

Toxicology of Gasoline



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Introduction



- ⌘ The toxicology of gasoline really is the study of a complex mixture of different chemicals.
- ⌘ The overall assessment is also complicated by the fact that there are thousands of different gasoline formulations in use.
- ⌘ Historical formulations are worth consideration because of their high levels of lead and benzene. Significant environmental lead contamination remains in soils and sediment.
- ⌘ Diesel emissions are primarily differentiated from gasoline by the greater amounts of harmful particulates released in the respirable range.

Gasoline, defined



- ⌘ Gasoline is the generic term for petroleum fuel used mainly for internal combustion engines.
- ⌘ This complex, volatile, and inflammable mix may contain over 500 saturated or unsaturated hydrocarbons having from 3 to 12 carbons.
- ⌘ A common gasoline formulation contains approximately 62% alkanes, 7% alkenes, and 31% aromatics, as well as alcohols, ethers, and additives (Caprino, 1998).

Components of Concern

- ⌘ Benzene; older formulations could have had 5% or greater, current formulations required to be 1% or less.
- ⌘ Oxygenates; added as a requirement of the Clean Air Act, such as methyl tert butyl ether (MTBE), ethyl tert butyl ether (ETBE), tert amyl methyl ether (TAME), and ethanol;
- ⌘ Manganese based compounds (based on neurotoxicity);
- ⌘ Lead, mainly remaining as deposited in soil and sediment.

Gasoline's Physical Properties



- ⌘ **Description** Colorless, mobile liquid with characteristic odor. Mixture of C4 to C12 hydrocarbons. The major components are branched chain paraffins, cycloparaffins, and aromatics. Highly flammable; dangerous fire and explosion risk.
- ⌘ **Specific Gravity** 0.72 to 0.76 at 60/60° F
- ⌘ **Boiling Point** Initial BP 39 ° C, after 10% distilled, BP 60 ° C, after 50% distilled BP 110 ° C, after 90% distilled BP 170 ° C, final BP 204 ° C.
- ⌘ **Solubility** Insoluble in water (apart from the oxygenate components); freely soluble in alcohol, ether, chloroform, and benzene.
- ⌘ **Flash Point** About (-45 ° C)
- ⌘ **IMIS** 1340

Exposure Pathways to Consider



- ⌘ Inhalation,
 - Direct inhalation of gasoline during occupational or direct use, such as customer refueling and home use.
 - Secondary exposure through dispersal of combustion byproducts into air and soil.

⌘ Ingestion, and

⌘ Dermal exposure.

Exposure Pathways to Consider



- ⌘ **Ingestion;** usually accidental, causes inebriation, vomiting, vertigo, fever, drowsiness, confusion, and cyanosis. Aspiration of gasoline causes bronchitis or pneumonia.
- ⌘ **Dermal exposure;** Exposure to the skin can cause slight burning, itching sensations and increased desquamation. Prolonged dermal exposure can cause systemic problems as well.

Health Effects



- ⌘ The range of health effects attributable to gasoline exposure are quite broad, and include both cancer and non-cancer health effects.
- ⌘ Renal and hepatic tumors,
- ⌘ Acute lung disorders, and
- ⌘ Other types of cancer.
- ⌘ Benzene is a well established leukemogen.
- ⌘ Non-cancer health effects also may occur such as mucous membrane irritation and dizziness.

High level exposures



- ⌘ Extremely high level exposures to gasoline vapor may result in dizziness, coma, collapse, and death.
- ⌘ Exposure to high nonlethal levels is usually followed by complete recovery, although cases of permanent brain damage following massive exposure have been reported (Klaxon, et al., 1996).
- ⌘ Atmospheric concentrations of approximately 2000 ppm are not safe to enter even for brief periods of time.

Tailpipe emissions



- ⌘ Important due to the high level of population exposure.
- ⌘ Tailpipe emissions represent the difference between formation of pollutants in the engine combustion process and destruction (through oxidation or reduction) of these pollutants in the exhaust system.
- ⌘ Catalytic converter is extremely important for destruction, yet effectiveness may vary based on multiple factors, including vehicle type and age, condition, gasoline formulation used, etc. (NRC, 1996).

Animal Studies and Lung Cancer



- ⌘ Most animal studies show no or minimal increases in lung cancer with exposure to engine exhaust emissions resulting from regular or unleaded gasoline.
- ⌘ In 1986, Heinrich reported exposing 80 female Wistar rats and 80 Syrian hamsters for 19 hours/day, 5 days a week for up to 24 months to exhaust from a 1.6L engine burning leaded fuel and operated on an urban cycle to produce chamber concentrations of 112 ppm CO or 207 ppm CO.
- ⌘ No increases in lung tumor incidence was observed.

Animal Studies and Lung Cancer, cont.



- ⌘ Roggendorf (1981) performed a similar study using 100 Wistar rats of both sexes for up to 28 months and reported inflammation, pneumonia, and emphysema of the lungs;
- ⌘ Suggested a greater propensity for infections;
- ⌘ however, no increase in lung cancer was found.
- ⌘ The authors did not measure whether this phenomenon was due to an immunosuppressive effect of the exposure.

Diesel studies differ in regard to lung cancer



- ⌘ Diesel gasoline exposure experiments have produced ample evidence of pulmonary carcinogenicity.
- ⌘ Studies have examined the difference between filtered and unfiltered diesel exhaust and found that the carcinogenicity of diesel is dependent on the presence of the particulate matter (Heinrich, et al. 1986).
- ⌘ In most studies of exposure to diesel exhaust, the range of particulates in unfiltered exhaust is usually between 3.5 and 4.2 mg particulates/m³.

Diesel, cont.



- ⌘ Studies of miners indicated a higher propensity of lung cancer which was associated with diesel emissions within the closed space of a mine.
- ⌘ Concern for diesel carcinogenesis arose partly from the observation of adsorption of mutagenic and carcinogenic compounds to diesel soot (Mauderly, 1994).
- ⌘ However, the particulates themselves are highly correlated with toxicity;

Diesel, cont.



- ⌘ Particle size seems to be strongly correlated with the adverse health effects, with PM 2.5 representing a significant cutoff.
- ⌘ Some authors have suggested that inhalation of diesel exhaust might act as a co-carcinogen by increasing the lung tumor response of rats to chemical carcinogens.

Applicability of Diesel Findings to Human health Risk Assessment



- ⌘ The applicability of these findings to human risk assessment is still in question, depending on whether a genotoxic or non-genotoxic mechanism is found.
- ⌘ The particulates from diesel exhaust has been shown to cause chronic inflammation, alveolar epithelial hyperplasia, and multifocal fibrosis (non-genotoxic mechanism).
- ⌘ Not all species exhibited lung tumors when exposed to diesel exhaust. In five different studies Syrian hamsters failed to exhibit any lung tumors after exposure periods up to 24 months.

Epidemiological Evidence



- ⌘ Boffetta et al. (1988) reported the results of the first two years of follow-up in the prospective mortality study of U.S. males conducted by the American Cancer Society.
- ⌘ Occupation, diesel exhaust exposure, and smoking history were obtained interviewing living subjects during enrollment.
- ⌘ They calculated a relative risk for lung cancer among diesel exhaust exposed subjects:
 - ⌘ 1.6 for railroad workers,
 - ⌘ 2.6 for heavy equipment operators, and
 - ⌘ 2.7 for miners who worked in mines where diesel equipment was operated.

Epidemiological Evidence, cont.



- ⌘ Mauderly (1994) summarized the results of fourteen case-control studies conducted between 1976 and 1990, with study periods ranging from 1 to 10 years, and between 376 and 6434 cases in each study.
- ⌘ Notably, all but two of these studies controlled for smoking and tobacco exposure. The relative risk ranges were from less than 1 to 2.4, and 12 of these studies reported a RR of 1.2 or greater.
- ⌘ As elevations of risk in the range of 20 to 50% (RR of 1.2 to 1.5) are at the approximate lower limit of practical detection in epidemiology, it may be that the true human lung cancer risk from diesel exhaust will never be resolved conclusively.

Environmental Concerns



- ⌘ MTBE contamination of groundwater, surface water, and direct Public Water Systems (PWS);
- ⌘ Historic deposition of lead into soils, especially in inner cities; which is highly correlated with blood lead levels;
- ⌘ All refineries, refueling sites (terminals and marine terminals) are 'dirty' to some degree;
- ⌘ Measured in industrial settings by sum of 'total petroleum hydrocarbons' either with or without diesel (TPH, TPH-D);
- ⌘ Good news is bioremediations for hydrocarbons becoming more and more effective.

Conclusion



- ⌘ In regard to the overall carcinogenicity of gasoline, risks cannot yet be identified with precision.
- ⌘ Reasons include the diverse and different constituents of gasoline (leaded, unleaded, oxygenated, reformulated gasolines).
- ⌘ Conflicting evidence in animal studies and lack of human studies (apart from occupational exposure to diesel gasoline), and
- ⌘ Inadequate information on population exposures (Caprino, et al. 1998).

Conclusion



- ☒ In summary, the potential for exposure exists during gasoline use in commerce in both occupational and everyday settings.
- ☒ Exposure to combustion byproducts excreted as air pollutants is also a daily occurrence for a majority of the population.

Research Needs



- ☒ Drawbacks associated with our understanding relate to the fact that gasoline is a complex mixture of potentially harmful constituents.
- ☒ Interactions among components within gasoline, as well as other air and chemical exposures, are not well understood.
- ☒ Additional research may allow refinement in formulation, manufacturing, and distribution methods, raising hope for further reduction in risk to human health.

Research Needs



- ☒ Modern unleaded gasoline presents less risk to human health due to the lower quantities of benzene and lead (Caprino, et al. 1998).
- ☒ The use of oxygenates has lowered harmful air emissions, however, it has raised emissions of other chemicals as well as polluting groundwater, surface water, and public water supplies.
- ☒ Additional study is required to determine specific oxygenates with lowest potential for harm (while still retaining beneficial properties).