4311

From the desk of
DR. ROBERT A. KEHOE

Mg. Zn/100 g tissue (wet)

	Weider	Wilcher	Donna Patakeles #1	#2
Kidney	1.15		1.60	1.75
Spleen	0.49		0.30	1.08
Pancreas	1.06			
muscle	0.29	2.60	1.55	1.70
Heart	1.56		1.5	
Lungs	0.67		R 0.83 L 0.63	0.67 0.53
Liver	1.46		2.33	2.01
Rib	0.80		1.67	1.13
Brain	0.74		0.30	
Bone of arm	—	Various parts 2.56 → 5.2 of arm		

Blood/Cow 5.3 - 5.7 mg kg

Human Blood 2.5 | mostly in erythrocytes

In man 7.58 mg/Kg - 3.33 mg/kg in plasma

1.5 mg - liter of urine

(Child Lungerhutter) ↓

	Child of 4 ↓	Employee Johnson Bronze Co (Scarnati)	Roy Leslie	Child Lungerhutter
	mg 100g		mg 100 g	
Kidney	1.17	1.67	2.00	1.40
Spleen	0.89	1.02	0.96	0.60
Pancreas	1.30	—	1.30	1.00
Muscle	4.65		1.85	
Heart	1.25	1.20	1.35	0.99
Lungs	0.61	1.02	0.56	0.46
Liver	3.15	2.55	2.65	1.10
Rib	—	3.93	4.07	0.80
Long Bone	—	3.72		
Brain	—	0.63	1.00	

Dr Ashe

I attach hereto our data or at least most of it on the Zinc content of human tissues, including 2 children, as compared to similar data on the 2 Donora cases

the results are scribbled down hastily but accurately. A glance at them will show nothing indicative of abnormal respiratory exposure to Zinc on the part of the Donora victims —

this does not prove anything, since

the fatalities may have been due to respiratory spasm (maintained) in persons near the ragged edge of anoxia, but it certainly does not add any strength to Hemeon's hypothesis

CK

January 25, 1950

Mr. Harvey Jordan
American Steel and Wire Co.
Rockefeller Building
Cleveland, Ohio

Dear Mr. Jordan:

I am one embarrassed guy. My current events are unforgiveably behind times. Only yesterday did I hear that you have been made president of your company. Please accept my belated congratulations and accept my sincere wishes for your success and happiness in your new job. Mrs. Ashe says, "He'll make out fine; he's a good guy."

I am forwarding to you three copies of the data accumulated on a pilot run to learn something of the toxicity of H_2SO_4 mist on animals. It is not to be considered a finished study by any means. We are doing additional work for our own interest. Dr. Philip Drinker at the Harvard School of Public Health in Boston is also investigating this problem. This material has already been paid for.

Warmest personal regards.

Sincerely,

WFA:rms

Wm. F. Ashe, M.D.

INDUSTRIAL HYGIENE FOUNDATION OF AMERICA, INC.

4400 Fifth Avenue
Pittsburgh 13, Pa.

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FINAL

REPORT ON THE DONORA SMOG

TO

American Steel and Wire Company

Cleveland, Ohio

January - May, 1949

By

W. C. L. Hemeon
Engineering Director

Industrial Hygiene Foundation of America, Inc.

By John F. McMahon
Managing Director

August 19, 1949

FINAL

REPORT ON THE DONORA SMOG

TO

AMERICAN STEEL AND WIRE COMPANY

CLEVELAND, OHIO

JANUARY - MAY, 1949

This is the final report on the findings of Industrial Hygiene Foundation in its investigations of certain phases of the Donora smog deaths and illnesses.

Resume of Investigations

In making this final report, it is desired to record the scope and limitations of the investigations by Industrial Hygiene Foundation.

The initial objectives were (a) to obtain any and all data pertinent to the causes of the illnesses and deaths, (b) to advise the company concerning a medical program, and (c) to outline a program of control that would insure that the plant's operators would never again be suspected of responsibility for any illnesses that might occur in the future in the town of Donora. These objectives were set forth in a memorandum to Mr. H. B. Jordan, dated November 8, 1948.

At a conference on December 2, 1948, the company announced that it had engaged the Kettering Laboratory of Applied Physiology, University of Cincinnati, to conduct similar investigations. It was subsequently made plain by the company that Industrial Hygiene Foundation, through mutual understanding, would not engage in studies within the plant, including stack effluent measurements and medical examinations.

The Foundation has made recommendations that may be summarized as follows:

(1) The U. S. Public Health Service should be asked to conduct thorough research (November 8, 1948). Such a broad investigation has been carried out.

(2) Meteorological studies should be carried out with a view to definition of synoptic meteorological factors during Donora week. Thus an effective use could be made of a special weather prediction service which could be integrated with whatever policy of investigation and operation might be decided upon in the future. To implement this recommendation, the services of Professor H. C. Willett, of Massachusetts Institute of Technology, Meteorology Department, were engaged. His two reports to Industrial Hygiene Foundation, dated February 5, 1949 and May 6, 1949, have been transmitted to the company. Copies were also provided to the U. S. Public Health Service.

(3) Activities concerning the medical program were discontinued as unnecessary, in view of the Kettering investigations. Prior to this, microscopic sections of lung tissues were obtained as autopsy material on one smog victim, by kindness of Dr. G. W. Ramsey, and these were sent to several outstanding pathologists. The expert opinions have been transmitted to the U. S. Public Health Service.

(4) Atmospheric studies, made on the morning of

October 31, were the subject of our report of December 14, 1948. These results were sent to the Pennsylvania Health Department's Division of Industrial Hygiene and to the U. S. Public Health Service.

Since the engagement of the Kettering Laboratory, Industrial Hygiene Foundation has had little or no contact nor discussion with any company official in respect to the overall problem, other than on matters related to the work of Professor Willett, referred to above.

However, certain investigations have been proceeding, as outlined below. On December 14, 1948, we reported on the composition of a sample of soot, obtained fortuitously from an electrostatic precipitator in the home of Mr. P. G. Hayes in Donora. That deposit constitutes, in effect, the essence of the solid constituents of the smog during the critical period of atmospheric pollution from Wednesday through Saturday, October 27-30, 1948. (The sample covered the period October 24 to November 1.)

We have conducted further examinations on this sample, and, in addition, have obtained similar samples from homes in Mt. Lebanon, Pennsylvania, and in Valencia, Pennsylvania, for comparison purposes. Further samples have also been obtained from the Hayes home for three different periods covering the months of January, March, and April. The results of these studies are the subject of the present report.

On the Significant Fraction of Smog

Considerable evidence exists tending to suggest that particulate rather than gaseous matter in the smog is the significant portion insofar as respiratory irritation is concerned. Strong support for this view is in the fact that electric precipitators remove the substances that aggravate asthmatic conditions. This is particularly so in the case of Mr. Hayes, in whose Donora home our electrostic precipitator deposit was obtained. Precipitators do not remove gases.

It has been suggested that gases adsorbed on the surfaces of the fine particulate matter of smog would be transported deeply into the lungs by reason of the penetrating power of fine particles (soluble gases cannot readily penetrate deeply), and thus be enabled to exert an irritant effect there.

A measurement was made of surface area of the smog particles by the low-temperature nitrogen adsorption technique. It was found to have 9.5 square meters of surface per gram. This enormous area is lower, however, than that of carbon blacks, but vastly greater than common dusts. The <u>maximum</u> adsorptive capacity of such a material can be estimated on the basis of known figures for chemical adsorption. If one assumed that sulfur dioxide gas molecules were chemically adsorbed, the total carrying capacity of the smog would be of the order 2 c.c. per gram. As will be shown, the quantity of water-soluble solids in the smog which have an irritating character is so much greater that we consider the gas adsorption hypothesis to be of relatively little interest.

Solution of sulfur dioxide in the water of the fog droplets could take place and similar reasoning applied.

However, the maximum possible concentration of sulfurous acid could not exceed 200-300 p.p.m. of SO_2 in water, and the total amount of SO_2 dissolved in the fog of a unit volume of air would be very low. Moreover, the rise in temperature of outside air, on entering a heated dwelling house, would result in evaporation of the fog droplets because of the reduction of relative humidity.

We conceived a hypothesis in the course of the investigation, upon which all our further studies have been based. It is that any substance producing a major irritation of the respiratory tract must do so by dissolving first in the fluids of the respiratory system, then, by whatever biochemical reaction, produce its effect on the tissues.

Methods of Examination

In conformity with the ideas described above, each sample of precipitator deposit was treated to extract the water-soluble fraction, following a preliminary extraction of tarry material by benzene. The water-soluble extract, dried at 110°C., was examined by spectrograph for identification of the principal metals, and chemical analysis then performed to determine the amounts of the metals shown to be present, as well as the other radicals of nonmetallic character. Results are given in Table 1.

Discussion of Results

Of outstanding interest is the fact that there is such a high proportion of soluble zinc in the Donora smog.

Even more surprising is the presence of appreciable amounts in the atmosphere of Mt. Lebanon and of Valencia. Also of interest is the presence of liberal amounts of ammonia in all samples, and likewise of sulfates (reported as SO_3).

The X-ray diffraction studies had disclosed the presence of zinc ammonium sulfate in the Donora sample and a similar X-ray pattern, though discernibly different, in the other samples. All evidence indicated this pattern to be due to a mixture of sulfates and chlorides.

In Table II, proprotions of zinc ammonium sulfate, ammonium sulfate, and zinc sulfate have been calculated with an indication of the amount of SO_3 left over for combination with other metals shown to be present in Table I.

The Donora smog is thus indicated as probably composed chemically in major degree of zinc ammonium sulfate and zinc sulfate. These two salts account for two-thirds of the water-soluble solids. The remainder is composed of chlorides, sulfates of iron and aluminum, calcium, magnesium, and the alkalis, sodium and potassium.

Sample 697, obtained in a Mt. Lebanon home using natural gas as fuel, and 698, in a Valencia home using coal as fuel, both show presence of enough soluble zinc, ammonia, and sulfate to account for about 9 and 13 per cent respectively of zinc ammonium sulfate. This is not, however, the major sulfate present, as is indicated by the liberal amounts of SO_3 left over even after assigning enough for all the ammonium sulfate that could be present. These two salts account for only 22 and 31 per cent respectively of all soluble salts. The remainder, obviously, are the sulfates and chlorides of Al, Fe, Ca, Mg, Na, and K.

TABLE I

COMPARATIVE COMPOSITION OF WATER-SOLUBLE EXTRACTS OF DONORA SMOG AND SMOGS FROM OTHER DISTRICTS*

	696	697	698	700	722	764
Silicon dioxide (SiO_2)	0.4	0.9	1.0	1.1	N.D.	N.D.
Zinc oxide (ZnO)	21.2	1.8	2.7	7.6	4.5	N.D.(low
R_2O_3	1.4	2.5	2.1	1.6	1.2	1.0
Calcium oxide (CaO)	3.3	6.2	1.6	5.8	3.6	8.3
Magnesium oxide (MgO)**	5.5	2.0	2.2	2.8	7.0	19.4
Sodium oxide (Na_2O)	4.0	2.4	6.4	3.1	3.1	2.9
Potassium oxide (K_2O By diff.)	5.5	2.5	---	3.1	---	4.4
Insoluble residue	4.8	6.2	17.1	6.4	1.6	14.9
Ammonia (NH_3)	4.9	4.3	5.7	9.7	8.1	9.8
Sulfur trioxide (SO_3)	31.3	27.7	37.6	35.5	30.8	35.2
Chloride (Cl)	8.7	5.0	3.2	6.7	9.3	7.4
Fluoride (F)	1.3					
Boron oxide (B_2O_3)	0.7					
Nitrate (NO_3)	0.1 (Max.)					
Cadmium (Cd)	0.0					
Beryllium (Be)			4.5***	0.2***		

* Source of "Trion" Precipitator Samples:

Sample Number	Date Collected	Location	Period of Collection
696	11-3-48	Home of P. G. Hayes Donora, Pennsylvania	10/24/48 - 11/1/48

Source of "Trion" Precipitator Samples (Continued):

Sample Number	Date Collected	Location	Period of Collection
697	1/12/49	Home in Mt. Lebanon, Pennsylvania (Gas-fired furnace)	
698	1/12/49	Home in Valencia, Pennsylvania (Coal-fired furnace)	
700	2/3/49	Hayes Home	1/5/49 - 2/3/49
722	3/16/49	Hayes Home	3/1/49 - 3/16/49
764	4/22/49	Hayes Home	3/16/49 - 4/22/49

** Magnesia precipitate calculated as MgO.

*** Parts per million, by weight.

Table II

CALCULATION OF AMOUNTS OF PRINCIPAL SALTS IN VARIOUS SMOG SAMPLES

	696	697	698	700	722	764
Zinc Ammonium Sulfate ($ZnSO_4 \cdot (NH_4)_2SO_4$)	58%	8.6*	13.2*	37.5	22.0	---
Zinc Sulfate ($ZnSO_4$)	7	No excess zinc				
Ammonium Sulfate ($(NH_4)_2SO_4$)	---	14.0	17.8	25.6	24.4	38.0
TOTAL	65%	22.6	31.0	63.1	46.4	38.0
Excess Sulfur Trioxide (SO_3)	3%	15.8	21.5	5.1	7.2	12.2

* Zinc content of these samples is no greater than a number of other metals, e.g.: Iron and Aluminum, Calcium, Magnesium, Sodium, and Potassium. Therefore, it would be as logical to calculate those sulfates instead.

The January and March smogs of Donora (700 and 722) contain much lower proportions of zinc, but just as much SO_3 as sulfates, and even more ammonia. The March-April sample (764) contains very small proportions of zinc--the actual amounts were not determined.

The chloride content of the Donora smog is seen to be appreciable, although it is also present in the Mt. Lebanon and Valencia materials. Clearly, zinc ammonium chloride could be present in considerable proportions as well as zinc ammonium sulfate.

The cadmium content of the Donora smog was too small to be found analytically, a fact of interest in relation to the potentialities of this metal from the standpoint of respiratory irritation.

Some soluble fluoride was found, but in very low quantity.

Sulfates

The origin of the sulfur in the sulfates found in Mt. Lebaonon and Valencia samples is obviously from the sulfur dioxide formed in the combustion of coal. Apparently, it unites with the metallic compounds, in the atmosphere, forming soluble sulfur salts, probably sulfites. It is well known that sulfites oxidize readily to sulfates.

These conclusions relieve one of the necessity for leaning on the hypothesis that has wide credence, that sulfur dioxide gas is oxidized to sulfur trioxide, which then combines with water to form sulfuric acid. We do not believe this occurs.

The air samples obtained in Donora near the zinc works, on Sunday morning, October 31, on which sulfates were determined, showed concentrations of 0.16 mgm. SO_3 per cubic meter. The sulfur dioxide concentration during the same period was about 0.4 p.p.m. or 1 mgm. SO_2 per cubic meter. Thus there was six times as much SO_2 in the atmosphere as sulfate--SO_3.

In the case of the Donora smog, it is logical to conclude that zinc particles, insoluble in water, were acted upon by atmospheric sulfur dioxide to form soluble zinc sulfite, which was then oxidized to zinc sulfate.

Ammonia

The ammonia found in Mt. Lebanon and Valencia atmospheres undoubtedly originates, also, from the distillation of soft coal that occurs where combustion is poor, the same circumstances that cause the evolution of smoke from chimneys.

The percentages found are, effectively, much greater than may at first appear because of the low molecular weight of ammonia. One per cent of NH_3 requires 4.7 per cent of SO_3; thus, in the Donora smog, the reported 4.9 per cent NH_3 will combine with 23 per cent of SO_3--clearly, a "little" ammonia "goes a long way."

Relative Atmospheric Concentrations

From the weight of material collected from the domestic electric precipitators, it is possible to calculate relative concentrations of particulate matter, though not absolute average concentrations. The Hayes "Trion" precipitator was handling recirculated air. The outside air entered the house by infiltration at some unknown rate. We can, however, determine the rate of deposition in grams per day and these figures are tabulated in Table III.

The concentration index is given for four periods in Donora. (Cleaning periods for the Mt. Lebanon and Valencia precipitators are not available.) It is seen that water-soluble salts were deposited during Donora week at a rate of 2.4 grams per day -- from 3.5 to 18 times as much as in subsequent periods.

The benzene-soluble fraction of the precipitator deposits represents the tarry material from coal. The water-soluble fraction may be said to reflect the effect of sulfur dioxide from whatever source. The ratio of the two, given in the last column, is of some interest as tending to show differences in makeup of the Donora smog during the different periods. There is no consistency in the ratios of ammonia and tarry material (not tabulated) which would be expected to show a relationship if they both originated from the same source.

Free Acid in Smog

References frequently made to free sulfuric acid in smog make interesting data of Table IV. Even if one assumes that titration to the neutral point, pH 7, represented free sulfuric acid, the quantity would be very small. Furthermore, the assumption is not valid: sulfates of the type present display pH values on the acid side. It is therefore reasonable to conclude that the amount of free acid

Table III

RELATIVE AMOUNTS AND ATMOSPHERIC CONCENTRATIONS OF TARRY MATERIAL AND WATER-SOLUBLE SALTS IN DONORA SMOG, COMPARED WITH OTHER DEPOSITS

Sample Number	Elapsed Days	Water Sol.	Benzene Sol.	Grams per Day Atmosph. Concent. Index: Water Sol.	Benzene Sol.	Insol.	Ratio Water Sol. / Benzene Sol.
696	9	22%	8%	2.4	0.9	7.8	2.7
697	---	12%	23%	---	---	---	0.5
698	---	14%	13%				1.1
700	29	11%	13%	0.13	0.15	0.85	0.9
722	15	15%	23%	0.67	1.0	2.8	0.7
764	37	13%	16%	0.16	0.26	1.1	0.8

Table IV

ACIDITY OF DONORA SMOG PRECIPITATE

Electrometric Titration with 0.1 Normal NaOH of sample Weighing 0.137 grams

CC Required to Raise pH to Indicated Value		pH
Start		5.4
0.2 cc		6.0
0.6 cc		7.0 Neutral
6.0 cc	Precipitate Formed	8.0
7.3 cc	Precipitate Formed	9.0

in the Donora smog is negligible.

Irritant Potential of Salts

We prepared some zinc ammonium sulfate in the laboratory, and volatilized some of it on an electric hot plate. On inhalation of the fumes, an irritation of the respiratory tract was noted. The concentration inhaled was low, but not measured.

Several rats were exposed to the volatilized fumes of this salt at a concentration of 50 mgm. per cubic meter. Immediate irritation of nasal passages and eyes was evident. The experiment was wholly preliminary and is not regarded as conclusive.

There are numerous instances in industrial operations of respiratory irritation from atmospheric suspensions of salts. Most significant in the present connection are the effects of zinc ammonium chloride, in common use in the galvanizing industry. We have recently had contact with two different operations in which irritation from volatilized zinc ammonium chloride was a significant factor. In one, conditions sometimes became intolerable, necessitating shutting the plant down until natural ventilation improved. The relationship between zinc ammonium chloride and zinc ammonium sulfate is close enough to warrant the conclusion that similar results would be noted from the latter.

Conclusion

The outstanding characteristic of the Donora smog was its irritating effect upon the respiratory tract. There is evidence that water-soluble metallic sulfates and chlorides in an extremely fine state of subdivision was the causative agent. The salts zinc ammonium sulfate, zinc sulfate, and ammonium sulfate were the principal ones in the Donora smog. The first and third of these are also present in the smog of other localities.