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An evaluation of the health risk of using a cerium-based diesel fuel additive in conjunction with a particulate filter

Health Risk of a Cerium Additive to Diesel Fuel

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The fuel efficiency and durability of diesel technology are particularly desirable in the transportation and construction industries. Concerns about the health effects of diesel particulate emissions have led to progressively stricter emission standards, which can be met only through new technologic advances and fuel modifications. The cerium-based fuel additive Eolys*, used in conjunction with a particulate filter, is one of the approaches being considered. However, this additive will result in emissions of cerium compounds and an increase in cerium in the ambient air and soil. HEI developed this report to provide a qualitative assessment of the possible health risk of cerium used as a fuel additive.

A limited number of short-term diesel engine tests have confirmed that cerium (20 to 100 ppm in the fuel) used with the particulate filter substantially decreases both particle mass (> 90%) and number (99%) concentrations in the exhaust. Despite the filter’s high efficiency in trapping particulate matter (PM), however, a small amount of cerium is emitted in the particulate phase of the exhaust. Cerium measured in emissions was found primarily in the oxide form and in particles less than 0.5 µm in diameter. Cerium mass relative to the total particle mass was between 3% and 18% based on two tests using two different types of filters.

Because cerium is present in soil and is being used in some vehicle manufacturing and other industrial processes, a baseline level exists in both ambient air and soil. The most recent measurements in the Los Angeles area report cerium levels of about 0.5 ng/m^3 in fine PM. The average cerium level in the earth’s crust worldwide has been estimated to be 20 to 60 ppm although higher levels have been measured in areas with anthropogenic sources of cerium. The one effort to estimate increases in environmental cerium concentrations from its use as a fuel additive suggested that the expected increase could be several orders of magnitude (in areas with a high volume of diesel traffic) and that cerium concentrations in soil may double over several decades. Specifically, an ambient cerium concentration of 0.6µg/m^3 was estimated along a highway and of 1.25µg/m^3 in a street canyon; concentrations due to deposition of cerium-containing PM in soil were predicted to be 5 to 30 ppm around roads with high traffic by the year 2050. Cerium in the soil may be absorbed into vegetation or may contaminate water, but the extent of such contamination cannot be estimated.

The main routes of exposure of the public to cerium-containing particles are inhalation and ingestion. Inhaled cerium is cleared from the respiratory tract by different pathways and at different rates depending on its solubility in body fluids. The clearance pathways include: mucociliary clearance to the mouth followed by swallowing and excretion via the feces; translocation to the pulmonary and tracheobronchial lymph nodes, and dissolution and absorption into the systemic circulation and distribution to various organs. Based on a 1978 classification by the National Council on Radiation Protection and Measurements

(NCRP), relatively insoluble cerium compounds (such as hydroxides and oxides) are cleared from the lung over a period of years. The more soluble forms (such as chlorides, phosphates, and nitrates used in many of the experimental studies) are cleared over a period of weeks. Insoluble forms are also less likely than soluble forms to reach the circulation and be deposited in other organs, while a proportionally greater amount would be found in the lymph nodes. Modeling of particle (1 μm in diameter) clearance estimated that about 80% of inhaled cerium deposited in the lung would clear through the gastrointestinal tract, about 5% to 15% would translocate to the systemic circulation, and the remainder would translocate to the lymph nodes. Circulating cerium deposits primarily in the liver and bones and then is slowly removed. Other organs that may accumulate some cerium are spleen, heart, and brain.

Cerium taken up by ingestion is excreted in the feces after transiting in the digestive tract. Studies in rodents fed cerium salts (in relatively soluble forms) showed that less than 0.1% of the ingested dose is absorbed by the gastrointestinal tract and distributed to other organs.

Literature on the health effects of cerium is limited. Inhalation of cerium is of more concern than ingestion because cerium is poorly absorbed by the intestine. Primary targets after inhalation of cerium are the lung and the associated lymph nodes; other organs could be affected via clearance through the blood. Case reports of workers occupationally exposed to rare earth metals (including cerium) describe a condition termed *rare earth pneumoconiosis* with pathologic features including interstitial fibrosis, granulomatosis, and bilateral nodular chest x-ray infiltrates. Although the disease sometimes is associated with accumulation of cerium in particles, the role of cerium in this complex disease is unclear relative to other metals or gases to which workers may also have been exposed.

The only animal inhalation study involved exposure of rats to cerium oxide particles substantially larger than those in diesel emission. The exposure concentrations ranged between 5 and 500 mg/m^3 for 13 weeks. Effects observed included lung discoloration, enlargement of lymph nodes and increased lung and spleen weight at all concentrations. In comparison, ambient levels of cerium are estimated to increase above baseline by 1.2 $\mu g/m^3$ in high traffic areas.

Studies of cerium injected systemically have shown that, once in the circulation, cerium can cause liver toxicity with a NOAEL of 1 mg/kg after a single intravenous injection and a LOAEL of 2 mg/kg for effects on liver detoxifying enzymes. Effects on other organs where cerium can accumulate (such as spleen, bones, and kidney) have not been studied.

In the worst case for human inhalation of cerium oxide, the estimated dose to the lung would be about 6 μg (or 0.09 μg/kg); if 5% of this dose is cleared to the blood (based on the NCRP model), the resulting blood dose would be 0.004 μg/kg. Although these dose estimates are based on assumptions, they are about six orders of magnitude lower than those shown to cause systemic effects in rats.

Behavioral effects (such as reduced activity and reduced forelimb grip) were observed after subcutaneous administration (cerium citrate, LOAEL 136 mg/kg) and inhalation exposure (cerium oxide, NOAEL 50 mg/m^3), respectively. These doses are higher than those shown to cause toxicity to the major target organs (liver and lungs).

One single-dose study on the effects of in utero intravenous administration reported reduced weight in newborn mouse pups, with a LOAEL of 80 mg/kg. The potential carcinogenicity of cerium-containing particles has not been studied in conventional rodent bioassays; mutagenicity studies have been negative.

Based on the limited data available, toxicity of cerium oxide appears to be small, and cerium oxide might not be of concern when inhaled or ingested at the low levels that would be encountered in the environment from the use of Eolys (estimated to be in the low μg/m^3 range in the air). The absence of more complete information precludes fully assessing the possible health effects of using cerium as a fuel additive. Ultimately, decisions about the use of the cerium additive, or other metal additives, need to be made in the context of a variety of factors besides information on exposure, rate of clearance from the body, and health effects. Other considerations are the additive's ability to reduce harmful emissions, its persistence in the environment, and the feasibility and cost effectiveness of this technology in comparison with other technologies that can achieve these reductions.

Review Of The Health Risk Of A Cerium Additive to Diesel Fuel

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Proposed Use of Cerium

- With particulate filter in diesel engines
- Alone or in combination with platinum in diesel engines

Goal Of Review

Evaluate and summarize information on:

- Diesel engine emissions
- Increases in cerium ambient levels
- Fate of inhaled cerium particles
- Effects of cerium to target organs

Intent was not of evaluating technology or comparing technology to other technologies

Effect of Cerium Additive on Engine

- Reduces soot combustion temperature
- Facilitates filter regeneration
- Improves life of the filter
- Causes small increases in particulate cerium content

Effect of Cerium + Filter on PM Emissions

- Reduction of PM mass > 90% in most tests
- Reduction of PM number > 99%
- Increase in cerium content in PM 0.02 to 500 nm in size
    - > 99% of cerium retained on filter during baseline operation
    - > 97% of cerium retained on filter during regeneration

Caveats

- Only few tests measured cerium content in emissions
- Effect of regeneration not studied
- Size of particles containing cerium not known

Exposure Information

- Baseline levels of cerium differ and are higher in urban areas
- Increase in the environment due to cerium emissions from additive estimated from following assumptions:
  - Filtration efficiency 92%
  - Cerium fuel content 100 ppm
  - 75% of diesel vehicles in 12 EU countries equipped with system by 2002

Ambient Cerium Levels

Air	**Soil**
• Baseline: 0.5 ng/m^3 • From cerium use (by 2010): – 1.25 µug/m^3 street canyon – 0.6 µg/m^3 highway	• Baseline: 20-60 ppm • From cerium use (by 2050): – 5-30 ppm along EU highways

Conclusions About Ambient Levels

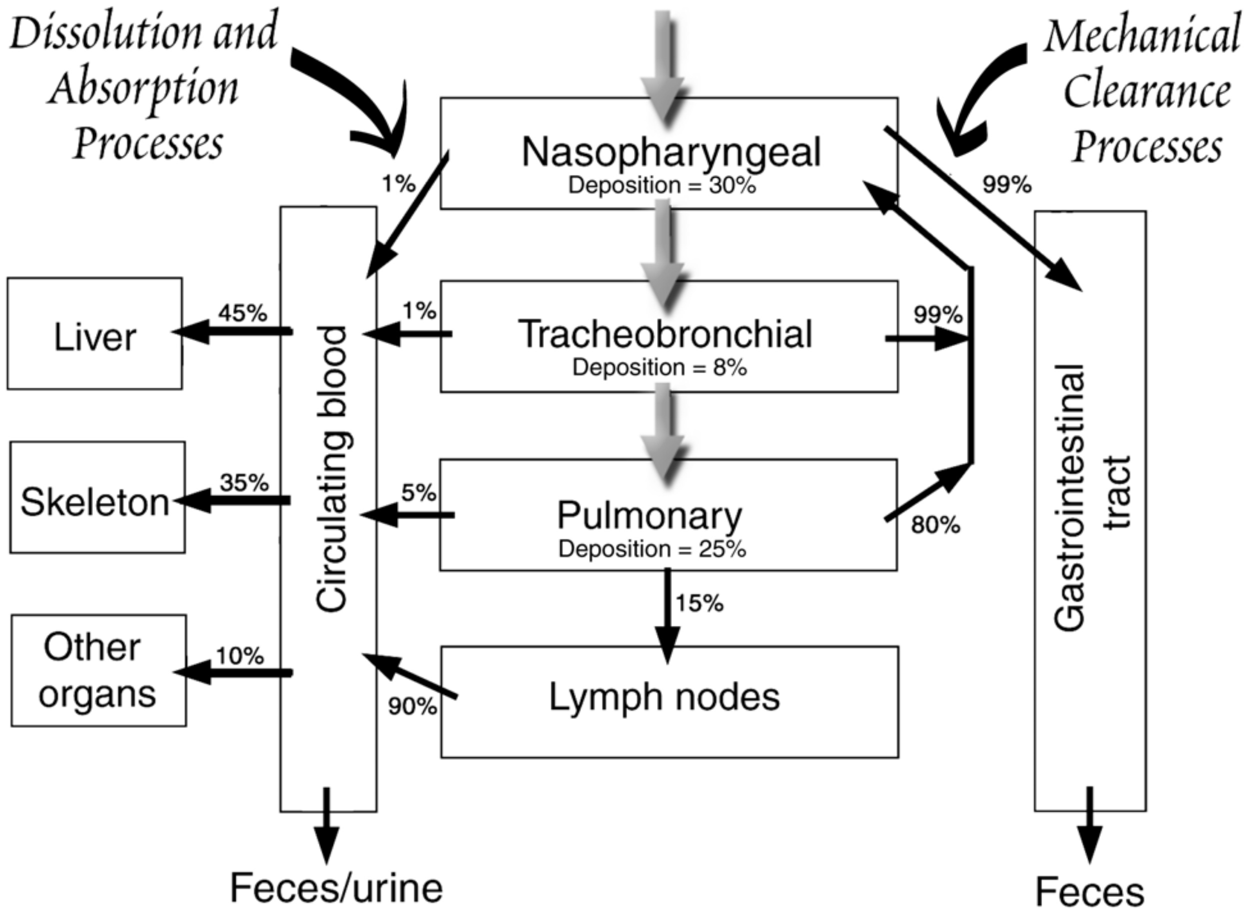
- Air concentrations might increase by several orders of magnitude in high traffic areas
- Soil levels may double over several decades

Fate Of Inhaled Cerium Particles

- Depends on size and chemical form of cerium
  - more soluble forms (nitrates, chlorides) clear faster (weeks) and higher percent of deposited translocate from the lung than less soluble forms (oxides, hydroxides), which clear slower (years)
- Cerium can translocate to lymph nodes and other tissues

Cerium-containing aerosol

(Slow clearance particles with a MMAD of 1 μM)



Target Organs After Cerium Uptake

Inhalation	Ingestion
• **Lung and associated lymph nodes** • Liver, skeleton, spleen, brain, heart	• Digestive tract • Cerium is poorly absorbed by digestive tract

Effects of Cerium to Target Organs

- A 13-week rat inhalation study reported increased lung weight, lymph node hyperplasia and discoloration, increased neutrophil count in blood
- Observations in workers associated exposure to cerium and other metals with rare earth pneumoconiosis, but role of cerium not clear

Effects of Cerium to Target Organs

- Gastritis and enteritis
- Decreased body weight

Systemic Effects of Cerium
(rodents)

- Liver toxicity: effects on enzymes, liver necrosis
- Neurotoxicity: reduced activity, exploration, and grip strength
- Immune sensitization: no effect
- Carcinogenicity: no chronic inhalation studies
- Fetal development: decreased pup body weight

Levels of Cerium Causing Effects

Food consumption	NOAEL: 60 mg/kg RE, 24 wks (ING)	
Lung damage	LOAEL: 5mg/m^3, 13 wks (INH)	
Liver function		NOAEL: 1 mg/kg (IV)
Behavioral effects	NOAEL: 50 mg/m^3, 13 wks (INH)	LOAEL:136 mg/kg (SC)
Fetal development		LOAEL: 80 mg/kg (IV)

Dose Comparisons

Rats (2.2 μm in diameter)	Humans (0.2 μm in diameter)
Lung dose	
LOAEL 5 mg/m^3 = 225 μg/kg/day	1.25 $\mu g/m^3$ = 0.09 μg/kg/day
Blood dose	
NOAEL = 1 mg/kg/day	5% of lung dose = 0.0045 μg/kg/day

Conclusions

- Amount of cerium absorbed is less after ingestion (0.1%) than after inhalation (5-15% of deposited, or about 1-6% of inhaled in the lung) may translocate to blood
- Effects in animals have been observed at doses 4-6 orders of magnitude greater than those estimated from inhalation of cerium in worst-case ambient concentrations

Conclusions (cont.)

- Cerium oxide appears to have little toxicity when inhaled or ingested for some period of time at the low levels caused by the cerium additive
- Data on health effects are not sufficient to fully assess human risk

Data Gaps

- Size of cerium-containing particles
- Effect of engine aging and regeneration on cerium emissions
- Effects of inhaled cerium (emission size)
  - on target organs over time (lung and lymph nodes, liver, heart;
  - cancer;
  - nervous system and developing organism

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