly negligible under best practice working conditions, due to the fact that phenol is consumed during the reaction.

### 1.4 Natural and further releases into the environment

#### Aquatic environment

As product of human metabolism phenol residues can be determined in urine with average concentrations of 25 mg/L (or 40 mg per person per day). Considering the European population as defined by the TGD a total release 540 t/a (regional model) and 4860 t/a (continental model).

Also animals eliminate phenol as a product of metabolism together with the urine and the faeces. Between 0.5 and 45 mg/l phenol were detected in the liquid manure (12 hours after excretion) produced by pigs (EC 2006). Usually, the liquid manure derived from livestock farming is spread over agricultural areas for the purpose of fertilisation. Release into sewage or surface water is expected to be of minor importance. However, due to the minor importance of this source and the ready biodegradability of phenol, significant exposure of the hydrosphere is not expected.

From industrial sources, it enters the environment from production and processing operations. Releases also occur due to the waste water from cooking plants and low-temperature carbonisation plants using hard coal and brown coal, from refineries, from pulp manufacture and landfill leachate. Phenol concentrations (for two sites) ranging from 68 to 720 mg/l were

determined in the waste water from cooking plants. Usually, the waste water is biologically purified in WWTPs before release into the receiving stream.

Phenol is sometimes also released via landfill leachate if leachate collection systems are not available. For example, concentrations of various phenols (phenol in a mixture with substituted phenols) were detected in 175 samples at a level of 49.2 mg/l (mean value) in landfill leachate in Germany.

### Atmosphere

Phenol is formed during the incomplete combustion of motor fuels. On the basis of the petrol consumption and the exhaust fumes which are formed during combustion in the engine, an emission of 270 t/a was estimated for the Netherlands. Based on this information total phenol emission can be extrapolated to 9000 t/a. However, as considerable reduction in the emission of phenol can be achieved through the use of charcoal filters, scrubber with liquid caustic soda and other measures, the release of 9000 t/a may be an overestimation for the present situation.

Phenol is formed during the combustion of organic substances. During measurements in the smoke gas of wood-fired tile stoves phenol was found in concentrations from 8 to 26 mg/m<sup>3</sup>. A total emission of 623 t/a results for the territory of Germany from combustion processes was estimated which can be extrapolated to 2,880 t/a for the total territory of the EU.

## **2. Environmental distribution and behaviour**

Compared to the EU-RAR as of 2006 (EU 2006) no additional data could be identified, which would require a modification of the conclusions drawn with respect to these endpoints.

### **2.1 Distribution**

Phenol is only slightly volatile from aqueous solution. Experimentally derived soil sorption coefficients (K<sub>oc</sub> values) for phenol are reported to be within the range of 14.0 L/kg to 91 L/kg exhibiting low adsorptive potential.

The calculated theoretical distribution in the environment (distribution model according to Mackay, level 1) clearly demonstrates that the hydrosphere is the target compartment for phenol in the environment:

Air:	0.8 %
Water	98.8 %
Soil	0.2 %
Sediment	0.2 %

### **2.2 Degradation**

Phenol introduced in water has been shown to be **readily biodegradable** in a considerable number of reliable investigations under a wide variety of conditions. This holds also true also for biodegradability in sediment as well as soil. Taking into account the ubiquitous occurrence of phenol in aquatic compartments, adaptation is to be assumed in the case of microbial inocula. Based on these valid data the following degradation rate constants were derived: WWTPs:  $k = 1 \text{ h}^{-1}$ ; water:  $0.05 \text{ d}^{-1}$ ; sediment:  $0.01 \text{ d}^{-1}$ ; soil:  $0.1 \text{ d}^{-1}$ .

Based on the physico-chemical properties of phenol and the rate constant for biodegradation of  $1 \text{ h}^{-1}$ , the total elimination from water in a WWTPs can be determined to be 87.4 %

(standard simple treat calculation). However, based on the best available techniques reference document the optimised biological treatment of wastewater ensures phenol to be removed by up to 99.9 % (CEFIC 2008; draft). In various degradation studies employing adapted microbial inocula removal rates in the range of 98.5-100 % were demonstrated (BUA, 1997).

In the atmosphere phenol reacts with photochemically formed hydroxyl radicals. A half-life of 14 hours ( $k_{\text{degOH}} = 0.051 \text{ h}^{-1}$ ) was calculated for the photochemical degradation in the atmosphere on the basis of an atmospheric concentration of the OH radicals amounting to  $5 \cdot 10^5$  molecules/cm<sup>3</sup>.

### 2.3 Bioaccumulation

As a conclusion from all available experimental results it can be stated that phenol has only a low bioaccumulation potential, which is also supported by the log Pow of 1.47. According to the equation of Veith et al. (1979) given in the TGD a BCF<sub>fish</sub> of 3.5 can be calculated from this value. For the further assessment the BCF of 17.5 found by Butte et al. (1985) is recommended by EU (2006).

## 3. Background levels

Only very few investigations are available with regard to the occurrence of phenol itself in the hydrosphere. They mostly contain only data on the quantity of steam-volatile phenols or on the Phenol Index (as summary parameters of all phenol compounds without substituted p-position). The Phenol Index based on the DIN 38409 include all substances which can be coupled oxidative like aromatic amines, so this results should be used with care. The available monitoring data are, in part, relatively old and cannot be assigned to the individual emission sources or the measured values. They only provide an indication of the orders of magnitude which are to be expected (if there are only data on the phenol index or  $\Sigma$ st. vol. phenols). As a product of human and animal metabolism phenol is a natural occurring substance (EU 2006).

The results of the investigations are summarised in the following table (EU 2006):

Location	Analysed substance	Period	Concentration in $\mu\text{g/l}$
3 German rivers	$\Sigma$ st. vol. phenols	1989 - 1991	6 - 450
Mulde near to Bad Dübén	$\Sigma$ st. vol. phenols	1988 - 1991	2 - 120
Elbe	$\Sigma$ st. vol. phenols	1989 - 1991	6 - 66
town well Berlin	Phenol Index	1986	<10 - 30
Müggelsee	$\Sigma$ st. vol. phenols	1988 - 1989	11 - 42
rain water Germany	Phenol	1989 - 1990	0.68-59.7
Emscher WWTP influent	Phenol Index	1994 - 2000	<10 - 1220
Emscher WWTP effluent	Phenol Index	1994 - 2000	<10 - 30
Rhein near to Lobith	$\Sigma$ st. vol. phenols	1983 - 1986	<0.1 – 2.0
2 Dutch rivers	Phenol Index	1983	5.7-15.7
Ijsselmeer	Phenol	1983	0.3 - 7
port of Rotterdam/Amsterdam	Phenol	1983	$\leq 260$
North sea	Phenol	1986	<0.1 – 0.88

Schelde	Phenol	1980 - 1988	2 - 5
Saar, different sites n = 290	Phenol	1990 - 1997	<10 - 20
Mosel, different sites n = 140	Phenol	1990 - 1992	<10 - 20
Rhein Setz n = 207	Phenol	1980 - 1992	<10 - 20

Σ st. vol. phenols = sum of the steam-volatile phenols

Monitoring data in German surface waters were determined 2002 within the water policy framework in streams of North Rhine-Westphalia. At 14 sites (typically with 3-5 measurements) phenol concentrations were found to be <0.01 µg/l (ELWASIMS, 2002).

In sludge from the wwtp Bottrop of the Emscher Genossenschaft (receiving the wastewater of INEOS phenol) a concentration of 1.2 mg/l phenol was measured in 2010 (Emscher Genossenschaft, 2010).

Quantitative determinations of phenol in the ambient air are only available to a limited extent. For example, investigations of the air were carried out in Gladbeck near Phenolchemie GmbH in 1987. However, it was not possible to detect phenol with a detection limit of 2 µg/m<sup>3</sup>. In the period 1967 to 1970 phenol concentrations of < 20 to 289 µg/m<sup>3</sup> were found in the air of the city of Cologne. In March 1991 a phenol concentration of 0.59 µg/m<sup>3</sup> was determined in the air in Rome. In January 1977 studies of the air were carried out in Paris. In sunny weather 2.1 to 5.1 µg/m<sup>3</sup> phenol were found, in the case of a cloudy sky the detected quantity was 0.7 to 8.2 µg/m<sup>3</sup> and in rainy weather it amounted to 5.4 µg/m<sup>3</sup>. Investigations involving the air of 8 cities in the USA during the period 1974 to 1978 revealed phenol concentrations (as mean values derived from the individual values) of 0.1 to 305 µg/m<sup>3</sup> (EU 2006).

With regard to the occurrence of phenol in soils, an investigation into contaminated soils at a gasworks near Copenhagen exists which reveals concentrations between 0.05 and 29 mg/kg. Other monitoring data of phenol in soils or ground water are not available (EU 2006).

The following regional environmental concentrations can be estimated for phenol:

PEC <sub>regional,aquatic</sub> =	1.9 µg/L
PEC <sub>regional, air</sub> =	0.026 µg/m <sup>3</sup> (EU 2006)
PEC <sub>regional, agr.soil</sub> =	0.172 µg/kg (EU 2006)
PEC <sub>regional, natural soil</sub> =	0.59 µg/kg. (EU 2006)

The PEC<sub>regional,-aquatic</sub> is based on the number given in EU 2006 (2.41 µg/L) but considering an updated percentage of waste water connected to WWTP.

## 4. Ecotoxicological information

Compared to the EU-RAR as of 2006 (EU 2006) no additional data could be identified, which would require a modification of the conclusions drawn with respect to these endpoints.

### 4.1 Aquatic environment

Reliable results from acute and long-term toxicity testing of three trophic levels (vertebrates, invertebrates, algae) are available. The most sensitive group was found to be fish with a

reliable NOEC of 77 µg/L obtained in a 60 day study with *Cirrhina mrigala*. Applying an assessment factor of 10 results in a PNEC freshwater of 0.0077 mg/L.

#### **4.2 Terrestrial environment**

Tests were performed with soil macro-organisms (earthworm acute, non-target arthropods long-term), plants and microorganisms. Furthermore a seedling emergence test with plants (*Latuca sativa*) and tests with microorganisms (dehydrogenase, N-mineralisation) are available. The earthworm acute toxicity test conducted equivalent to OECD 207 was selected as relevant test for the derivation of a PNECsoil. Based on the result (LC50 = 136 mg/kg soil) and taking into account an assessment factor of 1000 (according to the TGD) a PNEC soil=0.136 mg/kg soil is obtained.

### **5. Classification for the environment**

Due to its **ready biodegradability** in waste water, freshwater, sea water and sediment as well as its insignificant potential for bioaccumulation, phenol is not classified as dangerous/hazardous for the environment according to Directive 67/548/EEC and according to the Regulation (EC) 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regulation):

**According to Directive 67/548/EEC Annex 1 (environment): not classified**

**According to CLP - (EC) 1272/2008 (environment): not classified**  
L(E)C50 1-10 mg/L; readily biodegradable, no bioaccumulation

#### **Hazardous to the atmospheric environment:**

(Hazardous to the ozone layer: This includes substances which are listed in Annex I to Regulation (EC) No 2037/2000 of the European Parliament and of the Council on substances that deplete the ozone layer (1) and its subsequent amendments):

**Phenol is not listed in Annex I of (EC) No 2037/2000.**

**M-Factor:** No  
**Labelling** No Signal word and Pictogram for environmental hazards

## 6. References

- Cefic (2008): PHENOL Best available techniques reference document prepared by the CEFIC Phenol Sector Group (**draft**).
- BUA (1997): BUA-Stoffbericht 209 Phenol (Stand: 1997). Beratergremium für umweltrelevante Altstoffe, S. Hirzel Verlag, Stuttgart.
- CMAI (2010) CMAI Capacity Database – Capacity, Production and Use demand of Phenol 2004-2008 (Western Union and World). Chemical Market Associates, Inc.: <http://www.cmaiglobal.com>.
- EU (2006): European Union Risk Assessment Report PHENOL Revised Edition, EUR 22522 EN/1, ISSN 1018-5593, Luxembourg: Office for Official Publications of the European Communities, 2006.
- Emscher Genossenschaft (2010): Klärschlamm-Analysen Kläranlage Bottrop. Prüfbericht 39913036. EUROFINS Umwelt Ost GmbH, 07.07.2010.
- ELWAS-IMS (2002) Ministry of the Environment and Conservation, Agriculture and Consumer Protection of the German State of North Rhine-Westphalia; <http://www.elwasims.nrw.de>
- Ullmann's Encyclopedia of Industrial Chemistry (2005) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

## Appendix I

### Predefined Emission Scenarios

**Predefined emission scenarios Sheets are presented for acceptable environmental emissions in soil and surface water (PECsoil and PECsurface water).**

**The sheets contain maximum acceptable use volumes dependent on the local situation (e.g. ERC, dilution).**

**An according ECT-tool can be downloaded from the P&D REACH-Consortium web-page or the web-site of the producers. It is based on EUSES but with some simplifications to improve the user friendliness and to concentrate on the key-parameters**

## Predefined emission scenarios for Phenol (PECsurface-water)

Use volume (t/a)	Local Release factor (%)	Removal rate (%)	dilution factor (-)	Acceptable volume (t/a)	Defined for ERC	suitable also for ERC
Default		88,2	10			
Site specific		88.2 .. 99.5	30 ... 1500			
<36	100	88,2	10	0,36	4 8a 8d 10 b 11b	all
<100	6	93	100	101	1	all except 4 5 8a 8d 10b 11b
<100	2	88,2	60	107	2 6a 8b 8e	3 6d 8c 8f 10a 11a
<100	1	88,2	30	107	8c 8f	3 6d 10a 11a
<100	1	96	100 (sea release)	105	8c 8f	3 6d 10a 11a
<500	2	88,2	300 100 (sea release)	538	2 6a 8b 8e	3 6d 8c 8f 10a 11a
<500	1	99,2	100 (sea release)	529	8c 8f	3 6d 10a 11a
<500	1	96	50	529	8c 8f	3 6d 10a 11a
<500	1	88,2	150	538	8c 8f	3 6d 10a 11a
<1000	1	88,2	525	300	8c 8f	3 6d 10a 11a
<1000	1	96	100	1058	8c 8f	3 6d 10a 11a
<1000	0,2	98	100 (sea release)	1058	3	6d 10a 11a
<5000	1	88,2	1500	5382	8c 8f	3 6d 10a 11a
<5000	1	98,5	200	5645	8c 8f	3 6d 10a 11a
<5000	0,05	98,5	100 (sea release)	5645	11a	6d
<10000	1	99	250	10585	8c 8f	3 6d 10a 11a
<10000	0,2	88,2	600	10764	3	6d 10a 11a
<10000	0,05	92	100	10585	11a	6d
<20000	1	99,5	250	21170	8c 8f	3 6d 10a 11a
<20000	0,2	88,2	1200	21528	3	6d 10a 11a
<20000	0,05	88,2	300	21528	11a	6d

## Predefined Environmental Release Classes

ERC	Environmental Release Class	Default Release Fraction
ERC 1	Production of chemicals	6,00%
ERC 2	Formulation of preparations	2,00%
ERC 3	Formulation in articles	0,20%
ERC 4	Industrial use of processing aids	100,00%
ERC 5	Industrial use resulting in inclusion into or onto a matrix	50,00%
ERC 6a	Industrial use of intermediates	2,00%
ERC 6b	Industrial use of reactive processing aids	5,00%
ERC 6c	Production of plastics	5,00%
ERC 6d	Production of resins/rubbers	0,005%
ERC 7	Industrial use of substances in closed systems	5,00%
ERC 8a	Wide dispersive indoor use of processing aids in open systems	100,00%
ERC 8b	Wide dispersive indoor use of reactive substances in open systems	2,00%
ERC 8c	Wide dispersive indoor use resulting in inclusion into or onto a matrix	1,00%
ERC 8d	Wide dispersive outdoor use of processing aids in open systems	100,00%
ERC 8e	Wide dispersive outdoor use of reactive substances in open systems	2,00%
ERC 8f	Wide dispersive outdoor use resulting in inclusion into or onto a matrix	1,00%
ERC 9b	Wide dispersive outdoor use of substances in closed systems	5,00%
ERC 10a	Wide dispersive outdoor use of long-life articles and materials with low release	0,16%
ERC 10b	Wide dispersive outdoor use of long-life articles and materials with high or intended release	100,00%
ERC 11a	Wide dispersive indoor use of longlife articles and materials with low release	0,05%
ERC 11b	Wide dispersive indoor use of longlife articles and materials with high or intended release	100,00%

## Predefined emission scenarios for Phenol (Entry route: Sludge and aerial deposition, PECsoil )

Use volume (t/a)	Local Release factor water (%)	Local Release factor air (%)	Acceptable use volume (t/a)	Defined for ERC	suitable also for ERC
<3	100	100	3,2	4 8a 8d 10 b 11b	all 2 3 6a 6b 6c 8b 8e 9b 10a
<50	6	5	58	1	11a
<140	2	2,5	141	2	8b 8e 10a 11a
<300	2	0,1	304	8b 8e	10a 11a
<3000	0,16	0,05	3041	ERC 10a	11a
<6000	0,05	0,05	6387	ERC 11a	
any	dry sludge <100 mg/kg	air release below 230 t/a	any	all	
any	dry sludge <25 mg/kg	air release below 750 t/a	any	all	
any	dry sludge <10 mg/kg	air release below 1000 t/a	any	all	

## Predefined Environmental Release Classes

ERC	Environmental Release Class	Default Release Fraction
ERC 1	Production of chemicals	6,00%
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ERC 3	Formulation in articles	0,20%
ERC 4	Industrial use of processing aids	100,00%
ERC 5	Industrial use resulting in inclusion into or onto a matrix	50,00%
ERC 6a	Industrial use of intermediates	2,00%
ERC 6b	Industrial use of reactive processing aids	5,00%
ERC 6c	Production of plastics	5,00%
ERC 6d	Production of resins/rubbers	0,005%
ERC 7	Industrial use of substances in closed systems	5,00%
ERC 8a	Wide dispersive indoor use of processing aids in open systems	100,00%
ERC 8b	Wide dispersive indoor use of reactive substances in open systems	2,00%
ERC 8c	Wide dispersive indoor use resulting in inclusion into or onto a matrix	1,00%
ERC 8d	Wide dispersive outdoor use of processing aids in open systems	100,00%
ERC 8e	Wide dispersive outdoor use of reactive substances in open systems	2,00%
ERC 8f	Wide dispersive outdoor use resulting in inclusion into or onto a matrix	1,00%

ERC 9a	Wide dispersive outdoor use of substances in closed systems	5,00%
ERC 9b	Wide dispersive outdoor use of substances in closed systems	5,00%
ERC 10a	Wide dispersive outdoor use of long-life articles and materials with low release	0,16%
ERC 10b	Wide dispersive outdoor use of long-life articles and materials with high or intended release	100,00%
ERC 11a	Wide dispersive indoor use of longlife articles and materials with low release	0,05%
ERC 11b	Wide dispersive indoor use of longlife articles and materials with high or intended release	100,00%