## A Briefing Paper

# Probable Causes of Adverse Effects of Chronic Coal Dust Exposure on Human and Environmental Health

(preliminary analysis)

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**Summary:** Probable agents related to coal dust fall into the five categories summarized in this outline:

#### I. Coal dust as dust

- OSHA classifies coal dust in two categories based on whether the silica content is greater or less than 5%.
- Coal dust particles are thought to be one to ten microns in diameter. In general the smaller the particles the greater the inhalation risk is thought to be
- Dust in the absence of other factors is primarily a human health issue.
- Concern: Is silica content really the measure of potential adverse effects from coal dust?

#### II. Metals in coal dust

- A. Metals designated as hazardous air pollutants
  - Metals of greatest concern in UCMC appear to be lead (6.33 mg/kg (ppm)) and selenium (0.40 mg/kg (ppm)).
  - These metals may be both a human and environmental health concern through either inhalation or ingestion exposures.
  - Concern: How bioavailable are these to the surface of the coal particles?
- B. Metals promoting the formation of reactive oxygen species
  - Iron and possibly copper are the primary concerns. Neither content is available for UCMC.
  - These metals may not have to be bioavailable to be toxic.
  - Pyrite (iron sulfide) content of coal has been correlated with the incidence of CWP.
  - Concern: Neither pyritic sulfur nor iron content have reported for UCMC.

#### III. PAH in coal dust

- A. EPA priority pollutant PAHs
  - These are mostly four- and five-ringed PAH known to cause cancer in both animals and humans, including chrysene, benz(a)anthracene, and benzo(a)pyrene.
  - These are found in all fossil fuels but are more abundant as byproducts of combustion.
  - Concern: PAH levels are not known for UCMC.
- B. Three-ringed PAH

- The concern here is mostly phenanthrene and alkylphenanthrenes.
- This group of PAH are known to cause cardiac edema, various deformities, and death in juvenile fish at levels < 10 ng/g (pbb).</li>
- This group of PAH are not known to be toxic in humans.
- Concern: PAH levels are not known for UCMC.

### **Definitions & abbreviations:**

Bioavailability - the portion of a chemical which an organism encounters and is actually absorbed.

ACGIH - American Conference of Governmental Industrial Hygienists.

CWP - Coal Workers' Pneumoconiosis, sometimes called black lung.

EPA - United States Environmental Protection Agency.

OSHA - United States Occupational Safety and Health Administration.

PAH - polycyclic aromatic hydrocarbons.

UCMC - coal produced by Usibelli Coal Mine.

USGS - United States Geological Survey, now includes both biological and geological divisions.

<u>Discussion:</u> Coal and crude oil have much in common both in terms of geological formation and chemical composition, except that coal has lost most of its highly volatile parts and has been mineralized to become a solid rather than liquid. Like crude oil both physical properties and chemical composition of coal varies extensively from source to source, from coal bed to coal bed. Thus it is critical to have analyzes for the actual source material to accurately estimate the actual risks of exposure. Unfortunately only limited data on UCMC were available to this author at the time of this writing.

In their DDS-77 publication on Alaska Coal Geology, the USGS reported "In the Usibelli Coal Mine the coal is subbituminous with 7,570–9,430 Btu/lb (4,210–5,240 kcal/kg) on an as-received basis, 17.8 percent moisture content, 3.5–13.2 percent ash yield, and 0.1–0.3 sulfur (Barnes, 1967a). The sulfur content of the Usibelli coal ranks among the lowest of any United States coal (Rao and Wolff, 1981; Affolter and others, 1981). Affolter and others (1994) reported that the Usibelli mine coal contains high concentrations of lead and selenium and low concentrations of beryllium and mercury, all of which are designated as hazardous air pollutants (HAPs) by the 1990 Clean Air Act Amendment."

As part of its RFP on Coal Gasification (01/20/08) the Fairbanks Economic Development Corporation reported partial analyzes of UCMC, as provided to Golden

Valley Electric Association and analyzed by Hazen Research, Inc. The following Table gives the means and ranges of selected data for coal as received during the first three quarters of 2007.

Property (proximate)	Mean	Range
Moisture (%) (as received)	28.27	26.68-29.17
Moisture (%) (air dried)	8.47	2.10-14.98
Moisture removed by air drying (%)	69	44-91
Ash (%)	13.84	12.72-15.16
Volatile (%)	31.10	30.80-31.30
Fixed Carbon	26.79	26.58-26.98
Sulfur (%)	0.20	0.17-0.23
Cadmium (mg/kg)	0.22	<0.1-0.38
Lead (mg/kg)	6.33	3.0-10.0
Mercury (mg/kg)	0.08	0.04-0.14
Selenium (mg/kg)	0.40	0.22-0.57

There are three major characteristics which dictate much of the toxicity from exposure to coal dust: 1) The characteristics of the dust itself. 2) The metals available. 3) The PAH available. OSHA reports that exposure to coal dust can occur through inhalation, ingestion and eye contact.

Both OSHA and ACGIH characterize coal dust containing less than 5% silica as more toxic than that containing more than 5% silica. The latter is considered to have a toxicity similar to quartz. The University of Minnesota and U.S. Bureau of Mines report size distributions of coal dust particles of 1-10 microns in the haulage entries of three coal mines. There is general consensus that the smaller the particles the greater the inhalation risk is. Particles larger than 300 microns are not generally considered an inhalation hazard.

The OSHA *Health Hazard Information* states, in part: 1. Coal dust is a tumorigenic agent in experimental animals. Coal dusts were shown to be equivocal tumorigenic agents associated with lymphomas and, at the higher dose, adrenal cortex tumors in rats exposed to either 6.6 or 14.9 mg per cubic meter for 6 hours/day intermittently for 86 weeks. 2. Coal dust causes pneumoconiosis, bronchitis, and emphysema in exposed workers. Coal dust causes CWP.

There is not a consensus regarding the bioavailability of metals and "volatile" organic compounds found within samples of coal. Much of the uncertainty seems to arise from the fact that the accessibility of potential toxic substances to the biota varies as much as the nature of the coal itself. A hard dry anthracite coal probably does not provide access to any thing except the surface of the coal particles themselves. In contrast a soft wet subbituminous coal, such as that shipped through Seward, AK, probably provides fairly ready movement of potential toxic substances from the interior to the

surface of coal particles to be absorbed by various organisms. The fact that nearly two thirds of the water in the coal is transported to the surface during air drying proves the accessability of this water. Even if this water can not transport potential toxic substances to the surface, the very small size of the airborne dust particles creates a large surface area for the very small mass of individual dust particle.

The metals found within coal fall into two categories: Those which are directly toxic themselves, and those which are less toxic, or nontoxic, themselves but which are indirectly toxic by increasing the formation of very reactive oxygen species which are highly toxic. The first of these are the metals designated as hazardous air pollutants (HAPs) by the 1990 Clean Air Act Amendment. Their adverse health effects are well documented elsewhere.

Iron, and to a lesser extent copper, on the surface of particles are well known to enhance the formation of highly reactive oxygen species. The best known of these forms of oxygen are ozone and hydrogen peroxide, however the most dangerous is superoxide. All of these can kill tissue. Hydrogen peroxide and superoxide are so dangerous within cells that all organisms have special enzyme systems to help break them down rapidly. USGS and NYU School of medicine have shown a correlation between bioavailable iron, pyrite, and CWP rates. It is possible that these metals do not have to be bioavailable, and that bioavailable iron only appears important because it also correlates with pyrite (iron sulfide) content. Centers for Disease Control and Prevention (CDC) have also shown that coal dust in the lungs causes oxidative damage which can be measured by increased macrophage levels.

Compared to crude oil, most coals seem to have relatively low total PAH levels. The PAH content of UCMC is not available. However, Neff reports total PAH levels for coal as ~20 mg/kg and ~526 mg/kg in two separate publications. Both the amount and composition of PAH probably vary substantially with coal type and source.

All fossil fuels contain both aliphatic and aromatic molecules. Aliphatic hydrocarbons are long strings of carbon atoms usually connected to two other carbons and two hydrogen atoms. These are long stringy molecules with occasional branches. In the oil industry they are often called the "saturates" (because they contain few if any double bonds). Aromatic compounds are characterized by rings of six carbon atoms each attached to another carbon or a single hydrogen. The most common single ringed aromatic compounds are benzene, toluene, ethylbenzene, and xylene. Together these compounds are simply referred to as BTEX. Together BTEX and the lower boiling saturates make the fuel which powers our cars, boats and planes. They also contribute most of the acute toxicity of crude oil. This acute narcosis is not found in exposure to coal.

Polycyclic Aromatic Hydrocarbons are those formed by fusing two or more aromatic rings. These are flat molecules which in ball and stick models look a lot like chicken wire. If they do not have any side-chains attached to the rings, they probably were formed during poorly controlled combustion processes. As a class we call these pyrogenic PAH. In contrast the majority of PAH in oil and coal have short aliphatic sidechains. As a class these are the petrogenic PAH.

The four- and five-ringed pyrogenic PAH have been well studied are well known to cause cancer in both animals and humans. Many are listed among U.S. EPA's Priority Pollutant PAH. These are found at low levels in both crude oil and coal. Burning of tobacco, wood, gasoline, and fuel oil produces even more of these PAH.

At the time of the Exxon Valdez oil spill it was assumed that once crude oil had weathered to a solid form and no longer produced a sheen then the PAH it contained would no longer be bioavailable. By the mid-1990s it was apparent that injured herring and pink salmon populations were not recovering. NOAA Fisheries scientists from the Auke Bay Laboratory took oiled rock from intertidal spawning areas percolate water across these rocks and into egg trays in the hatchery. The only oil on these rocks was in varnish-like splotches. There was no liquid oil or even sheen from the rocks and the rocks did not come into contact with the eggs or emergent fry.

The results were completely unexpected at the time. The hatch rates for both herring and pink salmon were far lower than the controls. The fry that did survive had unusually high numbers of spinal deformities and skin lesions. When a cohort of seemingly health pink salmon fry were selected and released they returned two years later in much lower numbers than the control group. Much more recently, several research groups, including the NOAA Fisheries-NWFC-EDC group in Seattle led by Incadrona, and the one at Queens University in Canada led by Hodson, have shown that this toxicity in fish seems to start with an early larval stage cardiac edema which is caused by a fraction containing mainly three-ringed PAH. Prior to these studies toxicologists had assumed that the three-ringed PAH were relatively safe. They do not cause cancer, and they may still be safe in humans, but we know they can cause substantial adverse effects in the environment. We also know that these adverse effects result from 1000-time lower levels of PAH than were previously thought to be of concern. Three-ringed PAH are more abundant in both coal and crude oil than the cancer causing four- and five-ringed PAH. Neff's reports suggest that three-ringed PAH may be present in coal dust in the range of 100-200 mg/kg. Hodson reports cardiac edema in fish fry at 10 ng/g (0.010 mg/kg) three-ringed PAH. We will not know the actual PAH levels in the coal shipped through Seward until someone provides it.

Unlike the Precautionary Principle which counsels that we should not assume something is without adverse effects (safe) until we have proven it to be so, United States environmental law generally assumes a substance or process is safe until it is proven otherwise. There are enough questions regarding the safety of UCMC that we really should be seeking ways to minimize exposure to its dust.

About the author: Dr. French holds a PhD in Biological Chemistry from the University of Michigan and has over 30 years experience pursuing various aspects of environmental toxicology. He is a retired Professor from the UAF-School of Fisheries & Ocean Sciences. He is a long time member of the American Chemical Society, and the Society of Environmental Toxicology and Chemistry. He is a 28 year resident of Alaska and has lived in Seward, AK for the last ten years where he sits on the Seward Historic Preservation Commission, and represents the City of Seward on the Boards of Directors of Prince William Sound Regional Citizens' Advisory Council and Cook Inlet Aquaculture Association.