Research and Development

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Carcinogen Assessment of Coke Oven Emissions

The final report summarized herein is a source document developed primarily for use by the Office of Air Quality Planning and Standards, United States Environmental Protection Agency, to support decision-making regarding possible regulation of coke oven emissions as a hazardous air pollutant.

In the development of the assessment document, the scientific literature was inventoried and key studies were evaluated. The carcinogenicity and related characteristics of coke oven emissions are qualitatively identified. Measures of dose-response relationships relevant to ambient exposures and adverse health responses in the prospective observed environmental levels are also discussed.

This Project Summary was developed by EPA's Office of Health and Environmental Assessment, Washington, DC, to announce key findings of the research project that is fully documented in a separate report of the same title [see Project Report ordering information at back).

Introduction

Coke is a porous, cellular carbon residue produced from the carbonization of soft (bituminous) coal and used primarily in the steel industry's blast furnaces to make iron that is subsequently refined into steel.

A typical coke oven is 10 to 22 feet high. 36 to 55 feet long, and approximately 18 inches wide. A coking facility generally contains several batteries and each battery consists of 20 to 100 ovens. The coking cycle begins with the introduction of coal into the coke oven (charging) by means of a mechanical larry car which operates on rails on top of the battery. During the charging process the lids on

the charging holes are removed and the oven is placed under steam aspiration. This operation limits the escape of gases from the oven during charging so that they can be collected in the byproduct gas collector main for subsequent processing. Following the heating of the coal at 1046°C (1900°F) to 1100°C (2000°F) for 16 to 20 hours, the doors on each side of the oven are removed, and the coke is pushed by a mechanically operated ram into a railroad car called the quench car. The quench car is then moved down the battery to a quench tower where the hot coke is cooled with water.

where the hot coke is cooled with water. The reactions taking place in the coke oven can be characterized in three parts. In the first step, coal breaks down at temperatures below 700°C (1292°F) to primary products consisting of water, carbon monoxide, carbon dioxide, hydrogen sulfide, olefins, paraffins, aromatic hydrocarbons, and phenolic-containing and nitrogen-containing compounds. The second step occurs when the primary products react as they pass through the hot coke and along the heated oven walls at temperatures above 700°C (1292°F). This step results in the formation of aromatic hydrocarbons and methane; the evolution of hydrogen; and the decomposition of nitrogen-containing compounds, hydrogen cyanide, pyridine bases, ammonia, and nitrogen. The third step is the formation of hard coke by the progressive removal of hydrogen.

Human exposure to coke oven emissions occurs as a result of emissions released during the charging, coking (door, topside port, and offtake system leaks), and pushing operations. During these operations large quantities of sulfur dioxide, organic vapors, particulates, and coal tar pitch volatiles absorbed

to particulates can be emitted to the atmosphere. A detailed list of constituents found in coke oven emissions is given in the final report.

The Occupational Safety and Health Administration (OSHA) set a comprehensive standard for coke ovens emissions (29 CFR 1910.1029). This OSHA standard included requirements for exposure monitoring; medical surveillance; use of respirators, protective clothing, and equipment; training and education; and hygiene facilities and practices. The permissible exposure limit (PEL) as defined by the standard is an 8-hour time-weighted average of 150 mg/m³ of the benzene soluble fraction of total particulate matter.

Summary

Qualitative Assessment

The production of coke by the carbonization of bituminous coal leads to the atmospheric release of chemically complex emissions from coke ovens. The toxic constituents include both gases and respirable particulate matter of varying chemical composition. The emphasis in this document is on the toxic effects of the particulate phase of the coal tar pitch volatiles (CTPV) emitted from coke ovens, principally becuase this fraction contains polycyclic organic matter; however, the document also discusses the potential carcinogenic and/or cocarcinogenic effects of aromatic compounds (e.g., beta-naphthylamine, benzene), trace metals (e.g., arsenic, beryllium, cadmium, chromium, lead, nickel), and gases (e.g., nitric oxide, sulfur dioxide), which are also emitted from coke ovens.

The literature contains an extensive epidemiologic study of coke oven workers conducted at the University of Pittsburgh which showed that workers exposed to coke oven emissions are at an increased risk of cancer. A dose-response relationship was established in terms of both length of employment and intensity of exposure according to work area; i.e., at the top or the side of the coke oven. The relative risk of lung, trachea, and bronchus cancer mortality in 1975 was 6.94 among Allegheny County, Pennsylvania coke oven workers who had been employed five or more years through 1953 and worked full-time topside at the coke ovens. By comparison, side oven workers employed more than five years and followed through 1975 had a relative risk of 1.91, while nonoven workers employed more than 5 years had a relative risk of 1.11. Deaths from malignant neoplasms at all sites were also found to be dose-

related among the Allegheny County workers. Among non-Allegheny County coke oven workers employed more than five years at time of entry to the study (1951-1955), the relative risk in 1975 of cancer of the lung, trachea, and bronchus was 3.47 for full-time topside, 2.31 for mixed topside and side oven, and 2.06 for side oven. Although adequate smoking data were not available for either the Allegheny County or non-Allegheny County workers, it is not likely that differences in smoking habits could be of sufficient magnitude to negate the doseresponse effect. In addition to elevated mortality from cancer at all sites, and elevated mortality from cancer of the lung, trachea, and bronchus, there was significant (P < 0.05) excess kidney cancer mortality amoung white coke oven workers in Allegheny County (relative risk in 1975 of 8.50 for those employed five years or more through 1953 and 5.42 years for those ever employed through 1953). Prostate cancer mortality was found to be elevated significantly (P <0.05) for the nonwhite non-Alleghenv County coke oven workers ever employed or employed for five years or more (relative risks of 2.45 and 3.59 respectively in 1975) and for all workers at the coke ovens in Allegheny County ever employed through 1953 (relative risk of 1.67 in 1975).

Extracts of a topside coke oven sample and a sample obtained from a coke oven collecting main were shown to have skin tumor initiating activity in initiation-promotion studies in SENCAR mice. Coal tar, a condensate from coke oven emissions, was shown to be a skin carcinogen in several animal studies. Coal tar aerosols have been found to cause tumors of the lung in mice. Numerous other animal studies have shown constituents of coke oven tar and coke oven emissions to be carcinogenic.

Mutagenicity tests on the complex mixture of solvent-extracted organics of coke oven emissions were positive in bacteria. A complex mixture from the coke oven collecting main was mutagenic in bacteria and mammalian cells in vitro. In addition, a number of components identified in coke oven emissions are recognized as mutagens and/or carcinogens. Cell transformation was found in Balb/C 3T3 mouse embryo fibroblasts and Syrian hamster embryo cells treated with solvent-extracted organics of air particulates collected topside of a coke oven; however, these studies involve possibly significant contamination of the sample with ambient air particulates.

Quantitative Assessment

Several approaches are available to estimate the human lifetime respiratory cancer death rate from a continuous exposure of 1 μ g/m³ of the benzene soluble organics (BSO) extracted from the particulate phase of CTPV from coke ovens emissions.

Using a Weibull-type model, the estimated risk due to a 1 μ g/m³ unit exposure ranges from 1.30 x 10^{-8} for the 95% lower-bound zero lag-time assumption to 1.05 x 10^{-3} for the 95% upperbound 15-year lag-time assumption. Using a multistage-type model,the maximum likelihood estimates for the risk due to unit exposure range from 1.76 x 10^{-6} for the zero lag-time case to 6.29 x 10^{-4} for the 15-year lag-time case.

Since it is not known whether either of these models reflects the true doseresponse relationship at low doses, a range of estimates from zero to an upper bound is a more appropriate indicator of potenial risk. To obtain this upper bound, a linearized modification of the multistage model is used, giving a unit risk value of 1.26 x 10⁻³ as the highest potency amongst the four lag-time data sets. The lower bound of the range approaches zero.

A composite unit risk estimate is obtained from the multistage 95% upperbound estimates for each of four lagtimes by taking their geometric mean. This results in a composite estimate of 6.17 x 10⁻⁴, which is regarded as the most plausible upper-bound estimate.

It should be noted that the ranges of these results do not reflect the total uncertainty connected with these estimates. Other factors that could change the results, such as cigarette smoking rates and sex-race sensitivity differences, were not accounted for due to lack of sufficient information.

Conclusions

Coke oven workers were found to be at an excess risk of mortality from cancer at all sites, and from lung cancer, prostate cancer, and kidney cancer as a result of exposure to coke oven emissions. These risks may have been enhanced by smoking but are not believed to have been confounded by smoking. Both an extract from a coke oven main and coal tar, a condensate of coke oven emissions, were found to be carcinogenic in animal skin painting studies. In multiple experiments, mice exposed to coal tar aerosol developed lung tumors. Sample extracts from a coke oven topside sample and coke oven main initiated tumor formation in initiaion-promotion studies in mice. Coke oven door emissions were found to be mutagenic in bacteria. Numerous constituents of coke oven emissions are known or suspected carcinogens.

The findings of this document constitute sufficient evidence for carcinogenicity in humans, and sufficient evidence for carcinogenicity in experimental animals if the International Agency for Research on Cancer (IARC) criteria were used for the classification of carcinogens. Therefore, coke oven emissions would be classified in IARC category 1, meaning that this mixture is carcinogenic to humans.

Using a linearized multistage model and averaging the upper-bound estimates from multiple data sets, the most plausible upper-bound unit risk estimate is approximately 6.2×10^{-4} . This value is the estimated individual lifetime risk associated with a continuous exposure of 1 $\mu g/m^3$ of coke oven emissions in ambient air.

This Project Summary was prepared by staff of the Carcinogen Assessment Group, Office of Health and Environmental Assessment, USEPA, Washington, DC 20460.

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The complete report, entitled "Carcinogen Assessment of Coke Oven Emissions," (Order No. PB 84-170 182; Cost: \$19.00, subject to change) will be available only from:

National Technical Information Service 5285 Port Royal Road Springfield, VA 22161 Telephone: 703-487-4650

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