

Workshop on the Health Effects of HCl in Ambient Air

MICHAEL A. KAMRIN

*Institute for Environmental Toxicology, C-231 Holden Hall, Michigan State University,
East Lansing, Michigan 48824*

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This article presents a summary of the proceedings of the Workshop on the Health Effects of HCl in Ambient Air, held in Detroit, Michigan, on October 15, 1990. Participants addressed three topic areas: sources, levels, and chemistry of HCl in ambient air; toxicity of atmospheric HCl to humans and animals; and the need for future research on toxicity and exposure. Consensus conclusions related to each of these topic areas, arising from the deliberations of the workshop participants, are presented. These include: (1) atmospheric HCl will most commonly exist in the gaseous form; (2) long-range transport of HCl is probably of limited importance; (3) ambient HCl levels are in the low parts per billion range; (4) irritation of the upper airways appears to be the most sensitive indicator of exposure; (5) such effects are likely to occur only at exposure levels much greater than those measured in ambient air; and (6) future health research should focus on occupationally exposed populations and potentially sensitive subgroups, e.g., asthmatics. © 1992

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INTRODUCTION

The objectives of the Workshop on the Health Effects of HCl in Ambient Air were to evaluate (1) available information about sources, levels, and chemistry of hydrogen chloride in ambient air; (2) current knowledge about the toxicity of atmospheric hydrogen chloride to humans and animals; and (3) the need for future research on the toxicity of and exposure to hydrogen chloride in ambient air. To accomplish this, a group of 32 scientists representing a variety of disciplines and sectors met for a full day of intensive work on October 15, 1990, in Detroit, Michigan. The Workshop was coordinated by the Institute for Environmental Toxicology, Michigan State University.

In preparation for the meeting, participants were provided with a number of materials. Included were six articles describing experiments on the health effects of HCl (Malek and Alarie, 1989; Burleigh-Flayer *et al.*, 1985; Hartzell *et al.*, 1988; Kaplan *et al.*, 1988; Albert *et al.*, 1982; Sellakumar *et al.*, 1985); a summary of the National Research Council (1987) evaluation of HCl; and two review articles on the health effects of acid aerosols (Spengler *et al.*, 1990; Soskolne *et al.*, 1989a). One additional article describing a risk assessment of sulfuric acid (H_2SO_4) was distributed at the time of the meeting (Rao and Brown, 1989).

The Workshop began with three presentations to delineate the important health and environmental issues. Participants then were divided into smaller groups to facilitate discussion of the major questions. These breakout sessions were structured to identify areas of consensus and those requiring further study. All participants then met as a group to hear summaries of the breakout sessions and discuss the conclusions that were reached. The implications of the group conclusions for assessing human risk were also addressed during this final segment of the meeting.

This report contains summaries of each of the formal presentations followed by discussions of the issues raised in the respective presentations. The discussion sections summarize the views of the participants as expressed in both the breakout and the plenary sessions. In addition, the report reflects comments provided by participants subsequent to the Workshop in response to a draft version of this manuscript. While it was not possible to incorporate all comments of all individuals, this meeting summary reflects the consensus of the participants.

HCl IN AMBIENT AIR

Sources and Levels

The first speaker, Gerald Keeler (University of Michigan) discussed sources of HCl, the nature of HCl emissions and their atmospheric distribution and fate, and concentrations of HCl in ambient air. The two major sources of atmospheric HCl are fossil fuel burning and incineration of domestic and industrial waste (Sturges and Harrison, 1989; Lightowlers and Cape, 1988). The fossil fuel of most concern is coal. The amount of HCl generated from burning of coal depends on its chloride content which varies from 0.0029 to 0.095% (Gladney *et al.*, 1984; Olmez, 1990). The chloride content of fuel oils is generally low, as is the concentration in gasoline, where chloride is used as a scavenger for lead (Lightowlers and Cape, 1988; Pierson and Brachazek, 1983). The major contributors to the chlorine content in municipal solid wastes are polyvinyl chloride and paper (Lightowlers and Cape, 1988; Michigan DNR, 1986).

The relative contributions of incineration and coal burning can be estimated using information from existing facilities. A high-capacity resource recovery facility, operating 24 hr a day, 5 days a week, and burning 650,000 tons of solid waste (containing 6.5 lb HCl/ton) per year is estimated to emit uncontrolled emissions of about 2000 tons of HCl/year (Michigan DNR, 1986; Brunner, 1985). A high-capacity coal-fired power plant, burning 2,000,000 tons/year of bituminous coal (with an HCl content of 0.0925%), emits an estimated 1700 tons of HCl/year. Thus, these two types of sources appear to emit roughly equivalent amounts of HCl into the air. However, the source type that is the largest contributor to HCl in a particular geographical region depends on the amount and type of fuel consumed and the control equipment utilized on each facility.

In addition to the combustion of coal and solid waste, there are a number of other sources that contribute to HCl in ambient air. These include glass manufacturing, iron-steel manufacturing, the ceramic industry, cement production, the chemical industry, rocket firing, and natural sources, e.g., volcanoes and sea salt (National Research Council, 1976; Fenton *et al.*, 1980; Clegg and Brimblecombe, 1985). In most areas, these secondary sources contribute 10% or less to the total HCl emissions (Lightowlers

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and Cape, 1988; National Research Council, 1976). Some exceptions are found in the states of New Jersey and West Virginia, where such sources are more significant (National Research Council, 1976).

Environmental Distribution

The salient physicochemical characteristics of HCl are its high solubility in water, hygroscopic nature, strong reactivity, and complete ionization in solution (Lightowlers and Cape, 1988; National Research Council, 1976, 1987). Thus, the exact form of HCl in the atmosphere at a particular time and place will depend on atmospheric factors such as humidity and the presence of other constituents. However, from the above physicochemical considerations, it can be predicted that atmospheric HCl will most commonly be in the gaseous form.

Because of its solubility, HCl will rapidly dissolve in cloud water or rain and be readily washed out of the atmosphere. HCl is a reactive gas and is quickly removed from the atmosphere by almost any surface. Its dry deposition velocity is probably very similar to that of nitric acid (HNO_3) gas and is dependent upon meteorological conditions such as wind speed and vertical temperature profile. Although HCl may adsorb to inert particles when it is present at high levels and the humidity is high, it desorbs rapidly and is unlikely to be associated with particulates when it reaches the ground. Because of its reactivity, it may interact with gases such as ammonia (NH_3) and be neutralized. As a result of these removal processes, long-range transport of HCl from the source area is probably of limited importance and significant levels are more likely to be found closer to the emission source (Lightowlers and Cape, 1988).

Environmental Data

Few measurements of ambient HCl concentrations have been reported. Most of the measurements were performed in Europe during the past decade (Table 1) (Clegg and Brimblecombe, 1985; Pio and Harrison, 1987; Matusca *et al.*, 1984; Ruprecht and Sigg, 1990; Harrison *et al.*, 1989; Cadle *et al.*, 1985; Dasch *et al.*, 1989). As shown in Table 1, ambient concentrations are generally in the range of 1–100 nmol/m³, equivalent to about 0.025 to 2.5 ppb or 0.4–4 $\mu\text{g}/\text{m}^3$. Based on these data and physicochemical considerations, it is estimated that the maximum HCl concentrations in locally impacted areas will be from 20 to 30 ppb (30–45 $\mu\text{g}/\text{m}^3$). Some higher values have been reported but they are open to question due to the methodological difficulties (Pio and Harrison, 1987; Dasch *et al.*, 1989).

There are insufficient data to determine how concentrations vary with time of day, season, source, or area characteristics, e.g., urban vs rural settings. There are no measurements relating ambient concentrations to a particular source, and no direct assessments of excursions from the measured values. These data gaps suggest areas for further study.

Analytical Questions

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An issue related to the determination of ambient levels of HCl is the comparability of the different types of measurement techniques. Sampling methods for atmospheric

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TABLE 1
ATMOSPHERIC LEVELS OF HCl

Location/type	Season	Sample duration	Concentration range
			nmol M^{-3} (ppb)
Maritime/background Europe	All	Weekly	2-8 (0.05-0.2)
UK/rural	Summer	2-4 hr	27-82 (0.7-2)
UK/rural	All	Daily	7-50 (0.2-1.2)
UK/urban	All	Weekly	15-31 (0.4-0.8)
Switzerland	April 1982	1 hr	5-84 (0.1-2)
Dubendorf/urban	Winter 1985	Daily	0.8-82 (0.02-2)
Dubendorf/rural	March 1986	—	7-37 (0.2-0.9)
	Winter 1986/1987	—	4-87 (0.1-2.1)
Po River/rural	November 1984	Daily	3-13 (0.07-0.3)
Ljubljana/urban	February 1985	Daily	3-11 (0.07-0.3)
Linz/urban/industrial	Summer 1985	Daily	6-46 (0.15-1.1)
Wien/urban	Winter 1983/1984	Daily	3-43 (0.07-1)
Dortmund/urban	September-October 1980	Daily	10-310 (0.2-7.6)
United States			
N. Michigan/rural	Winter 1983/1984	Weekly	2-11 (0.05-0.3)
South Haven, MI	July 1990	6 hr	12-50 (0.3-1.2)
Ann Arbor, MI	August 1990	Daily	3-54 (0.07-1.3)

HCl must have a quantitative means for separation of gaseous HCl from aerosols which contain chloride ion. Furthermore, the sampling efficiency must be constant and independent of sampling conditions or there must be provisions for determining sampling efficiencies for each sample.

Methods that are commonly used are impingers/bubblers, absorbent tubes (silica gel), filter packs, and diffusion denuders. Filter packs, diffusion samplers, and denuders are considered the methods of choice and many of the measurements listed in Table 1 were generated using filter packs. Although there are questions about how well this method measures the species of interest, it is preferred since it provides an estimate of the upper bound on ambient concentrations.

One study has been performed comparing the filter pack and denuder methods for HCl determinations. This was done in Michigan under winter conditions and showed that the two techniques gave similar values (Dasch *et al.*, 1989). While this result is encouraging, additional comparisons are needed to determine whether this comparability holds for other sites and other times of the year. In addition, studies of the comparability of these methods with the other two measurement devices, impingers and absorbent tubes, are needed to assist in the interpretation of data already collected and to decide on the best and most cost-effective technique.

Discussion

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The question of the applicability of such ambient measures of HCl to human exposures was raised. The possible approaches to exposure assessment include dispersion

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modeling and personal monitoring. The dispersion modeling approach has one critical drawback in that it assumes that HCl can be treated as a nonreactive gas and this is known to be inaccurate. Thus, while such a model may be useful for assessing human exposure over short distances, its predictive power may decrease as distance and dispersion increase. The accuracy of personal monitoring techniques is subject to the same questions raised about the specificity, efficiency, and comparability of the various methods of measuring HCl levels in ambient air. Available techniques need to be carefully evaluated and calibrated before personal monitoring will be useful for exposure assessments.

HCl AND HUMAN HEALTH: EXPERIMENTAL STUDIES

Two speakers addressed the effects of acid exposure on human health. The first, Yves Alarie (University of Pittsburgh), reviewed the data collected from experimental studies. These studies show that the most common toxic reactions are sensory irritation of eye, nose, and throat; coughing; bronchoconstriction; and edema of conducting airways or alveoli.

There are very few reported studies on humans exposed to gaseous HCl (Lehmann, 1886; Matt, 1889; Lehmann *et al.*, 1908). Matt (1889) concluded that levels above 10 ppm ($15,000 \mu\text{g}/\text{m}^3$) lead to work impairment; above 50 ppm ($75,000 \mu\text{g}/\text{m}^3$) to work hindrance; and above 100 ppm ($150,000 \mu\text{g}/\text{m}^3$) to an environment in which work is impossible. It should be emphasized that these results were derived from studies of healthy adult males; no studies of possibly more sensitive human populations, such as children or individuals with preexisting pulmonary impairment, have been performed. A study of human exposure to large HCl droplets was conducted, but the experiment lacked clear definition of exposure. In addition, the results are relevant to acid fogs only, so that the usefulness of the work is limited (Fine *et al.*, 1987).

Acute studies on animals have been conducted at very high exposure concentrations, generally in the thousands of parts per million, so that the results are of questionable relevance to potential human health effects at much lower ambient concentrations (Darmer *et al.*, 1974; MacEwen and Vernet, 1974; Hartzell *et al.*, 1985; Kaplan *et al.*, 1985, 1988; Burleigh-Flayer *et al.*, 1985; Malek and Alarie, 1989). In addition, the use of rodents in many of these studies has been questioned because of anatomical and physiological differences between rodents and humans (Buckley *et al.*, 1984). However, rodents, like primates, exhibit bronchoconstriction when exposed to irritants such as HCl and the guinea pig has been used as a possible model for this response in humans (Kaplan *et al.*, 1985). It should be noted, however, that rodents differ markedly from primates in their lower airway response to HCl. Exposures to high levels of HCl cause pulmonary edema in rodents, but not in primates (Kaplan *et al.*, 1988). This difference appears to be due to differences in respiratory anatomy and the scrubbing ability of the upper airways.

There is very little information about long-term effects of HCl in either humans or animals. One study showed that exposure of rats to 10 ppm ($15,000 \mu\text{g}/\text{m}^3$) for 6 hr a day, 5 days a week, for a lifetime, leads to laryngeal hyperplasia (Sellakumar *et al.*, 1985). This can be considered a lowest observed adverse effect level, although it is not known whether this value is directly applicable to sensitive human subpopulations.

Considering the limited amount of HCl data and similarities in the chemistry of HCl and H_2SO_4 , it is useful to examine the extensive H_2SO_4 data base to see if it is

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consistent with the results of the HCl experiments. Based on short-term studies of H₂SO₄ exposure in humans, it appears that reversible airways construction occurs at 100–300 µg/m³ in sensitive individuals (Spengler *et al.*, 1990). Since higher levels of HCl are needed to produce similar effects, it appears to be a less potent irritant than H₂SO₄.

With respect to long-term effects, studies in cynomolgus monkeys indicate that 30 µg/m³ H₂SO₄ appears to be a clear no effect level and that 300 µg/m³ is the lowest effect level based on mild tissue irritation (Alarie *et al.*, 1975). Converting these concentrations to equivalent ones for HCl on a molar basis and taking into account the lower potency of HCl as an irritant, the level of HCl at which no effects would be expected is between 0.2 and 2 ppm (300–3000 µg/m³). These values are not very different from the 10 ppm no effect level reported in human workers and the 10 ppm lowest effect level seen in rodents. Thus, the H₂SO₄ data are consistent with and provide support for the no effect level values suggested by the results of the HCl studies.

Discussion

Utilizing the above analysis in conjunction with available literature, the participants concluded that, even though the data base is meager for both acute and chronic effects, it is possible to provide a good estimate of the no effect level for HCl. Based on the one long-term rodent HCl study showing laryngeal hyperplasia and the long-term H₂SO₄ study in monkeys, the no effect level in humans is predicted to be between 0.2 and 10 ppm. It was noted that the changes observed in experimental animals at the lowest effect levels were minimal and were not accompanied by losses in function (Alarie *et al.*, 1975). No comparable functional studies have been performed in humans. In addition, the participants examined published data from rodent carcinogenicity studies and concluded that there is no evidence that HCl is a rodent carcinogen (Selvakumar *et al.*, 1985; Albert *et al.*, 1982).

It was also evident from the discussion that the form of HCl is critical to the assessment of toxicity. If, as suggested by the physicochemical information, HCl molecules exist in a gaseous or nearly gaseous state in the atmosphere, they will likely become hydrated to a degree when inhaled into the upper airways. The majority of the resultant HCl microparticles will be scrubbed or neutralized in the upper airways in humans and thus will not be likely to result in significant pulmonary effects. This conclusion is consistent with results from studies in baboons which indicate that HCl does not move past the nasopharyngeal area even when exposure is at high levels, up to 10,000 ppm (Kaplan *et al.*, 1988).

One issue that was not resolved is the possible impact of HCl on sensitive human subpopulations. Although the most sensitive group is not known, one higher risk subpopulation that has been identified from H₂SO₄ studies consists of adolescents susceptible to asthma (Koenig *et al.*, 1989). Studies of effects of HCl inhalation on adolescent asthmatics might provide additional useful information. Such a study is presently underway at the University of Washington (Koenig, 1991). When the results of this research are available, they should help to better assess the potential health effects from HCl exposure.

HCl AND HUMAN HEALTH: EPIDEMIOLOGICAL STUDIES

The second speaker addressing human health concerns, Colin Soskolne (University of Alberta, Canada), summarized epidemiological studies of workers exposed occupationally to sulfuric acid. These data were included in the workshop because of the absence of epidemiological studies on the association between HCl and upper airway effects and because of the similarities between HCl and H₂SO₄ in the experimental studies discussed in the previous section.

In addition to published studies (Soskolne, 1982; Soskolne *et al.*, 1984, 1989a; Beaumont *et al.*, 1987; Steenland *et al.*, 1988), recently completed research has addressed the possible relationship between laryngeal cancer and long-term inhalation of sulfuric acid (Soskolne *et al.*, 1989b, 1990). These studies on workers from several industries suggest that long-term (>25 years), high-level H₂SO₄ exposure is associated with laryngeal cancer. After taking confounding variables (such as tobacco and alcohol consumption) into account, the studies indicate odds ratios in the 4 to 13 range for this type of exposure. Supporting the association, risk was found to decrease as exposure decreased.

In addition, by examining the pattern of odds ratios as a function of variable length exposure windows dating from first exposure through cancer diagnosis, it was possible to distinguish between total years of exposure and critical periods of exposure. This analysis suggests that the initial 25 years of high exposures contribute to the cancer incidence and that the 10 years prior to the cancer diagnosis contribute less to the effect.

Discussion

There are no epidemiological studies focusing solely on HCl, but some data were presented from a broad multifactorial occupational study suggesting that exposure of workers to 1 ppm (1500 µg/m³) of HCl for 15 years was not associated with lung cancer (Bond *et al.*, 1986). Unfortunately, details were not available, particularly with respect to possible effects on the upper airways, so it was not possible to compare this study to the sulfuric acid research. (Subsequent to the workshop, a more detailed analysis of the study was submitted for publication by Bond.) Even with such information, it appears that additional epidemiological data are desirable to assess whether there is any association between occupational hydrogen chloride exposure and chronic health effects, particularly those occurring in the upper airways.

The participants also concluded that the relevance of the sulfuric acid epidemiological data to HCl depends on whether the effects noted can be ascribed strictly to acidity, an issue that remains to be resolved. Even if acidity is the critical factor, there is reason to believe that the effects may be different because sulfuric acid, due to its greater hygroscopicity, will grow to a much larger particle size than hydrogen chloride in humid environments such as the upper airways and thus have the potential to cause greater effects at these sites.

CONCLUSIONS

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The participants in the Workshop were in general agreement about the scientific conclusions described above. They also reached consensus on the implications of these

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conclusions for assessing the risk of HCl in ambient air. First, measured levels of HCl in ambient air are about 1 ppb (0.025–2.5 ppb). These values are at least a few orders of magnitude less than the approximately 1 ppm (0.2–10 ppm) likely to cause either acute or chronic effects in humans. One area of uncertainty is possible effects on sensitive subpopulations. However, results from studies of H₂SO₄ exposure in sensitive groups suggest that they are only fivefold more sensitive than the general population (Spengler *et al.*, 1990). If these results are applicable to HCl, they suggest that ambient levels are unlikely to cause effects in such subpopulations.

Second, the form of HCl in ambient air (gaseous or with a very limited amount of hydration) and its physicochemical properties, especially hygroscopicity and reactivity, suggest that even if toxic effects in humans result from ambient exposure they will be limited to the upper airways. HCl will probably be effectively scrubbed from the inspired air at these levels of the respiratory system and will not penetrate into the deep lung in significant amounts. Another conclusion from physicochemical considerations is that human exposures will be limited in both time and space due to the transport and fate properties of HCl in ambient air.

Third, based on the limited geographical distances HCl is transported, it is clear that it is not a significant contributor to acid rain. However, in local areas, it could have environmental and economic impacts, such as corrosion. More careful examination of local movement of HCl is needed to assess the extent of such impacts.

In terms of future work, the consensus of the group was that additional health research should focus on epidemiological studies of exposed workers and of sensitive subpopulations. More environmental research is needed to quantify atmospheric HCl levels and determine their daily and seasonal variability. This work should include attempts to assess impacts of individual sources on ambient air concentrations. As part of this research, studies of the reliability and comparability of the four different measurement techniques—impingers/bubblers, absorbent tubes, filter packs, and diffusion denuders—should be undertaken.

In summary, the participants were able to reach general agreement about the levels of HCl expected in ambient air and the doses and types of adverse effects expected in humans who are exposed to such levels. The participants also identified additional areas of research that might provide additional useful information about HCl toxicity in humans.

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