NO_x, Fine Particle and Toxic Metal Emissions from the Combustion of Sewage Sludge/Coal Mixtures: A Systematic Assessment.

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ABSTRACT

This research project focuses on pollutants from the combustion of mixtures of dried municipal sewage sludge (MSS) and coal. The objective is to determine the relationship between 1) fraction sludge in the sludge/coal mixture, and 2) combustion conditions on a) NOx concentrations in the exhaust, b) the size segregated fine and ultra-fine particle composition in the exhaust, and c) the partitioning of toxic metals between vapor and condenses phases, within the process. The proposed study will be conducted in concert with an existing ongoing research on toxic metal partitioning mechanisms for very well characterized pulverized coals alone. Both high NOx and low NOx combustion conditions will be investigated (unstaged and staged combustion). Tradeoffs between CO_2 control, NO_x control, and inorganic fine particle and toxic metal emissions will be determined.

Previous research has yielded data on trace metal partitioning for MSS by itself, with natural gas assist, for coal plus MSS combustion together, and for coal alone. We have re-evaluated the inhalation health effects of ash aerosol from combustion of MSS both by itself and also together with coal. We have concluded that ash from the co-combustion of MSS and coal is very much worse from an inhalation health point of view, than ash from either MSS by itself or coal by itself. The reason is that ZnO is not the "bad actor" as had been suspected before, but the culprit is, rather, sulfated Zn. The MSS supplies the Zn and the coal supplies the sulfur, and so it is the *combination* of coal and MSS that makes that process environmentally bad. If MSS is to be burned, it should be burned without coal, in the absence of sulfur.

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INTRODUCTION

Municipal sewage sludge (MSS) is formed during wastewater treatment. Sludge is the largest by-product of wastewater treating plants and it's processing and disposal represent one of the most environmentally challenging aspects of the wastewater treating process [1]. As discharged, the sludge is contained in a dilute (0.25 to 12 wt%) aqueous suspension and contains hazardous compounds. A description of how sludge is generated can be found in [1].

One of the options currently being considered to improve the treatment of this sludge is a process involving heat treatment (to render the sludge biologically inactive) followed by dewatering, drying, pulverizing, and combustion [2]. The advantages of this combustion process are: a large reduction in disposal volume, thermal destruction of toxic organics, and recovery of the energy value of the carbon sources in the sludge [1]. However, there are a number of potential disadvantages including NOx formation (due to the high nitrogen content of most MSS), handling of the raw material (due to the toxicity of metals and dioxins in the feedstock), possible boiler slagging and fouling problems (due to the high inorganic content of the feedstock), and the release of toxic trace elements into the environment [3].

A study was conducted to investigate the partitioning characteristics of selected trace elements during the combustion of a dried, treated (Swiss Combi Process), and pulverized MSS at commercially relevant temperatures (i.e. combustion zone and post-combustion zone temperatures similar to those expected in commercial combustors. The objectives of this study were:

- to quantify the partitioning of selected major inorganic (silicon, iron, calcium, and aluminum) and trace elements (zinc, arsenic, selenium, and antimony) during combustion of MSS in a natural gas flame

- to quantify the partitioning of selected major inorganic (silicon, iron, calcium, and aluminum) and trace elements (zinc, arsenic, selenium, and antimony) during co-combustion of MSS with a well-characterized bituminous coal (Ohio 5/6/7 blend)

- to identify mechanisms where possible for trace element vapor-to-solid phase partitioning

- to explore synergistic effects for co-combustion of MSS with coal

This quarterly report is concerned with the last topic, namely the synergistic effects of co-combustion of MSS and coal. The specific issue addressed are synergistic effects of particulate matter, PM, emitted from the co-combustion of MSS and pulverized coal. Airborne particulate matter (PM) is an important environmental issue due to its association with acute respiratory distress in humans. Although the specific particle characteristics that cause lung damage remain unidentified, particle size, aerosol acidity, water-soluble transition metals, polyaromatic hydrocarbons, and particle composition have all been identified as possible contributors to respiratory distress. All of the above mentioned characteristics are contained in PM generated from the combustion of fuels, including coal or natural gas/municipal sewage (MSS).

It has been hypothesized that PM might be a source of bioavailable transition metals and inorganic compounds (Costa and Dreher, 1997; Dreher et al., 1997; Adamson et al., 2000). At the cellular level, it has been found that transition metals from PM induce a response by the release of inflammatory cytokines, acellular generation of hydroxyl radicals, and oxidative DNA damage (Carter et al. 1997; Maanen et al., 1999, Broeckaert et al., 1999).

Atmospheric PM is composed of a complex mixture of chemicals whose sources are anthropogenic (i.e. combustion) and natural (i.e. volcanoes, forest fires, oceans, and dust storms). However, not all atmospheric PM has the same chemical composition. Size segregated particle chemical composition is an important variable. Davison et al. (1974) have reported that toxic elements such as Pb, Se, Sb, Cd, Ni, V, Sn, and Zn in urban aerosols have equivalent mass diameters of the order of 1 μm, whereas, Fe, Al, and Si are more commonly found on particles that have a diameter greater than 2.5 μm (Rahn et al., 1971).

In a previously conducted study, the health effects associated from the inhalation of re-suspended coal and coal/MSS ash particles were addressed (Fernandez et al., 2001). From this study, it was concluded that coal/MSS ash particles led to a large increase in lung permeability than coal ash particles. Therefore from an health effects engineering point of view this paper addresses the following issues: 1) what are the relative severities of health effects of inhalation of ash aerosols from combustion of a) coal; b) coal plus MSS, c) MSS assisted by natural gas? 2) what are the "bad actors" (specific elements or combinations of elements in the particles) that cause lung injury, and what are possible mechanisms? 3) can lung injury from inhalation of the identified "bad actors" be diminished through engineering changes in the combustion process, specifically through addition of sorbents in the post flame?

As a corollary to responses to these questions, it was necessary to identify differences in the size segregated particle distribution, particle acid digestion analysis, and leachate analysis from ultra-pure water. From a health effects point of view, possible mechanisms of particle precipitated lung injury are inferred through time resolved health effects from sequences of 1 hour exposures per day at three time intervals, 3, 12, and 24 days of ash exposure.

MATERIALS AND METHODS

Particulate Source and Reagents. Gottelbörn coal ash samples were provided by the Institute for Process Engineering and Power Plant Technology at the University of Stuttgart. Combustion of coal was performed in a semi-industrial scale, 500 kW downfired pulverized fuel combustor having a 0.75 m diameter and ~7 m length. The first 4 m of the combustor are refractory lined while the remaining section is water cooled to simulate an industrial boiler section. The flue gas containing ash particles that were generated by the combustor passed through a bottoms hopper, air preheater (T=550 K), cyclone (T=500 K), and bag filter (T=480 K), respectively. Ash particles can be collected at the four previously listed locations. The ash particles used in the experiment as described in this paper were gathered at the surface of a baghouse filter, which exited the cyclone, and were reported to have a nominal mean diameter of 3.5 μm. Cenni et al., [1998] give a complete description of experimental procedure for the fuel combustion of coal and coal/MSS (municipal sewage sludge).

MSS assisted by natural gas were combusted in an 18 kW downfired pulverized fuel combustor which had a 0.15 m diameter and ~6 m length. This has been described elsewhere (Davis and Wendt, 2000). The first 1.22 m of the combustor is refractory lined while the remaining sections are made of pre-fabricated sections of Zicar. The furnace was designed to simulate the time and temperature histories and complex particle interactions of a commercial scale combustor. The feed rates of natural gas and MSS were 1.12 m^3/hr and 1.36 Kg/hr, respectively. Tables 1 and 2 provide some chemical and elemental characteristics of the solid fuels used in this study.

Particulate Re-suspension/Characterization. A solid particle re-suspension system, which has been previously utilized to conduct similar toxicological studies, was employed (Fernandez et al. 2001). The ash was re-suspended by the RBG-1000 and entrained into an air stream. The RBG-1000 was set at a pre-pressure of 2.5 bars (2.5 m^3/hr flow rate) and a plunger travel rate of 1 mm/hr. The entrained aerosols were diluted to yield breathable air/particulate stream at a concentration of averaged 1000 $\mu g/m^3$ for direct inhalation. A Berner low-pressure impactor (Hillamo and Kauppinen, 1991) (LPI) (11 stages with aerodynamic 50 % cut-off diameters ranging from 15.7 to 0.0324 μm) was used to size segregate the re-suspended ash samples. Prior to particulate size segregation polycarbonate substrates were sprayed with a mixture of Apiezon-L grease and hexane to prevent bounce off and were used as impaction surfaces (Moss 1986). The sprayed substrates were then placed in an oven at 75 ºC to drive off hexane for 30 minutes prior to particle collection. Each of the polycarbonate substrates was weighted before and after particulate collection and then acid digested in $3HF{:}1HCl{:}1HNO_3$. The digested particles were then analyzed by graphite furnace atomic absorption spectroscopy (Perkin Elmer 4110 ZL). An additional set of size segregated ash particles was utilized for water leaching studies. Each of the size segregated ash particles was deposited in plastic vials with 10 ml of ultrapure water (UPW). Prior to depositing the ash particles, the plastic vials were cleaned with a diluted solution of nitric acid for more than 24 hours prior to use. The vials, that contained the mixture of size segregated particles and UPW, were fixed on a Roto-Torque apparatus (Cole-Parmer) fixed speed rotator and allowed to rotate for 24 hrs in a dark environment. For the detection of sulfur leached chemical species, an ion chromatography apparatus (Dionex DX-500) was used. Additionally, 0.2 grams of coal or MSS ash particles were placed in a plastic vial with 10 ml of UPW. The supernatants from the mixtures were tested for changes in pH value.

Animals. Seventy-two pathogen free mice, C57BL/6NHsd, were randomly divided into groups of eight (30.0±4.3 g). Of the Seventy-two mice, fifty-six (seven groups) were selected to be exposed to coal or MSS re-suspended ash particles. The mice were housed 4 per cage with a 12-hr light/12-hr dark cycle at the Arizona Health Science Center animal facility (approved by the American Association for the Accreditation of Laboratory Animal Care) and fed a standard mice chow diet and tap water.

Particulate Exposure. The re-suspended particulates were drawn through a 24-port nose-only exposure chamber (IN-TOX, Albuquerque, NM) using a constant vacuum (~12 l/min). The nose-only exposure system was utilized in order to minimize ingestion of particulate matter during grooming and to more closely simulate occupational exposure. Four groups of the experimental mice were exposed to re-suspended coal ash particles for 1 hour/day for 1, 3, 12, and 24 consecutive days. Furthermore, three groups of the experimental mice were exposed to re-suspended MSS ash particles for 1 hour/day for 3, 12, and 24 days. The control set of mice was exposed to ambient air only. All of the mice exposed to aerosolized particulate were exposed to a concentration of ~1000 μg of ash particles per cubic meter.

Pulmonary function and respiratory permeability. To exclude transient changes immediately following particulate exposure, analyses were performed 24 to 30 hr after the final exposure. To ensure a deep state of anesthesia for the entire experimental period, the mice were anesthetized with an intramuscular injection mixture of ketamine HCL (80 mg/Kg; Parke-Davis, Morris Plains, NJ), xyline (10 mg/Kg; Mobay, Shawnee, KS), and acepromazine maleate (3 mg/Kg; Fermenta, Kansas City, MO). Tracheostomy was performed with the insertion of a Teflon intravenous catheter (20 gauge; Critikon, Tampa Bay, FL) serving as an endotracheal tube (Kent Scientific, Litchfield, CT) and given an intraperitoneal injection of gallamine triethiodide (8 mg/kg) to suppress spontaneous breathing. Airflow was measured with a pneumotachograph (Fleisch Instrumentation Associates) that was coupled to a differential pressure transducer (Validyne, Northridge, CA). Airflow and pressure signals were used to measure dynamic compliance. Pulmonary resistance was measured with a modified PEDS-LAB (Medical Associated Services, Hatfield, PA) pulmonary function system by the method of Rodarte (Rodarte and Rehder, 1986). The mechanical pulmonary functions were recorded and normalized to the weight of each animal. Lung permeability was measured with a 100 μl endotracheal instillation of a 100 μCi ^{99m}technitium labeled diethylenetriamine pentaacetate (^{99m}Tc-DTPA, 492 amu, physical half-life of 6.02 hr) bolus, followed by five tidal volume breaths of ambient air to disperse the ^{99m}Tc-DTPA. Lung permeability was then determined by monitoring the pulmonary clearance of ^{99m}Tc-DTPA over ten minutes using a Ludlum Model 2000 gamma counter (Ludlum, Sweetwater, TX).

RESULTS

Characteristics of Re-suspended Ash Particles

The *in-vivo* ash particle inhalation studies were conducted by utilizing a particle re-suspension system, (Fernandez et al., 2001). Aerosolized ash particulate concentrations on the order of 1000 μg/m^3 were achieved in these exposures. A concentration of 1000 μg/m^3 is about six and a half times the old EPA atmospheric 24 hour averaged, PM$_{10}$ particulate standard of 150 μg/m^3 (US EPA, 1990). However, the mice were only exposed to ash particulate for 1 hour per day.
The particles size distributions (PSD's) for the re-suspended ashes are illustrated in Figure 1. The particle size distributions are plotted in differential form. Therefore, the area under the curve between two particle sizes gives the corresponding mass fraction.

The particle size distribution for both ash types follows a similar particle distribution pattern. The PSD's for coal ash appeared to have three distinct modes (Linak et al., 2002). The PSD's for MSS ash appeared to have two modes with a very large mode center at ~2.5 μm. The three modes for the coal ash are centered at ~2.5 μm, ~0.25 μm, and ~0.025 μm, from large to small, respectively. The mean particle aerodynamic diameter for both ash particles is approximately 3.5 μm, however, MSS ash has the larger mode. In addition, the coal ash shows that the re-suspension of this ash particulate contains more particles in the fine mode, which is important for toxicological studies. Morrow (1964) and Hatch and Gross (1964) have demonstrated that aerosolized particles are deposited in different regions of the lung and their deposition depends on their aerodynamic size. The particle's deposition behavior is graphically illustrated by Boubel et al. (1994).

An important characteristic in ash particulate analysis is the pH of its supernatant. The pH value of the supernatant can be central in determining which elements will leach into solution (Brunori et al., 2001), therefore a small mass fraction of the ash particle may become bioavailable (Costa and Dreher, 1997), (Adamson et al., 1999), and (Dye et al., 1999). The pH value from the coal and MSS supernatant had a value of ~4.3 and 12.3, respectively. From this test, it is clearly illustrated that two set of ash particles have different chemical properties.

Numerous *in-vivo* and *in-vitro* studies have indicated that iron (Fe) may be involved in lung injury (Dreher et al., 1997), (Pritchard 1996), (Gavett et al., 1997), (Smith et al., 2000), (Guilianelli et al., 1993), and (Smith and Aust, 1997). However, an *in-vivo* study conducted by (Peters et al., 2000), in which animals exposed to the exhaust of an engine which combusted doped fuel with ferrocene, demonstrated no significant changes in health effects. Ferrocene is an organo-metalic compound that contains Fe.

Zinc (Zn) is also of particular toxicological interest. During the combustion of coal, many elements found in the coal particles are liberated into the gas phase. Due to their chemical properties and changes in temperature of the flue gas, layering of metals occurs during the evolving ash particles and some metals have the tendency to concentrate in certain particle size fractions. Zn is one elements commonly found in the submicrometer size fraction and in the surface of atmospheric fly ash. (Davison et al., 1974), (Linton et al., 1976), (Kaakinen et al., 1975) and (Amdur et al., 1986). Furthermore, (Amdur and Chen, 1989), (Chen et al., 1990), (Adamson et al., 2000), (Costa and Dreher, 1997), and (Fernandez et al., 2001) have elucidated that Zn may play a significant role in particle toxicity.

As it has been indicated, not all combustion generated ash particles are created equal. Therefore, a complete break down or acid digestion of the ash particles reveals their main elemental differences. The particle size segregated supernatant of the acid digestion was analyzed for the following elements: Al, As, Ca, Co, Cu, Fe, Mg, Na, Pb, Se, Si, V, and Zn. Analysis of the collected data revealed that the re-suspended coal ash particles contained a significant amount of Fe, Al, and Si. However, the results of Fe and Zn are of great interest and their respective distributions are demonstrated in Figure 2. As it is shown in this figure, Zn is more concentrated in the submicron region of the ash particles; while Fe is more apparent in the larger size of the particle size distribution.

The same, as to the coal ash particles, elemental analysis was carried out for the re-suspended MSS ash particles, with the exception of two elements Ca and Si. The results of the analysis indicated that Al, Fe, and Zn were the predominant elements found in these ash particles. Figure 3 displays the elemental distribution of Fe and Zn. If the elemental distribution of Fe and Zn are compared for the two re-suspended ash particles, it becomes apparent that in the MSS ash particles contained relatively the same amounts of Zn and Fe in the fine particle region. Furthermore, Fe was more concentrated in the fine ash particles of MSS then coal, but Zn was still a major constituent in this particle size range. Therefore, there is a distinct difference in chemical composition between the two ash particles.

From the UPW leaching analysis of the MSS ash particles, three chemical elemental components were detected: V, Zn, and Sulfur species. Sulfur species were found to be in greater concentration of the three elemental components by two orders of magnitude throughout the PSD. However, its greatest concentration was located in particles with a diameter greater than 1 μm. Zn and V were found in a lesser amount; but there was a difference between the two of them. V followed a similar trend as sulfur. However, Zn was more concentrated in fine particulate matter; which appears to agree with results obtained from (Davison et al., 1974), (Kaakinen et al., 1975), (Amdur et al., 1986), and (Linton et al., 1976). Analysis of the supernatant for iron, lead, and copper was also completed, however, these elements were not detected. Furthermore, no coal ash particles solubility in UPW has been determined.

Response to Inhalation of Re-suspended Ash Particles

(Hays et al., 1995) has previously determined that increased clearance of ^{99m}Tc-DTPA correlates with increased pathological injury. Furthermore, (Witten et al., 1985) has demonstrated that pulmonary clearance of ^{99m}Tc-DTPA is an extremely sensitive marker of lung injury. Increased lung permeability is an important parameter when attempting to understand the effects of various inhaled particulates on the respiratory system by allowing greater access of the toxicant to the lung interstitium and pulmonary circulation. For discussion purposes only, we shall, for the sake of simplicity and brevity, designate particles that cause significant positive changes in lung permeability, as being “harmful”, that is, likely to cause short term lung injury, in the short term. Those that cause negative or small changes in lung permeability, which will be designated, for the sake of brevity, as “relatively benign”. It must be emphasized, however, that these “relatively benign” particles can still cause inflammation, release of proteins, and long-term lung injury, and thus should not be given a clean bill of health.

Coal ash only. Figure 4 shows lung permeability results for exposure to coal ash alone. Mice that were exposed to coal ash particles for only one day, displayed a decrease in ^{99m}Tc-DTPA infiltration with a more significant change in the 3-day exposure. Mice that were exposed to ash particles for 12 days showed an adaptation or recovery to the ash particles and the permeability of DTPA was close to the control subjects. However, the mice that were exposed for 24 days started to display an increase in lung permeability. Therefore, a long-term exposure to the coal ash particles may start to weaken or reduce the capacity of the lung tissue to recover. It will be apparent later that this type of behavior is typical of particles that might be considered “relatively benign”, in that although there is initially some inflammation, causing a decrease in permeability, it is followed by a recovery to normal values after 24 days.

MSS ash only. Figure 5 shows similar data for exposure to ash from MSS assisted by natural gas. Mice that were exposed to re-suspended MSS ash particles displayed a similar lung permeability trend as the coal ash exposure. There was a significant decrease in lung permeability for mice that were exposed to 3 or 12 days, but mice exposed for 24 days appeared to start in a recovering phase. However, the lung permeability effect is somewhat different than for the coal ash particles.

Amdur and Chen, (1989) demonstrated that guinea pigs exposed to acidic aerosols had significant change in pulmonary functions (total lung capacity and vital capacity) response. In this study, the pulmonary functions (pulmonary resistance, compliance, and dynamic compliance) do not appear to be drastically changed. Of the three measured parameters, the noticeable parameter that changes with time is compliance. However, this parameter does not clearly show an obvious trend corresponding to lung injury. Therefore, it is difficult to use these parameters to determine the extent of lung injury.

A most important result is that MSS ash, by itself (or with combustion assisted by gas, as in this case) is “relatively benign”, or at least not noticeably less benign than coal ash by itself.

Coal+MSS ash. In comparison to the above, Figure 6 shows the previously published data of Fernandez (2001) in which the lung permeability changes, after 24 days, caused by re-suspended ash from a mixture of coal and MSS. The coal data for 24 days of one-hour exposure per day are roughly consistent with the 24-day data from Figure 4, after recovery has brought the permeability back to its original value. In contrast to both the coal alone data, and the MSS alone data, the coal+MSS mixture data show a very significant effect on lung injury. This suggests that it might be more environmentally benign to burn either coal or MSS by themselves, but not mixed in combination. When taken with the elemental data on Figures 2 and 3, the inference might be made that zinc plus some element present in coal (possibly sulfur) is the bad actor, but not necessarily zinc by itself. A more precise examination of the mechanisms behind this required special experiments involving combustion of doped distillate oil plus zinc and sulfur, as described below.

Doped distillate oil: zinc only and zinc plus sulfur . In order to generate zinc particles, doped distilled fuel oil was combusted in a cylindrical downflow reactor. The doping agents were zinc naphthenate and zinc naphthenate plus thiophene, in order to achieve a 100 ppm of both zinc and sulfur in the reactor’s flue gas. Particles were collected from a cyclone train (In-Tox, Albuquerque; NM) and a custom made filter system. The cyclone train consisted of two cyclones. The first cyclone was designed to remove particles larger then 10 μm in diameter while cyclone two was designed to remove particles larger than 2 μm. The custom made filter system was capable of collecting particles larger than 0.5 μm at 99% efficiency. The particles were collected on the surface of the filter. After several hours of running one type of experimental condition, the collected particles were removed and stored in a desiccated container until further use. Equilibrium calculations suggest that the particles collected would consist of ZnO without sulfur present, and of $ZnSO_4$ with sulfur present.

Figure 7 shows the PSD’s sampled from the furnace for particles from the Zn and Zn+S doped runs. There is one nucleation mode between 0.1 μm and 1μm, indicating that vaporization has occurred. In view of the nanosized aspect of this distribution it is unlikely, however, that the re-suspended particles that were inhaled by the mice had the same PSD’s.

Figure 8 presents the biological response to inhalation of these re-suspended particles. It displays results of the lung permeability k-value of mice exposed to re-suspended zinc oxide (ZnO) and zinc sulfate ($ZnSO_4$) ash particulate at various exposure time intervals, respectively. Even though both of these ash particles contained zinc, the physiological responses were quite different. In the case of ZnO particles, the k-value of the 3-day exposure mice set increased by a small amount but not statistically significant. The 24-day exposure mice set exhibited a significant decrease in lung permeability. The upper panel value in Figure 8 for the 12 day exposure is missing because of the expiration of experimental subjects while surgery was being performed.

The sulfated zinc particles, however, showed a different result on the lower panel of Figure 8. Any mice set exposed to these particles displayed an increase in lung permeability. A statistically significant change occurred for mice that were exposed for 12 days or more. Furthermore, the lung permeability increased as the exposure time, number of exposure days, increased. An increase in lung permeability can possibly pose a greater risk of allowing toxicants to come into contact with other organs. These data, with sulfur present, are consistent with the coal plus MSS data on Figure 6.

Mice that were exposed to ZnO and $ZnSO_4$ particles had an obvious physical appearance that was different then control mice. The nasal septum and paws were bright red; the nasal septum redness was also observed with mice that were exposed to re-suspended coal/RDF ash particles. In addition to the outside physical appearance, other observations that were very obvious to observed was the increase in difficulty capturing pulmonary functions, the brownish lung color (some exposed mice had lung with patchy white spots) in instead of the healthy pink color of the lung and hypersensitivity to bleeding. From transmission electron microscopy, it was observed that indeed a change had occurred to mice that were exposed to zinc oxide particles. Cells in the alveolar region displayed an obvious increase in lamellar bodies and connective tissue, which would confirm the observed decrease in lung permeability. Therefore, these (essentially pure) ZnO particles cannot be considered "benign", even though they may be so defined here from a lung permeability point of view. Sulfur addition had a very great effect on the cell count profile of the BALF. Whereas, the cell count decreased over time with the Zn only case, it actually significantly increased for the Zn plus sulfur case. There are possible biological reasons for this (Fernandez, 2002), but from an health effects engineering point of the important conclusion is that particle speciation is critical, as was apparent also from the lung permeability data (Figure 8).

<u>Health effects engineering to diminish lung injury from inhaled particles.</u> Figures 9 and 10 show the effects of kaolinite sorbent addition to the total PSD (Figure 9) and the elemental PSD (Figure 10). Sorbent was added above the dewpoint of the zinc vapor. Using the method of aerosol fractionation 30% of the Zn was reactively captured by the sorbent in the absence of sulfur and 40% was captured with sulfur present. Particles in the cyclone catch (nominally > ~2μm) can be assumed to contain only the sequestered zinc, and these were the particles for which their inhalation health effects were examined. Figure 11 shows that for both sorption cases in the presence and absence of sulfur, the approximate $1/d_p$ dependencies of Zn concentration to particle size, in the larger particle size range, suggest external surface or pore diffusion controlled reaction of the Zn on the kaolinite (in contrast to film diffusion controlled physical condensation). These larger particles containing sequestered Zn on kaolinite were re-suspended and applied to the mice in the IN-TOX mouse chamber. Lung permeability results are shown on Figure 12, and show the previously observed "relatively benign" behavior over time, similar to coal ash alone, and to other particulates, which did not cause a permeability, increase.

Clearly, the health effects of increased permeability, shown on the lower panel of Figure 8, have been engineered out by sequestering the zinc by kaolinite powder. This suggests that sorbent addition to the post flame region of a flame of coal and MSS might also engineer out the potentially bad health effects observed there.

CONCLUSIONS

The elemental composition and speciation of combustion generated particles is very important in determining the consequent health effects caused by their inhalation. The new field of Health Effects Engineering results from this observation, and is useful in identifying the effects of fuels and operating conditions on the health effects of the particles produced, and in devising combustion modifications to diminish potentially bad health effects.

Using increased lung permeability as a marker for incipient lung injury and also as a marker for subsequent transport of pollutants into the blood and to other organs, two types of behavior due to particles are observed. The first type of behavior manifests itself as an initial decrease of permeability (possibly caused by inflammation) followed by a recovery to initial values in 24 days. Most particles (ash from coal alone, ash from MSS alone, Zn without sulfur, sequestered Zn) follow this behavior. The second type of behavior manifests itself by a significant continuous temporal increase in lung permeability, which is undesirable because it allows greater access of impurities into the bloodstream. The only cases in this study that followed this behavior were ash from coal (containing S) and MSS (containing Zn) burned together, and particles formed from Zn and sulfur additives in oil burned together. This suggests that the “bad actor” for the previously reported coal+MSS health effects is the combination of Zn plus sulfur, rather than Zn alone.

Health effects engineering can be employed to diminish the health risk caused by burning fuels containing both zinc and sulfur. Injection of a kaolinite sorbent downstream of the flame, but above the Zn dewpoint, can sequester the Zn, and react it to form a new species that causes the first (relatively benign) type of lung permeability behavior, rather than the second (damaging) type of increased lung permeability behavior which is typical of incipient lung damage and cardiovascular injury. Future work should apply this concept to units burning coal and MSS, and perhaps also to other biomass mixtures and municipal waste incinerators.

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Analysis	Value	Units
Heat of combustion	6.647	MJ/Kg
Proximate		
Moisture	5.12	wt %
Volatile Matter	39.20	wt %
Fixed carbon	1.89	wt %
Ultimate		
Carbon	19.70	wt %
Hydrogen	3.08	wt %
Nitrogen	2.22	wt %
Chlorine	0.041	wt %
Sulfur	0.59	wt %
Ash	53.79	wt %
Ash Elemental Analysis		
Al_2O_3	19	wt %
CaO	8.8	wt %
Fe_2O_3	15	wt %
MgO	4.1	wt %
Na_2O	1.8	wt %
SiO_2*	36	wt %
As	6.7	ppmw
Sb	7.2	ppmw
Se	3.3	ppmw
Zn	664	ppmw

Table 1: Characterization of dried and processed municipal sewage sludge. * Major elements converted to oxides on a sulfur-free basis. Data reported is not normalized.

Analysis	Value	Units
Heat of combustion	30.52	MJ/Kg
Proximate		
Moisture	4.78	wt %
Volatile Matter	39.20	wt %
Ultimate		
Carbon	73.36	wt %
Hydrogen	4.82	wt %
Nitrogen	0.98	wt %
Chlorine	0.17	wt %
Sulfur	1.14	wt %
Ash	9.66	wt %
Ash Elemental Analysis		
Al_2O_3	23.6	wt %
CaO	2.7	wt %
Fe_2O_3	12.5	wt %
K_2O	3.1	wt %
MgO	2.7	wt %
Na_2O	0.4	wt %
P_2O_5	0.3	wt %
SiO_2*	42.5	wt %
TiO_2	1.0	wt %
Cd	0.8	ppmw
Cr	35	ppmw
Cu	24	ppmw
Mn	95	ppmw
Ni	24	ppmw
Pb	47	ppmw
Zn	64	Ppmw

Table 2: Characterization of Gottelborn coal. * Major elements converted to oxides on a sulfur-free basis. Data reported is not normalized.

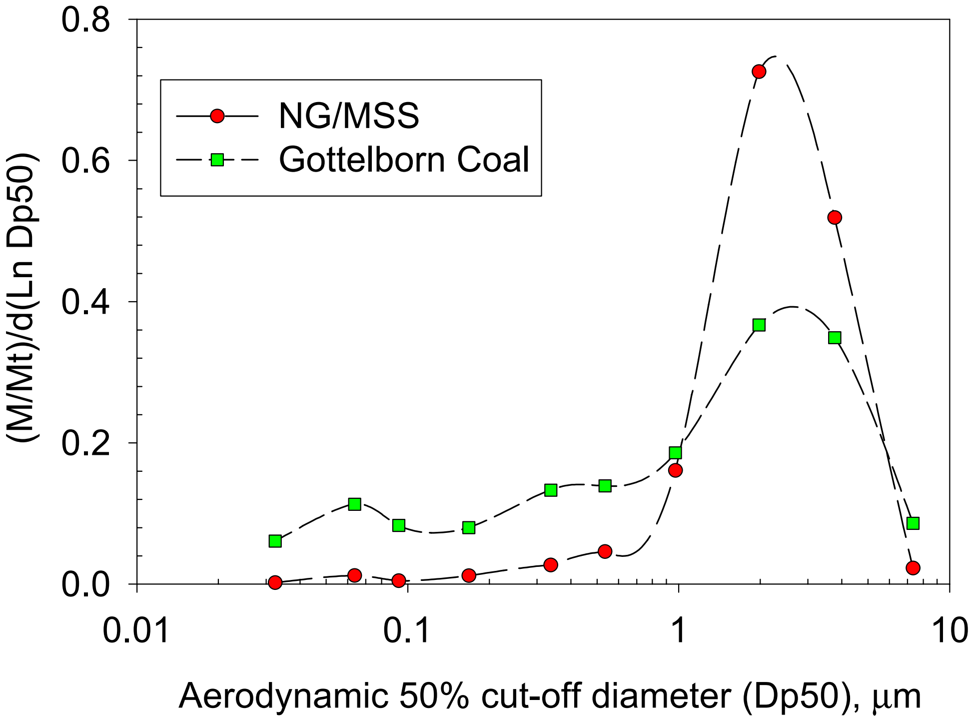

Figure 1. PSD's of resuspended ash aerosol from Gottelborn coal combustion (IVD, Stuttgart), and MSS combustion (UA)

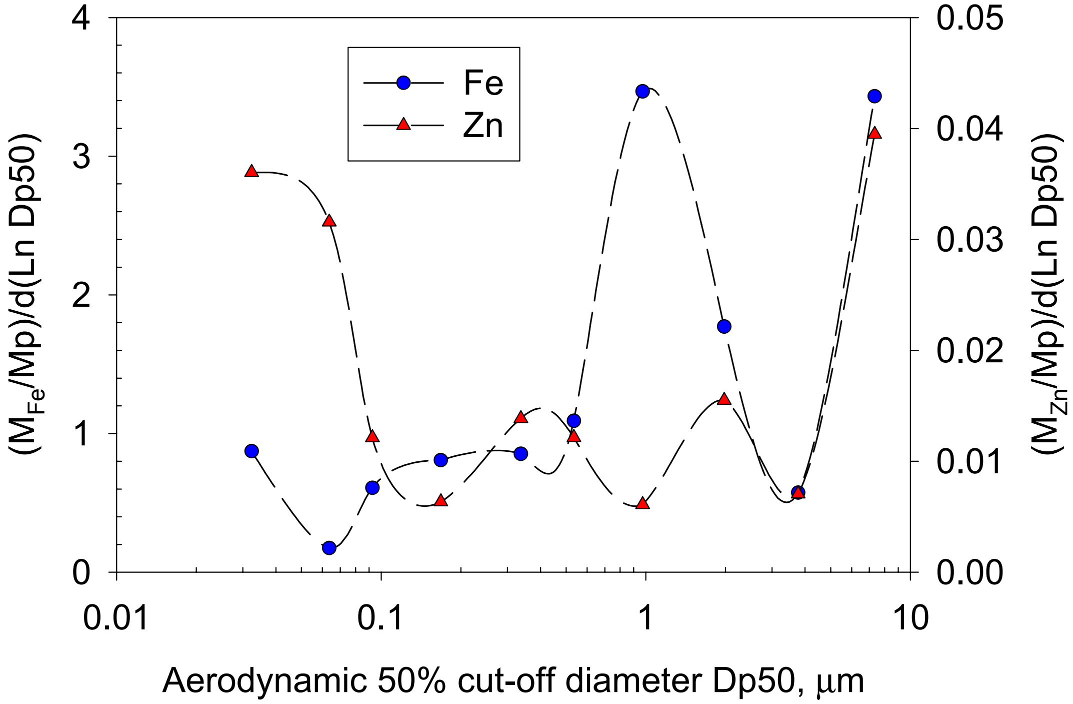

Figure 2. Gottelborn coal ash size segregated Fe and Zn composition.

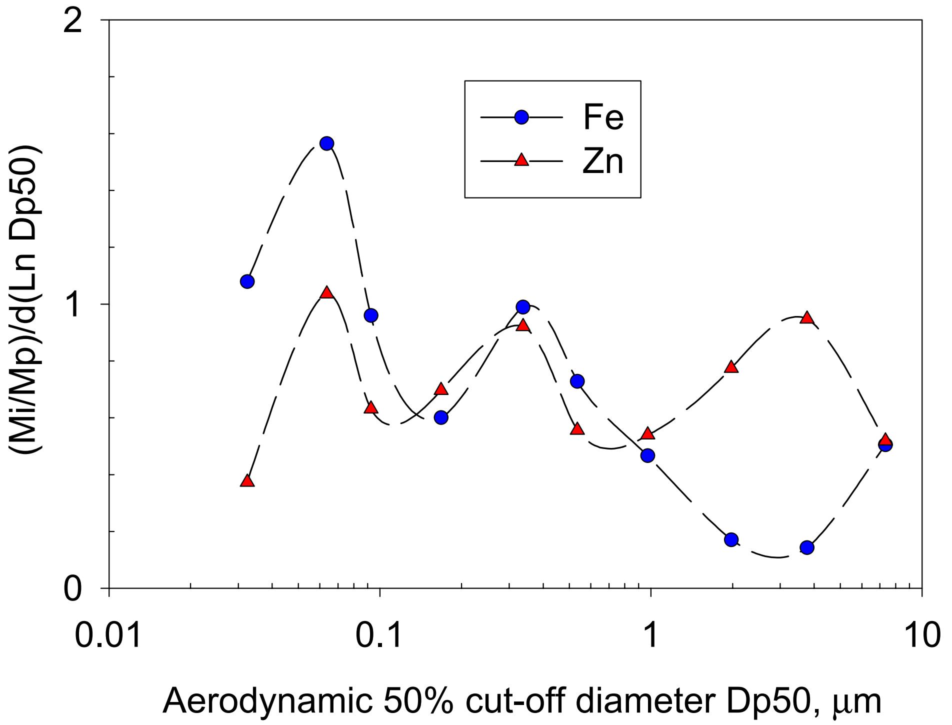

Figure 3: MSS ash aerosol size segregated Fe and Zn composition

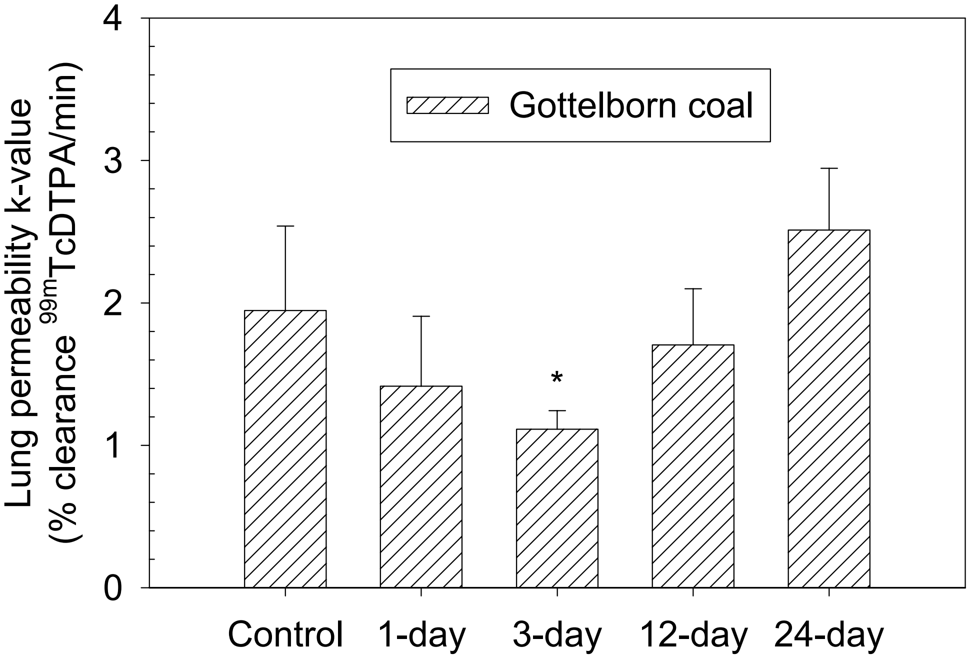

Figure 4. Coal ash inhalation. Lung permeability as a measure of lung injury. Lung injury after 1, 3, 12 and 24-day exposure.

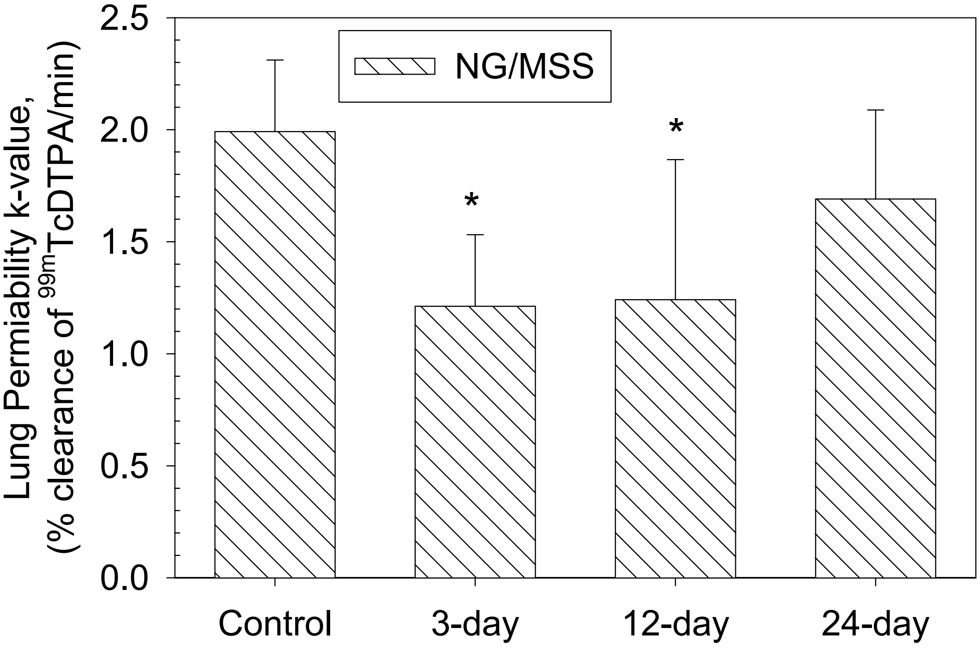

Figure 5. MSS (assisted by natural gas) ash. Lung injury after 3, 12, and 24 days.

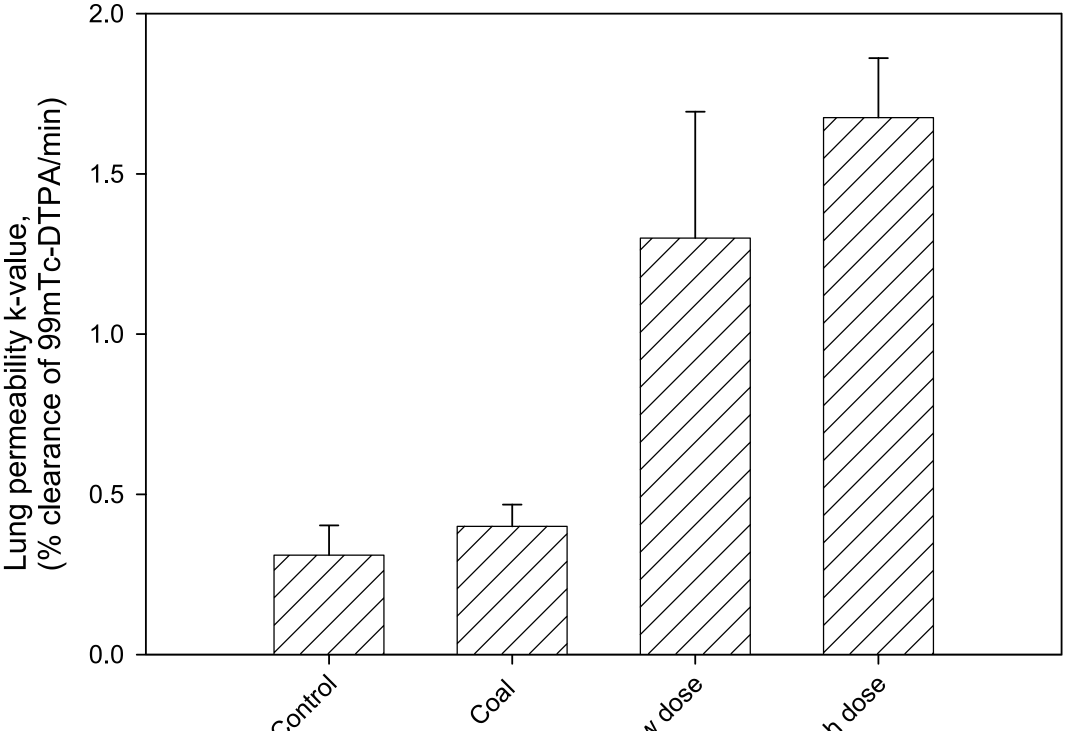

Figure 6: Coal + MSS ash. Significant increase in lung permeability (injury) after 24-day exposure, 1 hour per day. Low dose is 1000 μg/m^3, high dose is 3000 μg/m^3. Coal ash was inhaled at high dose.

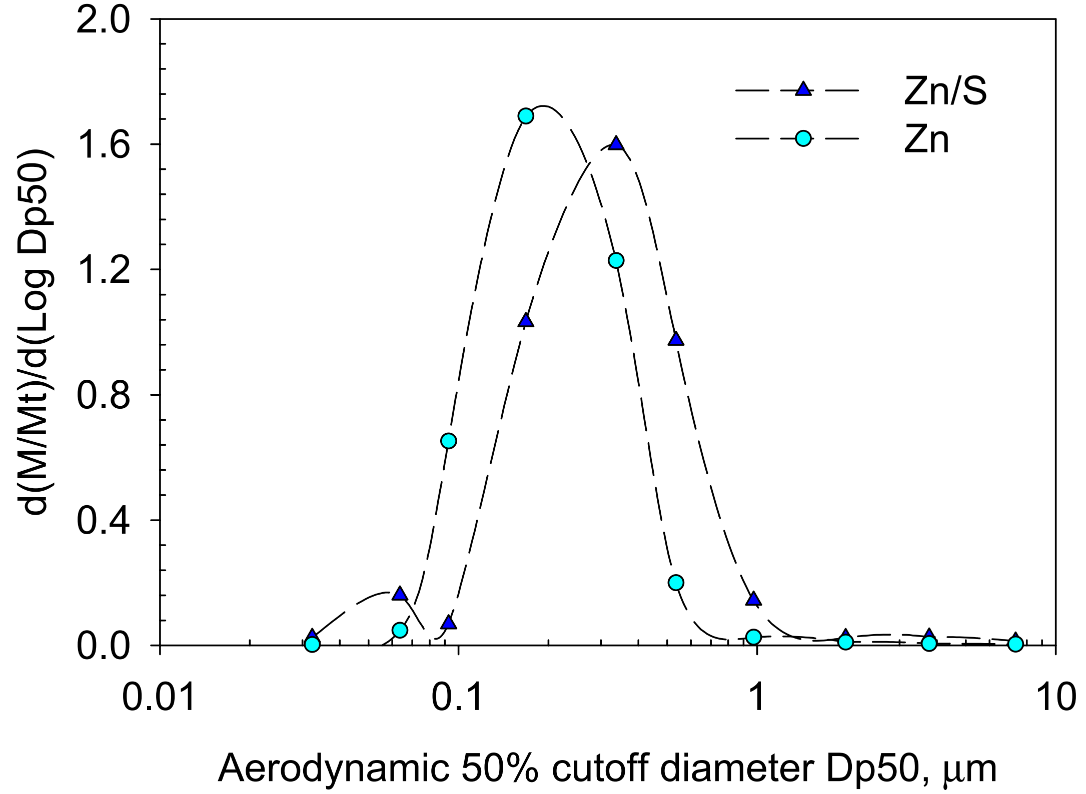

Figure 7 Particle size distributions of sampled particles from combustion of distillate oil with a) Zn only b) Zn + S.

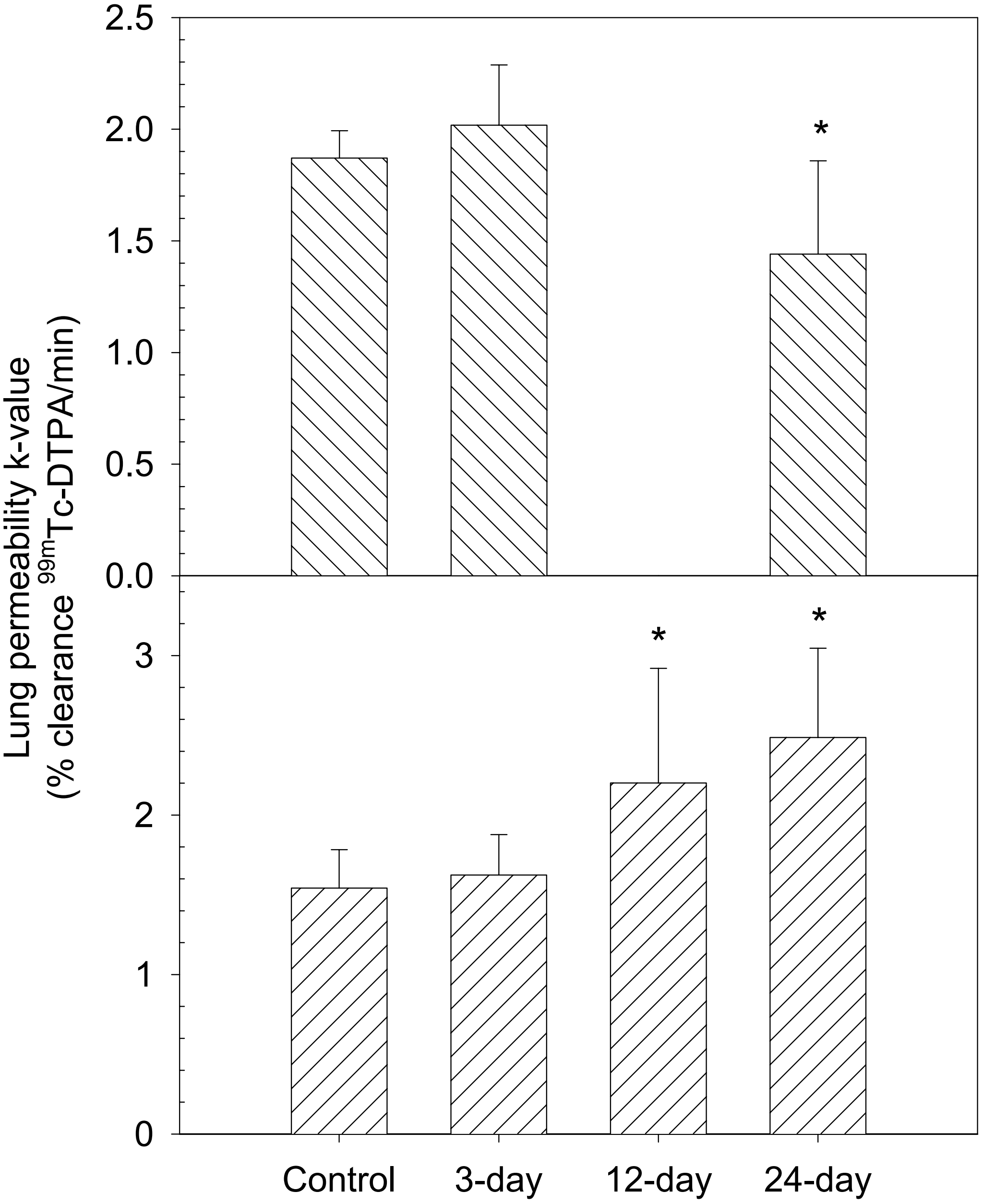

Figure 8 Doped distillate oil ash: lung permeabilities for ZnO aerosol (upper) and $ZnSO_4$ aerosol (lower) for various exposure periods (1 hour per day, ~ 1000μg/m^3).

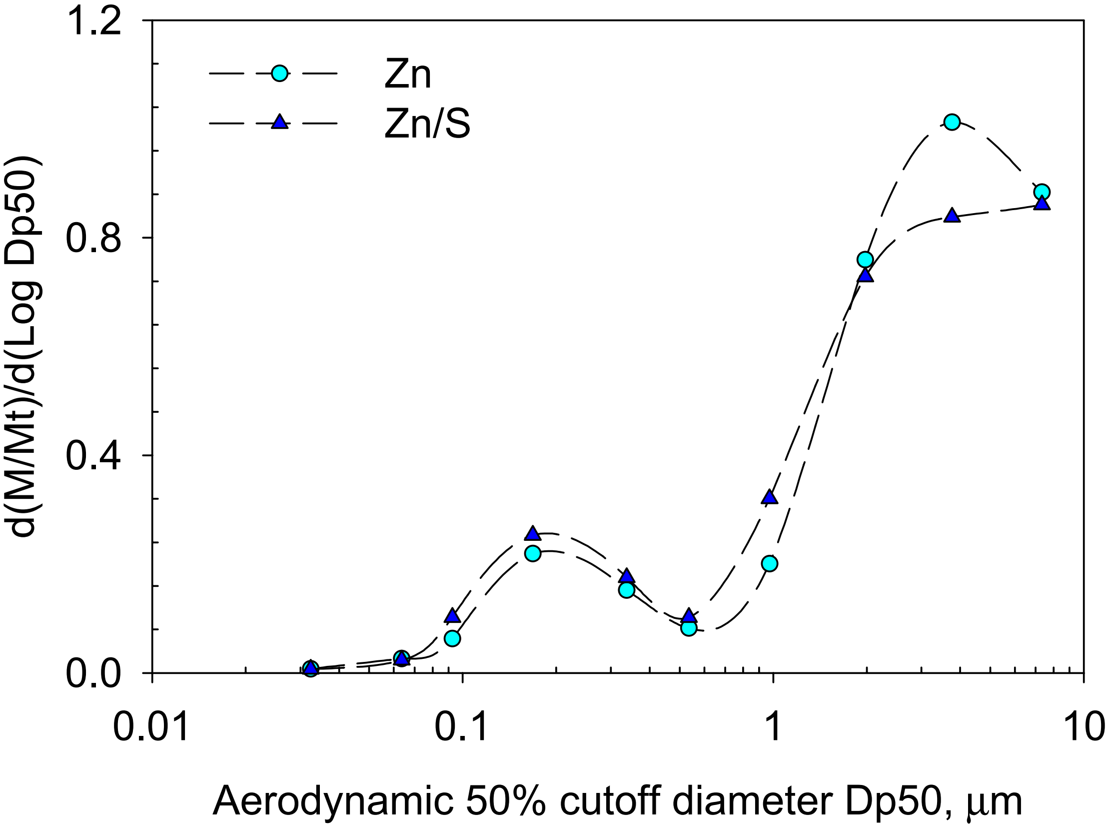

Figure 9 PSD from Zn plus kaolinite sorbent.

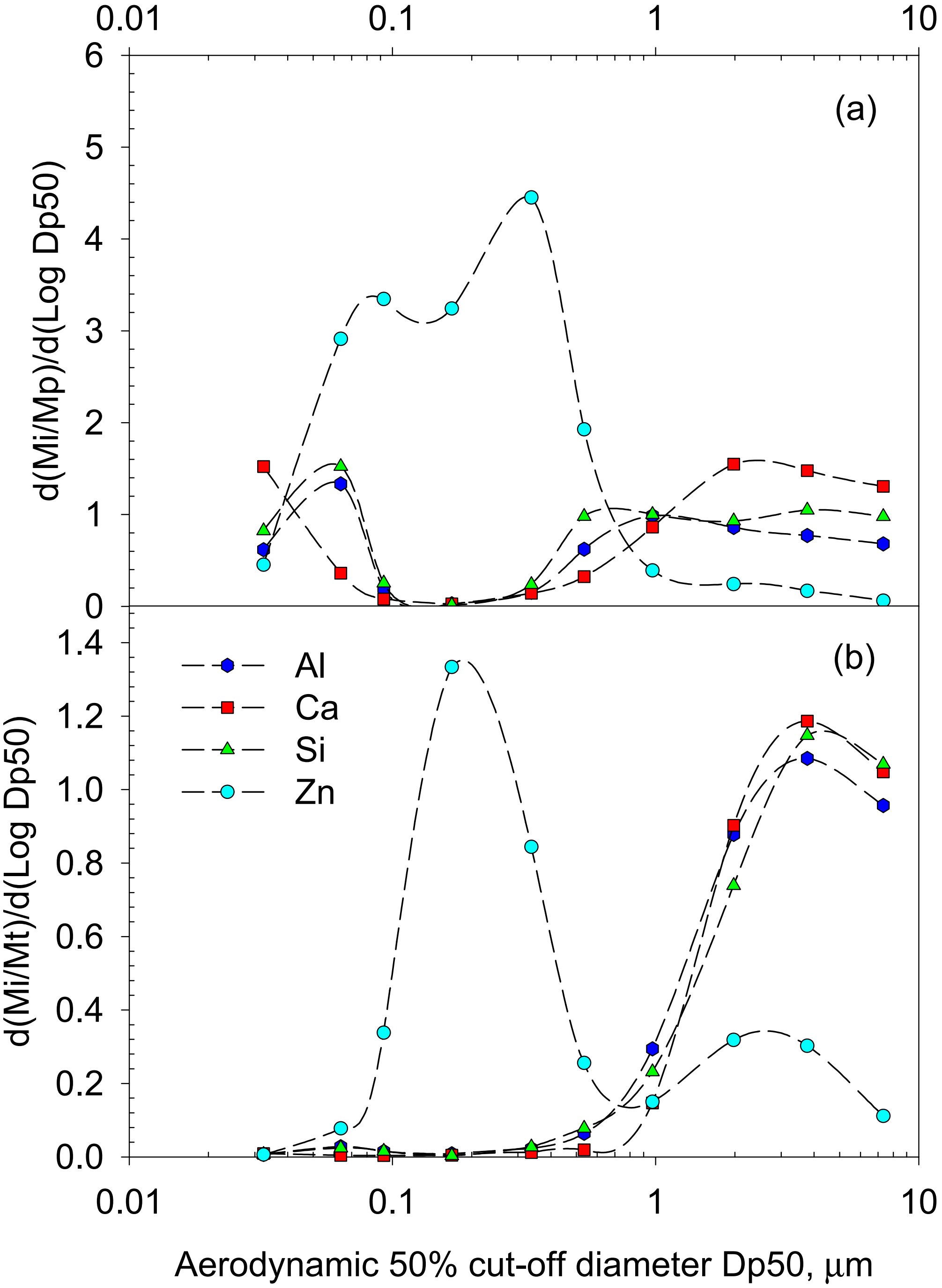

Figure 10 Elemental size segregated compositions a) without sorbent (upper) b) with sorbent (lower)

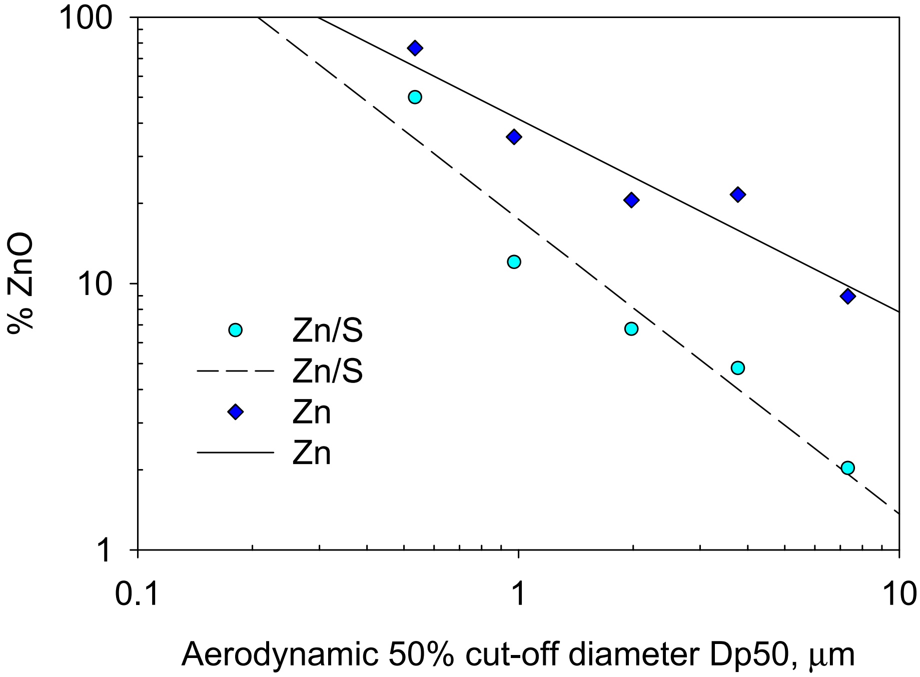

Figure 11 Composition/particle size dependence for large zinc containing particles after sorbent injection.

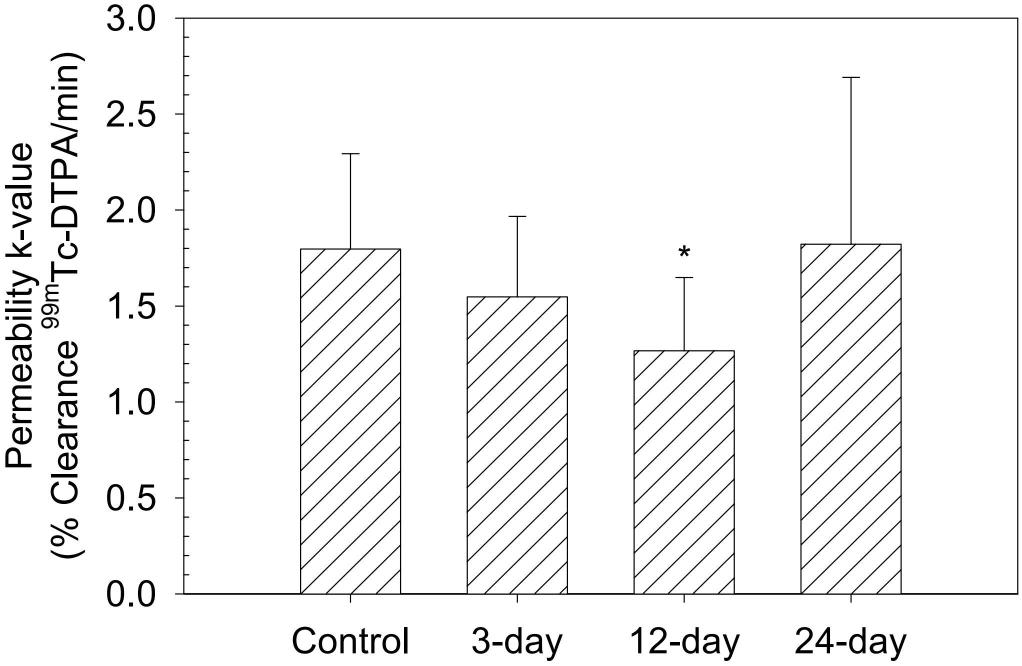

Figure 12: Sorbent addition: Lung permeabilities from sequestered zinc particles.