Chapter 1
Introduction

1.1. Background to the report

1. Previous reports by the Expert Panel on Air Quality Standards (EPAQS) have made recommendations to Government on non-occupational ambient air quality standards, with particular reference to the levels of airborne pollutants at which no or minimal effects on human health are likely to occur.

2. This report differs from previous reports in that the guideline values it recommends are not intended for use in national air pollutant standard setting. Instead, this report forms part of the Panel's current work programme in which it is advising the Environment Agency on some of the priority substances that it is responsible for regulating. Unlike the pollutants for which EPAQS has set air quality standards, these warrant special consideration for their emissions from a small number of point industrial sources and the guideline values are intended to protect local populations around these sites.

3. Scientists are often faced with a situation of uncertainty and this has been the case with EPAQS' assessments of the halogens and hydrogen halides. In recommending these guidelines there has been uncertainty both because the available data did not always apply to the actual chemical concerned and because the data were not usually obtained from the most susceptible groups of people (see Section 1.2.2 for a discussion of susceptible groups). In such cases, the Panel has divided the no observed adverse effect level (NOAEL) by a safety factor determined by the level of uncertainty (Renwick and Lazarus, 1998). This is in line with the precautionary approach favoured now in decisions concerning safety.

4. The guideline values recommended represent a level at which no significant health effects would be expected to occur over the short-term, specifically guarding against the effects of acute irritancy. They include a margin of safety so that slight exceedance would be unlikely to result in serious health effects. It should be noted, however, that for hydrogen fluoride and hydrogen iodide health effects resulting from longer-term exposure cannot be ruled out. EPAQS is currently investigating this issue and shall be producing an addendum to this report addressing the protection of human health over the long-term

against exposure to hydrogen fluoride and hydrogen iodide. The short-term guideline values are intended for use in the risk assessment of emissions arising from normal operating conditions. Separate guidelines are in place to deal with large releases during chemical incidents. Further information on the control and assessment of major accidental releases can be found on the Health and Safety Executive website at http://www.hse.gov.uk/hid/index.htm.

1.1.1 Development of the report

5. In order to facilitate the development of guideline values for a large number of compounds, the Environment Agency provided EPAQS with a peer-reviewed dossier on each of the substances under consideration. The dossiers included:
    - sources of the substance;
    - a summary of monitoring methods and UK ambient concentrations;
    - a review of relevant animal toxicity data;
    - a review and preliminary evaluation of existing literature on human toxicology and health effects; and
    - where possible, the identification of no observed (adverse) effect levels.

    These dossiers have been published as Environment Agency Research and Development Reports and are available on the Agency publications website (http://publications.environment-agency.gov.uk).

6. EPAQS used the dossiers to provide background information and as an aid to identifying the key studies on which to base their recommendations. When appropriate, members of the Panel went back to the original papers and supplemented these with additional research of their own. Air quality guideline values were reached through reviewing the available literature and the application of expert judgement.

7. For the selected halogens and hydrogen halides included in this report the number of reliable human studies that have been performed are few and so safety factors, in a range of two to ten, have been used to reflect both the uncertainty in extrapolating the data to the general population, which contains susceptible groups, and the confidence of the Panel in the scientific information available on which to base its judgements.

1.1.2 How the Environment Agencies will use the guideline values

8. The Integrated Pollution Prevention and Control Directive applies an integrated environmental approach to regulating industrial emissions from specified installations. This has been implemented in the UK through the Pollution Prevention and Control Regime.

9. When the Pollution Prevention and Control Regime is fully implemented, the Environment Agency will regulate approximately 4,000 of the potentially most complex and polluting industrial installations in England and Wales with many smaller installations

being regulated by local authorities. The situation is slightly different in Scotland where the regulator, the Scottish Environment Protection Agency, regulates all installations covered by the regime. The Northern Ireland Environment and Heritage Service is the environmental regulator for Northern Ireland.

10. The Pollution Prevention and Control Regime requires the regulator to ensure that 'no significant pollution is caused' and that conditions are included in the permit, subject to the application of the Best Available Techniques (BATs) that:
   - ensure a high level of protection for the environment as a whole;
   - have regard to the potential to transfer pollution from one environmental medium to another;
   - take account of an installation's geographical location and local environmental conditions;
   - are aimed at minimising long distance and transboundary pollution;
   - ensure appropriate protection of the soil and groundwater.

11. To gain a permit, operators will have to show that their proposals represent the BAT to prevent and minimise pollution from their installation. In order to assess the environmental impact of an installation or identify the BAT from a range of options, the Environment Agency in conjunction with the Scottish Environment Protection Agency and the Environment and Heritage Service is developing an assessment methodology known as H1: Guidance on Environmental Assessment and Appraisal of BAT. Operators are not required to use the methodology when making their application for a permit but it does provide a structured assessment process which addresses the specific requirements of the Pollution Prevention and Control Regime. Operators using an alternative approach would need to ensure that an equivalent level of assessment is made.

12. The H1 methodology consists of the following basic steps:
   - Define the objective and scope of assessment.
   - Generate options of techniques to control pollution.
   - Assess the environmental impacts of each option.
   - Evaluate the costs to implement each option.
   - Identify the option which represents the best available technique.

13. Environmental criteria are used within H1 primarily to:
   - assess the significance of releases to different environmental media and to screen out insignificant effects;
   - assess the relative effects of releases within and between different environmental media.

14. However, there are relatively few established environmental criteria that are suitable for use within the assessment methodology. For example, EPAQS have published standards for nine of the major air pollutants and the World Health Organization has set guideline values for 14 organic and 15 inorganic pollutants, including some for which standards have also been set by EPAQS. Overall, recognised air quality standards

are available for only approximately 31 different substances. This is to be compared with the 129 agents that are reported as being released to the air from industrial installations on the Environment Agency's Pollution Inventory and on the Scottish Environment Protection Agency's Scottish Pollutant Release Inventory.

15. In order to fulfil its regulatory role, the Environment Agency has developed environmental criteria known as *environmental assessment levels* (EALs) for different environmental media (air, water and land) for use within the H1 framework. A hierarchical approach has been used to develop EALs. For air, existing standards and guidelines are used as EALs; however, as there are only a limited number of appropriate values, EALs for most substances have been derived from occupational exposure values by the application of a simple safety factor (Environment Agency, 2003). The air quality guidelines proposed in this report by EPAQS will replace these less robust values for use within the H1 methodology.

1.2. General issues

1.2.1 Exposure to multiple pollutants

16. Individual industrial processes may release a wide variety of pollutants, which can include a number of the halides considered in this report. The principle hydrogen halide released is hydrogen chloride, which arises mainly from the burning of fossil fuels, especially the combustion of coal or oil. Since fossil fuels also contain trace amounts of the other hydrogen halides (hydrogen bromide, hydrogen fluoride and hydrogen iodide) these will be released in smaller quantities at the same time. Table 1.1 shows the releases of halogens and hydrogen halides by different industrial sectors as reported by the Environment Agency's Pollution Inventory in 2002.

Table 1.1 Releases of halogens and hydrogen halides from industry sectors reported in the Environment Agency's Pollution Inventory for 2002. (Data are for processes regulated under Integrated Pollution Control or Pollution Prevention Control by the Environment Agency in England and Wales. Nd indicates no data.)

Industry	**Bromine[1] (tonnes)**	**Chlorine[1] (tonnes)**	**Hydrogen bromide[1] (tonnes)**	**Hydrogen chloride[2] (tonnes)**	**Hydrogen fluoride[2] (tonnes)**	**Hydrogen iodide[1] (tonnes)**
Fuel and power production and associated processes	Nd	Nd	693	31710	2236	152
Metal production and processing	Nd	1.8	<0.1	586	237	Nd
Mineral industries	Nd	Nd	9.9	408	158	Nd
The chemical industry	0.7	26	0.2	63	<0.1	Nd
Waste disposal and recycling	Nd	<0.1	<0.1	146	<0.1	Nd
Other industry	Nd	Nd	Nd	Nd	73	Nd
Total (tonnes)	0.7	27.8	704	32914	2704	152

[1]Substance reported where release greater than one tonne per year or as required by the Environment Agency. Totals may underestimate actual release.

[2]Substance required to be reported by all operators.

17. In addition to hydrogen chloride from combustion processes, some installations will release one or more hydrogen halides from other processes or activities being undertaken on the site. For example, hydrogen fluoride is emitted from some aluminium smelters and ceramic processes and chlorine from a range of chemical processes, such as the manufacture of organic chemicals. Typically, however, releases are dominated by combustion-derived hydrogen chloride and process releases are generally small by comparison.

18. In this report, the effects of individual pollutants have been considered separately. However, the Panel recognises that ambient air that includes localities around an industrial plant contains a complex mixture of pollutants at differing concentrations. The effects of exposure to more than one pollutant may be additive (i.e., the sum of the individual pollutant effects), synergistic (i.e., greater than the sum of the individual pollutant effects) or antagonistic (i.e., less than the sum of the individual pollutant effects).

19. There is a paucity of information on the effects of complex mixtures of pollutants. Whether effects are additive, synergistic or antagonistic will depend on the pollutants involved, their likely mechanisms of effect and their concentrations.

20. The issue of the health effects of exposure to mixtures of air pollutants was considered by the Advisory Group on the Medical Effects of Air Pollutants in their Fourth Report in 1995 (MAAPE, 1995). They recommended caution when considering the effects of exposure to more than one pollutant and pointed out that the level of understanding of the mechanisms of possible interactive effects is even less well developed than the understanding of the mechanisms underlying the health effects of individual pollutants. For all the halogens and hydrogen halides, the prominent effect at low concentration is irritation. Thus it is likely that exposure to mixtures of these substances will be additive. The effects of mixtures of other pollutants with halogen and hydrogen halide gases is unknown and synergistic effects in some instances can't be ruled out.

21. This report deals with the direct effects of chemicals on health but the Panel recognises that there may also be interactions with biological components in the air. This is an area that requires further research.

1.2.2 Susceptible groups

22. Studies examining the impact of ambient air pollution have identified a wide range of sensitivities within the population. Certain individuals appear to be sensitive to pollution for genetic reasons, whereas others become vulnerable as a result of environmental or social factors. For example, socio-economic status has been shown to modify the effects of ambient air pollution associated with asthma hospitalisations (Lin *et al.*, 2003). These variations within the human population mean that individuals are likely to fall somewhere along a continuum of susceptibility. However, most safety factors are not based on strong scientific evidence nor are they necessarily accurate predictors of

outcomes. They merely attempt to allow for all perceived possibilities and compensate for a lack of knowledge (RCEP, 2003).

23. Age has been identified as a strong predictor of susceptibility to pollution. Young children and the elderly are considered to be more at risk from respiratory (breathing) and cardiopulmonary (heart and lung) disease associated with exposure to air pollution (Burnett *et al.*, 1997; Sunyer *et al.*, 2003). The specific issue of the greater susceptibility of children is dealt with in more detail in Appendix 1. A precautionary approach is widely adopted for very young children.

24. Subgroups of the population who acquire increased sensitivity to pollution include those with existing cardiovascular and respiratory disease.

25. It should be noted that susceptible groups are less frequently used either in chamber studies or in occupational assessments – further appropriate research into the health effects of air pollutants on such groups would be desirable.

1.2.3 Choice of averaging times and units of concentration

26. Chamber studies are conducted at concentrations that are held constant for their duration, often for several hours and sometimes with the subject undertaking exercise. Ambient exposures, on the other hand, are generally more variable, a fluctuation that is seldom reflected in average measurements. The adverse effects of halogens and their hydrogen halides are largely irritant and are thought to depend on peak concentrations. For these reasons it is preferable to measure exposures over short periods in order to capture any transient but significant peaks. However, for chemicals present at low levels, very short collection periods are not technically feasible as they may yield insufficient material for analysis. When recommending time periods for the guideline values the Panel has balanced these factors. It is considered that an averaging time of 1 hour is the lowest that is technically feasible for the guideline values proposed.

27. Concentrations of pollutants in air can be expressed in two ways: as the mass of pollutant per unit volume of air (expressed in this report as mg/m^3) or as the ratio of the volume of the pollutant to the volume of air in which it is contained (expressed in this report as parts per million or ppm). A more detailed explanation of these units is given in Box 1. In this report we have used the volume mixing ratio as the main unit of concentration. This is the appropriate unit to use if the toxicities of different gases, at different concentrations, are to be compared: the comparative toxic effects being dependent on the relative toxicological properties of the molecules and on the numbers present, but not on the masses of those molecules.

Box 1: Units used to express the concentration of gases in air

Concentrations of gases in air are expressed in two ways:

1. As the mass of gas in a specified volume of air, usually expressed as mg (one thousandth of a gram) or µg (one millionth of a gram) per cubic metre and generally written as mg/m^3 or $\mu g/m^3$.
2. As the ratio of the volume of the gas to the volume of air in which the gas is contained, usually expressed as a volume mixing ratio, that is parts per million (ppm) or parts per billion (ppb).

The mass concentration as expressed above will be dependent on the ambient temperature and pressure. The volume mixing ratio is independent of temperature and pressure, if ideal gas behaviour is assumed. The two systems of units are interchangeable.

Given that 1 mole of gas occupies 22.41 litres (l) at standard temperature and pressure (STP), and letting the gram molecular weight of the gas in question equal M,

$$1 \text{ mol} = M \text{ grams occupies } 22.41 \text{ l at STP}$$

Therefore, $$1 \text{ mg occupies } \frac{22.41}{M} \div 1000 \text{ l} = \frac{22.41}{M} \text{ ml}$$

As $$1\text{ppm} = 1 \text{ ml/m}^3$$

$$1\text{ppm} = \frac{M}{22.41} \text{ mg/m}^3$$

or $$1 \text{ mg/m}^3 = \frac{22.41}{M} \text{ ppm}$$

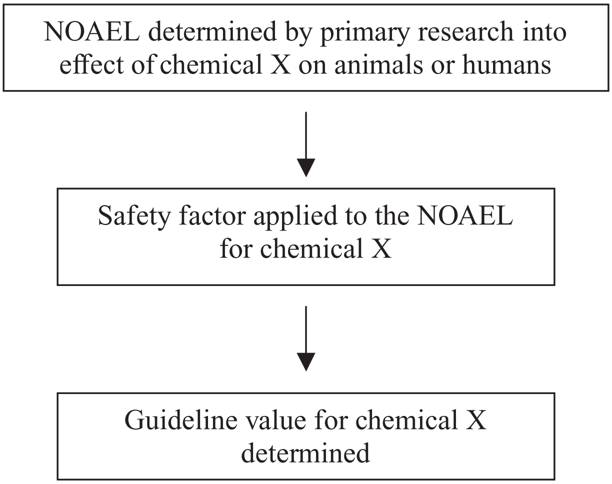
If ambient conditions of temperature and pressure need to be considered then the molar volume (22.41 l at STP) must be corrected:

$$\text{Molar volume at T°C and P millibars} = 22.41 \text{ x } \frac{273 + T}{273} \text{ x } \frac{1013}{P}$$

1.2.4 Safety factors

28. In its derivation of air quality guidelines, EPAQS has used the steps shown in Figure 1.1. It has taken account of the presence of susceptible groups in the general population by applying safety factors to the available human data. The values of the safety factors also incorporate the uncertainty of determining the no observed or lowest observed adverse effect levels (LOAEL) when the human data are sparse or inadequate. Justification of the safety factors adopted is given in respect of each individual compound in the specific sections. The basic rationale can be readily explained through the hydrogen halides. Hydrogen chloride proved to be the best starting point for the halide gases and a safety factor of 2 for this gas was applied by analogy with the method adopted by EPAQS in recommending the air quality standard for sulphur dioxide, another irritant acidic gas for which there is much more human data. Thus, a no observed adverse effect level (NOAEL) in subjects with mild asthma was considered to be 1 ppm for hydrogen chloride. The same starting value was assigned to hydrogen bromide because its irritant properties on the human lung were considered to be very similar to those of hydrogen chloride. Nevertheless, a higher safety factor of 5 reflected the uncertainty the Panel had because of the deficiency of human exposure data on hydrogen bromide itself. For hydrogen iodide a safety factor of 10 was used to reflect the uncertainty caused by the virtual absence of reliable human data on its irritant properties at low concentrations and because it has the potential to be a greater irritant at molar equivalent concentrations than hydrogen chloride is. The safety factors are summarised in Table 1.2.

Figure 1.1 Sequence of steps taken to arrive at a guideline value for a particular chemical pollutant.



29. In most instances, the information available on ambiguous, subjective reports of ‘irritation’ and odour detection was not regarded by the Panel to be sufficiently reliable or robust to be included. The exception was hydrogen fluoride in the one human exposure study in which symptoms of irritation of the upper and lower respiratory tract, as well as eye irritation, had been shown to be more reliable study endpoints for exposure to low concentrations of this gas (Lund *et al.,* 1997).

Table 1.2 Summary of safety factors used in arriving at the guideline value, averaged over a 1-hour time period, for each halogen and hydrogen halide.

Substance	NOAEL	Normal volunteers used ?	Volunteers with asthma used?	Safety factor	Guideline value (1-hour average)[1]
Chlorine	0.5 ppm	Y	Y	5	0.1 ppm (0.29 mg/m^3)
Bromine	0.05 ppm	Y	N	10	0.01ppm (0.07 mg/m^3)
Hydrogen fluoride	1 ppm	Y	N	5	0.2 ppm (0.16 mg/m^3)
Hydrogen chloride	1 ppm	Y	Y	2	0.5 ppm (0.75 mg/m^3)
Hydrogen bromide[2]	1 ppm	Y	N	5	0.2 ppm (0.70 mg/m^3)
Hydrogen iodide[2]	1 ppm	Y	N	10	0.1 ppm (0.52 mg/m^3)

[1]See Box 1 for an explanation of the units of concentration.
[2]Hydrogen chloride was used as a starting point for determining the guideline value.

1.3. Introduction to the halogens and hydrogen halides

30. In this report EPAQS recommend air quality guideline values for six halogens and hydrogen halides: chlorine (Cl_2), bromine (Br_2), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen fluoride (HF) and hydrogen iodide (HI). Some of these compounds are among the substances most frequently encountered by the Environment Agency in ambient air around industrial activities that do not currently have robust EALs. This group was therefore selected to be the first considered by EPAQS.

31. The halogens (fluorine, chlorine, bromine, and iodine) are a coherent series of elements with similar chemistry. Molecular weight increases from fluorine to iodine and chemical reactivity shows a downward trend with molecular weight. The lower atomic weight (and thus size) of fluorine and chlorine mean that these bind tightly within organic molecules and are difficult to displace, so chemical compounds of these halogens can be persistent. In contrast, bromine and iodine are more readily displaced and thus their compounds are generally less biopersistent. In terms of their reaction products with water, acid

strength increases from fluorine to iodine, but the oxidising strength of the hypo-halous acids also formed decreases, that is, hypochlorite is a stronger oxidising agent than hypobromite.

32. Because of the similar chemical properties of halogens and hydrogen halides, as well as the fact that a number of them have common sources, it is useful to consider them together. However, individual air quality guideline values have been derived on a substance-by-substance basis. For a number of compounds – in particular hydrogen iodide – where the literature on the health effects is sparse or non-existent, effects have been inferred from other similar substances being considered.

33. The halogens and hydrogen halides share the common property of irritancy to mucous membranes (the moist lining of airways). These irritant effects arise from the fact that these substances behave as strong acids in aqueous (water) media, i.e. they dissociate forming high concentrations of hydrogen ions that cause irritation. In the respiratory (breathing) tract the extent to which this impacts on symptoms largely depends upon their deposition in the nose or lung. Sensory irritant potency is particularly dependent upon the nature and specificity of interactions between the substance and irritant nerve receptors. The irritant potency depends upon a range of properties related to reactions at the site of deposition, physical properties such as aqueous (water) and lipid (fat) solubility and reactions with other tissue components that may compete with receptor stimulation (that is reactions that take place before the substance can cause irritation). Acid gases rarely exist in a pure gaseous state, but in a form that is partitioned between the gas and aqueous phases. They can also be adsorbed onto the surface of solid particles. These physical properties determine their bioavailabilty and thus the irritant outcomes of inhaling such gases. The studies used to inform current air quality guidelines have been based on exposure to substances in the gaseous phase. There is uncertainty surrounding their actual health effects. This needs to be taken into account when safety factors are chosen.

34. In 1998 the Health and Safety Commission's Advisory Committee on Toxic Substances (WATCH Panel) discussed the European Union criteria for classifying substances as respiratory tract sensory irritants (WATCH Panel, unpublished). It considered that ambiguous, subjective reports of ‘irritation’ that were not further qualified do not provide reliable evidence of the irritant potential of a chemical because the term ‘irritation’ can be used to describe a wide range of sensations including smell, unpleasant taste, ‘tickling sensation’ and dryness. Thus in reviewing its criteria for the European Union classification scheme for the supply of substances and preparations, the WATCH Panel considered that ambiguous, subjective reports of ‘irritation’ should be excluded, an approach that EPAQS has also adopted.

35. While acidity accounts for a high proportion of the irritancy of halides and hydrogen halides, the chemical nature of the reactive base may also contribute to stimulation of nerve receptors in the airways. This triggers subjective sensations such as cough, chest tightness and breathlessness and also reflex responses that can provoke bronchoconstriction,

increased mucus secretion and vascular engorgement, all of which may contribute to symptoms. In the case of more severe sensory irritancy involving the respiratory tract, subjective symptoms usually precede bronchoconstriction (constriction of the large air passages that lead to the lungs) and nasal obstruction.

36. There is limited information available concerning ambient concentrations of the halogens and hydrogen halides in the United Kingdom. The only reported ambient concentration data currently available from monitoring air quality are monthly mean concentrations for a small number of rural locations for hydrogen chloride and hydrogen fluoride. There are no short-term data – for example, at the 1-hour averaging period – for any of these substances and no reported data with which to assess population exposures.

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