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Processes and parameters influencing the oxidation of SO_2 and NO_X in plumes

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Steve Killeen

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Executive Summary

This report forms a part (Task 1) of the study commissioned by the Environment Agency entitled 'Atmospheric chemistry and regional ozone'. The main objectives of this study are:

1. To review the literature to identify the conditions under which unusual oxidation rates for sulphur dioxide (SO_2) and nitrogen oxides (NO_X) can occur in plumes from industrial releases.
2. To review the literature on the conversion of nitric oxide (NO) into nitrogen dioxide (NO_2) and to propose a practical methodsology to estimate the NO_2:NO_X ratio in plumes.
3. To demonstrate a practical method, based on advanced modelling, to estimate ozone (O_3) production from industrial plumes regulated by the Environment Agency and, if possible, to assess the suitability of the 'Reactivity Index' method.
4. This report addresses Task 1, with the main aim reviewing and assessing the literature in order to identify the conditions under which SO_2 and NO_X gases in the plumes of large industrial sources, such as power plants, can undergo enhanced oxidation.

Enhanced oxidation poses a particular regulatory risk. The estimation of this risk is complex as it invokes a number of competing and non-linear chemical pathways that lead to elevated concentrations of secondary pollutants. By their very nature, oxidation processes introduce non-linearities between the rates of primary emissions and the resulting concentrations, and thus can be difficult to quantify. To incorporate the correct description of these processes in assessment methodologies is therefore important for regulatory purposes.

Secondary pollutants can have important health and environmental impacts and thus nitrogen dioxide, ozone and fine particulates are of concern to regulators. It is important to fill the gaps in the regulatory models that currently exist concerning secondary pollutants from large industrial plumes. The findings contained in this report should help to develop improved assessment methods for the Environment Agency to use.

The main factors that influence the oxidation reactions of SO_2 and NO_X in plumes are reviewed. These include chemical composition of the background air, changes in light intensity between day and night and the influence of meteorological parameters such as humidity, wind speed and atmospheric stability. Key points are highlighted after each section of the literature review and are given below.

The reactions in plumes that involve sulphur dioxide oxidation can be summarised as:

1. the main gas-phase pathway is driven by the hydroxyl radical (OH), a daytime process;
2. the main liquid-phase oxidations are with O_3 when the liquid is near neutral, and with hydrogen peroxide (H_2O_2) when the liquid is more acidic, and both take place both day and night;
3. the liquid-phase oxidation rates are typically faster than those in the gas phase.

The reactions in plumes that involve NO_x can be summarised as:

1. liquid-phase oxidation of nitrogen species is not significant in plumes;
2. gas-phase oxidation by O_3 and other photochemical reactions are much more important;
3. generation of elevated O_3 by nitrogen oxide containing plumes requires the presence of volatile organic compounds (VOCs);
4. gas-phase oxidation of nitrogen species is much faster than that for sulphur species in the gas phase.

As the plume dilutes and encounters polluted atmospheres with high concentrations of VOCs the tendency to produce O_3 in the plume increases. As O_3 is an important oxidising species itself and can generate other oxidants through various reactions, its increase results in the enhanced oxidative capacity of the plume.

The review also reveals the lack of literature that deals directly with conditions that may lead to unusually high oxidation rates in plumes. The purpose of this review was not to undertake new work, but to bring together the general understanding in the area of factors that affect plume chemistry and in, particular, oxidation rates.

Contents

1 Introduction

This report addresses Task 1 of a larger study of atmospheric chemistry and regional ozone. It consists of a literature review to identify the conditions under which SO_2 and NO_X gases in the plumes of large industrial sources, such as power plants, can undergo enhanced oxidation.

Large industrial point sources produce NO_X (nitrogen oxides taken as the sum of nitric oxide, NO, and nitrogen dioxide, NO_2) and SO_2 (sulphur dioxide) as a result of combustion processes. Generally, SO_2 is produced from the combustion of sulphur present in the fossil fuel and NO_X is produced from the oxidation of atmospheric nitrogen (Hewitt 2001, Seinfeld 2004). Some fossil fuels may contain nitrogen in smaller amounts; of all the main fuels, coal has the greatest amount of nitrogen. The contributions from nitrogen fixation to fuel nitrogen from UK power stations can be found in the NAEI (National Atmospheric Emissions Inventory). The quantities of these gases produced depend upon process conditions such as temperature, which affects nitrogen fixation with oxygen in the air, and the purity of the fuel (e.g. sulphur content). The quantities of gases released to the atmosphere also depend upon the efficiency of any emission abatement technology (such as desulphurisation plant), where fitted. The emitted NO_x and SO_2 in the atmosphere can be oxidised by ozone and other oxidants as the plume travels away from the source. These oxidation reactions result in the production of gaseous NO_2 and secondary aerosol containing sulphates and nitrates $SO^2{}_4$ and $NO^-{}_3$. Ozone from the surrounding air is one of the reactants in the oxidation and is also generated as a by-product of the reactions. Both of these pollutant categories, gaseous NO_2 and the secondary aerosol particles have well recognised environmental implications, particularly on human health. It is therefore important to assess the impact of the point source plumes at various temporal and spatial scales in terms of their contributions to these pollutants.

The rates at which NO_X and SO_2 are oxidised to secondary pollutants are different for the background air and for plumes. Within a plume, the concentrations of these species and their rates of chemical reaction may vary by orders of magnitude compared to those in the surrounding atmosphere. The factors that affect this variability in the oxidation rates include the chemical composition of the plume, prevailing meteorology, time (day or night), age of the plume (distance from the source) and the chemical composition of the air in which the plume mixes (Cocks and Fletcher 1982, 1988, 1989, Burton *et al.* 1984, Janssen 1986, Clark and Cocks 1988, Janssen *et al.* 1991, Karamchandani and Seigneur 1999, Liang and Jacobson 1999, Mueller and Imhoff 2000, Seigneur *et al.* 2000).

1.1 Background of this study

The Environment Agency, as part of its obligations, is responsible for the regulation of emissions from large point sources, such as power stations. In September 1998 a widespread air pollution episode was observed in the areas of West Midlands and South Yorkshire resulting in the exceedances of SO_2, particulate matter less than 10μm in diameter (PM_{10}) and NO_2 objectives. The Environment Agency at that time commissioned various research studies to look into the causes of this episode with the particular emphasis on the contribution of large point sources (Environment Agency 2000, Harrison and Baggott 2000a, 2000b).

The study undertaken by the UK Met Office using the NAME model (Environment Agency 2000), to establish source attribution, concluded that more than one Environment Agency regulated source was responsible. Under the prevailing weather conditions, the study indicated that up to 95% of the simulated SO_2 concentrations at Birmingham, Ladybower, Nottingham and Stoke-on-Trent could result from the coal-fired power stations in northeast England.

In response to Environment Agency studies, the power generators TXU Europe Power Ltd (TXU) and PowerGen plc undertook their own studies of the 1998 episode (TXU and PowerGen 2000, Hewitt 2001). The report of TXU and PowerGen (2000) analysed the measured air quality and meteorology data and modelling results from the UK Met Office model NAME for the episode period. The TXU and PowerGen report (2000) did not agree with the findings of the Environment Agency (2000) report and concluded that the contributions from the power stations' plumes in northeast England were significantly lower than those reported in the Environment Agency (2000) report. We have not considered this work further, as it focused on the use of models rather than on the plume chemistry itself. However, there is a suggestion that fog may have been a complicating factor in the measurements of SO_2. Both reports should be consulted directly for more details on the specific studies.

The paper of Hewitt (2001) reviews the available literature on the atmospheric chemistry of SO_2 and NO_X emitted from power station plumes. The main findings from Hewitt (2001) and by Harrison and Baggott (2000a) are discussed in Sections 3.1.1 and 3.1.2.

In the light of the previous studies, the Environment Agency has commissioned this further work to investigate the contributions from large point sources. The emphasis is on the contribution of power station plumes to the ground-level concentrations of a suite of pollutants, such as O_3, NO_2, SO_2 and particles under typical and episodic meteorological conditions. In particular, this work should review any new relevant research and take account of new model developments in this field.

The current study is Task 1 of a larger project commissioned by the Environment Agency, which has the overall aim to develop methodologies to estimate the impacts of large point sources on regional air quality. The larger study comprises three separate, but interlinked and sometimes overlapping tasks, which are listed below.

1. Assessment of regional-scale plume chemistry for episodes;
2. NO/NO_2 conversion in plumes at short range; and
3. contribution of point sources regulated by the Environment Agency to regional ozone concentrations, particularly under episodic conditions.

This report addresses the literature review for Task 1 with the main objectives being:

1. to improve the understanding of processes that can lead to unusually high oxidation rates for SO_2 and NO_X and the formation of PM in plumes under episodic conditions;
2. to suggest any improvements in current methodologies to attribute the SO_2, NO_X and PM episodes to industrial sources.

Tasks 2 and 3 are addressed in separate reports as part of this overall study.

1.2 Structure of the report

The rest of the report is divided into two main sections:

1. A summary of the key reactions that are responsible for the oxidation of SO_2 and NO_X in the atmosphere. (This section is added to provide background to the discussion in the sections that follow.)

2. A review of the literature on the processes, parameters and factors that influence the oxidation of SO_2 and NO_X in plumes and in the background air.

The report on Task 2 addresses the conversion of NO to NO_2 in more detail and the report on Task 3 discusses CMAQ and NAME III modelling results to estimate stack contributions to regional air quality.

2 Major pathways of atmospheric oxidation of SO_2 and NO_X

The reactions that result in the oxidation of SO_2 or NO_X are the same in the background air and in the plumes. However, the rates at which these take place in the two environments can be considerably different. This section summarises the most important reactions that result in the atmospheric oxidation of SO_2 and NO_X, either in the gaseous or aqueous phase. For further background details on this subject, the reader is referred to standard text books (e.g. Brimblecombe 1996, Seinfeld and Pandis 1998, Jacob 1999, Hobbs 2000).

2.1 Atmospheric oxidation of SO_2

Sulphur dioxide is an acidic gas that is primarily produced from the combustion of fossil fuel containing sulphur, or from the oxidation of naturally occurring sulphur gases. The oxidation of SO_2 can occur either through gas or liquid phase processes.

2.1.1 Homogeneous oxidation

The gas-phase oxidation of SO_2 in the atmosphere primarily takes place through its reaction with the hydroxyl radical ($OH^{\cdot}$). This highly reactive radical is produced in the atmosphere from the reaction of oxygen atoms with water, or through other mechanisms such as the photolysis of nitrous acid (HONO) and hydrogen peroxide (H_2O_2).

A short summary of the homogenous oxidation of SO_2 has been provided by Derwent (2006, personal communication) and is given below.

The homogeneous, gas phase oxidation of SO_2, is driven primarily by its reaction with hydroxyl OH radicals (Blitz *et al.* 2003) through the reaction:

$$OH + SO_2 + M \rightarrow HOSO_2 + M \qquad 1$$

where M is a molecule of oxygen (O_2) or nitrogen (N_2) that removes the energy liberated in the reaction. The hydroxysulphonyl ($HOSO_2$) radical intermediate then reacts quickly with O_2 to form sulphur trioxide (SO_3) and an HO_2 radical (Atkinson *et al.* 2004):

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \qquad 2$$

SO_3 subsequently reacts with water vapour to form sulphuric acid (H_2SO_4):

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad 3$$

OH radicals are produced by the photolysis of O_3 in the presence of water vapour through the formation of excited oxygen atoms (O*) in the reactions:

$$O_3 + h\nu \rightarrow O^* + O_2 \qquad 4$$
$$O^* + H_2O \rightarrow OH + OH \qquad 5$$

where $h\nu$ represents a radiation photon. Another important source of OH radicals is through the photolysis of formaldehyde (HCHO), which produces hydroperoxy radicals (HO_2). These latter radicals are rapidly recycled to OH radicals through reactions with NO and O_3:

$HCHO + h\nu \rightarrow H + HCO$ 6
$H + O_2 + M \rightarrow HO_2 + M$ 7
$HCO + O_2 \rightarrow HO_2 + CO$ 8

$HO_2 + NO \rightarrow OH + NO_2$ 9
$HO_2 + O_3 \rightarrow OH + O_2 + O_2$ 10

There are, additionally, small sources of OH radicals from the photolysis of nitrous acid (HONO), nitric acid (HNO_3) and hydrogen peroxide (H_2O_2):

$HONO + h\nu \rightarrow OH + NO$ 11
$HNO_3 + h\nu \rightarrow OH + NO_2$ 12
$H_2O_2 + h\nu \rightarrow OH + OH$ 13

As the gas-phase oxidation of SO_2 primarily depends upon the concentration of OH radicals, it is largely restricted to daytime when the production of OH radicals is most favoured.

2.1.2 Heterogeneous oxidation

The heterogeneous oxidation of SO_2 proceeds through its dissolution in water from cloud and fog and its reaction with other dissolved species. The solubility of SO_2 in water can produce three dissolved S (IV) species depending upon the pH of the solution. At very low pH (<2) most of the SO_2 exists as $SO_2.H_2O$, in the pH range 2-7 it exists predominantly as HSO_3 and in basic solutions, pH >7, it occurs as SO_3^{2-} (Hoffmann 1986, Seinfeld and Pandis 1998, Hobbs 2000, Hewitt 2001).

The aqueous phase oxidation of SO_2 plays a more important role than its gas-phase oxidation. Although there are many pathways for the aqueous-phase oxidation of SO_2, the two most important include its reaction with dissolved O_3 and H_2O_2. In fact, the SO_2 reaction involving H_2O_2 is the most important oxidation pathway, but this oxidation route only operates efficiently in a near-neutral solution. As a result, this route is self-limiting because of the acidity it produces. Unless there is some means of limiting the build-up of acidity in the reacting droplets, the H_2O_2 route stops quickly.

Oxidation through the dissolved H_2O_2 route is promoted to an appreciable rate when ammonia (NH_3, the main alkaline gas in the atmosphere) dissolves in the reacting droplets and neutralises the acidity. The dissolved O_3 reacts with all the S(IV) species and does not show the pH dependence of the H_2O_2 oxidation. However, its overall rate is slower than that of the H_2O_2 route because of the lower solubility of O_3 in water compared with that of H_2O_2. The liquid-phase reaction of O_3 with SO_2 is faster compared with the reaction of the two species in the gas phase and is an important route of SO_2 oxidation at pH greater than 4. Other reactions are generally limited because of either the low solubility of other species or slow reaction rates. The reactions of SO_2 with dissolved O_3 and H_2O_2 are given below; they start with the dissolution of SO_2 in water to produce sulphite (SO_3^{2-}) and bisulphite (HSO_3^{-}) ions.

Dissolution of SO_2:

$$SO_2 + H_2O \rightarrow SO_2.H_2O \qquad 14$$

$$SO_2.H_2O + H_2O \rightarrow HSO_3^- + H_3O^+ \qquad 15$$

$$HSO_3^- + H_2O \rightarrow SO_3^{-2} + H_3O^+ \qquad 16$$

Oxidation with O_3:

$$S(IV) + O_3 \rightarrow S(VI) + O_2 \qquad 17$$

Oxidation with H_2O_2:

$$HSO_3^- + H_2O_2 \rightarrow SO_2OOH^- + H_2O \qquad 18$$

$$SO_2OOH^- + H_3O^+ \rightarrow H_2SO_4 + H_2O \qquad 19$$

In the presence of metals some reactions are catalysed and this can influence the yield of the products. Once sulphuric acid is formed it will react with atmospheric NH_3 to produce ammonium sulphate aerosol particles. NH_3 is a very important compound in the production of secondary aerosol as it is widely distributed in the natural environment because its emissions from agriculture are significant. It also plays a major role in the formation of ammonium nitrate (NH_4NO_3) aerosol. The droplets in which these reactions take place have to evaporate before they become particles and contribute to the total particulate matter (PM) levels. Raes *et al.* (2000) explain the importance of droplet evaporation in forming particles, particularly sub-micron particles. Thus a range of particle sizes is produced which contribute to the total atmospheric loadings of aerosol particles which in turn influences ground-level PM_{10} concentrations.

2.1.3 Key points of sulphur oxidation

1. The main gas-phase pathway is driven by OH, and is a daytime process.
2. The main liquid-phase oxidation occurs with H_2O_2 in near-neutral conditions and with O_3 for more acidic conditions, both of which can take place during day and night.
3. The liquid-phase oxidation rates are typically faster than those in the gas phase.

2.2 Atmospheric oxidation of NO_X

The initial emissions of NO_X from combustion sources largely consist of NO and a small fraction of NO_2 (typically around 5-10% of NO_x). A fraction of the primary emission of NO is then oxidised to NO_2, depending upon the meteorological conditions and the availability of suitable oxidants. The subsequent oxidation of NO_2 then results in the formation of HNO_3, which may, in turn, react with atmospheric NH_3 to form NH_4NO_3 aerosol particles.

2.2.1 Homogeneous oxidation

Nitric oxide may be oxidised by direct reaction with O_2; however, under usual ambient concentrations and normal temperatures this reaction is slow (Webb 1997, Seinfeld and Pandis 1998, Hewitt 2001). For power station plumes, characterised by high temperatures and high NO concentrations, the reaction, NO + NO + O_2 = $2NO_2$, is important in the post-flame gases and in the near-field plume chemistry. The temperature dependence of this reaction is sometimes used as a technique to minimise primary NO_2 emissions in the flue gases:

$$2NO + O_2 \rightarrow 2NO_2 \qquad 20$$

The oxidation of NO to NO_2 primarily takes place through ozone (O_3), the hydroperoxy radical (HO_2 radical or one of the alkylperoxy radicals (RO_2), as shown below:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad 21$$

$$NO + HO_2 \rightarrow NO_2 + OH \qquad 22$$

$$NO + RO_2 \rightarrow NO_2 + RO \qquad 23$$

During daytime, the gas-phase oxidation of NO_2 takes place largely through reaction with the OH radical, which leads to the generation of HNO_3. This reaction is faster for NO_2 compared with that for SO_2. This implies that under sunny conditions when the concentrations of OH radicals are high, the removal of NO_2 will be faster compared with the removal of SO_2 through the reaction:

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad 24$$

The excess energy generated from this reaction is removed by a third body (M), generally N_2, from the background air. During night-time, the major gas-phase oxidation mechanism includes the interaction of NO_2 with O_3 and the production of the nitrate radical (NO_3):

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad 25$$

Although during night-time there is no O_3 production from photochemical reactions, O_3 molecules are present in the atmosphere from the previous day and from entrainment processes.

As the NO_3 radicals are prone to rapid photolysis, this pathway is not significant during daytime. The NO_3 radicals produced at night by this reaction can transform into HNO_3 either through interaction with alkenes and aldehydes or through the production of dinitrogen pentoxide (N_2O_5). The N_2O_5 can then either decompose or partly hydrolyse to produce HNO_3. Seinfeld and Pandis (1998, p. 272) comment that the alkenes and NO_3 reaction (26) can have a significant rate because of the high concentration of the NO_3 radical compared with that of the hydroxyl radical OH.

$$NO_3 + \text{Alkene} \rightarrow \text{addition product} \qquad 26$$

$$NO_3 + RCHO \rightarrow HNO_3 + RCO \qquad 27$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad 28$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad 29$$

2.2.2 Heterogeneous oxidation

Theoretically, the aqueous phase oxidation of NO_X to HNO_3 is possible through reactions of dissolved NO, NO_2 and OH, as shown below:

$$NO_2 + NO_2 \xrightarrow{H_2O} NO_2^- + NO_3^- + 2H^+ \qquad 30$$

$$NO + NO_2 \xrightarrow{H_2O} 2NO_2^- + 2H^+ \qquad 31$$

$$NO + OH \rightarrow NO_2^- + H^+ \qquad 32$$

$$NO_2 + OH \rightarrow NO_3^- + H^+ \qquad 33$$

However, the general understanding regarding these reactions [(30) to (33)] is that their contribution in terms of HNO_3 production is insignificant. This is mainly because of two factors:

1. the very low solubilities of NO and NO_2 in water (Henry's Law constant $k_H = 10^{-2}$ moles litre^{-1} atmosphere^{-1}or less);
2. the very slow reaction rates under ambient conditions.

2.2.3 Formation of nitrate particles

A short summary of the formation of nitrate particles was provided by Derwent (2006, personal communication) as follows.

There are various routes in which NO_x is converted into nitrate particles, either through reactions of HNO_3 or of N_2O_5. The first class of reactions involves sea salts, in which HNO_3 and N_2O_5 form sodium nitrate ($NaNO_3$) aerosol on the surface of sea-salt particles by displacement of hydrochloric acid (HCl):

$$HNO_3 + NaCl \rightarrow HCl + NaNO_3 \qquad 34$$

$$N_2O_5 + 2NaCl + H_2O \rightarrow 2NaNO_3 + 2HCl \qquad 35$$

The second class of reactions involves carbonaceous particles of wind-blown dust and leads to the formation of calcium nitrate $Ca(NO_3)_2$ particles:

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \qquad 36$$

$$CaCO_3 + N_2O_5 \rightarrow Ca(NO_3)_2 + CO_2 \qquad 37$$

The formation of NH_4NO_3 proceeds through:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \qquad 38$$

This formation is reversible and NH_4NO_3 can decompose at higher ambient temperatures, particularly during summertime.

NO_2 is also oxidised to NO_y (NO_y = sum of all oxides of nitrogen, excluding N_2O) by reaction with peroxyacetyl radicals to form peroxyacetylnitrate (PAN) through:

$$CH_3COO_2 + NO_2 + M \rightarrow CH_3COO_2NO_2 + M \qquad 39$$

PAN is an important temporary reservoir species for NO_x because it is thermally unstable and decomposes back to peroxyacetyl radicals and NO_2. Since PAN is much longer lived than NO_2 it can act as a carrier of NO_x over long distances.

2.2.4 Key points of nitrogen oxidation

1. Gas-phase oxidation by O_3 and other photochemical reactions is much more important than liquid-phase oxidation of nitrogen species.
2. The gas-phase oxidation of nitrogen species is much faster than that for sulphur species. Conversion into nitrate particles occurs through various routes involving reactions with HNO_3 or N_2O_5.

3 Parameters and processes influencing oxidation of NO_X and SO_2 in plumes and the ambient atmosphere

This section is a review of the existing literature to draw together information on factors that may result in the enhanced oxidation of NO_X and SO_2 particularly in plumes. Many of the data presented here are expressed as a fractional conversion rate, or per cent per hour. This is not the usual way of expressing the rate of a chemical reaction, which is normally calculated in terms of the number of molecules of reactant that has reacted per second. However fractional conversion rates can be calculated from the concentrations of plume species, once a combined dispersion and chemistry model has been run.

The key difference in the plume and ambient atmosphere chemistry is the NO_X concentration, typically a few orders of magnitude higher in plumes than in ambient air. NO_X is responsible for the oxidant production and removal through a number of different pathways. The concentrations of oxidant in the plume result partly from the entrained atmosphere and partly from in-plume production. Most of the O_3 that is entrained in the early phase of the plume is quickly destroyed by the high NO concentration. This removes an important species that can produce oxidants. Later on as the plume dilutes, more O_3 is entrained from the ambient air. However the production of O_3 within the plume is restricted as the enhanced NO_2 takes up most of the OH produced. The levels of NO_X concentrations also play an important part in determining the gas-phase oxidation rate of SO_2, as they influence the availability of the OH radical concentrations.

This chapter discusses some of the recent reviews on plume chemistry. We also look at the chemical structure of the plume and the role of background air before examining the factors that influence oxidation rates in plumes.

3.1 Overview of recent reviews on plume chemistry

Two important reviews of the plume chemistry that resulted from the work following the 1998 episode, are Harrison and Baggott (2000a, 2000b) and Hewitt (2001). A further study by W.S. Atkins focused on the way the models were used, rather than the underlying chemistry, so it is not included here. We summarise the key points of these reviews to assess how the state of the art in this field relates to the questions that need to be answered in this project. The points of agreement between these reviews are also identified to understand the general consensus on the issues.

3.1.1 Harrison and Baggott (2000a,b) reports

The main objective of the report of Harrison and Baggott (2000a, 2000b) was to examine published information on the oxidation of SO_2 and NO_X in plumes of large industrial sources. The authors mention that most of the reviewed literature falls within a narrow time span, 1975-1981, which implies that this was the period when there was greatest interest in these aspects of plume research. Also most of the studies reviewed dealt with the oxidation of SO_2

rather than that of NO_X. These authors comment that the methodologies used in these studies were not optimal and various sources of errors in the studies were highlighted, such as not taking into account artefact formation during sampling and primary sulphate formation. They suggest that this may influence the results and the conclusions of the studies.

The variation in the estimated gas-phase oxidation rates of SO_2 in these studies appears to depend upon the availability of the OH radical. The rate varies from as low as 0.03% per hour, during night-time, to 3.2% per hour, under high OH concentrations in summertime. The authors mention that many of the studies have not taken into account the importance of heterogeneous mechanisms for SO_2 oxidation which may be more significant than gas-phase oxidation, particularly under cloudy winter conditions.

The authors suggest that under typical UK atmospheric conditions the loss of SO_2 through oxidation is estimated to be between 0.5 and 2% per hour. Therefore, even after 10 hours of travel time the loss will be about 20% at the most. The SO_2 loss from the plume becomes appreciable only after 20 hours of travel time and even then only when the most rapid loss rates occur.

The review suggests that the oxidation of NO_X through OH during daytime is faster than the oxidation of SO_2, and can result in a loss of up to 10% per hour from the plume. During night-time the main pathway is through the initial reaction with O_3 and the loss rate is significantly lower than in the daytime.

3.1.1.1 Key points

1. The gas-phase oxidation of SO_2 is greatest in summer.
2. Heterogeneous oxidation of SO_2 in cloudy, wintry conditions is more significant.
3. In the UK, SO_2 oxidation is about 0.5-2% per hour
4. SO_2 removal is only significant after about 20 hours travel time.

3.1.1.2 Hewitt (2001) report

The Hewitt (2001) review addresses specifically power-plant plumes. The author points out that the complete description of SO_2 and NO_X oxidation is restricted by the lack of measured data for NO_X oxidation in plumes; this includes the effect of the change in oxidant availability on its oxidation. Hewitt (2001) provides a summary of reaction-rate constants and values of observed oxidation rates. His conclusions from the reviewed literature can be summarised as follows.

Generally the loss rates of SO_2 and NO_X are lower in plumes than those in the background air, primarily because of oxidant limitation. The plume edges offer an intermediate loss regime.

In non-cloudy conditions, the gas-phase oxidation of SO_2 and NO_X occurs through interaction with the OH radical. However the loss rate is faster for NO_X by a factor of about 10 compared with that of SO_2. Moreover, the gas-phase oxidation for SO_2 occurs only during daytime, while the gas-phase oxidation of NO_X can take pace during night-time through the NO_3–N_2O_5 mechanism (see, for example, Jenkin and Clemitshaw 2000). Under cloudy conditions the rapid oxidation of SO_2 takes place through liquid-phase reactions, while for NO_X there are no significant liquid-phase oxidation pathways.

The dry deposition of gaseous SO_2 is faster than that for gaseous NO_X, but the nitrate aerosol is removed quickly compared with the removal of sulphate aerosol by dry deposition. The difference in the removal rates through various mechanisms results in the variation of sulphur to nitrogen (S:N) ratios as the plume travels downwind. Generally, in clear conditions the SO_2:NO_X ratio tends to increase, whereas the sulphate:nitrate ratio tends to decrease with travel time. The reverse of this happens under cloudy conditions.

The absolute oxidation rates of SO_2 and NO_X depend upon the chemical composition of the plume and the background air, as well as the ambient conditions. Under the most favourable sunny conditions a maximum loss rate of 3% h^{-1} for SO_2 and 30% h^{-1} for NO_X is possible, although in real conditions the loss rates may be lower because of oxidant limitation.

3.1.1.3 Key points

1. Loss of SO_2 and NO_X within plumes is oxidant-limited, whereas the plume edges offer an intermediary loss regime.
2. Gas-phase oxidation by OH is about 10 times faster for NO_X than it is for SO_2.
3. Gas-phase oxidation of NO_X via NO_3/N_2O_5 proceeds at night, but SO_2 has no similar night-time oxidation.
4. Liquid-phase oxidation for SO_2 is faster than its gas-phase oxidation.
5. There is no significant heterogeneous route for NO_X oxidation.
6. Maximum oxidation rates are about 3% h^{-1} for SO_2 and about 30% h^{-1} for NO_X, although the rates will be lower when oxidants are limited.

Although the two reviews differ in focus, analysis and the extent of literature cited, there are some points of agreement which can be summarised as follows:

1. The most important pathway for the gas-phase oxidation of NO_X and SO_2 is their reaction with the OH radical. Therefore, all the conditions that can result in an increased OH concentration favour the oxidation. These conditions occur on sunny days.
2. The reaction of NO_X with OH is faster than that with SO_2.
3. Liquid phase oxidation by H_2O_2 and O_3 is more important for SO_2 than it is for NO_X, and is also more efficient than its gas-phase oxidation.
4. Night-time oxidation rates in plumes are generally lower than daytime rates.

3.2 Chemical structure of the plume

Modelling and field studies have shown that the chemistry in the plume passes through distinct phases as it travels away from the emission source (Gillani *et al.* 1981, Karamchandani *et al.* 1998, Griffiths and Hill 2000, Mueller and Imhoff 2000). This section provides a synthesis of the information found in the literature.

A simple schematic diagram is shown in Figure 1 to illustrate the main phases in the life of an idealised plume as it mixes with polluted ambient air and undergoes chemical reactions in both the gaseous and aqueous states. The figure represents pictorially the main elements of plume chemistry that we have identified in the literature covered here. The boundaries drawn between the stages are not meant as geometric boundaries, but simply as conceptual domains.

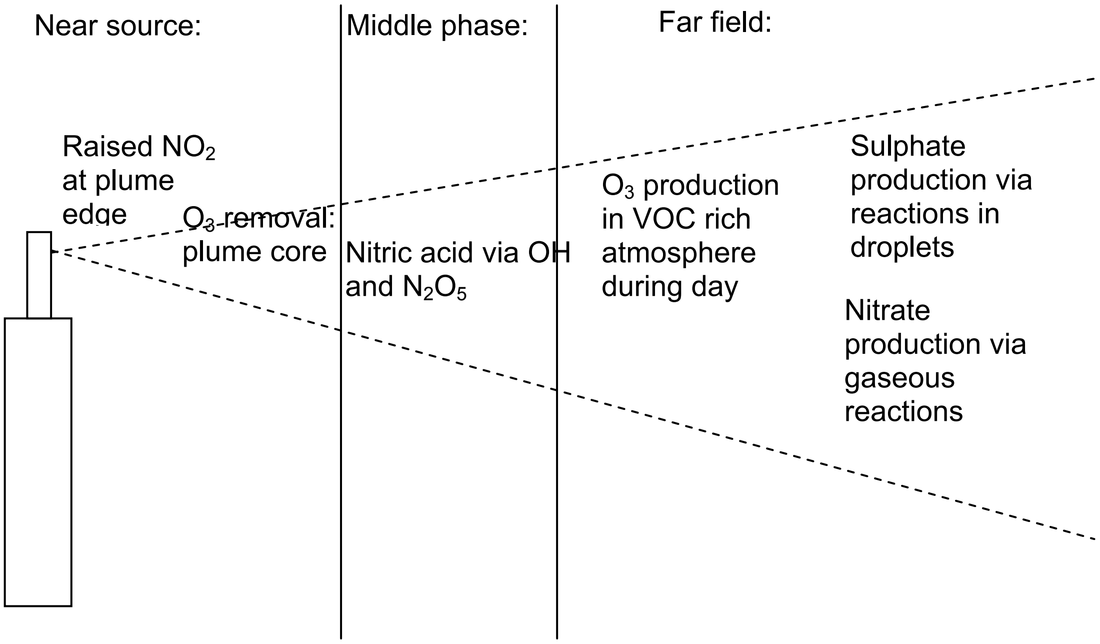

Figure 1: Schematic figure showing the phases of plume chemistry as the plume travels and mixes with ambient air to form the secondary pollutants NO_2, O_3 and secondary particulates. There are also important day/night changes and influences of meteorology that would need to be considered.

The first phase starts from the point of emissions and extends through the first few kilometres downwind, when the NO_X concentrations are very high. The characteristic of this phase of the plume is that the photostationary state applies during daytime. However, during night-time the photolytic dissociation of NO_2 does not occur. During this phase, the O_3 is titrated against high NO concentrations. The levels of O_3 are very low, generally less than 1 ppb, in the core of the plume causing the oxidation of NO to proceed very slowly. However, at the edges of the plume where the plume is in contact with background air and, therefore, exposed to higher O_3 concentrations, the NO oxidation proceeds faster. The radical concentrations in the plume are also very low resulting in the no appreciable production of aerosol.

During daytime, a second phase of the plume chemistry starts when the radical concentrations begin to increase sharply. The NO concentrations decrease because of the physical dispersion of the plume and the chemical removal processes. The radical concentrations increase because of a combination of mixing with background air containing these species and because of radicals produced from various photolysis reactions involving O_3, HONO, PAN and VOCs. During night-time, when the photolysis reactions do not occur, the concentrations of photolytic radicals decrease. However other radicals can be formed, such as NO_3 (Jenkin and Clemitshaw 2000), which result in the eventual production of HNO_3 through other mechanisms. The most important of these reactions is the one involving N_2O_5 [see reactions (26) to (29)]. During this phase, the concentrations of VOCs are still lower than that of NO_X and the O_3 concentration remains lower than that of the ambient concentration. Ozone concentrations start to rise as the plume moves further downwind and VOCs become involved in the chemistry. During this second or mid-range phase, appreciable amounts of NO_X and SO_2 are oxidised to produce aerosol through various gas- and liquid-phase reactions.

The final stage of the plume chemistry begins when the plume has travelled a long distance and is so diluted that the distinction between the concentrations of background and plume species is only minimal. At this stage, higher VOC concentrations are entrained and NO_X is diluted further. This may result in net O_3 production. The overall chemistry at this stage starts to resemble the chemistry of the background atmosphere.

It is recognised that Figure 1 may be an oversimplification of the processes. Hewitt (personal communication) has commentated that the three main phases of plume chemistry presented in Figure 1 may be useful in the regulatory context, but they are not that simple. It is correct to say that in the near field the primary pollutant concentrations are high and will dominate, removing oxidants and limiting oxidation. The rapid oxidation of NO_x in the gas phase to form nitrate implies that this process will dominate in the mid-field, and the subsequent slower oxidation of SO_2 means that this will dominate in the far field. Thus, Figure 1 does give a correct, if simple, representation of plume chemistry. The figure, however, does not take account of plume–background air mixing and it is possible that unexpectedly high plume–background air mixing may lead to *unusual* or *enhanced* oxidation rates of SO_2 and NO_x within the plume.

Unfortunately there is very little open literature on this particular area and it was not possible to pursue this further. The influence of meteorological factors on plumes, however, is discussed further in Section 3.6.

3.2.1 Key points

Plume chemistry can be considered to display distinct phases as the plume travels downwind. In the near-source phase:

1. high NO_X, photostationary state by day or O_3 and/or NO titration by night;
2. O_3 removal in the plume core inhibits NO oxidation;
3. fast NO oxidation at plume edges with surrounding O_3.

In the middle phase:

1. NO decreases with an increase in radicals during day from photochemistry;
2. at night other oxidising radicals such as NO_3 appear; the N_2O_5 pathway also appears;
3. O_3 then rises as VOCs become involved in the chemistry;
4. appreciable aerosols are formed in gas and liquid reactions.

In the final phase:

1. at large distances a highly diluted plume approaches ambient concentrations with more VOCs and less NO_X;
2. O_3 may now be produced.

The detailed model runs described under Task 3 of this project (Yu *et al.* 2007) are, in general, consistent with these key points.

3.3 Influence of season, release time and dispersion

Cocks and Fletcher (1988) investigated the influence of factors such as season, time of release and dispersion rate on the gas-phase chemistry in power-plant plumes dispersing in an atmosphere typical of rural emissions. However, before summarising their results we must emphasise that the work was undertaken using a simplified description of dispersion. A gas-phase kinetic scheme and a simple dispersion model were used to quantify these influences over a 24 hour period.

Cocks and Fletcher (1988) contains several tables, in which the following factors are summarised:

1. mean first-order rate constants for the oxidation of SO_2 in rural background air and in plumes;
2. concentration of oxidants and acids in plumes and in rural air after 24 hours;
3. first-order rate constants for the oxidation of SO_2 in rural background air and in plumes;
4. concentration of various oxidant and acid species at the end of 24 hours in plumes and in the ambient atmosphere.

The authors showed that the variation in the modelled oxidation rates could be explained in terms of the availability of various oxidants. These oxidants, in turn, are affected by a combination of factors such as season, time of release and dispersion rate. The study showed that the modelled concentrations of OH and other oxidants in the background air and plume show significant differences. The differences depend on the season (summer, spring and autumn, and winter), time of the release of the plume (06.00 hours, 12.00 hours, 18.00 hours and 24.00 hours) and on the rate of dispersion.

A similar modelling study, which investigated the effect of season, time of the release of plume and dispersion rate on the gas-phase chemistry of plume dispersing in an urban atmosphere (Cocks and Fletcher 1989), gave similar findings. In general, the interaction of plumes with urban atmospheres produced lower concentrations of the OH radical, which resulted in a decreased production of both HNO_3 and H_2SO_4.

The impact of the various factors cannot be generalised in a straightforward way as the three different impacting conditions (season, time of release and dispersion rate of the plume) interact to produce different overall impacts on the oxidation of SO_2 and NO_X under different combinations. For example, the dispersion rates under different seasonal conditions or, for that matter, under different plume-release times, show a different order of influence on the oxidation rates. However Cocks and Fletcher (1988) clearly demonstrate that the oxidation rates are significantly different in the ambient atmosphere and in plumes. Therefore control strategies based on ground-level measurements only may not be enough to assess the impacts.

Dispersion alters the concentrations in the plume, which affects the reaction rates. It also affects concentration gradients. We see below that inhomogeneous mixing is an important influence. The plumes show transversal and longitudinal concentration gradients, which are significantly different as the plume travels downwind and result in reaction rates that change significantly during its travel time.

A study based on a simulation from four models and measurements was undertaken by Janssen *et al.* (1990) to investigate the impact of travel time on the rate of non-linear chemical reactions that occur in the diluting plume. Janssen's work is reviewed in the Task 2 literature report (Middleton *et al.* 2007). The study suggests that for the first 5 km of travel the changes in concentrations in the plume primarily result from physical factors, such as dilution through dispersion. Conversion of NO at the early stages is therefore determined by mixing with the surrounding air. Therefore for accurate model predictions, the correct mixing rates need to be included. However as the plume travels further the chemical processes become important, but the timescales at which these reactions take place in various parts of the plume differ significantly. In the core of the plume, where the concentration of O_3 is very low and that of NO is very high, the timescale of reaction is about an hour, while at the plume edges, where the plume mixes with the ambient atmosphere, it is about 30 seconds. The timescales of the reactions constantly change as the plume moves because of the changes in the concentrations of the interacting species. Generally, chemical equilibrium exists at the core of the plume, as there is no O_3. The highest reaction rates exist at the edge of the plume, where both NO and O_3 exist in sufficient concentrations. The oxidation of NO to NO_2 can decrease by a factor of 10-20 after a distance of more than about 5 km from the source.

The short-term fluctuations of the reaction rates were investigated in a study by Bange *et al.* (1991), which infers that the rate of non-linear chemical reactions varies significantly. The study suggests that the model using these short-term fluctuating reaction rates gives a better agreement with the measurements than the model using hourly mean-dispersion parameters.

3.3.1 Key points

1. Cocks and Fletcher (1988, 1989) modelled gas-phase plume chemistry using an idealised dispersion model and found that oxidation rates depend upon oxidant availability, which in turn depends on season, time of day, entrainment and type of atmosphere (urban or rural). The study also suggests that oxidation may be slower in urban air.
2. They also found that dispersion rate affects the concentrations, which in turn affect the kinetics. Therefore, the rate constant alone does not predict directly the rate of oxidation. In addition, there may be multiple pathways.
3. Janssen *et al.* (1990) modelled plume inhomogeneity and developed a pseudo-empirical approach, which we discuss in the Task 2 literature review report (Middleton *et al.* 2007).

Results from comprehensive models in the Task 3 report of this project show the importance of both dispersion and oxidant availability in oxidising NO (Yu *et al.* 2007).

3.4 Influence of chemical composition of the background air

Janssen (1986) investigated the influence of chemical composition of the background air in which the plume mixes. The formation of NO_2 was both measured and modelled for Dutch and German power plants. A model that incorporated inhomogeneous mixing was used to simulate the results. The measurements were carried out using an equipped aeroplane for air measurements and an equipped van for ground-level measurements. Both chemical and physical processes were found to influence the oxidation of NO. The most important parameters to influence the oxidation of NO were the O_3 concentration and the wind speed. The O_3 concentration significantly influenced the initial rate of oxidation. However it was found that the amount of NO_2 was always greater than the O_3 consumed suggesting that molecular O_2 plays a role in the oxidation process.

The mixing of a plume into a VOC-rich environment has been found to provide an additional mechanism of NO to NO_2 oxidation, generalised as:

$$\mathrm{RH} + 2\mathrm{NO} + \mathrm{O}_2 \rightarrow \mathrm{Carbonyl} + 2\mathrm{NO}_2 + \mathrm{H}_2\mathrm{O} \qquad 40$$

Additional NO_2 is produced and some of it, under daytime conditions, photodissociates to produce O_3 (Webb 1997).

Measurement of O_3 in the plume of the Cumberland power plant using an instrumented helicopter was part of the Southern Oxidant Study (Luria *et al.* 1999). The results show that even after about 6 hours of travel the production of excess O_3 was limited to the edges of plume. However after sufficient dilution an O_3 concentration of 109 ppb was measured in the plume centreline, roughly 50-60 ppb above the background level. The results suggest that the power-plant plume regenerated O_3 once it had mixed with the urban plume and produced a peak of 120 ppb about 15-25 km downwind of the urban centre, Nashville. The O_3 productivity (the ratio of excess O_3 to NO_y and NO_z. NO_z is the sum of the oxidation products of NO_x, so that $NO_z = NO_y - NO_x$.) is found to be lower in an isolated power-plant plume than in a city plume. This is possibly caused by the production of nitrate, a termination product, in the power-plant plume. The nitrate was significantly higher in the power-plant plume compared with that of the city plume indicating a shorter chain length for the photochemical reaction mechanism. (Note that the O_3 concentrations, which reach 120 ppb, are similar in magnitude to the highest value of 106 ppb O_3 modelled during the model sensitivity runs of Task 3; see a separate report by Yu *et al.* 2007.)

High-resolution measurements of trace gas and particle levels were undertaken using airborne sampling techniques in the plume of the Cumberland coal-fired power plant (Mueller and Imhoff 2000). The measurements indicate that the primary sulphuric acid particles are produced in the first 5 minutes of release from the condensation of SO_3 (Mueller and Imhoff 1994a, 1994b), while the secondary particles are produced later. The measurements also show that photochemically active regions of the plume comprise only a small part of the plume compared with either chemically mature or inactive regions, and that the chemical structure of the plume changes dramatically as the plume ages. Each phase is characterised by different chemical mechanisms being dominant and having different oxidation rates.

Jenkin and Clemitshaw (2000) suggest that the production of excess O_3 depends upon the conversion of NO to NO_2 through paths other than those that utilise O_3, such as the reaction with peroxy radicals. These paths require VOCs as precursors. Hence an increase in the concentration of these radicals will favour the formation of O_3. The concentration of other oxidants is determined by differences between their production and destruction through various reactions.

3.4.1 Key points

1. The chemistry of plume oxidation depends on the concentration of the background species O_3 and VOCs.
2. Two important parameters which may increase the availability of O_3 in the plume are O_3 in the background air and wind speed.
3. Luria *et al. (*1999) studied the role of VOCs on plume chemistry. The O_3 concentration reached 120 ppb about 15-20 km downwind when the plume mixed with the urban background air, rich in VOCs. Our detailed Task 3 (Yu *et al*. 2007) report describes computer runs with concentrations up to 106 ppb O_3.
4. Overall, these results show the factors affecting oxidation include background O_3, VOCs and wind speed.

3.5 Diurnal variation in oxidation rates

Formation of NO_2, HNO_3, NO_3^- and SO_4^{-2} in power-plant plumes at night was investigated by Janssen *et al.* (1991) using modelling and aircraft measurements. A reactive plume model was used and the reaction rates calculated from the model were in good agreement with the measured values (the papers by Janssen discuss his modelling more fully; the Task 2 report refers to this in detail). The measurements and modelling suggest that the oxidation of NO differs during day- and night-time conditions. During daytime the plume is in the mixing layer, where NO interacts with the ambient O_3 and contributes towards the ground-level NO_2. At night-time the plume can be either above or below the nocturnal inversion layer, depending upon the stack height, and this changes the availability of O_3, which itself shows a vertical gradient. If the plume is above the inversion layer it reacts with relatively abundant O_3 and forms NO_2, but that NO_2 does not reach the ground level. However, if the plume is below the inversion layer, O_3 levels are lower after loss by dry deposition and, therefore, not much NO_2 is formed. The overall result is that during night-time plumes do not usually contribute much to the ground-level NO_2.

Measurements and modelling were also used to investigate HNO_3 formation during night-time above the nocturnal inversion, where relatively high O_3 is present. The measurements and modelling suggest that no appreciable amounts of SO_4^{-2}, NO_3^- and HNO_3 are detected in the plume at night-time. The model calculated a maximum of about 0.2 ppb of HNO_3 formed in the night in the plume at a distance of 20 km.

3.6 Effect of meteorological parameters and travel time on oxidation rates

The model results (Janssen 1986) showed a small and insignificant difference between unstable (Pasquill B-C) and neutral (Pasquill D) atmospheres for the mixing rate parameter, k_m. The measured and modelled results showed higher oxidation rates at increased wind speeds. This may result from an increased amount of air diffusing and mixing into the plume, and therefore an increase in the availability of O_3. Janssen (1986) suggests that it is important to take account of the inhomogeneous mixing to avoid large deviations from the photostationary equilibrium. Webb (1997) also suggests the mixing of the plume near the source with ambient air is not complete and it reduces the oxidation of NO with O_3.

Springston *et al.* (2005) carried out aircraft measurements in the plume from a coal-burning power plant in Texas, USA. They sampled the plume out to 60 km with a travel time of about 5 hours. They found that O_3 production is more efficient further from the stack. Similarly, they found that aerosol particles changed with the ageing and dilution of the plume. Also observed was a marked increase in the accumulation-mode particles (D_p > 100 nm) because of particle growth via gas-particle conversion. The O_3 production efficiency ranged from about 0 near the stack to 5-6 molecules for each molecule of NO_x further downwind.

Using a gas–aqueous photochemical model, Liang and Jacobson (1999) investigated the effect of water content, pH and temperature on the oxidation of SO_2. It was found that the aqueous-phase oxidation of S(IV) through aqueous H_2O_2, O_3, OH and CH_3OOH is sensitive to pH, liquid water content, temperature and radiation. The aqueous-phase oxidation of SO_2 was found to be much slower in aerosols than in clouds. When aerosols are present during clear days the aqueous-phase oxidation is insignificant compared with the gas-phase oxidation of SO_2. However, during winter days when the temperature is low and the relative humidity is high, the aqueous-phase oxidation can increase significantly. The oxidation of

SO_2 through CH_3OOH is insignificant under all cases. The major sinks of SO_2 are H_2O_2 and O_3 in the aqueous phase at $pH < 5$ and > 6, respectively. Aqueous OH may become important when the pH is between 5 and 6 and H_2O_2 is depleted at high water content. O_3 is important when $pH > 4$ and water content is > 1 g m^{-3}. However when the pH is initially above 6, oxidation of SO_2 with O_3 reduces the pH and the reaction with H_2O_2 then becomes dominant. The study suggests that the uncertainties in the oxidation rates can result in significant errors in the estimates.

The simulation of sulphate formation in a major power-plant plume was undertaken by Seigneur *et al.* (2000) using the reactive photochemical model ROME. The modelling was carried out for four sets of conditions: two dry days, one foggy day and one hypothetical day with foggy conditions favourable to sulphate formation. Under dry-day conditions gas-phase chemistry resulted in a very little formation of sulphate, less than 1.5% h^{-1}. The largest amounts of sulphate formation in the plume took place under foggy conditions via three mechanisms:

1. firstly, through H_2O_2 when H_2O_2 concentration was higher than that of SO_2 in the background air;
2. secondly, with O_2 in the presence of iron and manganese;
3. thirdly, through the reaction with O_3, particularly at the plume edges where pH is higher than at the plume centre.

All three mechanisms of oxidation are non-linear with respect to SO_2 emissions. The simulation data indicate that a 44% reduction in emissions of SO_2 resulted in about a 20% decrease in total sulphate concentration (plume and background).

3.6.1 Key points

1. Atmospheric moisture must be included in the form of aerosol chemical kinetics for plume oxidation of SO_2.
2. To simulate SO_2 oxidation to secondary particulates is a complex problem requiring sophisticated modelling. Factors such as humidity, cloud and even fog should be considered.

3.7 Factors influencing particle formation in plumes

Karamchandani and Seigneur (1999) used a reactive plume model to simulate the formation of sulphate and nitrate aerosol under various atmospheric conditions in plumes. They found that the rate of formation of secondary aerosol changes as the plume mixes with the background air, and that the rate of oxidation of SO_2 and NO can be very different in the plume and background air. Simulations were performed for summer conditions, daytime and day–night transition, and winter conditions, night-time and night–day transition.

For *summertime* simulations the findings can be summarised as:

1. significant formation of HNO_3 or H_2SO_4 only begins after 20-40 minutes (i.e. 5-10 km downwind) of plume travel time for the morning and noon simulations;
2. for the 17.00 hours simulation the formation of HNO_3 begins after 5 hours of travel time, no H_2SO_4 was produced and the plume excess nitrate was 4-7 times higher than the plume sulphate level;
3. NO_2 oxidation was seven times faster than the SO_2 oxidation with OH.

In the first few kilometres, because of the removal of most of the O_3 and the associated decrease in other oxidants, the oxidation rates were lower in the plume compared with those in ambient air. However, as the plume travels and dilutes the oxidation rates matched or sometimes exceeded those in the ambient air.

For the summer daytime simulation, rises in O_3 concentrations increased those of HNO_3. This resulted from an increase in the NO_2 formed, while H_2SO_4 showed a slight decrease in formation, possibly caused by greater competition for OH from the increased NO_2.

For the summer noon start time, increasing O_3 increased the production of HNO_3, which becomes significantly higher in the nocturnal period through the NO_x–N_2O_5 mechanism. The summertime 17.00 hours simulation showed the highest change with an increase in the O_3 concentration. Radical levels were high enough to initiate the HNO_3 formation and there was a dramatic increase in HNO_3. The peak concentration was higher by a factor of five compared with that in the base case.

The summertime simulations suggested that increasing the hydrolysis rate had no influence on the formation of HNO_3. However when the simulation period entered into the night-time the effect started to become visible and the peak concentrations during these periods were twice as large compared with those in the base case. However, this increase was proportionally smaller than the increase in the hydrolysis rate (by a factor of 10).

Decomposition of PAN could result in the formation of significant amounts of radicals. In this study, PAN concentrations were increased from 0.2 to 10 ppb and showed a significant effect on the concentrations of O_3, NO_2, H_2SO_4 and HNO_3. For a summertime 07.00 hours simulation the H_2SO_4 and HNO_3 showed an increase from the start and the peak concentrations were about a factor of five higher compared with those in the base case.

The effect of increasing VOCs concentration by factors of five and 10 was investigated for the concentrations of O_3, H_2O_2 and HNO_3 at the plume centreline. The summertime 07.00 hours simulation showed that O_3 started to increase from the start of the simulation, and the O_3 peak was more than four times higher, compared with that in the base case. The effect on H_2O_2 became significant after a travel time of about 5 hours, when the plume dilutes sufficiently in the atmosphere with increased concentrations of VOCs. The study also showed that the formation of HNO_3 was a good indicator of a VOC-limited environment and the formation of H_2O_2 is favoured when the environment is NO_x-limited

For *winter-time* simulations the findings can be summarised as:

1. In all the winter simulations starting at 21.00, 00.00 and 03.00 hours, an increase O_3 concentration did not influence the HNO_3 formation until sunrise. The reason is that, because of the prior removal of O_3, there was no NO_3 radical. Once sunrise occurred, HNO_3 formed from the reaction of NO_2 and OH.
2. In winter simulations for the 21.00 hours case, the effect of increasing PAN was less significant compared with that in the summer case. This possibly resulted from lower temperatures and the decomposition of PAN.
3. An increase in temperature from the base case by 10 and 20^{o}C for the winter 21.00 hours simulation showed an increase in the formation of H_2SO_4 and HNO_3 that resulted from an increased formation of OH.

The study suggested, as do several others (Kleinman *et al*. 1997, 2001, Sillman 1999, Sillman and He 2002, Daum *et al.* 2003, Sillman *et al.* 2003), that the atmospheric chemistry cannot easily be separated into either NO_X-limited or VOC-limited regimes. The usual understanding of these terms is:

1. *NO_x-limited chemistry* when there is ample oxidants, so the chemistry depends strongly on the availability of nitrogen compounds;
2. *VOC-limited chemistry* when VOCs are not in abundance and thus restrict the chemistry.

In the case of a VOC-limited atmosphere, OH radicals are taken up by NO_2 to form HNO_3, while in the case of an NO_X-limited atmosphere, OH radicals combine to form H_2O_2. This can be used to infer whether an atmosphere is either NO_X- or VOC-limited. Thus in a VOC-limited atmosphere formation of HNO_3 is favoured, while in a NO_X-limited atmosphere formation of H_2O_2 is favoured. This was observed from the results of this simulation: for about the first 300 minutes, when the atmosphere is still VOC-limited, H_2O_2 does not start to form appreciably. However, once the plume becomes sufficiently rich in VOCs and becomes NO_x-limited, the formation of H_2O_2 increases significantly and the formation of HNO_3 starts to decline, which can facilitate the formation of H_2SO_4.

3.7.1 Key points

1. Plume mixing and inhomogeneous concentrations are important. The chemistry changes across the plume as well as passing through identifiable phases downwind.
2. Background O_3 and VOCs may also need to be considered in regulatory scenarios.
3. Atmospheric moisture is important for O_3 formation as well as for secondary particulate production via aerosol kinetics.
4. Day–night differences should be considered, especially in the regulation of NO_2. Note that changes in atmospheric stability are linked to the diurnal cycle, as are changes in light intensity.

Based on the literature reviewed here it has not been possible to recommend a simple methodology, or rule of thumb, for the overall production of the secondary pollutants O_3 and fine particulates in plumes in moist rural or moist urban atmospheres. Thus the processes associated with secondary pollutants constitute a significant gap in our current predictive capability and pose a regulatory risk. It is therefore advisable to conduct detailed studies with advanced modelling methods, which would include treatment of the aerosol phase, before any simple screening approach is suggested for the regulation of plumes in typical UK atmospheres.

4 Key findings and discussion

This section summarises the main report findings in terms of conditions that may lead to enhanced oxidation of NO_X and SO_2 in plumes. It also raises some wider points that the Environment Agency may wish to consider in developing its future assessment methods.

The main points that arise from the literature review are:

1. The gas-phase oxidation for SO_2 primarily proceeds through its reaction with the OH radical. Therefore, sunny days, when the excess production of this radical is favoured, result in an enhanced gas-phase oxidation of SO_2.
2. The liquid-phase oxidation for SO_2 is much faster than its gas-phase oxidation. The increased amount of water in the atmosphere caused by cloud, fog, humidity and other forms results in the enhanced oxidation of SO_2 through this pathway. The rate of heterogeneous oxidation for SO_2 also depends on the concentration of dissolved oxidising species, such as H_2O_2 and O_3. Between these two species, H_2O_2 is more important than O_3 as its solubility in water is higher. This pathway for SO_2 oxidation depends upon the pH of the resulting solution in which the reaction takes place. The oxidation of SO_2 through H_2O_2 takes place at near neutral conditions. The reaction between SO_2 and H_2O_2 can stop quickly, as it results in a build-up of acidity. The presence of acid-neutralising species, such as NH_3, is therefore important to maintain this oxidation process.
3. The conditions that result in the enhanced oxidation of SO_2 in liquid-phase reactions include the presence of a high water content in the atmosphere and of oxidising agents, such as H_2O_2 and O_3. This is particularly so for H_2O_2 and in the presence of NH_3. Therefore, the heterogeneous oxidation of SO_2 is more significant in cloudy, wintry conditions.
4. The gas-phase oxidation of NO_X by OH is about 10 times faster than that for SO_2. Therefore, during sunny days the gas-phase oxidation for NO_X is significantly higher than the gas-phase oxidation of SO_2.
5. The presence of secondary pollutants, such as PAN, which can produce significant amounts of radicals on decomposition, could result in the enhanced oxidation of $NO_\mathbf{x}$ and SO_2.
6. The plumes show different chemical regimes as they move away from the source because of the changes in both the chemical composition of the plume and the availability of oxidants. The rates of reactions and types of reactions that dominate in the three plume phases (near source, middle range and far field) are different, and depend on the time of day and the chemical composition of the background air.
7. The conditions in which high background and plume mixing can take place, bringing more oxidants in, may lead to unusual oxidation rates of NO_X and SO_2. Such conditions include turbulent mixing under high wind speeds bringing more oxidants and oxidant precursors.
8. All the conditions that lead to high oxidant concentration produce enhanced oxidation of NO_X and SO_2.

The regulation of large plumes requires consideration of the wider context of air quality across Europe. There are a number of points that should be borne in mind:

Plumes may travel large distances along which they entrain ambient air and undergo a variety of gas- and liquid-phase reactions depending on the composition of the surrounding air, its moisture content, the time of day, the season and the ambient conditions. To develop practical schemes to assess the potential plume impacts it is necessary to consider long-term trends in the pollution climate, which will be influenced by European controls on the emission sources.

AQEG (2007) has produced a report on the likely consequences of climate change on air pollution and their interaction. This report provides a thorough discussion of our current understanding and should be consulted when future regulatory options are considered. We suggest that a rise in background O_3 concentration may result in increased oxidation within plumes. It is recommended that modelling studies be conducted to explore systematic changes in the assumed O_3 background levels. In the Task 3 reports, we propose using modelling tools (for example, NAME III or CMAQ models) to be tested for the Environment Agency.

For example, in Task 3 the model NAME III was used to simulate an idealised plume that contains just nitrogen oxides. It demonstrated oxidation by the surrounding O_3 and VOCs. Such sensitivity studies for a simple plume using a range of O_3 background concentrations can explore the effects of rising O_3 levels on plumes of the sort regulated by the Environment Agency. While it stimulates ideas, this project was not intended to provide resources for model validation, so any results from simplified cases are for illustration purposes only.

5 Summary

The oxidation of power-station plumes is complex, invoking a number of competing chemical pathways. By their very nature, the production rates are not necessarily proportional to the primary emissions rates, and can be difficult to quantify. If the concentrations arising from a given source or sources are uncertain, then their regulation will also be difficult. Secondary pollutants can have important health and environmental impacts: NO_2, O_3 and fine particulates are of current concern to regulators. It is therefore important to fill the gap in the regulatory modelling capability, which currently exists regarding secondary pollutants from large industrial plumes. No simple methodology for immediate use emerged from the literature studied here. This is an important finding and may have implications for the future direction of research sponsored by the Environment Agency.

An aim of this report was to review and assess the literature to identify the conditions under which *unusual* oxidation rates for SO_2 and NO_X gases in the plumes of large industrial sources, such as power plants, can occur. In this review, the only direct reference found from the literature on factors that affect *unusual* oxidation rates related to foggy conditions (Seigneur *et al.* 2000).

The plumes from large industrial sources exhibit chemistry that is significantly different from the chemistry of background air. The differences depend upon a complex combination of factors such as the chemical composition of the plume and background air, time of day, travel distance and prevailing meteorology.

Keeping all factors constant, such as time of day, meteorological conditions and the composition of the background air, plumes show distinct phases (short range, mid range and long range), which are dominated by different chemical reactions and reaction rates. Therefore, the resultant products and their relative quantities are also different. These differences can generally be attributed to dilution as plumes move horizontally and vertically, and mix with the background air.

The most important factor responsible for the differences in the chemistry that takes place in the background air and in the plume is the NO_X concentration, which can be a few orders of magnitude higher in plumes compared with that in the background air.

The oxidation rates of SO_2 and NO_X in plumes depend upon the availability of various oxidising species, radicals and molecules involved in gas- or liquid-phase interactions. The availability of these species, in turn, is a complex function of season, time of day, chemical composition of the background air and plume, and ambient conditions, such as relative humidity and dispersion in the vertical and horizontal planes.

Within a large plume, the oxidation rates vary by many orders of magnitude. For example, in the plume core almost all O_3 is titrated by NO and reaction rates are very slow, while at the plume edges, where the plume is in contact with the background air, the reaction is much faster.

Gas-phase plume chemistry during daytime in the early stages of the plume is determined by the photochemistry of NO_X and O_3, which results in the generation of radicals that oxidise NO_X and SO_2. Therefore, all the conditions that can favour the formation of radical species, such as high temperature and sunshine, result in the enhanced oxidation of NO_X and SO_2. The oxidation of NO_X will be about 10 times faster than the oxidation of SO_2 through this mechanism.

Heterogeneous chemistry does not play any appreciable role in the oxidation of NO_X, but it is the most important pathway for the oxidation of SO_2. Therefore, all the conditions that enable this chemistry to take place enhance the oxidation of SO_2. Such conditions include high relative humidity, fog, clouds and the presence of liquid aerosol.

Gas-phase oxidation of SO_2 is mainly restricted to daytime, while the gas-phase oxidation of NO_X can still continue through the production of the NO_3 radical and N_2O_5 in the dark. The gas-phase oxidation of SO_2 shows marked seasonal variation in the order summer > spring and autumn > winter. This order corresponds to the availability of OH concentrations, the main oxidant for SO_2.

Hewitt (personal communication) provided the following points:

1. Both plumes and background air exhibit non-linear behaviour with respect to secondary pollutant formation. It is therefore very difficult to interpret changes in the ratios of individual primary and secondary compounds without the use of sophisticated chemistry and transport models
2. In a plume, *unusual* or enhanced oxidation rates of SO_2 and NO_x would occur if there are *unusual* or enhanced concentrations of oxidants present, or if an *unusual* or enhanced oxidation route is available. In a power-station plume, the concentrations of oxidants may be higher than expected if very *unusual* or enhanced mixing of background air into the plume occurs. This would lead to *unusual* or enhanced oxidation rates of SO_2 and NO_x within the plume. This situation may arise in very turbulent conditions, and allow O_3 or O_3 precursors (VOCs) to enter the plume by the excessive entrainment of background air. Without models of plume-fringe activity it is not possible to quantify the degree of enhancement in O_3 concentrations that this can lead to, and hence it is not possible to quantify the resultant degree of enhancement in SO_2 and NO_x oxidation rates. However elevated O_3 concentrations have repeatedly been observed in plume fringes (Hewitt 2001). Therefore it can be suggested that exceptionally *unusual* or enhanced mixing of background air into the plume in very turbulent conditions may lead to unusual or *enhanced* oxidation rates of SO_2 and NO_x in the bulk of the plume.
3. In a power-station plume the iron- and/or manganese-catalysed oxidation of S(IV) is normally limited by the low concentrations of these metals. However, should there be *unusual* concentrations of metals in the plume (perhaps because of unusually high metal concentrations in the fuel and/or a failure in emission-control equipment), the aqueous-phase oxidation of SO_2 may proceed much more rapidly than expected. Similarly, unusually high concentrations of VOCs in the emitted gases may give rise to higher than expected O_3 concentrations early in the plume evolution.

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