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# A Reduced-Form Model to Predict Long-Term Ozone Concentrations in Europe

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## Preface

In the preparation process for the Second Sulphur Protocol of the Convention on Long-range Transboundary Air Pollution, integrated assessment models played an important role in identifying cost-effective strategies for reducing SO<sub>2</sub> emissions in Europe. Applying this effect-based approach to other environmental problems (e.g., photo-oxidants) seems appealing. In view of the timetable adopted for the current preparation of an updated Protocol on emissions of nitrogen oxides, an integrated assessment tool for ozone is required in the very near future.

The paper presents an outline of an integrated assessment model for tropospheric ozone in Europe, with modules on emissions, emission control technologies and costs, ozone formation and environmental impacts. In its central part the paper focusses on the core element of such an approach, i.e., a concise description of the relationships between the precursor emissions (nitrogen oxides and volatile organic compounds) and regional ozone levels, which must be computationally efficient for use in an integrated assessment model.

Critical levels, i.e., threshold levels protecting vegetation from damage, have been recently established using long-term exposure measures. Consequently, to be suitable for integrated assessment models, source-receptor relationships should be able to describe the long-term changes of ozone, e.g., over a six-month period. Based on numerous scenario runs of the EMEP ozone model, polynomial source-receptor relationships have been statistically identified. Using national annual emissions of NO<sub>x</sub> and VOC, the model predicts regional responses of the six-month mean of early afternoon ozone concentrations. From this concentration measure, excess exposure as used in the definition of the critical levels can be derived. The paper introduces the methodology of the approach, evaluates the results and discusses areas of further work.

The suggested model formulation can be incorporated into the framework of an integrated assessment model, enabling (i) the assessment of costs and environmental benefits from alternative strategies to reduce precursor emissions and (ii) the identification of cost-optimized strategies to achieve environmental targets.

## **Acknowledgements**

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We also thank Prof. Anton Eliassen from the EMEP Meteorological Synthesizing Centre West (Oslo) and Prof. Achim Sydow from the German National Research Center for Information Technology (Berlin) for their positive support of the work presented in this paper.

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# 1. INTRODUCTION

## 1.1 Purpose of the Paper

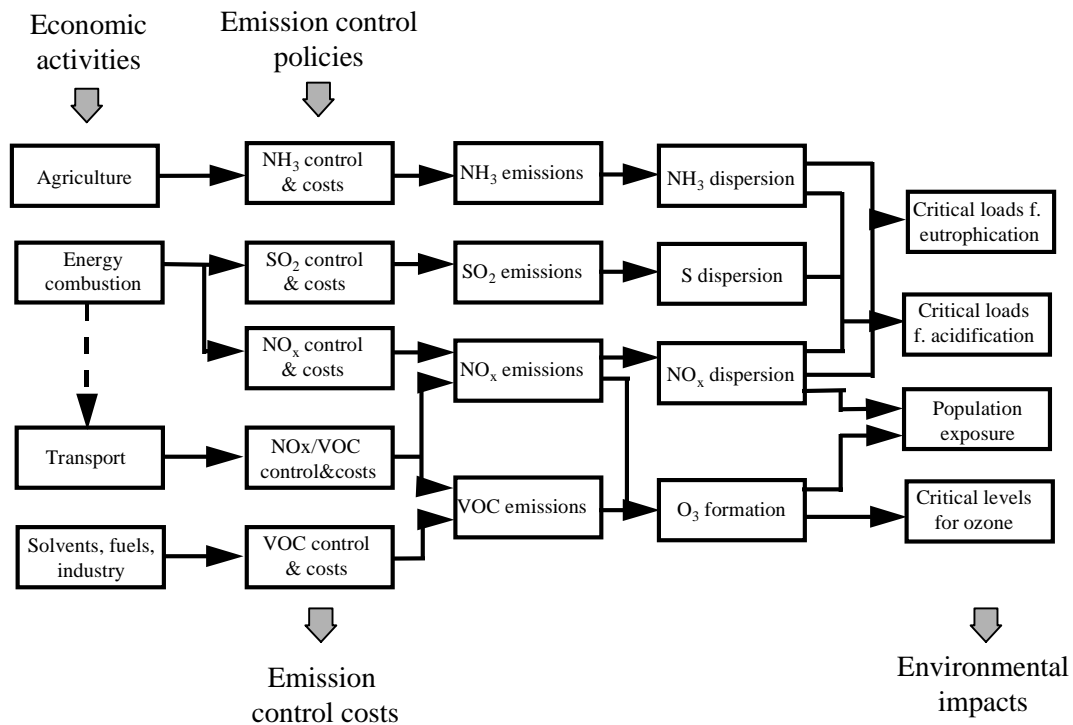
This paper outlines the current stage in the development of an integrated assessment model for tropospheric ozone in Europe. The authors are well aware of the fact that, at the time of writing this document, many of the described elements are not yet in their final shape; not all parts of the model are completed yet, nor are many improvements, which have been recognized by the authors as important or desirable, implemented.

The remainder of Section 1 outlines the general concept of and the experience with integrated assessment models for control of air pollution. Section 2 provides a brief overview of the various elements of an integrated assessment model for tropospheric ozone. Focussing on the core element, Section 3 presents an approach for deriving simplified source-receptor relationships between precursor emissions and tropospheric ozone in Europe. Issues for further work and conclusions are the subjects of Sections 4 and 5.

## 1.2 Integrated Assessment of Strategies to Reduce Air Pollution in Europe

The RAINS (Regional Air Pollution INformation and Simulation) model (Alcamo *et al.*, 1990) was developed by IIASA's Transboundary Air Pollution project as an integrated assessment tool to assist policy advisors in evaluating options for reducing acid rain. Such models help to build consistent frameworks for the analysis of abatement strategies. They combine scientific findings in the various fields relevant to strategy development (economy, technology, atmospheric and ecological sciences) with regional databases (Figure 1). The environmental impacts of alternative scenarios for emission reductions can then be assessed in a consistent manner ('scenario analysis'). A further refinement in developing strategies is the search for cost-effective solutions. Integrated assessment models enable the identification of those strategies that minimize the costs required to achieve a set of environmental targets ('optimization').

In recent years, the European implementation of the RAINS model has been used to support the negotiations on an updated Sulphur Protocol under the Convention on Long-range Transboundary Air Pollution (LRTAP), by deriving guidelines for international reductions of sulphur dioxide (SO<sub>2</sub>) emissions in Europe. Earlier protocols under the Convention had been formulated in terms of uniform percentage reductions in national emissions compared to a base year. However, RAINS and other integrated assessment models indicated that such flat-rate, source-oriented approaches do not necessarily produce cost-effective solutions (UNECE, 1990). The Second Sulphur Protocol made use of an alternative, effect-oriented approach, in which the extent of emission reductions is guided by the impacts that emissions from a given source have on sensitive ecosystems. One of the crucial factors leading to the development of effect-based abatement strategies was the development and political acceptance of the critical loads/levels concept. Critical loads/levels quantify the ability of ecosystems to absorb acid input without causing damage and so provide a threshold level for maintaining sustainable conditions.



**Figure 1** Structure of the RAINS model

The scenario eventually adopted as a guideline for the negotiations on the Second Sulphur Protocol aimed at reducing current excess deposition, i.e., the gap between current deposition levels and the critical loads, by at least 60% everywhere in Europe. Whereas the resulting deposition targets can be derived from a comparison of the current deposition levels with the critical loads, the cost-minimal allocation of abatement measures had to be identified with the optimization feature of the RAINS model.

Although emissions from several pollutants contribute to acid deposition, the Second Sulphur Protocol limited its scope to emissions of SO<sub>2</sub> only, mainly due to the need for a renewed agreement on sulphur emissions after expiry of the first Sulphur Protocol in 1993. For the future, the highest priority is being given to the development of a strategy for the second step of the Protocol concerning the Control of Emissions of Nitrogen Oxides. The improved cost-effectiveness of effect-based approaches, as implemented in the Second Sulphur Protocol, has resulted in a general wish for maintaining the effect-oriented principle in the negotiations on reductions of nitrogen emissions.

Reducing nitrogen emissions based on environmental effects will be a rather complex process. The interrelation of several environmental effects (acidification, eutrophication, tropospheric ozone, human health, etc.) establishes a multi-effect problem, and the involvement of several emitted compounds adds a multi-pollutant dimension. The RAINS model is being developed further to maintain its applicability within this framework. One major avenue of development is the inclusion of ground-level ozone (O<sub>3</sub>).

## 2. CONCEPT OF AN INTEGRATED ASSESSMENT MODEL FOR OZONE

The formation of ozone in the atmospheric boundary layer involves chemical reactions between nitrogen oxides ( $\text{NO}_x$ ) and volatile organic compounds (VOCs)<sup>†</sup> driven by solar radiation. Stated briefly, the aim of an integrated assessment model for tropospheric ozone is to describe the relationship between ozone exposure and the emissions of the  $\text{NO}_x$  and VOC precursors in such a way that the costs and effectiveness of emission reduction strategies within Europe can be quantified. To achieve this requires the integration of information from each of the following areas:

- current and future emissions of  $\text{NO}_x$  and VOCs, both man-made and natural.
- the abatement technologies available for  $\text{NO}_x$  and VOCs, and their costs.
- a concise description of the source-receptor relationships, taking account of meteorological influences on ozone formation.
- studies of the effects of ozone on agricultural crops, forests and human health, leading to the establishment of critical levels for ozone.

This information must be organized in such a way that scenario analysis (exploring the costs and environmental impacts of alternative emission reduction scenarios) and optimization (the systematic search for cost-effective solutions) will be possible.

The following sections provide a brief overview of the basic modelling concepts developed for the various elements of the envisaged integrated assessment tool. Since the ultimate aim of the exercise is to evaluate alternative emission control options against their environmental impacts, the sequence of the description starts from the environmental impacts and goes stepwise back up to the sources of emissions.

### 2.1 Environmental Impacts of Tropospheric Ozone

Within Europe interest in ground-level ozone has intensified in recent years, with increasing experimental evidence that ozone can have adverse effects on crops, trees, materials and human health. Studies of the impacts of ozone have resulted in the apparent consensus that critical levels for ozone in order to protect natural vegetation, agricultural crops and forests can best be established with long-term exposure measures, in particular, by the 'accumulated excess ozone' concept. Currently, a threshold concentration of 40 ppb is proposed for both crops and trees. This exposure index is referred to as AOT40, the accumulated exposure over a threshold of 40 ppb (Fuhrer and Achermann, 1994). For agricultural crops the accumulated exposure should be calculated for daylight hours, defined as those hours with a mean global radiation of  $50 \text{ Wm}^{-2}$  or greater, and for three months (May-July, except in areas where this period is inappropriate). The current proposal for forest trees recommends that the cumulative exposure be calculated for daylight hours during a six-month period (Kärenlampi and Skärby, 1996). Work is underway to map the receptors at risk

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<sup>†</sup> The term VOC is used in this paper to refer to all volatile organic compounds except methane



for all of Europe (Hettelingh and de Leeuw, 1994). A basic function of an integrated assessment model will be to predict the AOT40 for crops and trees over all of Europe in response to changes in the precursor emissions and to compare them with the stock at risk.

With regard to human health, it has recently been proposed that the criterion for ozone within the WHO air quality guidelines be changed from a one-hour limit value to an eight-hour mean of 60 ppb (Younes, 1995). Therefore, integrated assessment models should also be capable of producing an indication of the frequency of days with eight-hour means larger than 60 ppb under different emission reduction scenarios.

In conclusion, it can be stated that current thinking on environmental impacts (including human health) puts increasing emphasis on long-term exposure. This has an important bearing for atmospheric ozone models applicable for an integrated assessment since models must be capable of calculating ozone levels over an extended time horizon of several months rather than focussing on single episodes of a few days.

## **2.2 Source-Receptor Relationships for Tropospheric Ozone**

The formation of ozone involves chemical reactions between  $\text{NO}_x$  and VOCs driven by solar radiation, and occurs on a regional scale in many parts of the world. The timescale of ozone production is such that ozone concentrations build up in polluted air over several days under suitable weather conditions, and this pollutant and its precursors can be transported over considerable distances and across national boundaries. An integrated assessment model for ozone needs to be able to relate ozone exposure to changes in the emissions of ozone precursors. These source-receptor relationships need to be valid for long-term ozone exposure, in line with the proposed critical levels, and applicable on the scale of Europe.

For application in an integrated assessment model for ozone, the source-receptor relationships need to be valid for a variety of spatial patterns of emission sources and for a range of emission levels, and not restricted to the present-day situation alone. For this reason, attempts to define these relationships solely on the basis of recent ozone measurement data are likely to prove inadequate. Instead, the ozone formation description needs to be based on mathematical models that have gained widespread international acceptance.

Within the framework of an integrated assessment model, source-receptor relationships must be computationally efficient to enable the numerous scenario runs for analyzing costs and benefits from a wide range of control strategies. Furthermore, extended uncertainty and robustness analyses will be necessary to derive solid conclusions from the model, taking into account the gaps and imperfections of the available databases and models. In many cases, methodologies for such analyses require sufficiently simple formulations of the underlying models. In addition, optimization analysis has proven to be a powerful feature in the integrated assessment process for the Second Sulphur Protocol. Optimization of the entire chain from the sources of emissions, over the costs for controlling them, up to the regional impacts on ozone levels, however, also requires sufficiently simple source-receptor relationships.

It is possible to envisage several ways of condensing the results of more complex models of ozone formation in order to construct a simplified means of representing source-receptor relationships, and investigations in this area have proceeded on parallel paths. This paper describes work carried out on one of the possible approaches, in which statistical techniques are used to describe the important relationships between ozone and its precursors.

Section 3 of this paper introduces the simplified approach developed at IIASA to describe relationships between precursor emissions and long-term ozone levels. It must be kept in mind that, in the overall context of an integrated assessment model, the aim of such an approach is solely to provide source-receptor relationships which are computationally efficient to enable cost- and optimization analysis of alternative emission reduction strategies. In contrast to conventional, more detailed atmospheric models of ozone formation, a simplified approach of this sort does not try to explain the chemistry of ozone formation.

### **2.3 Emissions of Precursor Substances and Costs for Reducing them**

The main purpose of an emissions and control costs module within an integrated assessment model is to estimate current and future sources and volumes of the relevant precursor emissions and to assess the potential for, and the costs of, reducing them. As described later in this paper, the simplified description of source-receptor relationships developed for this model takes annual, national emissions of nitrogen oxides and volatile organic compounds as an input. According to the CORINAIR 1990 emissions inventory carried out as an international European effort coordinated by the European Environmental Agency, the major sources of these emissions are transport activities, power generation and district heating, industrial combustion and solvent use (Table 1). Emission estimates in IIASA's integrated assessment model for tropospheric ozone are based on the latest CORINAIR data.

The sources of NO<sub>x</sub> emissions, their possibilities for control and the associated costs have already been modelled in the context of the RAINS-acidification model (Amann, 1989). With some updates this module is also applicable for the assessment of ozone abatement strategies.

Methods for projecting VOC emissions have been explored by Olsthoorn (1994). With a split into traffic-related emissions (on-board emissions, gasoline distribution, etc.) and other sources (mainly solvent use), a consistent scenario development will be possible. Caliandro has compiled an inventory of control options for VOC emissions and of the associated costs as a basis for an integrated assessment model (Caliandro, 1994). Her inventory distinguishes control options for mobile sources (gasoline and diesel engines), industrial painting, printing, metal degreasing, non-industrial solvent use, chemical industry and refineries. For each of these groups the most important options and their costs have been identified. With this information, together with CORINAIR data on the source strengths of each of these emission categories, the development of cost curves will be feasible in the near future.

**Table 1** Sources of NO<sub>x</sub> and VOC emissions in Europe in 1990 (Source: EEA, 1995)

Sector	NO <sub>x</sub> emissions		VOC emissions	
	Emissions (kt)	%	Emissions (kt)	%
Transport (inc. gasoline distribution)	10205	56.8	8077	46.1
Power generation and district heating	4527	25.2	1057	6.0
Industrial combustion	2457	13.7	157	0.9
Production processes	393	2.2	1232	7.1
Solvent use	-	-	4946	28.2
Others	374	2.1	2051	11.7
<b>Total</b>	<b>17956</b>	<b>100.0</b>	<b>17520</b>	<b>100.0</b>

## 2.4 Optimization

The optimization mode of integrated assessment models can be a powerful tool in the search for cost-effective solutions to combat an air pollution problem. In the RAINS model, optimization techniques have been used to identify the cost-minimal allocation of resources in order to reduce the gap between current sulphur deposition and the ultimate targets of full critical loads achievement. The outcome of the optimization was used as a starting point for the political negotiations on the second sulphur protocol. According to the nature of the problem (i.e., the linear source-receptor relationships for sulphur transport), linear programming techniques have been applied.

In the case of tropospheric ozone, a systematic search for cost-effectiveness appears even more attractive. The facts that several pollutants (NO<sub>x</sub> and VOC emissions) are involved, and that important non-linearities between precursor emissions and ozone levels have been recognized, cut the likelihood of 'intuitive' solutions being identified in the scenario analysis mode. At the same time, these aspects also increase the complexity of the problem and, therefore, the demand for optimization techniques.

For simple cost-minimization, the objective function of the optimization problem can be formulated as

$$\sum_{i=1}^N c_i \rightarrow \min \quad [1]$$

s.t.

$$c_i = f(n_i, v_i) \quad [2]$$

$$[O_3]_j = f'(n_i, v_i, \dots) \leq f''(AOT40_{lim}, \dots) \quad [3]$$

with  $i$  denoting emission sources (countries),  $j$  the receptor sites,  $n_i$  the emissions of  $NO_x$ ,  $v_i$  the emissions of VOC,  $c_i$  the combined costs of reducing  $NO_x$  and VOC emissions in country  $i$ ,  $[O_3]_j$  the ozone concentrations at a receptor  $j$  and  $AOT40_{lim}$  the relevant ozone exposure critical level. Depending on the type of the function in Equation [3] and the number of emitter countries and receptor sites to be considered, the optimization task becomes a large-scale non-linear problem. To solve such a problem, the function derivatives (the Jacobian matrix) must also be available. Using source-receptor relationships according to Equation [9] (see Section 3.5.2), an initial test sample for 25 receptors sites ( $j$ ) and 21 emission sources ( $i$ ) has been successfully solved with three alternative optimization packages (Zawicki, 1995).

Further work will be necessary to implement the full-scale optimization feature. In addition, the pioneering character of many elements of the integrated ozone model elements (cost curves, source-receptor relationships, exposure thresholds for environmental impacts, etc.) as well as concerns about gaps and quality of the European databases used for the implementation, call for advanced methods of uncertainty and robustness analysis in order to derive solid conclusions from the model framework.

In the long run, policy relevance can be enhanced by combining the optimization for ozone according to Equations [1] to [3] with cost curves for sulphur and ammonia emissions and constraints on critical loads for acidification and eutrophication, thereby creating a comprehensive tool for multi-pollutant/multi-effect strategies.

### 3. A SIMPLIFIED DESCRIPTION OF OZONE FORMATION

#### 3.1 Introduction

An integrated assessment model for ozone needs to be able to relate ozone exposure to changes in the emissions of ozone precursors. These source-receptor relationships need to be valid for long-term ozone exposure, in line with the proposed critical levels, and applicable on the scale of Europe. They should be based on a mathematical photo-oxidant model that has gained widespread international acceptance.

For practical reasons, the calculation of ozone exposure in an integrated assessment model needs to be computationally efficient. A number of ways of constructing a simplified description of ozone formation may be envisaged, ranging from those in which the emphasis is placed on the chemical processes to others that rely on statistical methods. Several authors have described procedures designed to reduce the computational burden of the chemical schemes employed in detailed photochemical models (Venkatram *et al.*, 1994; and references therein). The work described here took a statistical approach, in order to construct a simplified model to summarize the results obtained from a more comprehensive photochemical model. In contrast to many conventional, more detailed atmospheric models of ozone formation, a simplified approach of this sort does not try to explain the chemistry of ozone formation.

Before describing the development of the simplified model itself, it is appropriate to provide some background information about atmospheric ozone and the detailed photo-oxidant models that have been used to describe aspects of its formation behaviour in a European context. Section 3.2 outlines the salient features of the ozone formation process. A very brief review of some of the available photo-oxidant models is given in Section 3.3, together with a more detailed description of the EMEP ozone model, selected here as the basis for the present study. Subsequent sections describe the approach taken in developing a simplified model, the design of the regression model at the heart of this concept, and the sampling strategy adopted in order to construct the regression model. Finally, the results of several evaluation tests are presented in Section 3.6.

#### 3.2 Ozone Formation

This section provides an outline of the atmospheric chemistry and other factors affecting the formation of ozone in the atmospheric boundary layer. This is by no means a comprehensive description, but is intended rather to illustrate some of the important features of the process.

##### *Atmospheric chemistry*

There are no emissions of ozone directly into the atmosphere; all the ozone found there has been formed by chemical reactions in the air. Most of the ozone is produced and resides in the stratosphere at altitudes between 12 and 40 km. Some stratospheric ozone is transported downwards through the troposphere into the atmospheric boundary layer and is

finally removed at the earth's surface. This naturally occurring flux is supplemented by in-situ photochemical production of ozone in the troposphere, the most significant in-situ production occurring in the atmospheric boundary layer close to the surface. In this region, it is the reactions of primary pollutant gases, specifically nitrogen oxides and organic compounds, driven by the action of sunlight, which are responsible for enhanced ozone formation.

The chemical production of ozone ( $O_3$ ) in the atmosphere requires the recombination of atomic oxygen ( $O(^3P)$ , a ground state oxygen atom) and molecular oxygen ( $O_2$ ). In the troposphere, photodissociation of nitrogen dioxide ( $NO_2$ ) is the only significant source of oxygen atoms:



Clearly, this process depends on sufficient solar energy (represented by  $h\nu$ , the product of Planck's constant,  $h$ , and the frequency,  $\nu$ , of the solar radiation). The recombination of atomic and molecular oxygen:



(where  $M$  can be any inert molecule such as nitrogen or oxygen) to produce ozone may be followed by the rapid reaction of ozone with nitric oxide ( $NO$ ):



to regenerate  $NO_2$ . In a relatively unpolluted atmosphere, a photochemical steady state is achieved during hours with sunlight, and, in the absence of other processes that convert  $NO$  to  $NO_2$ , the ozone concentration is linked to the  $NO_2 / NO$  concentration ratio:

$$[O_3] = J_1 [NO_2] / k_3 [NO] \quad (4)$$

where  $J_1$  is the  $NO_2$  photolysis rate and  $k_3$  is the rate constant for reaction 3.

Any processes, other than reaction with ozone, which convert  $NO$  to  $NO_2$  will facilitate net production of ozone during daylight. Such processes are possible in polluted atmospheres containing volatile organic compounds (VOCs), originating primarily from pollutant emissions but also from natural sources like vegetation. The chemistry of the polluted troposphere is very complicated because of the presence of numerous VOCs of various classes (e.g. alkanes, alkenes, aldehydes, ketones and aromatic hydrocarbons) and the added complexities in the chemistry of these organic species. A full description of their role in atmospheric chemistry is clearly beyond the scope of this paper; the following outline of the important atmospheric reactions of the alkanes is intended merely to illustrate the salient features with regard to ozone production. More complete discussions may be found in several review articles (e.g. Atkinson, 1990; National Research Council, 1991).

The initial step in the important chain of reactions involving VOCs is attack by hydroxyl radicals ( $OH^\bullet$ ). In a sunlit, polluted atmosphere the two main sources of this

species are (i) the ultraviolet dissociation of ozone followed by rapid reaction with water vapour,



(where  $\text{O}(^1\text{D})$  is an electronically excited oxygen atom and  $\text{H}_2\text{O}$  is water) and (ii) the photochemical dissociation and subsequent reactions of aldehydes and ketones.

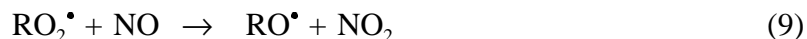
In the illustrative case of alkanes (represented by  $\text{RH}$ ), reaction with the  $\text{OH}^\bullet$  radical yields an alkyl radical ( $\text{R}^\bullet$ ):



which is rapidly converted to an organic peroxy radical ( $\text{RO}_2^\bullet$ ):

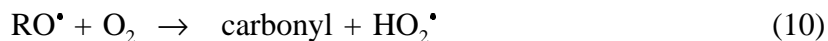


The peroxy radicals are able to oxidize  $\text{NO}$  to  $\text{NO}_2$  :



and thus, in conjunction with reactions 1 and 2, lead to increased ozone production.

The alkoxy radical ( $\text{RO}^\bullet$ ) produced in reaction 9 may react with oxygen to form an aldehyde or ketone, depending on the nature of  $\text{R}$ , and a hydroperoxy radical ( $\text{HO}_2^\bullet$ ) :



although they may also decompose or isomerize to other alkyl radicals and carbonyl compounds which can then react further. The hydroperoxy radical is another important trace component of the atmosphere which can also oxidize  $\text{NO}$  to  $\text{NO}_2$  with the regeneration of a hydroxyl radical:

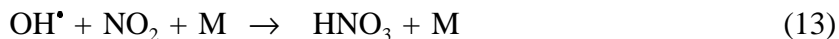


with the result that further oxidation of VOCs, and further ozone formation, can occur. Reaction of the hydroperoxy radical with ozone:

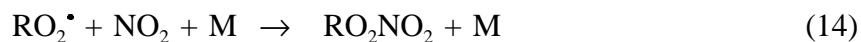


is another mechanism by which the chain-propagating hydroxyl radical can be regenerated.

The main process which removes free radicals, and therefore opposes the ozone-producing reactions, is the combination of hydroxyl radicals with nitrogen dioxide to form gaseous nitric acid (HNO<sub>3</sub>) :

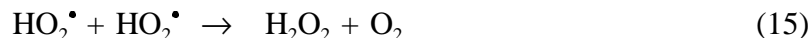


Peroxy radicals also react with nitrogen dioxide to form peroxy nitrates:



Many of the peroxy nitrates are unstable and so do not effectively remove radicals. However, the more stable ones do act as radical sinks and can build up as significant secondary pollutants. One important example of such a compound is peroxyacetyl nitrate (PAN), formed in reaction 14 when the R fraction represents the acetyl group.

Reaction between peroxy radicals can also act as a radical loss process. One example is the self-reaction of hydroperoxy radicals:



which is the major route for the formation of atmospheric hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

The preceding description of the photochemical production of ozone is applicable to the polluted atmospheric boundary layer. It is worth noting that some ozone formation can also take place in the absence of anthropogenic emissions of VOCs. In the clean, unpolluted troposphere, the atmospheric chemistry is largely determined by the reactions of methane (CH<sub>4</sub>) and its degradation products, formaldehyde (HCHO) and carbon monoxide (CO). The hydroxyl radical reaction is again the important initial step (see, for example, National Research Council, 1991) but its rate of reaction with methane is much slower than with non-methane VOCs and, consequently, methane has a much longer tropospheric lifetime than the VOC species. In the lower troposphere, especially in polluted areas, the chemical reactions of the non-methane VOCs dominate those of methane and carbon monoxide.

It should be emphasized that the preceding description of tropospheric ozone production is necessarily simplified and incomplete; for example, important night-time reactions have been entirely omitted from the discussion. However, even this simple outline serves to highlight the most important factors involved.

#### *Emissions, meteorology and other physical processes*

Clearly, the enhanced production of ozone depends on emissions into the atmosphere of nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) and volatile organic compounds. As indicated earlier in Table 1, emissions of NO<sub>x</sub> arise mainly from the combustion of fossil fuels; the most important sources are motor vehicles and power plants. Major anthropogenic sources of VOCs in the atmosphere include emissions resulting from the use of solvents, motor vehicles (both exhaust and evaporative emissions) and the chemical and petroleum industries. In addition, there is increasing recognition that biogenic, or natural, emissions of VOCs, mainly from trees and other vegetation, can also be important in some circumstances.



While the emissions of ozone precursors are obviously essential for ozone formation, meteorological factors also exert a crucial influence. Ozone production in an air mass containing  $\text{NO}_x$  and VOC compounds will occur only if the weather conditions are favourable. Firstly, it will be clear from the preceding description of ozone formation chemistry that the intensity of the incoming solar radiation must be high since this is the driving force behind the photochemistry of ozone production. Temperature is also important since it influences the rates of many of the chemical reactions involved. Other conditions favourable to ozone formation are low windspeeds and a persistent, well-defined boundary layer. These conditions allow sufficient build-up of precursor concentrations, contained within a limited volume, for long enough to generate ozone and other secondary pollutants before the polluted air is dispersed into the free troposphere above the boundary layer.

A major sink for tropospheric ozone is removal by deposition to terrestrial surfaces, termed dry deposition. This process is regulated by stomatal uptake in vegetation canopies which depends on light, temperature and humidity. As a result, the dry deposition of ozone shows strong diurnal and seasonal cycles with daytime and summertime maxima.

The concentration of ozone in the atmosphere will clearly be influenced by the rates at which the chemical mechanisms proceed. Additionally, both large- and local-scale mixing processes occurring in the troposphere will affect ozone concentrations measured at ground level. During the day, any pollutants within the atmospheric boundary layer, having a depth of approximately 1 km or so, are generally well mixed. Following sunset and subsequent cooling at the surface, the depth of the boundary layer may contract to perhaps a few tens of metres above the surface. During night time, in the absence of significant ozone formation, the ozone concentration within the shallower boundary layer decreases due to deposition to the surface and, in areas subject to emissions of  $\text{NO}_x$ , through reaction with NO (reaction 3). At sunrise, convective processes break down the nocturnal stratification; ozone trapped aloft overnight is mixed down to the surface and its ground-level concentration rises. As a consequence of these processes, a diurnal variation in ozone concentration is observed at many locations. Topographical features may influence the strength of this variation. Sites on elevated ground are exposed more frequently to free tropospheric air and may be less frequently capped by a nocturnal inversion layer. Similarly, land/sea breezes help to sustain mixing processes at coastal locations. In both these cases there may be a dampening of the diurnal cycle.

#### *Consequences for ozone control policies*

It is evident from the preceding discussion that the ratio between  $\text{NO}_x$  and VOC concentrations in the atmosphere is an important factor, not merely the presence of these compounds. When the reactions of peroxy radicals with NO (reactions 9 and 11) proceed more rapidly than reactions between peroxy radicals (e.g. reaction 15) or the reaction of the hydroperoxy radical with ozone (reaction 12), the result is net ozone formation. The balance between these opposing tendencies is determined by the  $\text{NO}_x$  / VOC ratio. In very remote locations, mainly in parts of the southern hemisphere, the  $\text{NO}_x$  concentrations may be so low that the reactions of  $\text{HO}_2$  with ozone and other peroxy radicals dominate, leading to net ozone removal. The  $\text{NO}_x$  concentrations in the atmospheric boundary layer over continental areas in the northern hemisphere, however, are generally high enough that the reactions of peroxy radicals with NO dominate, leading to ozone production.

There is a further complication when  $\text{NO}_x$  concentrations are particularly high. In this case, the hydroxyl radicals, which propagate VOC oxidation and conversion of NO to  $\text{NO}_2$ , are scavenged by the relatively high concentrations of  $\text{NO}_2$  (reaction 13). The  $\text{NO}_2$  effectively competes with the VOCs for the OH radical, reducing the production of  $\text{RO}_2$  and  $\text{HO}_2$  radicals, and inhibiting the formation of ozone. This feature of tropospheric chemistry has important implications for the development of ozone control strategies. If, in these circumstances, the  $\text{NO}_2$  concentration is decreased, there will be a greater number of OH radicals available to react with the VOCs, leading to greater formation of ozone. Hence, a reduction in the atmospheric  $\text{NO}_x$  level may result in an increase in ozone concentration.

### **3.3 Photo-oxidant Models**

The formation of tropospheric ozone involves the complex interaction between precursor emissions, photochemistry, transport and deposition. The complete representation of these processes in a mathematical model is currently impossible, and the great variety of models developed to study the ozone formation processes have all been simplified, to a greater or lesser extent, in one or more of these areas. Both Eulerian, or grid, and Lagrangian, or trajectory, models have been constructed, using different spatial and temporal scales, and employing chemical mechanisms of varying complexity, as deemed appropriate for each model's main purposes. Because of the complexities of the processes involved, these models themselves are complex and computer-intensive.

The following section gives a brief survey, based largely on the review of UK PORG (1993), of some of the main photo-oxidant models developed for use in Europe, with an indication of each model's main area of application. Generally, they have all been used to assess aspects of emissions control policies.

#### **3.3.1 *European Photo-oxidant Models***

Within the UNECE European Monitoring and Evaluation Programme (EMEP) a Europe-wide ozone model has been developed from the Norwegian photochemical trajectory model (Eliassen ., 1982) at the Meteorological Synthesizing Centre-West in Oslo. The EMEP ozone model (Simpson, 1992a, 1993, 1995) is a single-layer Lagrangian model with a variable depth which extends from the ground to the top of the atmospheric boundary layer. The meteorological data requirements are met by the Norwegian Numerical Weather Prediction model. The EMEP model uses a chemical mechanism in which each important VOC class is represented by one or two members whose chemical degradation is followed explicitly. Further details of the model are given in Section 3.3.3. The EMEP model has been designed with the purpose of simulating ozone formation over long periods of time (one month to one year) and over the whole of Europe, so that the likely effects of emission control measures on long-term ozone concentrations can be estimated.

The EURAD modelling system has been developed within the EUMAC sub-project of the EUROTRAC (European Experiment on Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe) project. This model comprises three main modules: an emissions model, a mesoscale meteorological model and a chemical transport model. The chemical transport model is based on the RADM

(Regional Acid Deposition Model) model (Chang *et al.*, 1987), adapted from North American to European conditions (Hass *et al.*, 1991). RADM is an example of an Eulerian grid model. EURAD uses a variable resolution in both the vertical, up to the height of the lower stratosphere, and the horizontal directions, with usual grid sizes of 20-80 km. The EURAD model uses the RADM II chemical mechanism (Stockwell *et al.*, 1990) which employs nine VOCs and more than 80 organic reactions in addition to the reactions involving the small molecules and radicals containing C, O, H, N and S atoms. The model has been applied to several episodes to estimate the transport and chemical transformations of environmentally relevant trace gases. Several applications have focussed on photo-oxidant formation on a European scale.

In addition to the UNECE EMEP and EUROTRAC/EURAD models, which have been supported internationally, there are a number of national photochemical modelling activities which have addressed the regional scale formation of ozone.

The LOTOS (LOnG Term Ozone Simulation) model (Bultjes, 1991) has been developed at the TNO institute in the Netherlands as a follow-up to the European implementation of the RTM-III model of the Systems Application Inc. within the joint Netherlands and Federal Republic of Germany PHOXA programme (Meinl & Bultjes, 1984). The LOTOS model is an Eulerian grid model with three vertical layers up to about 2.5 km and a parameterized surface layer. The horizontal grid resolution is 1° latitude x 2° longitude, with a total of 35 x 35 grid cells covering much of Europe. The meteorological data required are taken from the output of the Norwegian Numerical Weather Prediction model. The LOTOS model incorporates the Carbon-Bond IV mechanism (CBM-IV) which describes the behaviour of seven VOCs using 34 organic reactions in addition to the reactions involving the small molecules and radicals containing C, O, H, N and S atoms. Results of model simulations for the period April-October 1985 have been reported (Roemer *et al.*, 1993).

The RTM-III model has been used to examine regional-scale ozone formation during three separate photochemical episodes during 1980 and 1982. It is ideally suited to the assessment of the impact of precursor emissions controls across large areas of Europe during such ozone episodes, although the emissions data requirements of this model are considerable.

The characteristic feature of the UK Harwell photochemical model (Derwent & Jenkin, 1991) is the complete and explicit chemical mechanism used, involving 69 VOC species and almost 700 reactions. The model concentrates on the chemical processes in the atmosphere and adopts a simple, two-layer Lagrangian trajectory model approach using illustrative straight-line back trajectories of up to six days in length, representing the weather conditions in a typical photochemical episode. Studies with this model have focussed on elucidating some basic features of regional ozone formation, and it has been used to investigate the relative importance of individual VOC species in forming ozone.

This area of study has been continued at the Swedish Environmental Research Institute with the IVL model, in which the chemistry has been extended to include more than 100 VOC species and over 1000 chemical reactions.

The MPA model has been developed at the RIVM institute in the Netherlands. It is a two-layer Lagrangian trajectory model employing 96-hour back trajectories to four receptor

points within the Netherlands. The model includes emissions, non-linear atmospheric chemistry using the CBM-IV mechanism, dry deposition, exchange between the boundary layer and the free troposphere, and fumigation between the two modelled layers. It has been used to calculate both long-term averaged and episodic ozone concentrations (de Leeuw & van Rheineck Leyssius, 1991).

The Danish DMU model (Zlatev *et al.*, 1992) is Eulerian with one layer (the boundary layer) and uses 150 km grid resolution. This is another of the models that takes its meteorological data from the Norwegian Numerical Weather Prediction model. The DMU model uses the CBM-IV chemical mechanism.

Stedman & Williams (1992) have described a simple trajectory model using a boundary-layer box followed along 96-hour trajectories. Ozone production is driven by VOC emissions - on a 50 km x 50 km grid - using a seasonally-dependent hydroxyl radical concentration. Both the box height and the OH concentration are calculated as simple step functions of the daily maximum temperature at the receptor, the only other model input. The emissions of NO<sub>x</sub> are ignored. As a result of its simple linear formulation, this model is able to separate the contributions to ozone from different emitter countries. This model is designed for real-time ozone forecasting applications in the UK.

### **3.3.2 *Choice of Model as Basis for Simplified Approach***

A simplified description of ozone formation suitable for incorporation into an integrated assessment model needs to be based on a photo-oxidant model designed to calculate ozone concentrations over long periods and covering the whole of Europe.

To this end, the work was carried out in collaboration with EMEP's Meteorological Synthesizing Centre - West, and the results of the EMEP ozone model (Simpson, 1992a, 1993, 1995; Labancz, 1993) provide the basis on which a simplified ozone formation module has been built. The EMEP model has been selected for this analysis for several reasons: (i) the EMEP model has repeatedly undergone extensive peer review and its structure and results have been compared with other ozone models (see Section 3.3.3); (ii) the EMEP model is readily available for calculating ozone levels over all of Europe over a time period of six months, which is in line with the requirements established by the definition of the critical levels, and the calculation of the necessarily large number of scenarios is a practical proposition with this model; (iii) since the model(s) developed by EMEP are created in an international cooperative effort and approved by the international EMEP steering body, their results receive both scientific and political acceptance within the framework of the Convention on Long-range Transboundary Air Pollution, where negotiations on the next nitrogen protocol will be carried out. Therefore, relying on the EMEP model increases the chances of general acceptance of the integrated assessment tool.

It should be stressed, however, that in principle the construction of simplified source-receptor relationships could also be based on results of other photo-oxidant models, provided the required scenario runs are available for all of Europe for a time period of six months. Indeed, one method of making comparisons between complex photo-oxidant models might be to construct statistical models - such as the one presented in this paper - summarizing the

results of the complex models, and then use the calculated coefficients (of the statistical models) as a means of comparing basic model responses.

The following sections provide an overview of the EMEP model and briefly describe the work carried out to implement this model within a parallel processing environment. It should be pointed out that the EMEP ozone model is by no means static; it continues to be updated to reflect developments in both the understanding of the physical and chemical processes involved and the availability of new data on the emissions of pollutants, whether from anthropogenic or natural sources, chemical reaction rates, deposition velocities, background concentrations, etc. The following description of the EMEP model concentrates on the version used in constructing the simplified model, with indications of recent revisions that are pertinent to future work on the simplified model.

### **3.3.3            *Description of the EMEP Ozone Model***

The EMEP ozone model is a single-layer Lagrangian trajectory model which calculates concentrations of photochemical oxidants every six hours for a set of up to 740 arrival points (on a 150 km x 150 km grid) covering the whole of Europe. Columns of air in the atmospheric boundary layer are followed along specified 96-hour trajectories, picking up emissions of NO<sub>x</sub>, VOC, CO and SO<sub>2</sub> from the underlying grid. The height of the air column, the mixing height, containing the bulk of the polluted air is reset at 1200 GMT each day from radiosonde data. Along each trajectory the mass conservation equations are integrated, taking into account emission inputs, photolysis and chemical reactions, dry and wet removal, and the influence of meteorological parameters. These equations are solved numerically, currently using the quasi-steady state approximation method with a fixed time step of 15 minutes.

The six-hourly meteorological data required by the EMEP model are taken from the output of the Norwegian Numerical Weather Prediction model. Wind velocity data permit calculation of 96-hour back-trajectories to any point in the EMEP grid. The ozone model simulates the exchange of boundary-layer air with free-tropospheric air as a result of convective clouds. Photolysis rates are adjusted for cloud cover, and temperature data are used to calculate appropriate chemical reaction rates and in estimating both natural VOC emissions and the emissions of NO<sub>x</sub> from soils. Other meteorological data are used in estimating deposition velocities, which are calculated as a function of atmospheric stability, latitude, time of year and time of day.

The anthropogenic emissions of NO<sub>x</sub>, VOC and SO<sub>2</sub> used in the model are based, as far as possible, on data supplied officially at a national level. The emission inventory includes estimates of SO<sub>2</sub> and NO<sub>x</sub> emissions from ship traffic in the Atlantic Ocean, North Sea and Baltic Sea. When not otherwise available directly, emissions of CO are estimated by scaling the anthropogenic VOC emissions. For use in the ozone model, the emissions data (prior to 1990) are spatially disaggregated on to the 150 km x 150 km EMEP grid. For 1990, emissions estimates are available on a 50 km x 50 km grid, and the EMEP model has recently been updated to make use of the better resolution. The SO<sub>2</sub> emissions and emissions of NO<sub>x</sub> from high-level sources are assumed to vary sinusoidally over the year with a maximum in January and a minimum in July. By contrast, anthropogenic VOC emissions are kept constant from one month to the next. Both low-level NO<sub>x</sub> emissions and anthropogenic VOC

emissions are assumed to follow a simple diurnal variation with daytime emissions three times greater than those during the night.

Natural emissions of both VOCs and NO<sub>x</sub> have been included in the EMEP ozone model. Natural emissions of VOCs are represented by the emissions of isoprene from forests and agricultural crops (Simpson *et al.*, 1995). These are calculated at each time step using surface temperature data, land-use data for each grid square and published emission-temperature relationships. Estimates of NO<sub>x</sub> emissions from soils are based on temperature and a simple categorization of type of land cover.

The chemical mechanism of the EMEP model has recently been updated (Simpson *et al.*, 1993; Simpson, 1995) and now comprises 136 reactions, including 25 photolysis reactions. The model calculates explicitly the concentrations of 61 chemical species. Six organic species - ethane, n-butane, ethene, propene, o-xylene and ethanol - are used to represent the emitted anthropogenic VOCs. Their proportions have been chosen to reflect current understanding of the mix of species and chemical reactivities of actual VOC emissions. In the version of the model used for this study, the same VOC speciation is used to represent man-made emissions from anywhere in Europe. More recent versions of the EMEP model allow a larger number of emitted VOC species and the use of different VOC species profiles for different source sectors in different countries. Methane is treated in the model as a tropospheric background species. Initial concentrations of all species at the start of each 96-hour trajectory are taken from previous model calculations, if available; otherwise a set of assumed background tropospheric concentrations, based on appropriate measured data or tropospheric model calculations, is used.

The EMEP ozone model has been applied to the summer periods of 1985, 1989 and 1990 (Simpson, 1992a, 1993; Labancz, 1993) and has been used to assess the effects of various scenarios of precursor emission reductions (Simpson, 1992b, 1993; Simpson & Styve, 1992).

A number of comparisons with ozone measurements have been reported, the extent of such comparisons being limited in practice by the availability of reliable measurement data. Model calculations of daily maximum ozone (boundary layer average) for July 1985 have been compared with observed maximum concentrations at 24 rural sites in north-west Europe (Simpson, 1992a), assuming that at this time of year there will be good thermal mixing of the boundary layer in the afternoon, when both modelled and observed concentrations usually peak. The modelled concentrations generally lay within 30% of the observed values, with a tendency towards over-prediction. The quality of the comparison was clearly very site-dependent, with correlation coefficients varying from -0.06 to 0.88; the median value of the correlation coefficients was 0.49.

Comparisons of EMEP model estimates of surface ozone concentrations with observations have been made for the April-September periods of both 1985 and 1989 at nineteen selected sites (Simpson, 1993). For the 1985 data the correlation coefficient between modelled and observed concentrations varied over a wide range, from -0.05 to 0.66. The 1989 results, however, showed much more consistent quality across nearly all months and across all sites, with correlation coefficients ranging from 0.54 to 0.73. The modelled six-

month mean concentrations generally lay within about 20% of the measurements. For this period the ozone episodes were well reproduced at all sites.

A similar comparison for 1990 has also been reported (Labancz, 1993). The level of agreement between modelled and measured values was similar to that for 1989, with correlation coefficients in the range 0.55 - 0.75 for the small number of sites reported. The most recent comparison exercise undertaken (Malik *et al.*, 1996) also used 1990 measurements but involved modelled values generated with the revised version of the EMEP model designed for use with emission inventories on a 50 km grid. The model generally gave a slight over-prediction of the six-month mean of daily maximum ozone - with a median difference of 12% between modelled and measured values - except at the highest ozone concentrations. The correlation coefficients at over 40 sites were found to vary from 0.42 to 0.75.

Some of the uncertainties associated with the modelling process have been addressed by comparisons with other chemical mechanisms and other photochemical oxidant models. The chemical mechanism formerly employed in the EMEP model has been shown (Derwent, 1993) in polluted situations to give ozone concentrations well within the central range of results from the 25 mechanisms tested. The same conclusion was drawn for the EMEP mechanism's predictions of PAN and hydrogen peroxide. In addition, and significantly in the present context, the EMEP chemical mechanism generated ozone responses to 50% reductions in either VOC or NO<sub>x</sub> emissions that also lay well within the central range of control scenario responses.

The EMEP model has been compared with both the three-layer Eulerian LOTOS model and the single-layer Eulerian Danish DMU model for July 1985 (Iversen, 1991), with a closer comparison between the EMEP and LOTOS models (Simpson & Builtjes, 1991). All three models predicted a similar spatial distribution of ozone across Europe, with average concentrations in the sequence LOTOS > DMU > EMEP. When the LOTOS and EMEP model results were compared with observations, it was found that, at specific locations, the LOTOS model gave clearly higher ozone levels than both the EMEP model and the measurements. The two models' predictions of maximum ozone were more closely correlated than their predictions of mean ozone. Generally, the EMEP model predicted lower average ozone concentrations than the LOTOS model but showed greater variability with lower minima and higher maxima. The differences between these two models were ascribed, in the main, to the greater tropospheric ozone concentrations used as boundary conditions in the LOTOS model.

The responses of the EMEP and LOTOS models to emissions reductions were also compared to investigate whether the models would provide different policy guidance. This comparison was conducted for 50% reductions in the emissions of (i) NO<sub>x</sub>, (ii) VOCs and (iii) both NO<sub>x</sub> and VOCs with respect to maximum, daily and monthly mean ozone concentrations. Although the comparison of the effects of emission controls revealed differences between the two models for particular days, the overall results were similar. The EMEP model tended to indicate that NO<sub>x</sub>-only emission controls were less effective at reducing ozone across a large part of Europe than the LOTOS model showed. For VOC reductions, the two models predicted similar spatial patterns of ozone decrease across Europe

but the EMEP model gave a greater size of reduction. The models showed very similar responses for the scenario in which both NO<sub>x</sub> and VOC emissions were reduced.

Another model intercomparison involving four photo-oxidant dispersion models - EMEP, LOTOS, EURAD and REM3 - has also been reported recently (Hass *et al.*, 1996). This study, in which as far as possible each model was run in its normal manner, focussed on the simulation of a six-day ozone episode in early August 1990 at four receptor sites for which measurements were available. All four models showed reasonable agreement with measurements. Differences in model performance were found but these differences depended on the specific meteorological situation, location and time; no general trend was evident. The model responses to NO<sub>x</sub> and VOC emission reductions, though, showed substantial differences, despite general agreement about the direction of the response. The EURAD model tended to show a more pronounced response to anthropogenic emission reductions than the other models. The differences between the models were also found to vary from one receptor site to another. General conclusions could not easily be drawn, however, since the comparison was limited to one particular episode of only a few days duration.

The role played by biogenic VOCs in ozone formation over Europe and their influence on the predicted effects of reducing anthropogenic emissions have been investigated using the EMEP ozone model (Simpson, 1995). Estimates of biogenic isoprene emissions in Europe are subject to considerable uncertainty, perhaps by a factor of five (Simpson *et al.*, 1995). The implications of this uncertainty for model predictions of control strategy effectiveness in Europe have been assessed (Simpson, 1995), with the conclusions that uncertainties in isoprene emissions are not very important for the evaluation of long-term ozone scenarios in Europe but must be considered for episodic ozone events.

#### **3.3.4 *Parallelization of the EMEP Model***

Operation of the EMEP model on the mainframe computer used by the Norwegian Meteorological Institute is rather time- and resource-intensive. Carrying out the large number of scenario runs (see Section 3.5.3) necessary for constructing the simplified ozone model is therefore an expensive undertaking. To simplify and accomplish this task, the EMEP model has been transferred to a parallel computing environment, which resulted in a significant decrease of computing time (Unger, 1996). This work was carried out for IIASA, specifically in relation to the simplified ozone model, by GMD FIRST - Institute for Computer Architecture and Software Technology of the German National Research Center for Computer Science - in Berlin.

To adapt the EMEP model to parallel computing, the computational tasks were subdivided into a number of subsets and distributed to individual parallel processors (nodes), where they can be carried out simultaneously. The results are then passed back to the host node.

For Lagrangian trajectory models (like the EMEP model), computations of the chemical equation schemes along the individual trajectories can be easily separated and distributed to parallel nodes. Significant efficiency improvements have been achieved by carefully balancing the loads (i.e., minimizing the idle time) of the nodes. Owing to differences in meteorological conditions, the trajectories often have different lengths. It



**Table 2** Computing times of the EMEP Model for 10 trajectory arrival times on the FIRST'S MANNA platform

Number of nodes	Maximum number of trajectories on each node	Computing time (seconds)	Speed-up factor
1	734	1789.18	1.00
2	380	891.21	2.01
3	260	597.60	2.99
4	200	450.42	3.97
5	170	362.85	4.93
6	140	303.87	5.89
7	120	261.51	6.84
8	110	229.42	7.80
9	100	205.39	8.71
10	90	185.52	9.64
11	86	169.07	10.58
12	80	156.55	11.43
13	75	148.10	12.08
14	70	136.35	13.12
15	66	128.67	13.91
16	63	121.87	14.68
17	60	116.37	15.37
18	57	109.86	16.29
19	52	105.01	17.04

transpires that the computational work for each trajectory is nearly proportional to the number of grids cells touched by the trajectory. To optimize the load of the parallel nodes, the lengths of the trajectories are therefore precalculated by the host node. This provides a basis for distributing all trajectory-related calculations equally among the available parallel nodes. Furthermore, the field dimensions of some variables (particularly those relating to the number of emitter countries touched by a trajectory) can also be reduced accordingly. A further improvement was achieved by utilizing the idle time of the host node - during the trajectory calculations for step  $k$  on the parallel nodes - for computation of the trajectory lengths for the following step  $k+1$ .

The parallel version of the EMEP model has been implemented on two computer platforms at the GMD in Berlin: on the MANNA computer system developed by GMD and on a PARSITEC GD PowerPlus machine. Table 2 lists the computing times for different numbers of parallel nodes for the MANNA platform, for a test set of ten trajectory arrival times. A full scenario run on this platform with 20 nodes for six months and 734 grids takes about two hours.

### **3.4 Concept of the Simplified Model for Ozone**

The approach taken here for developing simplified source-receptor relationships between ozone exposure and the emissions of ozone precursors has been to divide the description into three parts.

#### *1. Atmospheric Boundary Layer*

The first aspect concerns the source-receptor relationships between precursor emissions and the concentrations of ozone in the atmospheric boundary layer; the EMEP ozone model has been shown to give reliable estimates of ozone concentrations during the afternoon period when daily maximum values are most likely to occur. The development and testing of the regression model constructed to describe these source-receptor relationships are the subjects of Sections 3.5 and 3.6.

#### *2. Ground Level*

It is then necessary, in a second step, to relate the boundary layer mean ozone concentrations to the ozone exposure at ground level (AOT40), the effects-related parameter that must be calculated during an integrated assessment. The reasons for adopting this indirect approach to estimating the AOT40 values are discussed in Section 4.1.1.

Because the EMEP model is designed to cover the whole of Europe, it uses a relatively large grid size of 150 km. However, an integrated assessment model for ozone needs to consider the effects of ozone exposure on ecosystems that may be much smaller than this. Observational evidence for small-scale spatial variation in ozone exposure at ground level is well-established (Angle & Sandhu, 1986; UK PORG, 1993). Therefore, the diurnal variation of ozone exposure at ground level (AOT40) at a particular location would be calculated from the boundary layer average ozone concentration for the area, taking local factors into account as necessary. These factors will include features such as altitude, distance from the coast and local emissions of NO<sub>x</sub>. Analyses of ozone measurement data, aimed at identifying the important features and investigating ways of incorporating them into an integrated assessment model for calculating the AOT40, are reported separately (Kettunen *et al.*, 1994). Small-scale mapping of ozone exposure in Europe is being carried out at RIVM in The Netherlands (de Leeuw, 1995), and shows that the calculated ozone fields are very heterogeneous in heavily populated areas and in complex terrain. The incorporation of such information into the integrated model is discussed further in Section 4.1.2.

### 3. Free Troposphere

A third concern is related to the contributions to ground-level ozone from the free troposphere (see also Section 4.2). An initial feasibility study carried out recently suggests that the boundary layer ozone response can be up to 50 percent of the free tropospheric ozone perturbation (Wojcik, 1995). The response depends strongly on latitude, season and distance to the coast. Further work will be necessary to quantify this influence and to establish relationships to emissions of precursor substances, including the contribution from aircraft, not only in Europe but potentially in the entire northern hemisphere.

#### 3.5 Simplified Source-Receptor Relationships

Before outlining the development of the regression model constructed to describe the source-receptor relationships between precursor emissions and the concentrations of ozone in the atmospheric boundary layer, a brief overview of the patterns of behaviour in Europe, as determined by the EMEP ozone model, is presented. This is done using the mean, over six months, of ozone concentrations during the early afternoon, well-mixed period.

##### 3.5.1 Ozone Isopleth Diagrams

The EMEP ozone model has been used to investigate the relationships in different areas of Europe between mean boundary layer ozone concentrations and changes in the emissions of  $\text{NO}_x$  and VOCs, using emissions and meteorological data appropriate to the summer of 1989.

A convenient way to illustrate the results of these investigations is by means of ozone isopleth diagrams. Such diagrams have been most commonly used, particularly in North America, to show how maximum ozone concentrations depend on the initial concentrations of  $\text{NO}_x$  and VOCs on a particular day at a specific location. Lines of constant value, or isopleths, of the maximum ozone concentrations are constructed by connecting points having the same ozone concentration but corresponding to various initial conditions. Ozone isopleth diagrams in this form provide a concise representation of the effect of reducing initial  $\text{NO}_x$  and VOC concentrations on peak ozone concentrations and, in the past, they have been used quantitatively to develop ozone control strategies as part of the U.S. EPA's empirical kinetic modelling approach (EKMA) (Gipson *et al.*, 1981).

The isopleth diagrams used in this section are constructed rather differently, although there are obvious similarities in appearance. Firstly, the ozone statistic depicted by the isopleths is the mean, over the six-month summer period, of the early afternoon ozone concentrations calculated by the EMEP model. Secondly, in the version used here, ozone is shown as a function of the percentage reduction in emissions of  $\text{NO}_x$  and VOCs across Europe. Thus, the top right-hand corner of each diagram represents the base case without any reduction in precursor emissions.

Two broad patterns of ozone formation may be distinguished, as illustrated by the isopleth diagrams shown in Figure 2. The grid squares investigated, and the general pattern found in these grids, are identified in Figure 3.

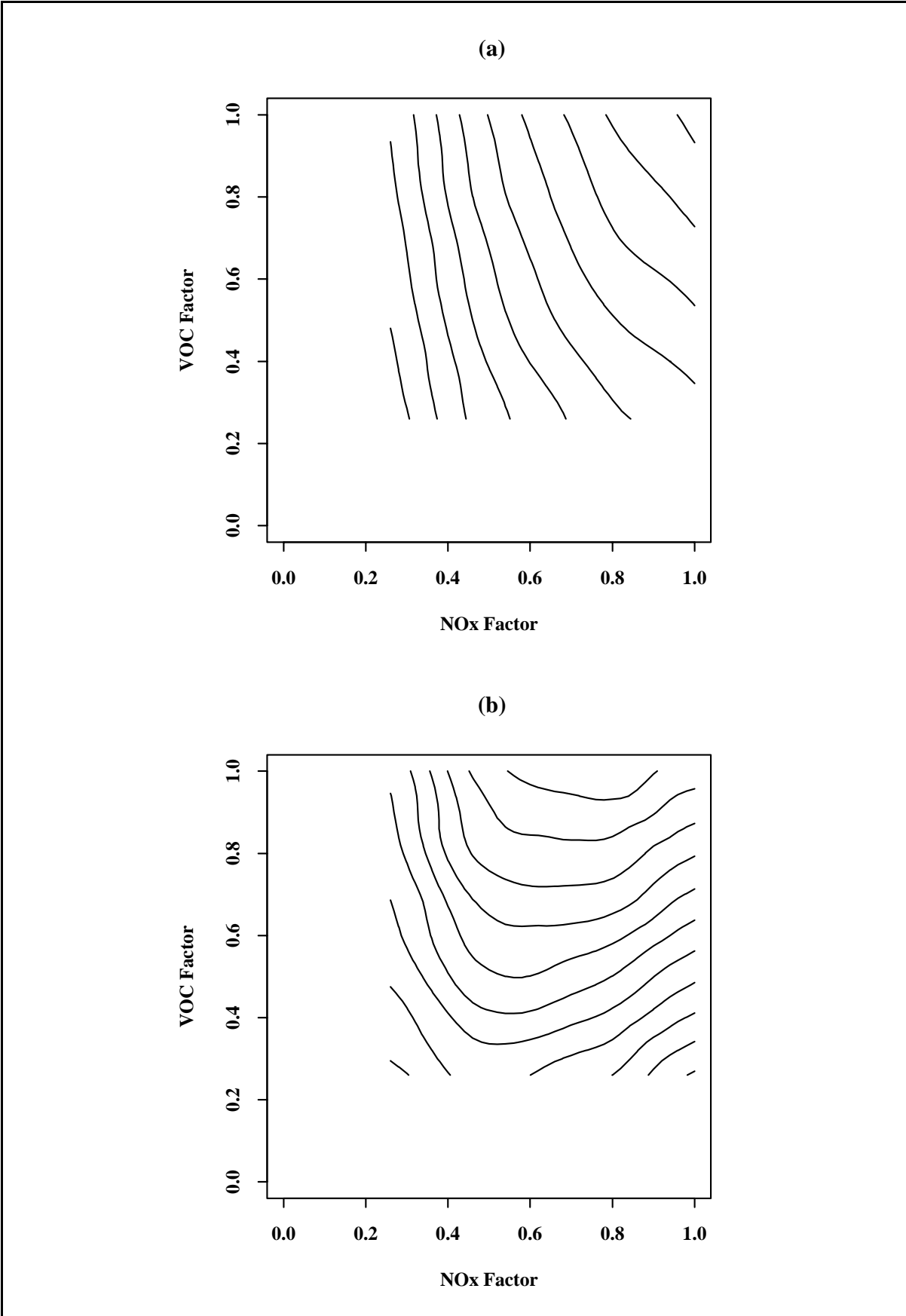
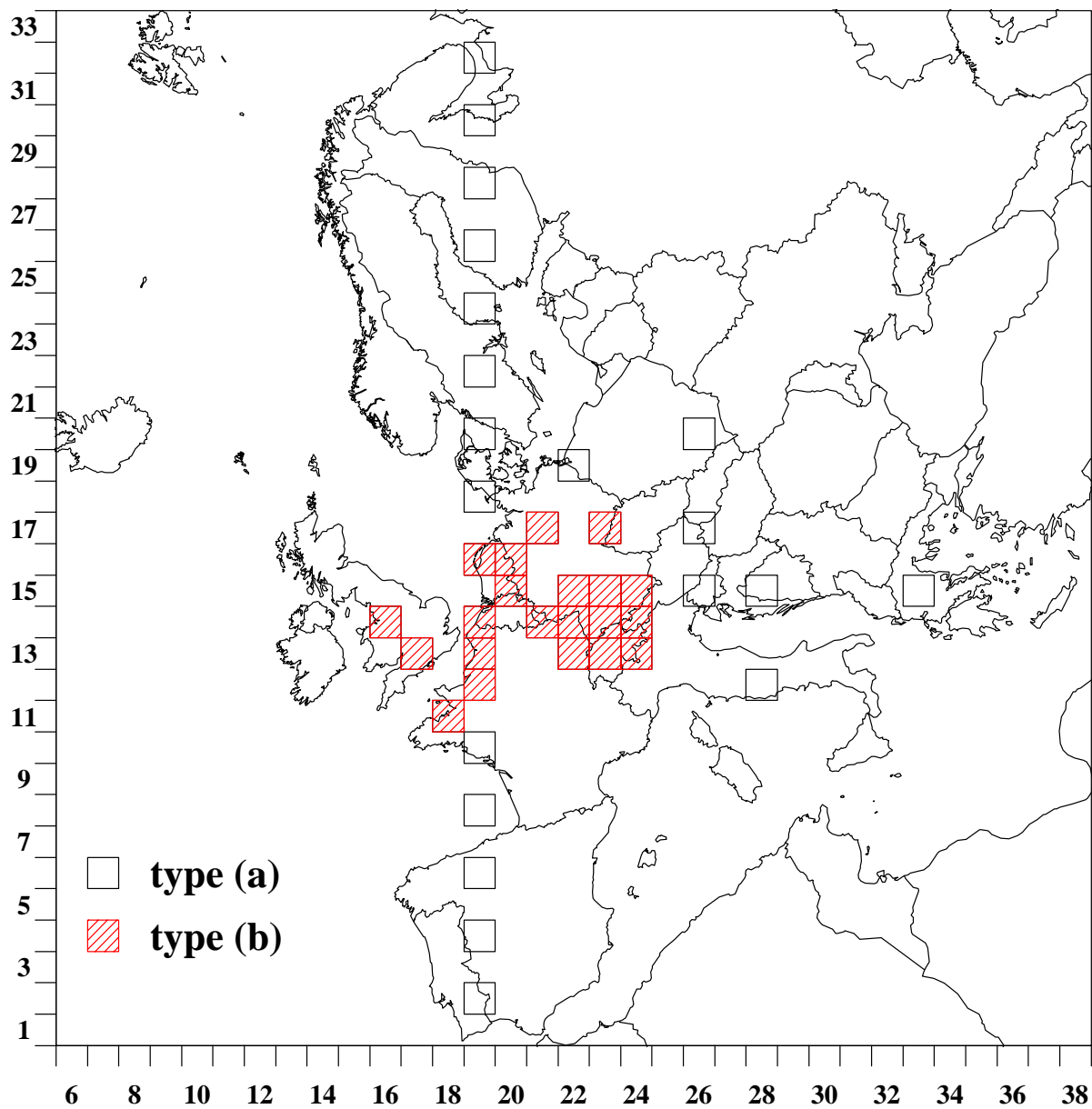


Figure 2 Typical patterns of ozone formation behaviour in Europe



**Figure 3** European grid squares showing (a) linear or (b) non-linear ozone formation behaviour

In northern, southern and eastern areas of Europe, the typical pattern of ozone formation behaviour corresponds to the isopleth diagram of Figure 2(a). Reductions in VOC emissions are seen to exert only a minor influence on mean ozone concentrations. The importance of the  $\text{NO}_x$  / VOC ratio in determining ozone production, and the underlying atmospheric chemistry, were discussed in Section 3.2. In these regions the  $\text{NO}_x$  / VOC ratio is relatively low. There is an ample supply of peroxy radicals ( $\text{RO}_2$  and  $\text{HO}_2$ ) to convert  $\text{NO}$  to  $\text{NO}_2$  and, thus, lead to ozone production. Decreasing the available  $\text{NO}_x$  leads directly to a decrease in ozone. In these circumstances, ozone formation is limited by the availability of  $\text{NO}_x$ , and the atmospheric chemistry system is said to be  $\text{NO}_x$ -limited. In such regions, reductions in emissions of  $\text{NO}_x$  are likely to be effective in reducing ozone concentrations,

but ozone is relatively insensitive to reductions of VOC, and to changes in the VOC species distribution, at constant  $\text{NO}_x$ .

For NW Europe, however, the isopleth diagram of Figure 2(b) shows a different picture. The isopleths form a ridge dividing the diagram into two areas. On the left of the ridge, corresponding to the greatest reductions in  $\text{NO}_x$  emissions, the system tends towards the  $\text{NO}_x$ -limited case. On the right of the ridge, the  $\text{NO}_x$  / VOC ratio is relatively high and the  $\text{NO}_2$  concentrations are sufficiently great that  $\text{NO}_2$  competes with VOCs for reaction with the OH radical, as discussed in Section 3.2. In this region of the diagram, reducing VOC emissions results in lower ozone concentrations; to a large extent, ozone shows a linear dependence on VOC emission changes (Simpson, 1992b). However, ozone concentrations may be increased, at least initially, by  $\text{NO}_x$  reductions in the absence of concurrent reductions in VOC emissions.

### 3.5.2 *Design of the Simplified Model*

This section outlines the development of a regression model designed to provide a simplified description of the source-receptor relationships between precursor emissions and the concentrations of ozone in the atmospheric boundary layer, in line with the first part of the overall concept given in Section 3.4.

The simplified source-receptor relationships need to be able to predict changes in ozone concentration at a receptor grid resulting from emission abatement strategies adopted in various European countries. Emission estimates at a national level were considered to be the most appropriate for this purpose, and the regression model uses national, annual emissions of  $\text{NO}_x$  and VOCs as explanatory variables. For the model discussed in this paper, the mean early afternoon ozone concentration over the six-month summer period was adopted as the response variable to be predicted. Basic ideas about which terms should be included in the simplified model were developed from the published results of studies made using the EMEP ozone model and experience of this latter model's behaviour gained during earlier efforts to develop a simplified model for calculating daily ozone concentrations.

Simpson (1992b) investigated the relationship between mean ozone concentrations and VOC emissions and concluded that there is considerable linearity, in the sense that a 5x % reduction in VOC emissions from a given country results in 5 times the reduction in mean ozone that an x % reduction produces. He also showed that the change in ozone per unit VOC emission reduction depended on the extent of any simultaneous  $\text{NO}_x$  emission changes.

Ozone isopleth diagrams constructed from the results of EMEP model calculations, such as those in Figure 2, almost invariably show a relatively simple form. Earlier IIASA studies into the possibilities of developing a simplified regression model for predicting daily ozone concentrations (Heyes & Schöpp, 1995) made use of non-parametric methods. The results suggested that a multi-dimensional quadratic spline could be used to reproduce the main features of the relationship between ozone and the emissions of its precursors.

The simplified "daily" model also made use of the concept of "effective" emissions, suggested by recent studies with the EMEP model (Simpson, 1995) which showed that exchange processes between the boundary layer and the free troposphere could have a

significant impact on the final ozone concentrations. The EMEP model includes two processes by which boundary-layer air can be mixed with free tropospheric air, *viz.* day-to-day increases in mixing height and the venting effect of cumulus clouds. For some sites, at least, the consequent losses of ozone, NO<sub>x</sub> and VOCs from the boundary layer could be considerable. To allow for these effects, emissions along the trajectory were weighted by the amount of dilution that subsequently takes place within the air mass (Simpson, 1995) to give the dilution-weighted or "effective" NO<sub>x</sub> and VOC emissions used as variables in the regression model.

On the basis of the ideas outlined above a general formulation for the simplified "seasonal" model was developed. In subsequent sections the following abbreviations are used for model variables:

$v_i$	-	annual national emissions of non-methane VOCs from emitter country $i$
$n_i$	-	annual national emissions of NO <sub>x</sub> from emitter country $i$
$ev_j$	-	"effective" emissions of VOCs, including natural sources, at receptor $j$
$en_j$	-	"effective" emissions of NO <sub>x</sub> , including natural sources, at receptor $j$
$evn_j$	-	"effective" natural emissions of VOCs at receptor $j$
$enn_j$	-	"effective" natural emissions of NO <sub>x</sub> at receptor $j$
$\bar{x}$	-	seasonal mean of variable $x$

The mean, early afternoon ozone concentration at receptor  $j$ ,  $[O_3]_j$ , is assumed to be a function of the nmVOC and NO<sub>x</sub> emissions,  $v_i$  and  $n_i$  respectively, from each emitter country  $i$ , and the mean "effective" emissions (of NO<sub>x</sub> and VOCs),  $en_j$  and  $ev_j$ , experienced at the receptor over the period in question. The general model formulation adopted is:

$$\overline{[O_3]}_j = k_j + \sum_{i=1}^M (a_{ij}v_i + b_{ij}n_i + c_{ij}n_i^2) + \alpha_j \overline{en}_j^2 + g(\overline{en}_j, V) + \overline{en}_j \sum_{i=1}^M h_{ij}n_i \quad [4]$$

where  $M$  is the number of emitter countries considered,

$V = \{v_1, v_2, \dots, v_M\}$ ,

and the non-linear function  $g()$  is given either by:

$$g(\overline{en}_j, V) = \overline{en}_j \sum_{i=1}^M d_{ij}v_i \quad [5]$$

or by:

$$g(\overline{en}_j, V) = \beta_j \overline{en}_j \overline{ev}_j \quad [6]$$

The mean "effective" emissions are given by:

$$\overline{en}_j = \sum_{i=1}^M \overline{E}_{ij} n_i + \overline{enn}_j \quad [7]$$

$$\overline{ev}_j = \sum_{i=1}^M \overline{F}_{ij} v_i + \overline{evn}_j \quad [8]$$

where  $E_{ij}$ ,  $F_{ij}$  depend on the meteorology and are obtained from EMEP model calculations, and  $enn_j$  and  $evn_j$  represent the "effective" natural emissions of  $\text{NO}_x$  and VOCs, respectively.

For the initial stages of evaluating this model, an heuristic approach was taken to decide which terms, if any, could be dropped from the model. Such experiments led to the conclusion that the following linear regression model contained sufficient information for the present purpose:

$$\overline{[O_3]}_j = k_j + \sum_{i=1}^M (a_{ij} v_i + b_{ij} n_i + c_{ij} n_i^2) + \alpha_j \overline{en}_j^2 + \overline{en}_j \sum_{i=1}^M d_{ij} v_i \quad [9]$$

In order to decide which emitter countries should be included in the model, the emitter countries were ranked on the basis of their contribution to the "effective"  $\text{NO}_x$  emissions experienced at each receptor  $j$ . For the purpose of testing this model formulation, the highest eleven contributors to "effective"  $\text{NO}_x$  were included in the equation, i.e.  $M$  was set equal to 11. This choice was based on an assessment of the EMEP model results for a small number of receptor sites, in an attempt to include in the simplified model all the most influential emitter countries (for a given receptor) yet exclude those which had very little effect. It is recognized that there may be potential collinearity problems with this model formulation which need further investigation. This issue is discussed in Section 4.5.

It is apparent from the use of the  $v_i$  variable to represent annual, national total non-methane VOC emissions in equation [9] that this model formulation is not designed to allow for any potential effects on ozone formation of different VOC species profiles. The neglect of VOC speciation effects is discussed further in Section 4.3.

The formulation of the simplified "seasonal" model given in equation [9] above is the one constructed for 25 European receptor grids, as described in the next section, and used for the model evaluation tests described in Section 3.6.



It is of interest to relate the terms of equation [9] to the physical and chemical processes that determine ozone formation in the atmosphere. Possible interpretations are:

- $k_j$  includes the effects of background concentrations of  $O_3$  and its precursors, and natural VOC emissions;
- $a_{ij}v_i$  provides the linear country-to-grid contribution from VOC emissions in country  $i$ , allowing for meteorological effects;
- $b_{ij}n_i$  provides the linear country-to-grid contribution from  $NO_x$  emissions in country  $i$ , allowing for meteorological effects;
- $\alpha_j en_j^2$  takes account of the average non-linearity (in the  $O_3 / NO_x$  relationship) experienced along trajectories arriving at receptor  $j$  and any non-linear effects local to that receptor;
- $c_{ij}n_i^2$  serves essentially as a correction term to allow for non-linearities occurring close to high  $NO_x$  emitter countries;
- $d_{ij}en_jv_i$  allows for interactions between  $NO_x$  and VOCs along the trajectories.

The coefficients  $a_{ij}$  and  $b_{ij}$  may also be regarded as a composite source-receptor matrix.

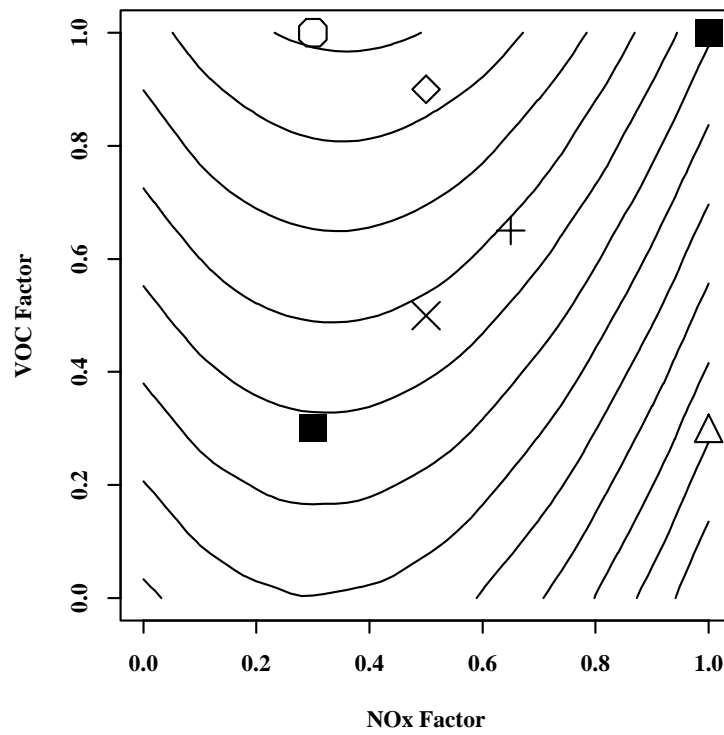
### 3.5.3 *Sampling Design*

The simplified model has been designed as a regression model that relates the six-month mean early afternoon ozone concentration to national, annual emissions of  $NO_x$  and VOCs. For this purpose the data sample, upon which the regression analysis is to be based, must also include cases with reduced emissions. Obviously, actual monitored data are available only for the current emission levels. To overcome this lack of data, the sample was constructed from numerous runs of the EMEP model, carried out using 1989 emissions data and meteorological data for the period April-September 1989. Consequently, the simplified model can be considered to be a summary of the full EMEP model, limited to the response of mean ozone levels to changes in national  $NO_x$  and VOC emissions.

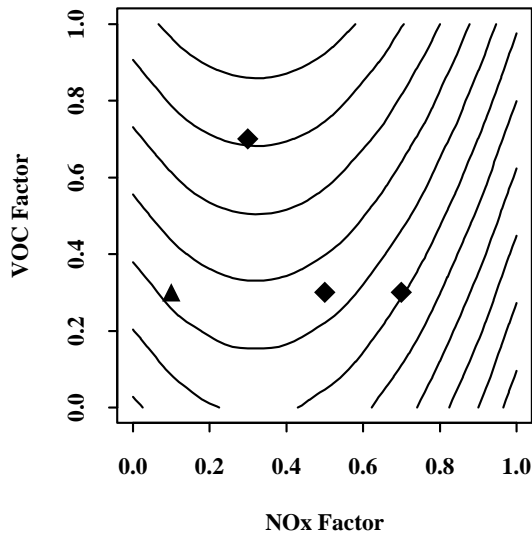
Although there exists a wide variety of statistical methods to fit optimally the overall response surface, for this analysis it was considered important that the model should be applicable to any areas of non-linear behaviour (see Figure 2b) likely to be encountered as a result of realistic emission control policies. The primary emphasis, then, was placed on a close representation of the EMEP model's behaviour (i) around the current emission levels and (ii) at the lowest emission levels considered to be technically achievable. This second point was taken to be 70% reductions of both  $NO_x$  and VOC emissions. The basic idea in developing the summary was to approximate as well as possible the derivatives of ozone concentrations with respect to changes in precursor emissions for these two (extreme) points.

With this goal in mind, the regression model has been built upon two "base" cases with uniform emission reductions across all European countries and, for each of the 21 emitter countries considered in this analysis, six scenarios in which emissions from single countries only have been reduced. In total, this design resulted in  $2 + (6 \times 21) = 128$  scenario cases.

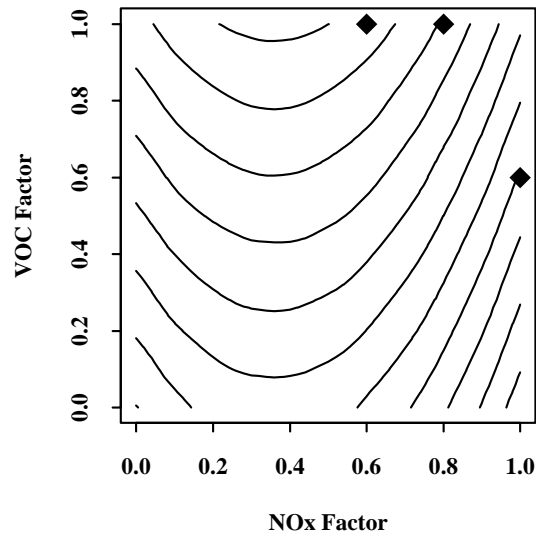
(a) Uniform emission reduction scenarios - 'base cases'



(b) Individual country reductions around lower base case



(c) Individual country reductions around upper base case



**Figure 4** Ozone isopleth diagrams illustrating the emission reduction scenarios used in fitting and testing the seasonal model

The emission reduction scenarios used to fit the model are shown on the ozone isopleth diagrams given in Figure 4. The two “base” cases are shown in Figure 4(a) as filled squares (■), superimposed on an isopleth diagram that has been calculated for uniform emission changes in all emitter countries. At these points the model is intended to fit as well as possible. Figure 4(a) is also used to indicate the percentage reductions used for five 'validation' scenarios discussed later in Section 3.6.1.

Three scenarios per country were calculated around the upper base case, two involving  $\text{NO}_x$  emissions changes and one involving VOC. These scenarios are shown as filled diamond symbols (◆) in Figure 4(c). The isopleth diagram in this figure shows the effect on ozone of emission reductions from just one emitter country (the most influential for this receptor grid), while emissions from all other sources are maintained at their base case level. The filled diamond symbols in Figure 4(b) indicate the corresponding three scenarios calculated for every emitter country around the lower base case. The background isopleth diagram for Figure 4(b) shows the effect of emission reductions from the same country for the same grid as Figure 4(c), but now with both  $\text{NO}_x$  and VOC emissions from all other countries reduced by 70%. The receptor grid used for the isopleth plots in these examples is rather extreme in showing a ridge in the isopleths at such low  $\text{NO}_x$  factors (i.e. large  $\text{NO}_x$  reductions). This illustrates why it was considered necessary, in subsequent development of the regression model for ozone, to calculate a further scenario involving 90% reductions of  $\text{NO}_x$  from a small number of emitters in NW Europe, in order that the regression model could “see” over the ridge. This additional scenario is shown on Figure 4(c) by means of a filled triangle symbol (▲).

The sampling strategy outlined above was adopted in order to construct a regression model for the main purpose of evaluating the proposed model formulation. Further discussion of the issues involved in the experimental design can be found in Section 4.5.2.

As noted previously, the regression model attempts to explain the mean over six months of the early afternoon concentrations of ozone, reflecting the situation in the well-mixed boundary layer. For practical reasons, however, the regression model is based on the six-month mean of ozone concentrations associated with 1200 GMT arrival trajectories as calculated by the EMEP model.

To test the performance of the simplified ozone model, analysis has been restricted to 25 receptor sites across Europe. Some of these sites are located along a hypothetical north-south cross-section of Europe, covering a wide range of  $\text{NO}_x$  / VOC ratios. Additional sites have been selected to explore the model behaviour for other places in central, eastern and southern parts of Europe.

### 3.6 Model Evaluation

This section compares results from the simplified 'seasonal' model with runs of the full EMEP model. To provide a solid basis for judgement of the performance of the seasonal model, three types of comparison were carried out:

1. Uniform reductions of NO<sub>x</sub> and VOC emissions across Europe;
2. Ranges of reductions of NO<sub>x</sub> and VOC emissions separately in individual countries;
3. Multi-national, non-uniform emission reduction scenarios.

#### 3.6.1 Uniform Emission Reductions

Comparisons between the models for cases involving uniform emission reductions were undertaken in two ways: (i) using five 'validation scenarios' of different combinations of NO<sub>x</sub> and VOC emission reductions; and (ii) by comparing the ozone isopleth diagrams produced by the two models.

##### *Comparison for five validation emission reduction scenarios*

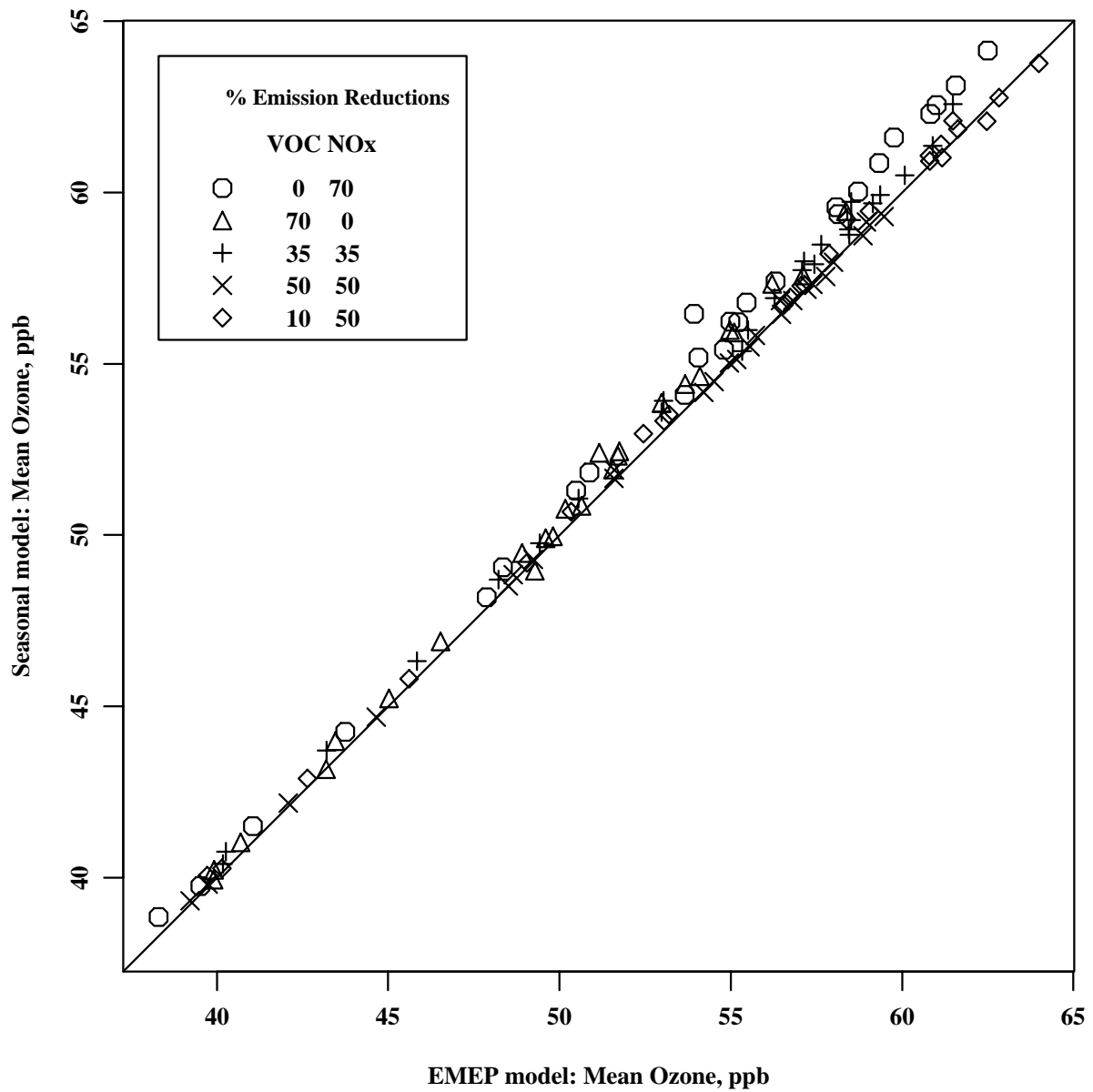
It has been mentioned above that 128 scenario runs provided the basis for fitting the EMEP model. In addition, five 'validation scenarios' have been calculated, with uniform reductions in all emitter countries, to provide an independent basis for testing the model's performance. Figure 4(a) shows the positions of the five emission reduction scenarios (indicated by the +, × and open symbols) used. Test runs were performed for all the 25 receptor grids for which the seasonal model has been constructed.

The seasonal model's predictions of the mean ozone concentration in each of the five validation scenarios have been plotted against the corresponding EMEP model results in Figure 5. The agreement between the two models is generally very good, although in some instances, i.e. at some of the receptor sites, the seasonal model overestimates the ozone concentration for the scenario in which NO<sub>x</sub> emissions are reduced by 70% while VOC emissions remain unchanged from the base case.

##### *Comparison of ozone isopleth diagrams*

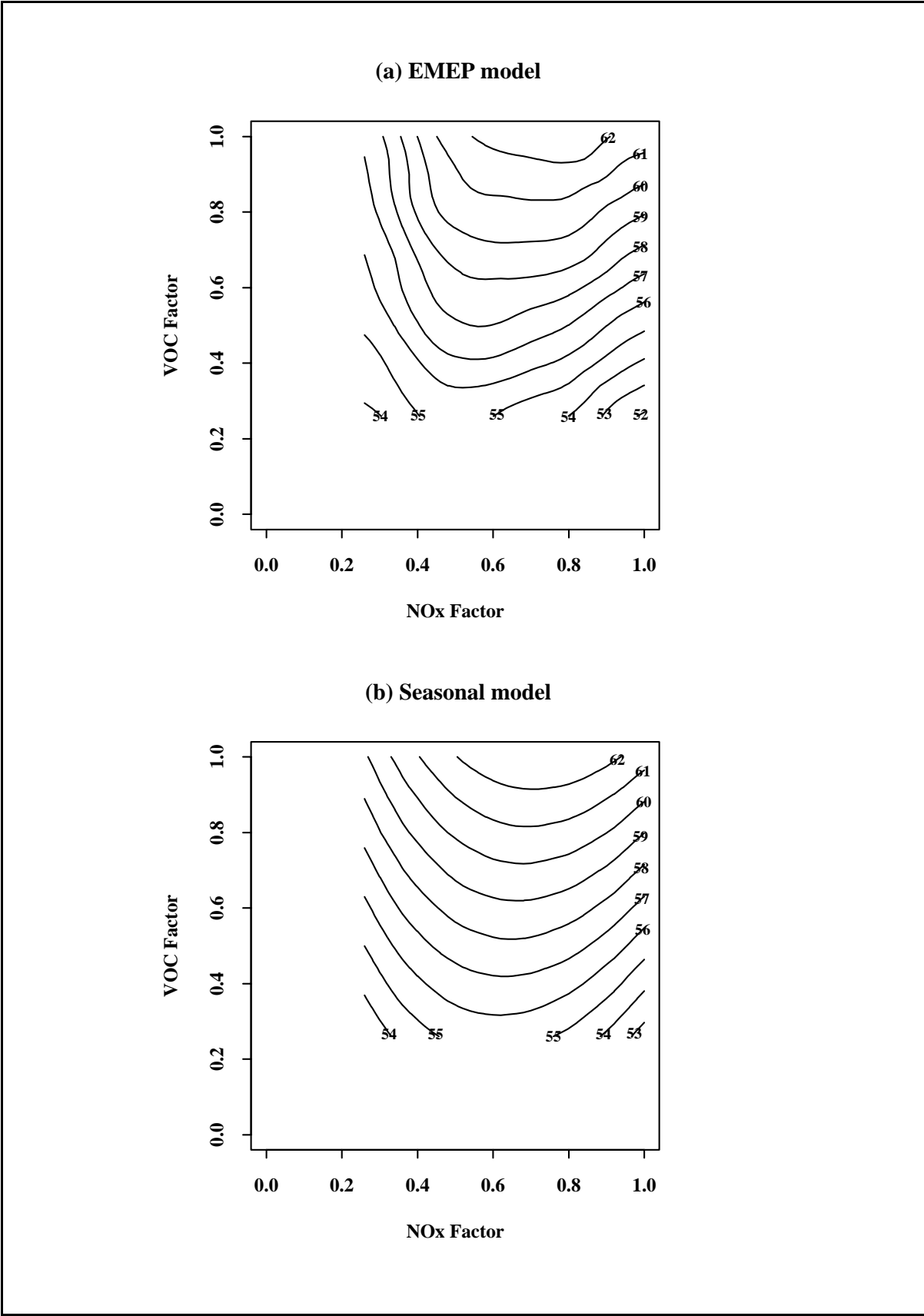
Many of the comparisons presented in this paper apply to the Schauinsland receptor site, a place in the Black Forest in the south-west of Germany. Although most of the comparisons have also been carried out for all the other 24 test sites, the presentation in this paper focusses on this site because of its clear non-linearity in ozone concentrations with regard to NO<sub>x</sub> emissions. To capture the non-linearities at such a point accurately is a tough benchmark for any simplified ozone model.

Figure 6 compares the ozone isopleth diagrams for Schauinsland, constructed from EMEP model calculations, with the corresponding diagram produced from predictions of the seasonal model. The overall shape of the isopleths is reproduced rather well by the seasonal model, although any irregularities in the isopleths are inevitably smoothed out.



**Figure 5** Comparison between IIASA's seasonal model and the EMEP model at 25 sites for five emission reduction scenarios

Ozone isopleths at other European sites show different shapes, as demonstrated in Figure 2. Validation runs with the seasonal model reveal, however, that the simplified model is capable of capturing both the shape and the absolute magnitude of the response of ozone concentrations with a quality comparable to the Schauinsland case, at least for the sites examined up to now.



**Figure 6** Comparison of ozone isopleth diagrams (showing ozone concentration in ppb) for Schauinsland for 1989 produced by the EMEP model and IIASA's seasonal model

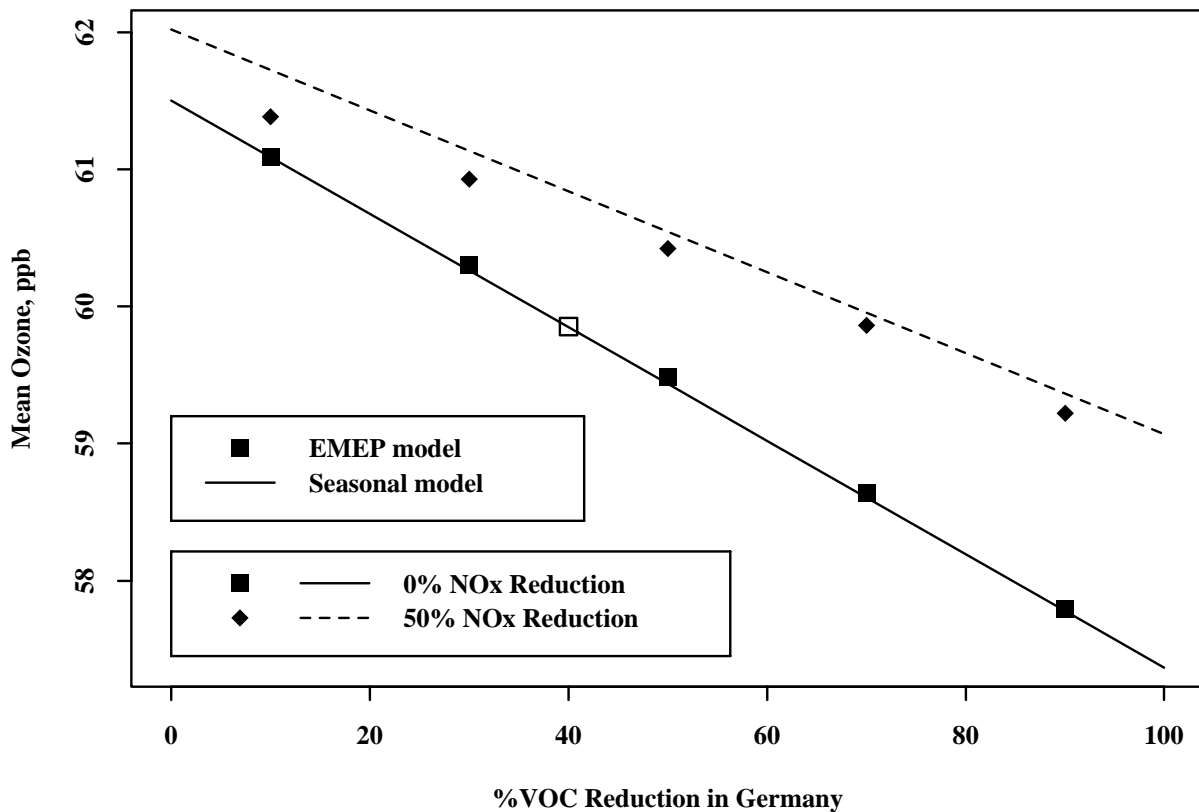
### 3.6.2 Individual Country Emission Reductions

Owing to the computational volume involved with scenario calculations, validation scenarios exploring the impacts of emission reductions in single countries have so far been limited to the Schauinsland receptor site.

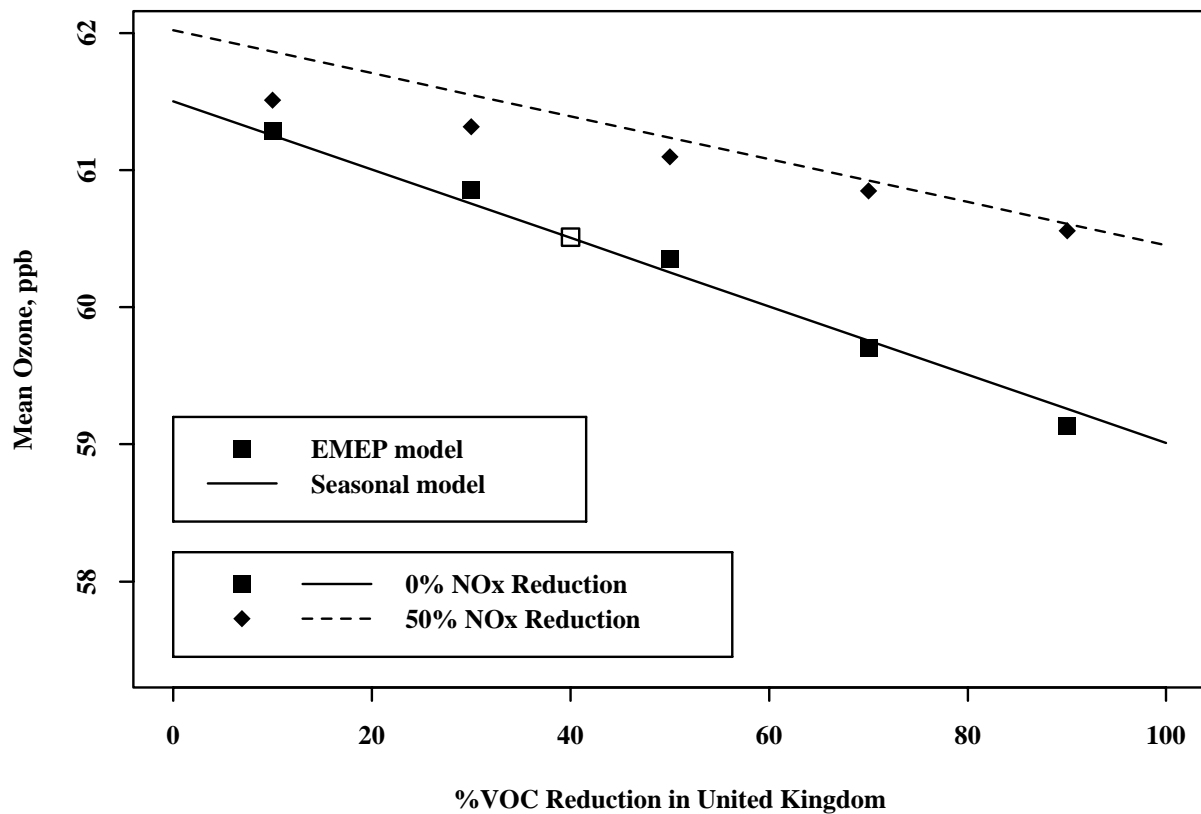
#### *Reduction of VOC emissions*

As already demonstrated by Simpson (1992b), changes in ozone are rather proportional to changes in VOC emissions. This behaviour was reproduced very well by the seasonal model, which showed excellent agreement with the EMEP model for Schauinsland for the eleven scenarios (i.e. eleven different emitter countries) investigated in which VOC emissions from a single country were reduced while all  $\text{NO}_x$  emissions and all VOC emissions from other countries remained at their base case levels. Figures 7 and 8 compare the seasonal model's predictions of mean ozone at Schauinsland as a function of VOC reductions in Germany and the UK, respectively, with the corresponding EMEP model results. In these, and subsequent, figures the empty squares (white) indicate scenarios used for constructing the seasonal model, whereas the filled symbols depict the verification cases.

When these eleven scenarios were repeated with  $\text{NO}_x$  emissions from all emitter countries reduced by 50%, however, a slight discrepancy between the models is apparent, with



**Figure 7** Mean ozone at Schauinsland for 1989 as a function of VOC reductions in Germany; uniform  $\text{NO}_x$  reductions everywhere



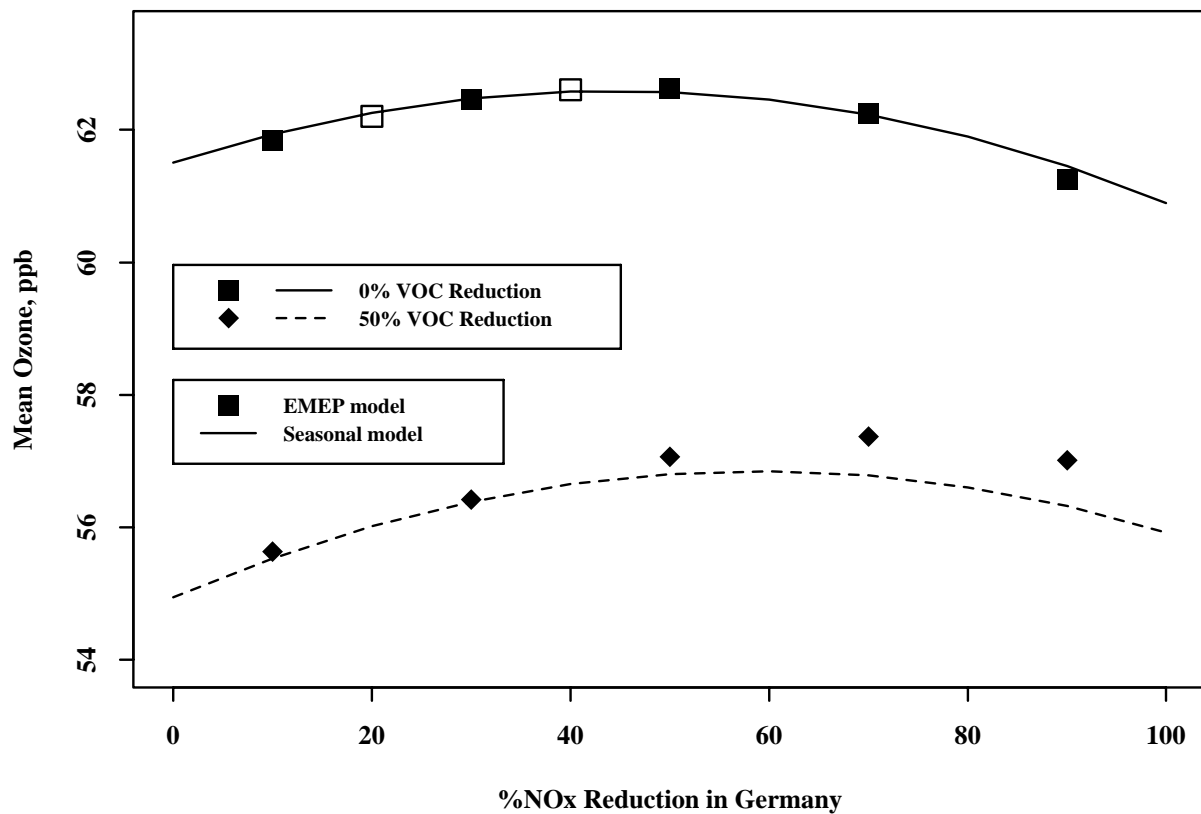
**Figure 8** Mean ozone at Schauinsland for 1989 as a function of VOC reductions in the UK; uniform NO<sub>x</sub> reductions everywhere

the seasonal model producing an overprediction of ozone concentration. The results suggest that this discrepancy is greatest for the case where all countries make 0% VOC and 50% NO<sub>x</sub> reductions; agreement between the models improves as greater VOC emission reductions are made in (each of) the single emitter countries. The comparisons between the seasonal and EMEP models for the 50% NO<sub>x</sub> reduction case are also shown in Figures 7 and 8 as a function of VOC reductions in Germany and the UK, respectively.

#### *Reduction of NO<sub>x</sub> emissions*

A more difficult situation occurs for the response of ozone concentrations to changes in NO<sub>x</sub> emissions. Figure 9 compares the reaction to changes in Germany's NO<sub>x</sub> emissions for the Schauinsland receptor site. Again, the empty squares (white) indicate the scenarios used for constructing the seasonal model, whereas the filled symbols depict the verification cases. The agreement between the two models is satisfactory, both for base case VOC emissions and when VOC emissions from all emitter countries are reduced by 50%, with minor deviations for high NO<sub>x</sub> reduction cases.





**Figure 9** Mean ozone at Schauinsland for 1989 as a function of NO<sub>x</sub> reductions in Germany; uniform VOC reductions everywhere

### 3.6.3 *Multi-national Emission Reductions*

Predicting the response to non-uniform, multi-national emission reductions may be considered as one of the most difficult tasks for a simplified ozone model. To test the performance of the seasonal model, three sets of emission reduction scenarios (each involving a range of reductions in UK NO<sub>x</sub> emissions in combination with emission reductions in up to four other emitter countries) have been examined:

- (a) reductions of NO<sub>x</sub> emissions by 40%;
- (b) simultaneous reductions of NO<sub>x</sub> emissions by 70% and VOC emissions by 50%;
- (c) reductions of NO<sub>x</sub> emissions by 70%.

The UK was selected as the primary emitter country in these tests because EMEP model calculations indicate strong non-linearities in the ozone response to changes in UK NO<sub>x</sub> emissions, both in the UK itself and in other countries. For each of the three cases above, the following tests have been carried out:

- (1)  $x$  % reductions of the emissions in the UK;
- (2)  $x$  % reductions of the emissions in the UK and Germany;
- (3)  $x$  % reductions of the emissions in the UK, Germany and France;
- (4)  $x$  % reductions of the emissions in the UK, Germany, France and the Netherlands.

Examples of the results of these comparisons are presented in two ways:

- (i) showing sequences of changes in ozone as emissions are reduced in additional countries;
- (ii) showing changes in ozone as a function of UK NO<sub>x</sub> emission reductions.

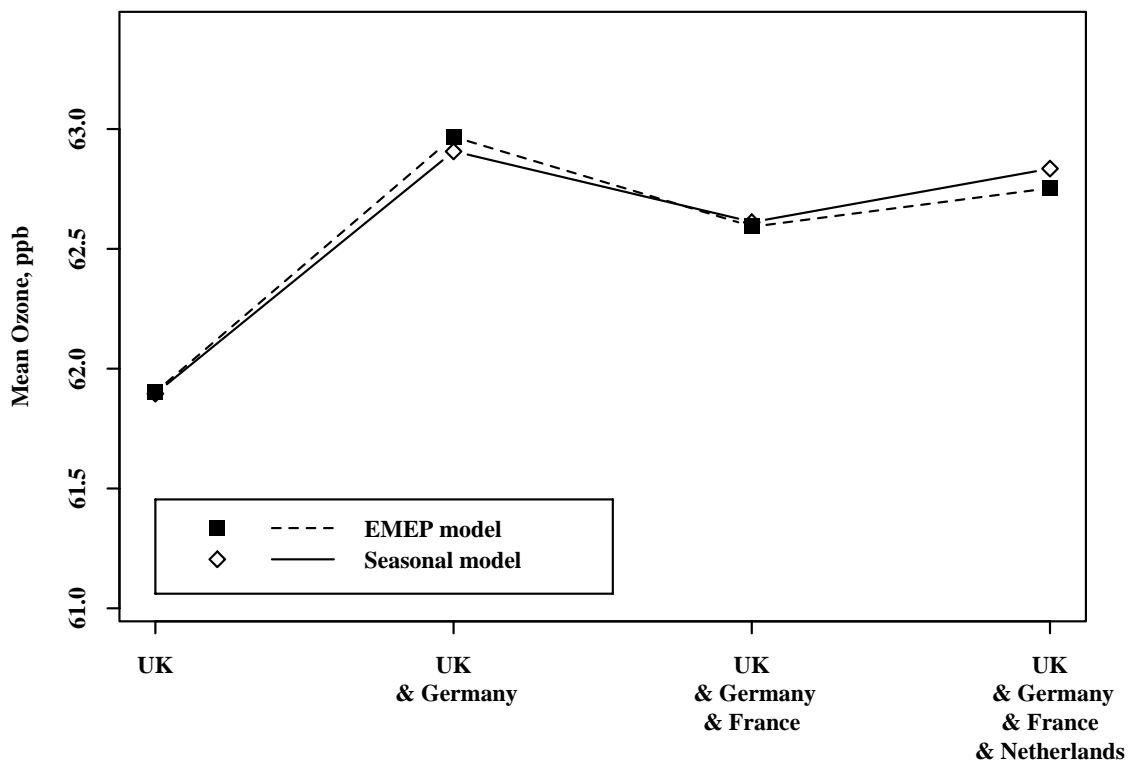
These comparisons have been carried out for all of the 25 receptor sites. For reasons of brevity, however, this paper can show only a small selection of the results.

#### *Reductions of NO<sub>x</sub> emissions by 40%*

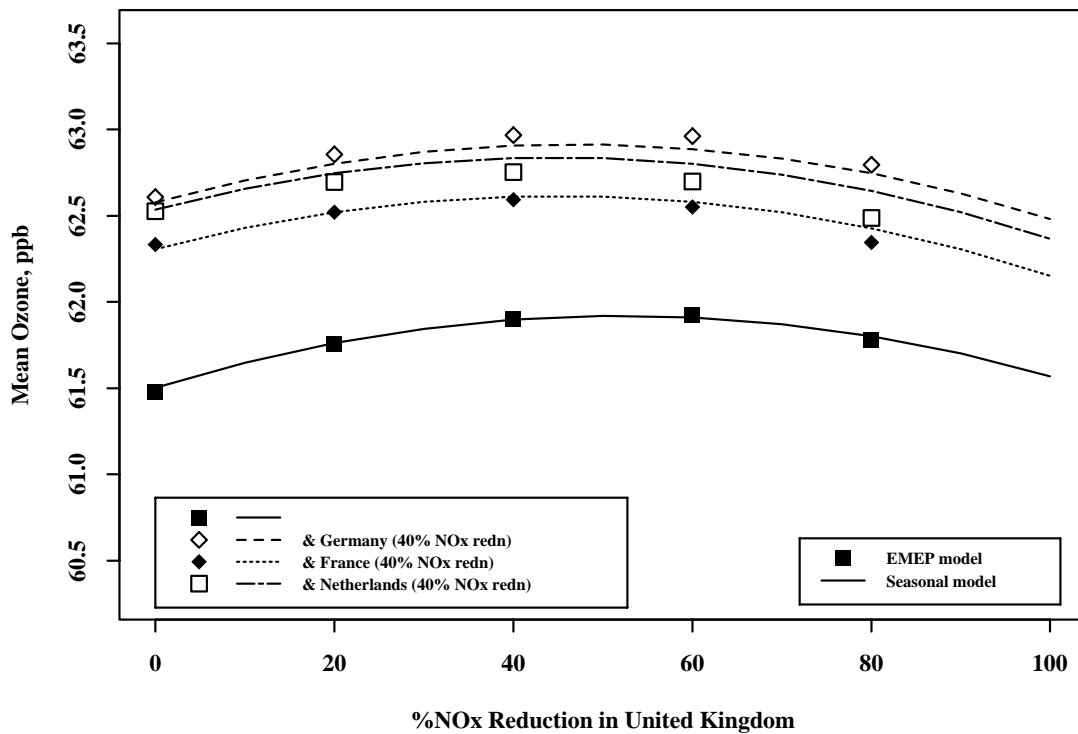
In this set of tests the changes in mean ozone brought about by NO<sub>x</sub> emission reductions in the UK were examined; additional 40% NO<sub>x</sub> reductions were included in the scenario in a stepwise fashion, firstly from Germany, then France and then also from the Netherlands. The VOC emissions were maintained at their 1989 base case levels. For NO<sub>x</sub> emission reductions of 40% from the above sequence of emitter countries, the seasonal model captures both the direction of the changes in ozone and the absolute magnitudes remarkably well (with a maximum difference of less than 0.7 percent) at all 25 receptor sites. As an example, Figure 10 displays the changes in mean ozone at the Schauinsland receptor site for sequential reductions of the NO<sub>x</sub> emissions (by 40%) in the UK, Germany, France and the Netherlands.

When the impacts of variations in the UK NO<sub>x</sub> emissions are examined, it is evident that the good agreement between the models exists across a large proportion of the range of NO<sub>x</sub> reductions in the UK. Figure 11 illustrates this for the Schauinsland receptor site. For reductions in UK NO<sub>x</sub> up to 60%, the greatest difference at any receptor, apart from one site in the UK itself, amounts to 0.7%. Larger discrepancies occur for cases with 80% NO<sub>x</sub> reductions but this is not unexpected in view of the scenarios employed to construct the model in this initial analysis. The largest NO<sub>x</sub> reductions used in these tests lie outside the range over which the seasonal model can be expected to give reliable results. A similar reason lies behind the larger discrepancies seen at one of the UK receptor sites; the NO<sub>x</sub> reductions used in fitting the model did not extend far enough to capture the change in sign of the ozone response to NO<sub>x</sub> emission changes at this particular receptor.

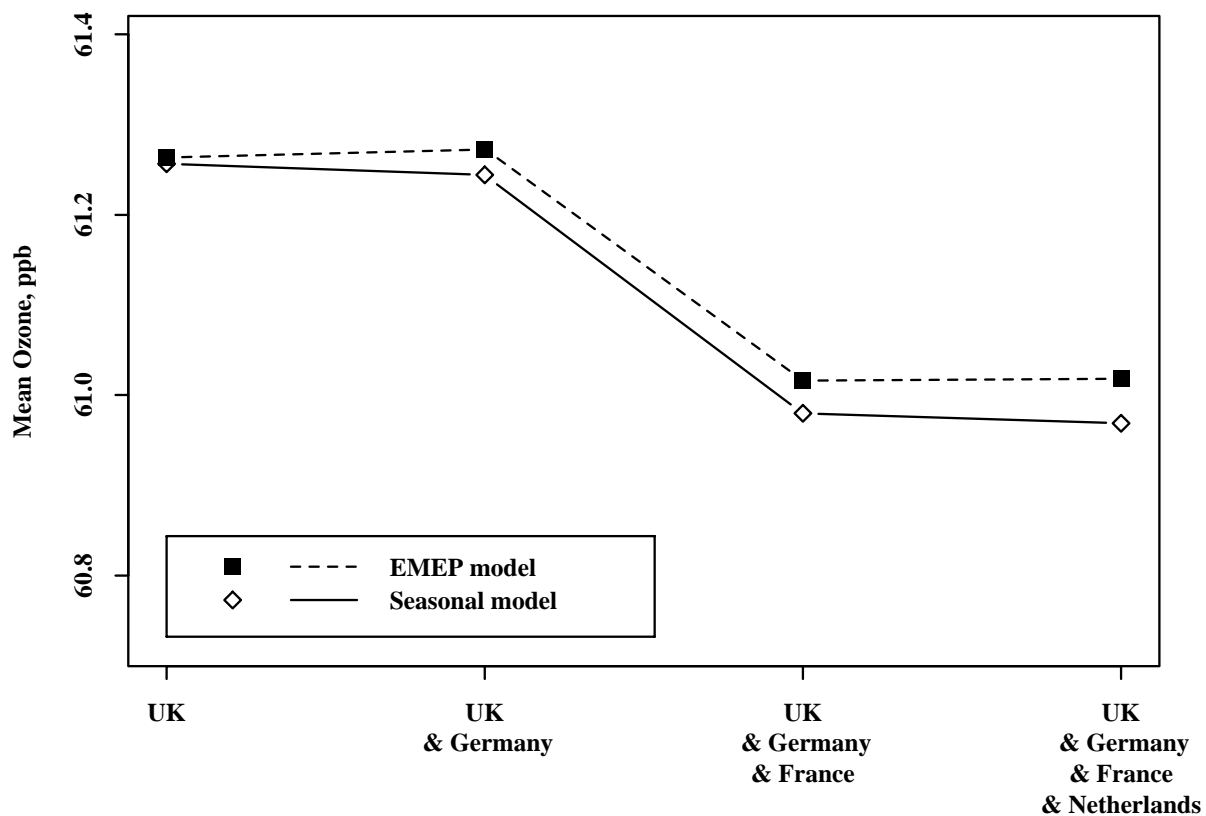
The shape of the response curve was found to be strongly dependent on the site under inspection. At Schauinsland, for example, 40% reductions of NO<sub>x</sub> emissions in Germany, UK and the Netherlands lead to an increase of ozone according to the EMEP model, whereas reductions in France cause ozone concentrations to decrease. At other locations, such as a receptor grid in Italy, NO<sub>x</sub> reductions in the above-mentioned countries always result in a decrease in ozone. The results for the Italian receptor grid, for sequential reductions in NO<sub>x</sub> emissions from the four emitter countries, are shown in Figure 12. Again, in this respect, the seasonal model reproduces the behaviour of the EMEP model very well.



**Figure 10** Mean ozone at Schauinsland for 1989 for a sequence of emission reductions of 40%  $\text{NO}_x$  in the UK, Germany, France and the Netherlands



**Figure 11** Mean ozone at Schauinsland for 1989 as a function of  $\text{NO}_x$  reductions in the UK, with additional  $\text{NO}_x$  reductions in Germany, France and the Netherlands (0% VOC reduction)



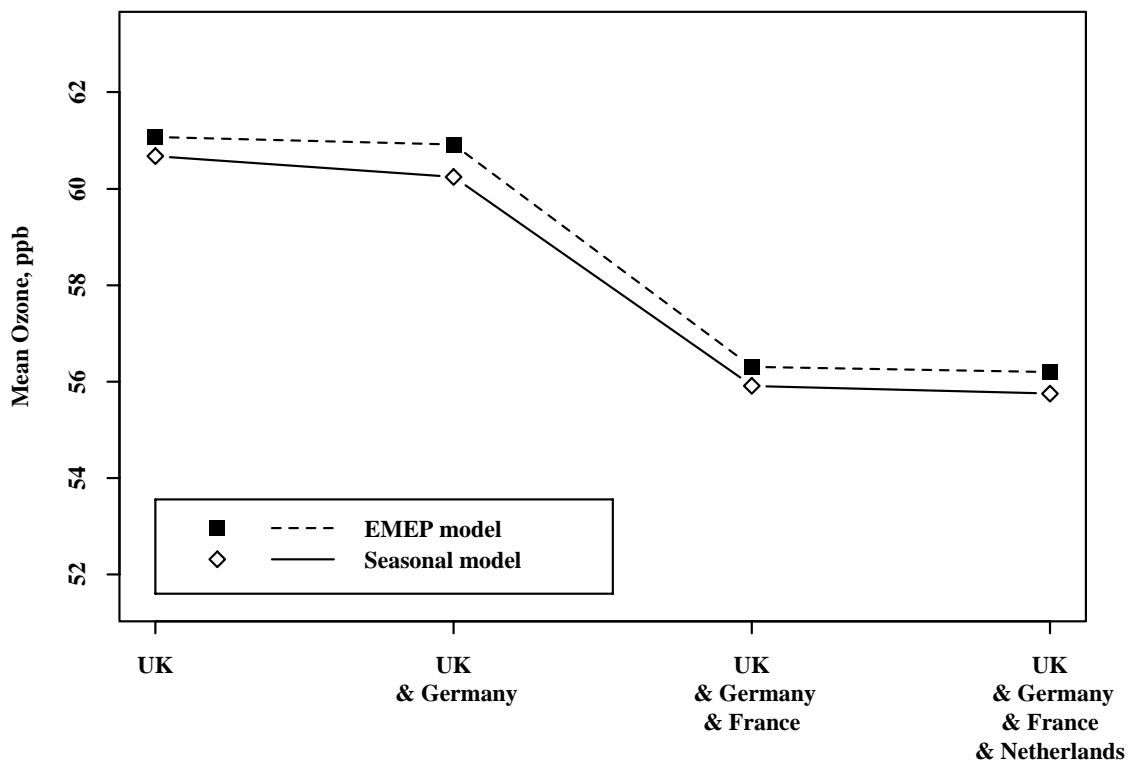
**Figure 12** Mean ozone at a receptor grid in central Italy for 1989 for a sequence of emission reductions of 40% NO<sub>x</sub> in the UK, Germany, France and the Netherlands

*Simultaneous reductions of NO<sub>x</sub> emissions by 70% and VOC emissions by 50%*

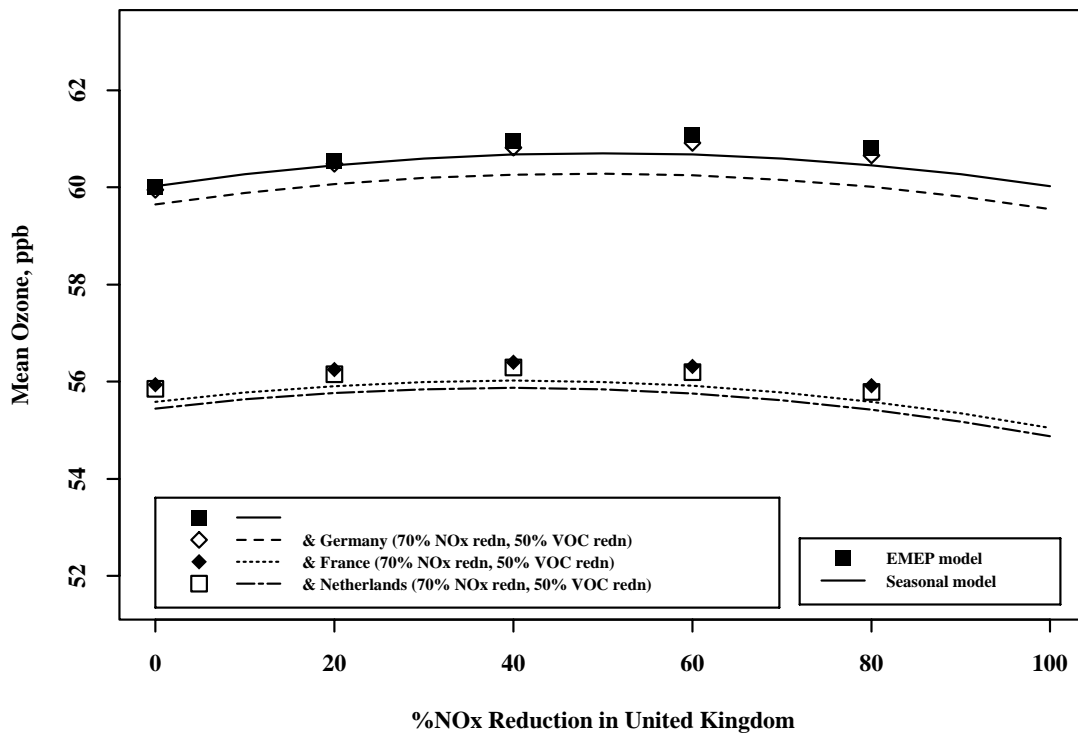
A second set of comparisons focusses on simultaneous reductions of NO<sub>x</sub> and VOC emissions.

Figure 13 displays the changes in ozone at a receptor grid in western France, following sequential emission reductions in the UK, Germany, France and the Netherlands. Reductions in NO<sub>x</sub> and VOC emissions by 70% (or 60% in the case of the UK) and 50%, respectively, cause decreases in ozone at this location. The seasonal model manages to capture the direction and the absolute magnitudes of the changes, but shows a small but consistent bias for all of the four examined cases. This bias occurs consistently over the entire range of NO<sub>x</sub> reductions carried out in the UK (Figure 14).

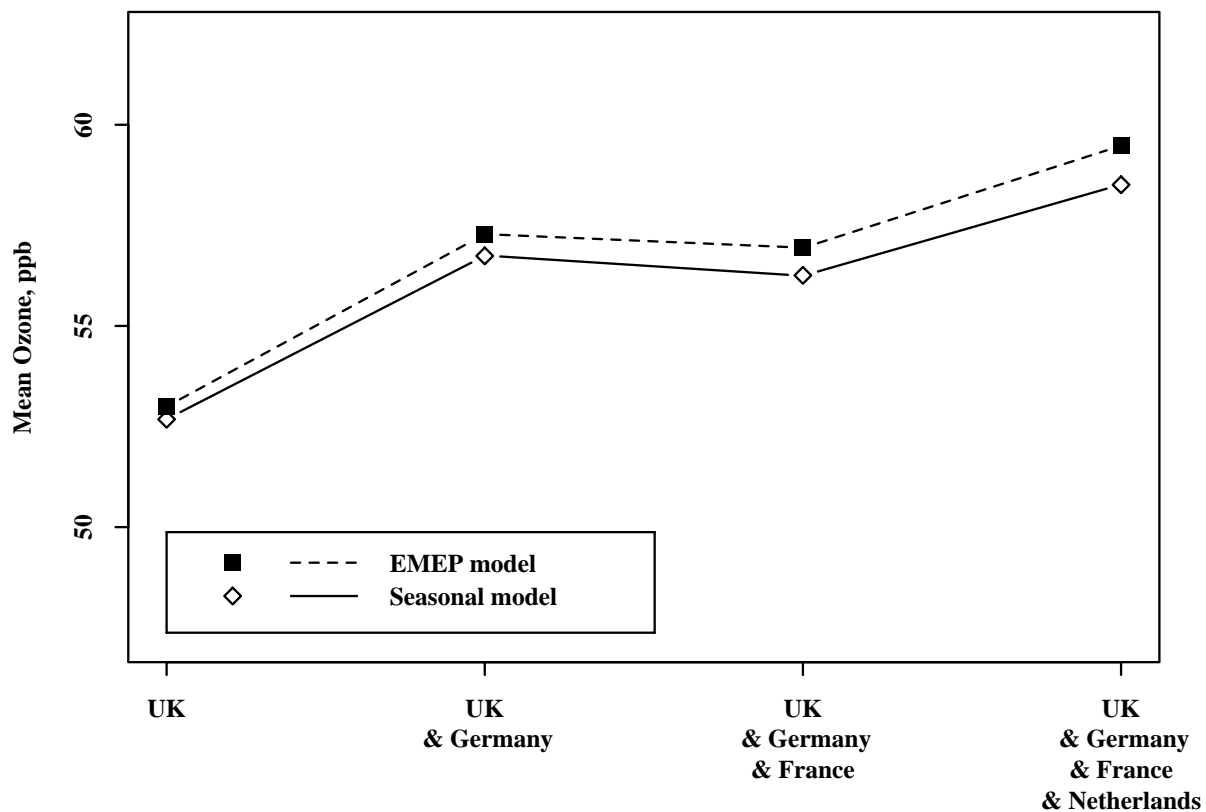
Whereas simultaneous reductions of NO<sub>x</sub> and VOC emissions are found to have a decreasing effect on ozone in western France (and many other sites), the opposite direction can be observed for receptor grids in the Netherlands (Figure 15), for example. From the standpoint of model comparison, however, the fit between the seasonal model and the EMEP model is again good for these receptors.



**Figure 13** Mean ozone in W. France for 1989 for a sequence of emission reductions of 70% NO<sub>x</sub> and 50% VOC in the UK, Germany, France and the Netherlands



**Figure 14** Mean ozone in W. France for 1989 as a function of NO<sub>x</sub> reductions in the UK, with 50% VOC reduction and additional reductions in Germany, France and the Netherlands

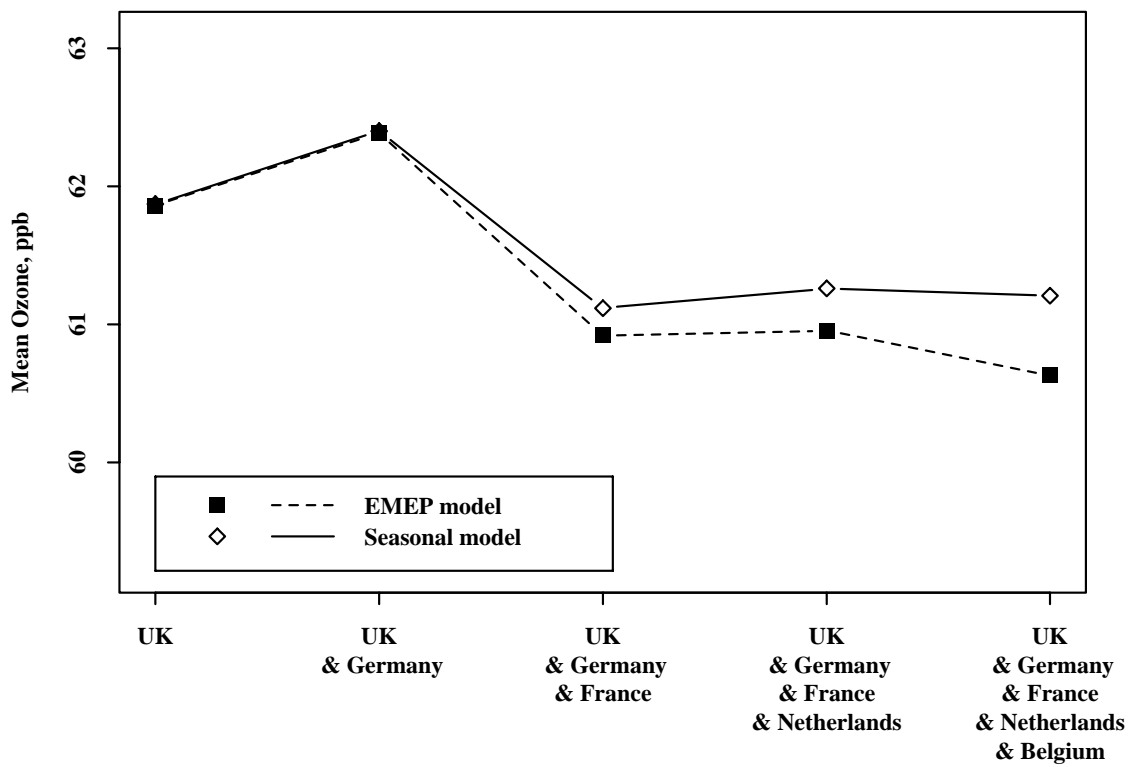


**Figure 15** Mean ozone at a receptor in the Netherlands for 1989 for a sequence of emission reductions of 70% NO<sub>x</sub> and 50% VOC in the UK, Germany, France and the Netherlands

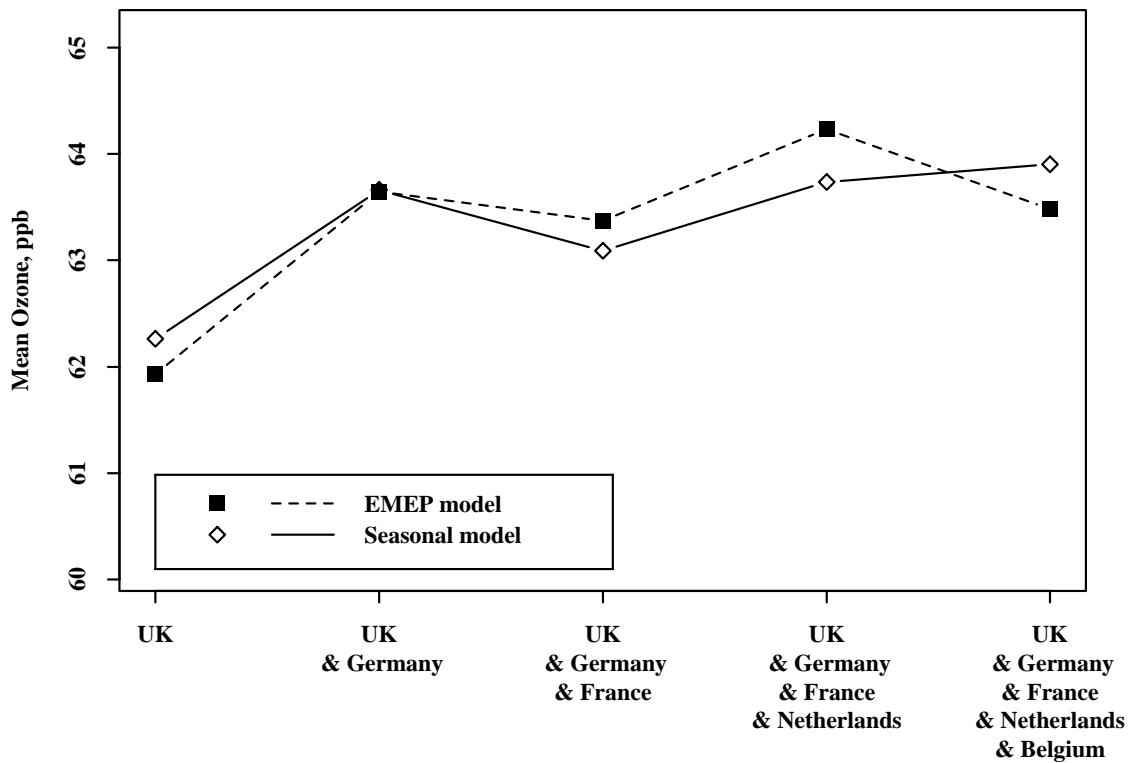
The median percentage absolute difference between the seasonal model and EMEP model for this set of tests across all 25 receptors is about 0.6%. The greatest discrepancy, again excluding one receptor grid in the UK, was found to be 1.03 ppb, or 1.7% of the EMEP model result. This difference occurred at a site in Belgium within the 'high NO<sub>x</sub>' region of Europe, for the scenario in which UK NO<sub>x</sub> emissions are reduced by 60% and additional emission reductions also take place in Germany, France and the Netherlands.

*Reductions of NO<sub>x</sub> emissions by 70%*

Finally, comparisons have been carried out for the extreme case of a 70% NO<sub>x</sub> / 0% VOC reduction. It must be mentioned that this should be considered as a hypothetical case, since it is technically impossible to achieve such NO<sub>x</sub> abatement levels in Europe without simultaneous reductions in VOC emissions. In all European countries such drastic reductions of NO<sub>x</sub> emissions can only be achieved by applying three-way catalysts to passenger cars. Such catalysts, however, reduce both NO<sub>x</sub> and VOC emissions together, roughly at the same rate. This test should, therefore, be considered only as a formal check of the performance of the seasonal model in a range of low NO<sub>x</sub> emissions, without a realistic chance that any policy scenario could ever get into this area.



**Figure 16** Mean ozone at Schauinsland for 1989 for a sequence of emission reductions of 70% NO<sub>x</sub> in the UK, Germany, France, the Netherlands and Belgium



**Figure 17** Mean ozone in Belgium for 1989 for a sequence of emission reductions of 70% NO<sub>x</sub> in the UK, Germany, France, the Netherlands and Belgium

For Schauinsland, a reasonable fit of the seasonal model for a wide range of country reductions was obtained (Figure 16), with a lower performance for cases with extremely low NO<sub>x</sub> emissions. For one site in Belgium in a 'high NO<sub>x</sub>' region, the seasonal model produced a difference in the direction of the change in ozone concentration when the 70% NO<sub>x</sub> reduction in Belgium itself was included in the scenario (Figure 17). However, this was the only observation of a difference of this sort between the models throughout the series of comparison tests.

## **4. DISCUSSION AND FURTHER WORK**

Despite the encouraging comparison between the simplified ozone model and the EMEP model in the evaluation tests carried out so far, a number of important areas of the model development require further work. Several of these have been highlighted in earlier sections of this paper. Discussion of these issues is amplified below.

### **4.1 Calculation of the AOT40 Ozone Exposure Index**

The currently proposed ozone exposure index, AOT40, was briefly outlined in Section 2.1, while Section 3.4 described the approach taken in this work towards developing a simplified model in order to estimate ozone exposures resulting from changes in emissions of ozone precursors. This involves the description of source-receptor relationships for mean boundary-layer ozone concentrations (Section 3.5), followed by the derivation of local ozone exposure (AOT40) from the mean boundary-layer concentrations. Two aspects of this approach merit further discussion: (i) the reasons for modelling mean ozone concentrations in the boundary layer rather than AOT40 directly, and (ii) the incorporation of local factors into the determination of AOT40 values.

#### **4.1.1 *Response Variable: Mean Ozone or AOT40***

As explained in Section 3.4, the development of the simplified ozone model has followed a tiered approach in which the first step is to estimate boundary layer average ozone concentrations - and these represent average conditions over an area of the order of 150 km x 150 km - and then, in a subsequent step, these mean concentrations are related to a ground-level ozone exposure index (AOT40) relevant to a much smaller area, taking local factors into account as necessary. The question arises: why not model AOT40 directly?

A number of reasons lay behind the indirect approach taken in estimating AOT40 values. The first, and most important, is that the AOT40 function is, by its nature, discontinuous since it involves a threshold value of 40 ppb. This would lead to an additional, undesirable non-linearity problem, particularly in areas of Europe where the mean ozone concentration over the summer is around 40 ppb.

A second reason for avoiding the use of AOT40 as the response variable in the regression equation arose from the necessity of estimating separate AOT40 values for trees



and crops, based on different exposure periods. Furthermore, the definition of the AOT40 exposure index has been actively debated and revised in recent times, as more experimental data on ozone impacts became available. Any future revisions might pose problems for a regression model designed for estimating an earlier version of the AOT40 measure. Finally, the question of the validity of AOT40 values calculated from the EMEP model results - for O<sub>3</sub> concentrations at just two points in time during daylight hours - also counted against estimating the AOT40 directly.

The difficulties posed by the fact that the AOT40 is a step function may not be insurmountable, however. Over the last few years several different indices of ozone exposure have been proposed and evaluated within the research community, including some that did not make use of an artificial threshold concentration as a cut-off point. Instead, a cumulative integrated exposure index can be developed by weighting individual hourly mean concentrations of O<sub>3</sub> and summing over time. A sigmoidal weighting function has been proposed (Lefohn & Runeckles, 1987) for this purpose. The proposed sigmoid function is of the form:

$$w_i = \frac{1}{[1 + M \cdot \exp(-A \cdot c_i)]} \quad [10]$$

where  $M$  and  $A$  are positive arbitrary constants,  
 $w_i$  is the weighting factor for concentration  $i$   
and  $c_i$  is concentration  $i$ .

The use of a sigmoidally-weighted index with constants  $M$  and  $A$  set equal to 4403 and 126 ppm<sup>-1</sup>, respectively, has been reported (Lefohn *et al.*, 1988). This was referred to as W126. Such an index includes hourly average concentrations as low as 40 ppb, has an inflection point near 65 ppb, and gives an equal weighting of 1 to hourly average concentrations of 100 ppb and above.

Using an ozone exposure index based on such a sigmoidal weighting function would circumvent the problem of discontinuity inherent in the AOT40 index. This approach may be worth exploring for the further development of the simplified seasonal ozone model in the future.

#### 4.1.2 *Local Variation of AOT40*

The approach taken in this work requires the estimation of AOT40 ozone exposure index values from the boundary layer average ozone concentrations predicted by the proposed regression model. In order to achieve this, information is required about the diurnal variation in ozone concentrations experienced at ground level. The boundary layer average value provides a good estimate of ground-level ozone concentrations during the afternoon period in summer, when the boundary layer is expected to be well-mixed.

Because the EMEP model is designed to cover the whole of Europe it uses a relatively large grid size of 150 km, and the ozone concentrations calculated by the proposed regression

model will be appropriate to this scale. However, an integrated assessment model for ozone needs to consider the effects of ozone exposure on ecosystems that may be much smaller than this. For the reasons outlined in Section 3.2, the ozone diurnal variation pattern at a particular location depends on factors such as the local topography, distance from the sea, and magnitude of local NO<sub>x</sub> emissions (due to urban areas, for example). These local factors need to be taken into account in estimating AOT40 values. The approach taken here is based on an examination of ozone measurement data across Europe, in relation to diurnal variation patterns and local factors such as those mentioned above (Kettunen *et al.*, 1994).

A number of studies related to this question have been reported, although generally for a smaller spatial scale. For example, Fowler *et al.* (1994) have presented maps of the spatial distribution of ozone exposure in the UK, allowing for the effects of altitude. Their investigation of UK summertime ozone measurements, omitting data from coastal and urban sites but using rural sites only, focussed on the ratio between the total number of hours with ozone above a threshold concentration and the number of hours during the 1200-1800 period with ozone above the same threshold. A simple linear function was fitted to the relationship between this ratio and the site altitude, in order to interpolate ozone exposure between measurement sites taking account of altitude effects.

Altitude was also investigated in a study of the effects of complex terrain on ozone distributions in Austria (Loibl *et al.*, 1994) but, in this case, the variable used was relative altitude (above the valley floor). An empirical function was derived using summertime ozone measurements assuming that ozone concentrations were dependent on relative altitude and time of day. In this study a logarithmic function was chosen to model the dependence of ozone concentration with relative altitude.

North American studies of the frequency of occurrence of a number of characteristic ozone diurnal variation patterns have been reported (Böhm *et al.*, 1991). Cluster analysis has been used to group sites with similar ozone regimes (Böhm *et al.*, 1995).

For the integrated assessment application, further work is necessary to investigate how best to incorporate local factors into the estimation of AOT40 values. The approaches taken in the studies outlined above have provided useful starting points but need to be extended to be applicable across Europe. The goal is to derive relevant criteria that can be mapped on a sufficiently small scale across Europe. Related work in this area is also being carried out at RIVM in The Netherlands (de Leeuw, 1995); small-scale mapping of ozone exposure in Europe shows that the calculated ozone fields are very heterogeneous in heavily populated areas and in complex terrain.

## **4.2 Influence of the Free Troposphere**

The regression model given in equation [9] relates boundary layer mean ozone to the annual NO<sub>x</sub> and VOC emissions from a number of emitter countries. The only explanatory variables used in this model are the NO<sub>x</sub> and VOC emissions themselves and the related "effective" emissions. Other factors such as the free tropospheric background concentrations of ozone and precursor species are not included explicitly in the regression but their influence is incorporated into the constant term,  $k_j$ . Thus, the regression model is strictly valid only for

the free tropospheric conditions used in generating the data set for fitting the model. If the free troposphere plays a significant role in determining boundary layer ozone concentrations in Europe, then this influence should be incorporated explicitly into the regression model. Work on this topic has been started in order to investigate the temporal trends in free tropospheric concentrations (of ozone and precursors), assess the impacts of possible future changes in the free troposphere, and consider, if necessary, how best to include such factors in the simplified ozone model.

An initial feasibility study carried out recently suggests that the boundary layer ozone response can be up to 50 percent of the free tropospheric ozone perturbation (Wojcik, 1995). The response depends strongly on latitude, season and distance to the coast. Further work will be necessary to quantify this influence and to establish relationships to emissions of precursor substances, including the contribution from aircraft, not only in Europe but potentially in the entire northern hemisphere.

### **4.3 VOC Speciation**

There are a number of reasons why a given mass emission of different VOC species would be expected to contribute differently to photochemical ozone formation. Most importantly, differences in the rate coefficients for the OH + VOC reaction (reaction 7 in Section 3.2) lead to different rates of VOC oxidation and, consequently, different rates of ozone production. Chemical structure also plays a role by determining the extent to which it is possible for the product(s) of the initial OH reaction to undergo further degradation resulting in additional ozone formation. However, the higher the molecular weight of the VOC species, the lower will be the volume mixing ratio (for a given mass emission), and the lower the ozone formation potential.

Studies using models that incorporate sufficiently complete chemical mechanism schemes have been used to demonstrate the different ozone formation potentials of different VOC species during ozone episodes (Hough & Derwent, 1987; Derwent & Jenkin, 1991). A variety of ranking schemes have been proposed (e.g. Carter & Atkinson, 1989; Lowi & Carter, 1990; Derwent & Jenkin, 1991) in attempting to simplify comparisons between VOC species in this respect. Modelling studies have also shown, however, that there can be considerable variability in such ranking schemes depending on factors such as the elapsed time considered (Derwent & Jenkin, 1991), the geographical location, and the severity of ozone episode (Simpson, 1992b).

In the light of these findings, careful consideration was given to the question of whether or not to include VOC speciation as an explicit factor in the simplified model, in which the emphasis is placed on predictions of long-term ozone concentrations on a European scale.

As explained earlier, the simplified source-receptor relationships have been derived from the results of the EMEP photo-oxidant model. This model uses a simplified chemical mechanism in which each important VOC class is represented by one or two members with degradation chemistry included explicitly. In the version of the EMEP model used here, the emissions of anthropogenic non-methane VOCs are represented by six species: ethane,

n-butane, ethene, propene, o-xylene and ethanol. Comparisons of a large number of different chemical mechanism schemes have shown (Derwent, 1993) that the EMEP chemistry gives results for ozone (and PAN and H<sub>2</sub>O<sub>2</sub>) that lie well within the central range of results from all the mechanisms considered.

The evidence available from EMEP model calculations for long-term ozone suggests that the effects of changes to the VOC species profile are relatively small compared to the effects of changes in total non-methane VOC emissions. The results of sensitivity analyses (Simpson, 1992a) showed that the effect of increasing the reactivity of the VOC mixture was relatively small, with 1% - 7% increases in monthly mean (of daily maximum) ozone concentrations across a range of receptor sites.

The published sensitivity studies, which had been performed for July 1985 conditions, were supplemented by a series of further model experiments examining the influence of each 'emitted' VOC species in turn. These used a simplified 'box-model' version of the EMEP model run over a five-day period, using constant meteorological parameters and typical values for the rates of emission of NO<sub>x</sub>, man-made VOCs and natural VOCs (represented by isoprene). The emission rates remained unchanged during the simulation period (as though the air mass had remained stationary for five days over one emission area), although diurnal variations were incorporated. For each of the six representative VOC species in turn, the simulation was repeated several times with the proportion of that species in the total VOC emission varying between zero and twice the default value. In order to keep the total VOC mass emissions constant in each case, the amounts of the remaining VOC species were adjusted as necessary, maintaining the same proportionality between them.

Under the conditions of this simulation, it was clear that varying the proportions of the alkenes within the selected range had very little effect on the predicted ozone concentrations; a 100% change in the proportion of either alkene resulted in a difference of less than 1% in the ozone concentration. Changing the o-xylene proportion had a rather more noticeable influence, but the overall effect was still limited to a 3% change at most in ozone for a 100% change in o-xylene. In all cases, the extent of the ozone response depended on the elapsed time. This was most obvious for n-butane; during the first three days, an increase in the n-butane percentage caused a decrease in ozone. During the fourth day the ozone concentration appeared to be largely independent of the amount of n-butane assumed. Subsequently, an increase in the proportion of n-butane resulted in increased ozone compared to the base case. Over the whole period the ozone changes fell in the range 0% - 4% for a 100% change in n-butane. The effects of varying ethane or ethanol were very small, at least within the range selected. Of course, these results depend on the conditions assumed and they would be affected, in particular, by significantly different assumptions about the emissions of NO<sub>x</sub> and isoprene. However, they do serve to illustrate that the influence of VOC speciation changes in the EMEP model is a relatively minor one.

One further factor against the inclusion of VOC speciation effects in the simplified model is the level of uncertainty in current estimates of species profiles. Although progress in VOC emission inventory work has been considerable in recent years, estimates of aggregated VOC emissions remain more uncertain than NO<sub>x</sub> and SO<sub>2</sub> emissions inventories, for example. The level of uncertainty inherent in VOC species profiles is greater still.

Taken together, these factors - the comparatively small effects of changes in VOC species profiles and the large uncertainties in speciation estimates - suggest that the additional complexity that would result from inclusion of VOC speciation in the simplified model is not justified at the present stage of model development.

The regression model described in Section 3.5.2 uses national, total non-methane VOC emissions as an explanatory variable, making no explicit recognition of the different species profiles that may exist for VOC emissions from different source sectors and different countries. Therefore, in its present form, the regression model is unable to take account of any effects arising from potential changes in overall VOC species profiles as a result of particular emission abatement strategies.

#### **4.4 Interannual Meteorological Variation**

Measurements of ground-level ozone within Europe, and some modelling studies (Simpson, 1993), show that there are considerable year-to-year variations in mean summertime ozone concentrations, in the spatial patterns observed and in the number and severity of ozone episodes. These differences are ascribed to differences in meteorological conditions from one year to the next.

The regression model described in this paper has been based on modelled results from one six-month period, April-September 1989, in order to evaluate the proposed formulation. In constructing a full version of the simplified model, for use within an integrated assessment framework, it will clearly be essential to use data from several years to allow for the effects of interannual meteorological variability, i.e. it will be necessary to perform EMEP model calculations for the summer periods of a number of years.

Further work also remains to be done on the question of how to interpret the importance of interannual variations for the environmental impacts of ozone exposure on different types of ecosystems.

#### **4.5 Potential Collinearity Problems**

The emission reduction scenarios used in the EMEP model calculations carried out to provide a data set for fitting the regression model were described in Section 3.5.3. It was acknowledged that this experimental design might easily lead to collinearity problems. In fact, no serious problems of this nature have been encountered so far. However, for some receptor grids there have been indications of minor occurrences, as evidenced, for example, by instances of coefficients with the "wrong" sign. The collinearity question needs further attention before full EMEP model calculations to receptor grids across Europe are performed. Several areas in which improvements are possible are discussed in the following sub-sections.

#### 4.5.1 *Regressor Selection*

The proposed simplified ozone formation model is a linear regression model (containing quadratic terms) with many potential variables. In such a case, the question of regressor selection is very important.

This problem is quite common in statistics (e.g., Weisberg, 1980). In applying statistics several regressions may be calculated, each of which explains the same dependent variable. In such cases it is necessary to choose the equation which best satisfies some given criterion. So far, in modelling equation [9] above, this choice has been made through an intuitive thought process, considering goodness of fit, reasonableness of the sign and magnitude of the estimated coefficients. The use of statistics such as Student's t and F-value played an important role in this process. As the method is to be applied to receptor grids throughout Europe, a more systematic selection process will be needed in future.

The statistical decision theory has developed a number of information (selection) criteria. Amongst them, the Akaike Information Criterion (AIC) and the Schwartz-Bayesian information criterion (BIC) are the most popular.

One of the main advantages of AIC lies in its simplicity. There is no problem of subjective specification of an arbitrary significance level to test the models, and comparisons are not restricted to models which are nested or hierarchically ordered. From the maximum likelihood value of the model estimation, the AIC can be found by:

$$AIC = -2\log(\text{likelihood}) + 2K \quad [11]$$

where  $K$  is the number of parameters in the tested model variant. A model with a minimum value of AIC is chosen to be the best-fitting model among several competing models. But it is also necessary to go beyond an automatically selected model and examine the criterion more closely. It is important to know why the AIC will favour a particular model. In this respect, AIC emphasizes the goodness of modelling, an important aspect for the response surface in this study.

The AIC is not intended to identify a true model, which in this case is the full EMEP ozone model. The model is best among its competitors in the sense that it gives the closest approximation to the true model for the chosen data design. Naturally, the model could change as a function of sample size and selection. Particularly with a larger sample, the parameters of a model can be estimated more reliably. This leads to some further questions:

- the best design of the full model experiments to obtain a good data set for the regression;
- incorporation into the selection criteria of prior information about coefficients;

which are discussed below.

#### 4.5.2 *Experimental Design*

In designing the sampling strategy for this work, it was considered important that the simplified model should be applicable to any areas of non-linear behaviour likely to be encountered as a result of realistic emission control policies. The experimental design of the EMEP model calculations used to provide a data set for the regression model will determine the range within which the regression model may be applied. The simplified model is not intended to be used outside this range, i.e. no extrapolation is employed. The intended range of application is, therefore, an important factor in designing the sampling strategy.

The range of model application in the present study was based on a consideration of the relevant emission sources, their applicable abatement technologies and potential control policies. It is likely that international cooperation among the member countries of the UNECE LRTAP Convention and their will to solve the problems arising from air pollution will result in an overall reduction of emissions. According to the countries' current reduction plans reported to the UNECE (UNECE, 1995), total European emissions of  $\text{NO}_x$  and VOC will decrease by the turn of the century by around 20-30%. Some countries indicate that reduction levels of 70-80% might be achieved by 2010 (compared to 1990 emissions). Only a few countries forecast a freeze of emissions at their current levels or a slight increase.

Emission reduction scenarios involving changes of only one pollutant (either  $\text{NO}_x$  or VOCs) are very unlikely. This is because the regulations on emissions from traffic, which are already in place in most European countries, result, in most cases, in reductions of both pollutants. Secondly, emission limits imposed on stationary sources in the European Community by various directives will result in further reductions of nitrogen oxides (LPS Directive) and volatile organic compounds emissions (proposed IPPC Directive on organic solvents and EC Directive 14/63 on storage and distribution of liquid fuels).

The experimental design adopted in this work, as described in Section 3.5.3, aimed to represent the behaviour of the EMEP ozone model as well as possible within the range between two points: (i) close to current emission levels, and (ii) at a point representing the maximum emission reductions considered technically feasible. Based on the considerations above, this second point was taken to be 70% reductions of both  $\text{NO}_x$  and VOC emissions.

This experimental design seems to be reasonable on the basis of the consideration of likely emission reduction scenarios given above. However, it is recognized that such a design is not necessarily optimal. Alternative strategies could provide the same amount of information from fewer sample runs, taking into account information and expert knowledge from the emissions module of the integrated assessment model. Further work on this question is still required.

#### 4.5.3 *Use of Prior Information on Coefficients*

The regression currently used in the simplified model does not yet make use of any prior information about the coefficients. However, some such information can be obtained from a consideration of the chemistry involved in ozone formation, briefly outlined in Section 3.2. One important cause of non-linearity when  $\text{NO}_x/\text{VOC}$  ratios are high is the

reaction (numbered 13 in Section 3.2) between the OH radical and NO<sub>2</sub>, leading to the formation of nitric acid, which is removed relatively quickly from the atmosphere. As a result of reaction 13 there are fewer OH radicals available to react with VOCs, and ozone formation is consequently inhibited. In this situation, increases in NO<sub>x</sub> lead to reductions in ozone. Therefore, the signs of the quadratic terms in  $n_i^2$  (for the emitter country) and  $en_j^2$  (for the receptor) in equation [9] must be negative.

A further step in this direction could be based on the assumption that the quadratic term in  $n_i^2$  should be included in the regression only for emitter countries where the local NO<sub>x</sub>/VOC ratios are high.

Another potential way to incorporate the effects of high NO<sub>x</sub> around the source could be to find a NO<sub>x</sub> emission "adjustment" which, for a particular emitter, is the same for all receptors. For example, it may be possible to determine a coefficient  $q_i$  such that the terms in  $n_i$  and  $n_i^2$  in equation [9] can be replaced in the following manner:

$$b_{ij}n_i + c_{ij}n_i^2 \rightarrow b'_{ij}(n_i + q_in_i^2) \quad [12]$$

where  $q_i$  is unique for all receptor grids. In this way the total number of coefficients in the regression would be reduced.

#### 4.5.4 *Use of Daily Variability Information*

The simplified model described in this paper is based on seasonal means of all variables, calculated from the daily data resulting from the EMEP model runs. These available daily data constitute additional information which could be used in developing a simplified ozone formation model. One option would be to improve the "daily" version of the simplified model described by Heyes & Schöpp (1995). There is also another way to make use of this additional information in formulating the seasonal model.

The set of daily data could be split according to the prevailing meteorological conditions. As is clear from the brief discussion of ozone formation in Section 3.2, solar radiation is a very important factor in the ozone production process. The daily model (Heyes & Schöpp, 1995) used the NO<sub>2</sub> photolysis rate (available as an output from the EMEP model) as a convenient explanatory variable to reflect this fact. The NO<sub>2</sub> photolysis rate could instead be used in the seasonal model to group the daily data.



The advantage of this "splitting" may be seen by considering the mean ozone concentration for the group of days with "high" NO<sub>2</sub> photolysis rates. For these days, the following characteristics might be expected:

- greater ozone values but also a larger response in the mean ozone concentration to changes in the emissions of precursors;
- fewer emitter countries crossed by the air mass trajectories resulting in a reduced number of potential regressor variables;
- less mixing with the free troposphere on days with high solar radiation;
- the diurnal variation of ozone for these episodes has been well studied, making it easier to establish a relationship between the "seasonal mean" of high-NO<sub>2</sub>-photolysis-rate ozone and local exceedance of a threshold.

Furthermore, days with low NO<sub>2</sub> photolysis rates might also exhibit common characteristics with regard to ozone formation, e.g. the greater influence of background ozone concentrations.

As a result of the expected similarities within such groups or subsets of the data, it should be possible to use fewer coefficients within the subsets. There is, of course, the added complication of combining the subsets within the seasonal model.

This approach provides a way to describe the frequency distribution of ozone concentrations and, therefore, will provide additional information for ozone episodes. This will require further consideration of the VOC speciation question in the context of episodes of peak ozone concentrations.

#### **4.6 Further Statistical Aspects**

There are two other statistical aspects to this study that merit further investigation:

- Functional Form of the Model; and
- Spatial Correlation of Errors

##### *Functional Form of the Model*

As currently formulated, the regression model has a simple quadratic form. For strong source-receptor relationships further investigation of the functional form is warranted. One idea is to replace the part,  $b_{ij}n_i + c_{ij}n_i^2$ , by a general non-parametric function, such as a spline or higher order polynomial, to test whether such a formulation would improve the quality of fit.

##### *Spatial Correlation of Errors*

In order to construct simplified representations of ozone source-receptor relationships throughout Europe, it will be necessary to use EMEP model results for all (land-based) EMEP grid squares. Neighbouring receptor grids might well be influenced by similar disturbances, e.g. experience similar meteorological conditions. Therefore, the errors for neighbouring

grids are potentially correlated. Since it does not use this information about neighbouring grid squares, the regression will not be biased but the normal least squares method is no longer efficient. Spatial general least squares methods, however, can make use of this information.

## 5. CONCLUSIONS

The development of an integrated assessment model for tropospheric ozone requires a simplified yet reliable description of ozone formation in order to represent the source-receptor relationships involved. This paper has demonstrated how such an ozone formation module can be constructed using a regression surface to summarize, in effect, the results obtained from numerous calculations performed by the EMEP ozone model.

Based on a large number of scenario runs of the full EMEP model, a simplified model has been developed to produce relationships between sources of emissions (i.e., annual emission levels of NO<sub>x</sub> and VOC) and mean concentrations of early-afternoon ozone levels over a six-month period. These relationships are simple enough to enable quick calculations of a large number of emission control scenarios and also enable the optimization of emission reductions schedules aiming at an optimal (cost-minimal) use of resources to attain specified target levels of ozone concentrations.

The simplified model has been tested and compared against results of the full EMEP model for 25 sites in Europe. Over a wide range of realistic emission levels the simplified model reproduces the EMEP results sufficiently well, typically with a difference of less than 1.3 percent.

The model presented in this paper is an initial version of simplified source-receptor relationships for tropospheric ozone in Europe. Further work will be necessary to refine the model. Some important aspects requiring further attention are:

- the estimation of AOT40 values, taking account of local factors,
- the explicit incorporation of the impacts of free tropospheric ozone,
- the inter-annual meteorological variability, and
- the use of daily data to provide more information on ozone episodes, taking the influence of VOC speciation into account.

Despite these potential improvements, the results up to now are rather encouraging and give realistic hope for the successful construction of an integrated assessment model for tropospheric ozone in Europe.

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