United States
Environmental Protection
Agency

Air and Energy Environmental
Research Laboratory
Research Triangle Park NC 27711

Research and Development

EPA/600/S7-85/041 Jan. 1986

EPA

Project Summary

Hydrogen Chloride and Hydrogen Fluoride Emission Factors for the NAPAP Emission Inventory

David C. Misenheimer, Rebecca E. Battye, Michael R. Clowers, and Arthur S. Werner

While sulfuric and nitric acids are considered primary precursors of acid deposition, contributions of hydrogen chloride (HCl) and hydrogen fluoride (HF) are also significant. This report summarizes the findings of a study to identify and characterize sources of emissions to the atmosphere of HCl and HF. Emission factors were identified for each major source category based on the most recent data available and were used to develop nationwide emissions estimates for base year 1980. Descriptions of each source category, controls commonly used for each source, and an assessment of the accuracy of emission factors are also included. Major sources of HCl are coal combustion, waste incineration, and organic chemical manufacture. Sources of HF include coal combustion and the production of primary aluminum, HF, and phosphate fertilizers.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The focus of emission inventory activities within the National Acid Precipitation Assessment Program (NAPAP) is to estimate emissions of pollutants of concern to the acid deposition phenomenon. While sulfuric and nitric acids are considered primary precursors of acid deposition, contributions of hydrogen chloride (HCl) and hydrogen fluoride (HF) are also significant. This report presents emission factors for HCl and HF from significant sources of these pollutants.

Discussion and Procedure

A literature search was conducted to identify significant anthropogenic emissions sources and estimate emission rates for each source. The emission factors summarized in Table 1 were developed from the most recent data available. When available, emission factors based on tests performed by a sound methodology and accompanied by adequate background data were chosen. Emission factors were evaluated on a scale of A through E: A represents data from a large data base covering a good cross section of the industry, determined from valid test methods, and with a high confidence level; E represents data from a small data base, not necessarily representative of the industry, and with a low confidence level; and B through D represent data with intermediate confidence levels. National emissions estimates for base year 1980 were calculated by multiplying the level of activity (production/use rates) for each source category in 1980 (or as close to base year 1980 as possible) by the emission factor for that source. National emissions estimates provide a measure of the relative importance of each source category.

HCl is emitted from coal combustion, waste incineration, and organic chemical manufacture. Approximately 660,000 tons of HCl was emitted in 1980; over 89 percent of the total resulted from coal combustion. HF was emitted from various sources at the rate of 90,000 tons/year. Coal combustion, comprising 78 percent of the total, and primary aluminum production, comprising almost 15 percent, are the major HF sources. Other sources include the fertilizer and HF manufacturing industries.

The rates at which HCl and HF are emitted during coal combustion are functions of coal composition and air pollution control techniques. A study of coal combustion in utility boilers conducted by the Bureau of Mines found that most of the chlorine in coal volatilizes and forms HCl. There is a need for additional scientific data which directly assess the chemical form of fluorine emitted during coal combustion. In lieu of such data and because of the chemical similarity between fluorine and chlorine, it is assumed that all fluorine in the feed coal reacts to form HF.

Data compiled in 1979 on trace element compositions in coal were obtained from studies by TRW and GCA and were used to calculate emission factors for coal combustion in utility and industrial boilers. Factors calculated for bituminous coal burned in utility boilers are 78.8 lb HCl/10^9 Btu and 9.4 lb HF/10^9 Btu. These factors were assigned an A ranking due to the number of tests conducted, availability of information concerning accuracy, and types of test methods used. Recent data (1985) developed by the Department of Energy's Pittsburgh Energy Technology Center from laboratory tests on bituminous coal in utility boilers resulted in emission rates of 690 lb chlorine/10^9 Btu/percent chlorine and 870 lb fluorine/10^9 Btu/percent fluorine. Dividing by the chlorine and fluorine contents of the coal and assuming that emissions are in the form of HCl and HF result in emission factors of 28 lb HCl/10^9 Btu and 4.7 lb HF/10^9 Btu. These factors compare favorably with those developed from the TRW/GCA studies.

Scrubbers, electrostatic precipitators (ESPs), cyclones, and baghouses are used frequently on coal-fired utility boilers as flue gas control techniques. The primary purpose of these controls is to remove particulate matter from the flue gas stream. The efficiency of wet scrubbing devices has been reported at about 80 percent for HCl and HF emissions from

Table 1. Emissions of Hydrogen Chloride and Hydrogen Fluoride

Source	Emission Factor[a]		Emissions tons/yr	Emission Factor Accuracy Rating
	--HCl--			
Coal Combustion				
Utility Boilers				
Bituminous	78.8	lb/10^9 Btu	458,200	A
Anthracite	35.5	lb/10^9 Btu	310	A
Lignite	1.0	lb/10^9 Btu	270	A
Industrial Boilers				
Bituminous	78.8	lb/10^9 Btu	121,000	A
Anthracite	35.5	lb/10^9 Btu	530	A
Lignite	1.0	lb/10^9 Btu	40	A
Residential Boilers				
Bituminous	60.5	lb/10^9 Btu	1,300	C
Anthracite	120	lb/10^9 Btu	1,300	C
Lignite	35.1	lb/10^9 Btu	--	C
Propylene Oxide Manufacture	7.46	lb/ton	2,140	B
Incineration				
Municipal Waste	5.0	lb/ton[b]	75,000	E
Industrial Waste	5.35	lb/ton[b]	--	E
Liquid Waste	1.19	lb/ton[b]	--	E
By-product HCl Production				
(without final scrubber)	3.0	lb/ton	--	C
(with final scrubber)	0.2	lb/ton	--	C
	--HF--			
Coal Combustion				
Utility Boilers				
Bituminous	9.4	lb/10^9 Btu	54,670	A
Anthracite	7.2	lb/10^9 Btu	60	A
Lignite	1.2	lb/10^9 Btu	310	A
Industrial Boilers				
Bituminous	9.4	lb/10^9 Btu	14,400	A
Anthracite	7.2	lb/10^9 Btu	110	A
Lignite	1.2	lb/10^9 Btu	50	A
Residential Boilers				
Bituminous	6.87	lb/10^9 Btu	150	C
Anthracite	4.95	lb/10^9 Btu	50	C
Lignite	6.34	lb/10^9 Btu	--	C
HF Manufacture				
Tail Gas Vent				
Uncontrolled	25.0	lb/ton	--	E
Controlled— Caustic Scrubber	0.2	lb/ton	21.3	E
Primary Aluminum Production				
Anode Baking Furnace	0.52	lb/ton	--	A
Prebaked Reduction Cell	4.9	lb/ton	9,300	A
Prebaked Fugitive Emissions	1.2	lb/ton	--	A
Vertical Soderberg Stud Cells	0.6	lb/ton	1,800	A
VSS—Fugitive Emissions	4.9	lb/ton	--	A
Horizontal Soderberg Stud Cells	1.9	lb/ton	2,200	A
HSS—Fugitive Emissions	2.2	lb/ton	--	A
Phosphate Fertilizer Industry				
Phosphoric Acid Production				
Reactor	0.37	lb/ton[c]	--	C
Condenser	0.043	lb/ton[c]	--	C
Controlled Emissions	0.010	lb/ton[c]	150	C
Gypsum Ponds	0.42	lb/ton[c]	6,400	D

able 1. (Continued)

Source	Emission Factor[a]	Emissions tons/yr	Emission Factor Accuracy Rating
Triple Superphosphate Manufacture			
Reactor/Dryer (granulor)	*21.0 lb/ton[d]*		*A*
Controlled (granulor)	*0.24 lb/ton[d]*	*0.21*	*A*
Diammonium Phosphate Manufacture			
Dryers and Coolers	*0.3 lb/ton[d]*	--	*A*
Ammoniator/Granulator	*0.3 lb/ton[d]*	--	*A*
Controlled Emissions	*0.08 lb/ton[d]*	*245*	*A*

mission factors are based on the rate of production for the specific source category unless therwise noted; for readers more familiar with the metric system: 1 Btu = 1.055 kJ, 1 lb = 0.454 g, and 1 ton = 907.2 kg.
he emission factor units are lb HCl/ton material burned.
he emission factor units are lb HF/ton phosphate rock processed.
he emission factor units are lb HF/ton P_2O_5.

ituminous-coal-fired utility boilers. Bag-ouses which have sorbent or alkaline naterials introduced may remove a sub-tantial amount of HCl and HF. A study of he use of nacholite and sodium bicar-onate as dry sorbent resulted in a 95 to 3 percent HCl removal. However, under rmal operating practices, baghouses, SPs, and cyclones have no significant ffect on removal of HCl or HF.

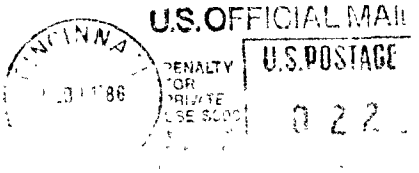
Another control technique, flue gas desulfurization (FGD), is used to remove ulfur oxides from coal combustion. Data ave indicated that FGD is at least 95 ercent effective in removal of HCl. No data are available to quantify removal fficiencies of HF.

Several emission factors received low ratings because of limited data. Factors or HCl from residential boilers, HCl manufacturing, and waste incineration received intermediate to poor rankings because of the few plants actually tested and the absence of information on test methodology. Factors for HF emissions from residential boilers, phosphoric acid production, and HF manufacture were assigned intermediate to low rankings based on the few studies, absence of information concerning accuracy of test methods, and the number of assumptions made in determining these factors. Additional data which address emission rates of HCl and HF from these sources would be beneficial.

D. Misenheimer, R. Battye, M. Clowers, and A. Werner are with GCA/Technology Division, Chapel Hill, NC 27514.
***J. David Mobley** is the EPA Project Officer (see below).*
The complete report, entitled "Hydrogen Chloride and Hydrogen Fluoride Emission Factors for the NAPAP Emission Inventory," (Order No. PB 86-134 020/AS; Cost: $11.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268



Official Business
Penalty for Private Use $300

EPA/600/S7-85/041