Bull. Environ. Contam. Toxicol. (1997) 59:702-707

Bulletin of Environmental Contamination and Toxicology

Phenol Concentrations in Air and Rain Water Samples Collected near a Wood Preserving Facility

S. K. Allen, C. W. Allen

Indiana State University, Department of Health and Safety,
Terre Haute, Indiana 47809, USA

Received: 21 April 1997/Accepted: 21 August 1997

Over the past two decades, increasing numbers of trace organic compounds have been determined in atmospheric air and water samples. These include polycyclic aromatic hydrocarbons (PAH), nitrated PAH, polychlorinated biphenyls (PCB), phenols, aldehydes, ketones, carboxylic acids and aromatic alcohols, many of which are of concern due to their toxic and potentially carcinogenic properties. In many cases, the distribution and fate of these compounds are only poorly understood. There have been a number of reports in the literature concerning the tropospheric distribution of a variety of phenolic compounds. The tropospheric concentration of phenol and a variety of substituted phenols associated with residential wood burning has been reported in several studies (Hawthorne et al. 1992; Hawthorne et al. 1988; Hawthorne et al. 1989). Phenols have been shown to be present at high concentrations in urban rainwater and ambient air (Leuengerger et al. 1985; Shah and Heyerdahl 988), but there have been no reports describing the concentrations of phenols in air and rainwater impacted by emissions from the wood preserving industries, despite their high emission rates from these industrial processes (Graedel 1978).

The human health effects resulting from the emission of pollutants from wood preserving plants have not been well characterized. Of particular concern is the ability of phenols and cresols to be absorbed through the skin which has been demonstrated in humans (Zenz 1988). Skin painting studies reviewed in U.S. EPA (1984) and Bruce et al.(1987) suggest that phenols may be promoters and/or weak skin carcinogens in mice. Phenol vapors are highly irritating to the skin, eyes, and mucous membranes. Since phenols and cresols are readily absorbed through the skin, prevention of contact with vapors and liquids is suggested by the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Act of 1970 (OSHA) (1985). It is important to note that such standards are based on short-term exposures to phenols and cresols. The health effects of long-term exposure to low levels of phenols and cresols are not well characterized. However, because phenols and cresols have been demonstrated to be harmful to humans as well as other living organisms, there is an interest in determining the concentrations of these compounds in the ambient air and rainwater.

Correspondence to: S. K. Allen

In addition to the adverse effects to human health, nitrated phenols in the atmosphere have been implicated as possible contributors to forest decline (Rippen et al. 1987). Nitrated aromatics are formed by atmospheric photochemical reactions of aromatic compounds such as phenols and creosols with hydroxyl radical and nitrogen dioxides (Nojima 1983). Nitrophenols and nitrocreosols have been observed in the ambient atmosphere in both the gas and particle phases, as well as in fogwater, rainwater, and snow (Richartz et al. 1990). Although some nitrated phenols are included in the Environmental Protection Agency's list of priority pollutants, few data are available about their atmospheric concentrations.

The purpose of this study was to provide detailed information on the occurrence and quantity of phenols in urban air and rainwater in areas downwind of coal tar creosote wood preserving plants. These data have not been previously reported in the literature.

MATERIALS AND METHODS

Terre Haute, IN, was chosen as a primary site for sample collections, wood pulping and preserving are still viable industries in this urban location. The wood preserving industry uses more pesticides than any other industry worldwide. The major chemicals used for this purpose are creosote, pentachlorophenol and CCA (copper, chrome, and arsenate) (Mueller et al. 1989). Coal tar is the primary source of creosote for the wood preserving facility located in Terre Haute. Creosote is a complex mixture of compounds with diverse chemical structures and chemical properties. Coal tar creosote is composed of approximately 85% PAH, 10% phenolic compounds, and 5% N-, S-, and O- heterocyclics (Mueller et al. 1989). Of the two hundred or more compounds which make up the complex mixture of creosote, only a few are present in a high mole fraction. Phenol is a major constituent of creosote, it is volatile and is water soluble. It is thus a good marker compound for the presence of creosote in air and rainwater. Certain phenols have been previously identified as atmospheric markers of wood smoke (Hawthorne et al. 1992; Hawthorne et al. 1988; Hawthorne et al. 1989), arising from the incomplete combustion of wood lignin. Since phenolic compounds make up about 10% of coal tar creosote and they have been used in previous studies as atmospheric markers, phenol was chosen as the marker compound for this study. Thus, air and rainwater samples impacted by creosote emissions were analyzed for phenol concentrations.

Air and rainwater samples were collected between July 1995 and October 1995. Sample collections were limited to rain events that occurred during the wood preserving plant operations, Monday through Friday, 7:30 a.m. to 5:30 p.m. Ambient air and rainwater samples were collected concurrently during the first 30 minutes of each rain event. All samples were collected 100 yards down wind of the facility.

Air samples were collected using a LaMotte Air Sampling Pump, Model (3345-3494), and a LaMotte general purpose bubble impinger, Model (0938-B) containing 20 mL. of 0.1 M NaOH. The air sampling pump was calibrated at a flow rate of two liters of air per minute. After 30 minutes of sampling, the contents of the impinger were transferred to a high-density polyethylene bottle. The samples were stored in the dark at 5°C until analysis. Phenol was determined in all samples within forty-eight hours after collection.

All samples were acidified to pH 2.5 with 10% phosphoric acid and filtered using an all-glass filtration apparatus (Schleicher and Schuell) with a 0.47 mm Teflon filter just prior to analysis. The pH value for each sample was measured using an Orion Model 710 pH meter with a Ross combination pH electrode. A three point calibration using NIST traceable buffers (Fisher) was used for all pH measurements.

Rainwater samples were collected using a 9" x 13" x 2" collection vessel. After 30 minutes of sampling, the contents of the vessel were transferred to a high-density polyethylene bottle. The samples were stored in the dark at 5°C until analysis. Phenol was determined in all samples within forty-eight hours after collection. Rain events which produced less than 20 mL. of rainwater were eliminated from the study.

All rainwater samples were acidified to pH 2.5 with 10% phosphoric acid and filtered using an all-glass filtration apparatus (Schleicher and Schuell) and 0.47 mm Teflon filter just prior to analysis. The pH value for each sample was measured using an Orion Model 710 pH meter with a Ross combination pH electrode. A three point calibration using NIST traceable buffers (Fisher) was used for all pH measurements.

Phenol (99%), was obtained from Aldrich. Sodium hydroxide (ASC reagent) was obtained from Fisher. Phosphoric Acid (ASC reagent) was obtained from Baker. Purified water for preparation of standards and for preparation of HPLC mobile phase was obtained by passing in-house deionized water through a four bowl Barnstead E-Pure laboratory water purification system yielding water with >18 MΩ resistivity. Acetonitrile (HPLC grade) was obtained from Burdick and Jackson.

The high-performance liquid chromatograph (HPLC) used for all experiments reported herein incorporated a Spectra-Physics model P-200 pump with an Applied Biosystems model 785A UV-Visible detector with a Rheodyne manual injector incorporating a 50 mL. sample loop and a 150 x 4.6 mm reversed-phase C_{18} column (Alltech) for determination of phenol. All analyses were carried out under isocratic elution conditions using a 50 % acetonitrile and 50 % water mixture for the mobile phase at a flow rate of 1 mL. per minute. Phenol was detected at $\lambda = 222$ nm.

A calibration plot was constructed for phenol. The standard concentration values for phenol were chosen such that they bracketed the range of phenol concentration present in the samples. The multi-point calibration curve was then used to quantify the phenol present in samples.

RESULTS AND DISCUSSION

The results of phenol analysis are reported in Table 1. As can be seen by an examination of the data, the phenol concentrations are well above those reported in the literature for winter urban air due to wood smoke emissions. The phenol concentrations in Terre Haute air reported herein range from 4.1 µg/m^3 to 15.7 µg/m^3. As can be seen in Table 1, the lowest measured phenol concentration in Terre Haute air was found to be twice as high as the highest reported phenol concentration in the Hawthorne study (1992), which was conducted between November 1988 and February 1989, in Minneapolis, MN and Salt Lake City, UT, and reported phenol concentrations in winter urban air samples in the range of 279 ng/m^3 to 2410 ng/m^3. The authors of this study did not report phenol concentrations in rainwater. The Hawthorne study concluded that these concentrations were significant enough to pose a human health risk (Hawthorne et al. 1992).

In addition, the mean value for phenol concentrations in Terre Haute rainwater was 18.1 µg/m^3 which is well above the 280 ng/m^3 reported in the Leuenberger study (1985) done in Portland, Oregon, 1985. The mean value for phenol concentrations in Terre Haute ambient air of 9.7 µg/m^3 was roughly 30 times higher than the mean phenol concentration of 0.380 µg/m^3 reported in the Leuenberger study.

In addition, as can be seen by an examination of the data, the expected aqueous phase concentration based on Henry's law as reported in Table 1 is much higher than the actual rainwater phenol concentration. In fact, the actual phenol concentrations found in Terre Haute rainwater were only three to four percent of the expected equilibrium aqueous phase concentration based on Henry's law. This indicates that the amount of phenol present in air parcels sampled exceeded the amount that could be scavenged by raindrops under the conditions prevailing at the time of sampling. This is in agreement with previous studies (Leuenberger et al. 1985 and Atkinson et al 1992).

The phenol concentrations reported here are at least an order of magnitude higher than results from previous studies where phenol concentrations in air and water samples collected in urban areas were reported. In fact, the concentration levels of phenol found in Terre Haute, IN are high enough to cause eye irritation and skin disorders in humans according to the EPA. The EPA and the World Health Organization (1980) have stated that long-term exposure to phenol could be dangerous since phenol is suspected of being a tumor promoter and has the ability

Table 1. Measured phenol concentrations in Terre Haute air and rainwater.

Date of Sample Collection	Ambient Air Concentration ($\mu g/m^3$)	Rain Water Concentration ($\mu g/m^3$)	Expected Aqueous Phase Concentration Based on Henry's Law* ($\mu g/m^3$)
20 July, 1995	14.1	23.5	752.8
2 August, 1995	10.0	20.6	536.4
4 August, 1995	4.1	7.9	216.4
9 August, 1995	4.7	10.4	254.1
2 September, 1995	15.7	28.2	856.3
Mean	9.7	18.1	

* Henry's Law constant: 4.57 x 10^{-4} L·ATM/mole at 25°C

to mutate mammalian cells. Because the health effects of long-term exposure to low levels of phenol are not well characterized, epidemiological studies are needed in order to assess the risk associated with such exposures.

REFERENCES

Atkinson R., Aschmann S, Arey J (1992) Reaction of OH and NO_3 radicals with phenol, cresols, and 2-nitrophenol at 296 ± 2 K. Environ Sci Technol 26: 1397-1403

Bruce R, Santodonato J, Neal M (1987) Summary review of the health effects associated with phenol. Toxicol Ind Health 3: 535-68

Graedel T (1978) Chemical Compounds in the Atmosphere. Academic Press. NY

Hawthorne S, Krieger M, Miller D, Mathiason M (1989) Collection and quantitation of methoxylated phenol tracers for atmospheric pollution from residential wood stoves. Environ Sci Technol 23: 470-475

Hawthorne S, Miller D, Barkley R, Krieger M (1988) Identification of methoxylated phenols as candidate tracers for atmospheric wood smoke pollution. Environ Sci Technol 22: 1191-96

Hawthorne S, Miller D, Langenfeld J, Krieger, M (1992) PM-10 high-volume collection and quantitation of semi- and nonvolatile phenols, methoxylated phenols, alkanes, and polycyclic aromatic hydrocarbons from winter urban air and their relationship to wood smoke emissions. Environ Sci Technol 26: 2251-62

Leuenberger C, Ligocki M, Pankow J (1985) Trace organic compounds in rain. Identities, concentrations, and scavenging mechanisms for phenols in urban air and rain. Environ Sci Technol 19: 1053-58

Mueller J, Chapman P, Pritchard P (1989) Creosote-contaminated sites. Environ Sci Technol 23: 1197-201

NIOSH (1985) NIOSH recommendations for occupational safety and health standards. Morb. Mort. Wkly. Rpt. 34(suppl); 4s-31s

Nojima K, Kawaguchi A, Ohya T, Kanno S, Hirobe M (1983) Studies on photochemical reaction of air pollutants. Identification of nitrophenols in suspended particulates. Chem Pharm Bull 31: 1047- 1051

Richartz H, Reischi A, Trautner F, Hutzinger (1990) Nitrated phenols in fog. Atmos Environ 24A; 12: 3067-3071

Rippen G, Zietz E, Frank R, Knacker T, Klopfler W (1987) Do airborne nitrophenols contribute to forest decline? Environ Technol Lett 9: 475-482

Shah J, Heyerdahl E (1988) National ambient volatile organic compounds (VOC's) data base update. EPA Report 600/3-88/010*(a).* U.S. Government Printing Office: Washington, D.C.

Shah J, Heyerdahl E (1988) Distribution of volatile organic chemicals in outdoor and indoor air Environ Sci Technol 22: 1381-88.

U.S. Environmental Protection Agency (1984) Health effects assessment for phenol. EPA 540/l-86/007, PB86-134186

U.S. Environmental Protection Agency (1980) Ambient water quality criteria for phenol. EPA 440/5-80-066. U.S. Government Printing Office, Washington, D.C.

Vigo County Air Pollution Control Department. (1994) Vigo county air pollution control inspection report. Western Tar Products

Zenz C (1988) Occupational medicine principles and practical applications. Mosbey Year Book. Boston