

Emission factors programme Task 1 – Summary of simple desk studies (2003)

A report prepared for the Department for Environment, Food and Rural Affairs; the National Assembly of Wales; the Scottish Executive; and the Department of Environment in Northern Ireland

Report

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Executive Summary

This report has been prepared for the Department for the Environment, Food and Rural Affairs; the National Assembly of Wales; the Scottish Executive; and the Department of Environment in Northern Ireland by **netcen** (an operating division of AEA Technology) under the contract EPG 1/3/195 - Emission factors for air pollutants.

The Department for Environment Food and Rural Affairs (DEFRA) Air and Environment Quality (AEQ) Division is responsible for maintaining the UK National Atmospheric Emissions Inventory (NAEI). The NAEI is maintained by **netcen** on behalf of DEFRA. As part of the ongoing quality control of the NAEI the quantitative uncertainty in the national emission total of each component pollutant in NAEI is reviewed annually. Based on the findings of this review project EPG 1/3/195 aims to characterise and minimise uncertainty in the emission factors used in the compilation of the NAEI. The project objectives (Tasks) are set and reviewed annually; these comprise data collection and evaluation via literature review, personal contact with industrial representatives, direct source measurement and other means as appropriate.

Task 1 comprises small, simple, pieces of research or information purchases in order to improve generally minor parts of the NAEI. The task included the purchase of publications and the gathering of information from industry via telephone contacts with trade associations and industrial process operators.

A number of areas where research could be done was identified and inventory improvements have been proposed in the following areas :

- Flat glass production (Cd, Cr, Pb, Se, Zn)
- Primary lead/zinc production (Cd, Pb, Hg, Zn)
- Carbon Tetrachloride manufacture (HCB)
- Car refuelling using unleaded petroleum (VOC)
- Nickel refining (Ni)
- Lime production (Ca)
- Manufacture of chromium based chemicals (Cr)
- Process emissions from crude oil refineries (Benzene)
- Non-aerosol carcare products (VOC)
- Maturation of whisky (VOC)
- Glass fibre manufacture (Cr)
- Use of trichloroethylene as a cleaning solvent (VOC)

These items were all investigated except for the zinc production. Some further items of research have also been included when opportunities arose for improvements to the inventory to be made through this type of simple research.

The research has covered the following additional areas:

- adhesives use (VOC)
- landfill gas combustion (PM₁₀ , Benzene, NO_x , N₂O, CO, CH₄ , VOC)
- sewage gas combustion (PM₁₀ , Benzene, NO_x , N₂O, CO, CH₄ , VOC)
- pesticide use (POPs)

- manufacture of pressure sensitive tapes (VOC)
- tyre manufacture (VOC)
- chlorinated solvent manufacture (HCB)
- malting (VOC)
- creosote use (VOC)
- wood products manufacture (PM₁₀)
- alumina production

In addition, a briefing note on fireworks emissions was prepared.

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1 Introduction

This report has been prepared for the Department for the Environment, Food and Rural Affairs; the National Assembly of Wales; the Scottish Executive; and the Department of Environment in Northern Ireland by **netcen** (an operating division of AEA Technology) under the contract EPG 1/3/195 - Emission factors for air pollutants.

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This report provides a summary of work undertaken to improve the NAEI using simple desk-based studies to target specific sections of the NAEI with high uncertainty.

2 Methodology

Small, simple, pieces of research were carried out or information purchased in order to improve generally the consistency, comparability and accuracy of the NAEI. These general objectives allow an improvement in the uncertainty of the emission estimates in the inventory.

The task included the purchase of publications and the gathering of information from industry via telephone contacts with trade associations and industrial process operators. At the start of the project, a number of areas where research could be done was identified, and these are detailed below with associated key emissions :

- Flat glass production (Cd, Cr, Pb, Se, Zn)
- Primary lead/zinc production (Cd, Pb, Hg, Zn)
- Carbon Tetrachloride manufacture (HCB)
- Car refuelling using unleaded petroleum (VOC)
- Nickel refining (Ni)
- Lime production (Ca)
- Manufacture of chromium based chemicals (Cr)
- Process emissions from crude oil refineries (Benzene)
- Non-aerosol carcare products (VOC)
- Maturation of whisky (VOC)

- Glass fibre manufacture (Cr)
- Use of trichloroethylene as a cleaning solvent (VOC)

These items have all been investigated except for the zinc production. Some further items of research have also been included when opportunities arose for improvements to the inventory to be made through this type of simple research.

The research has covered the following additional areas:

- adhesives use (VOC)
- landfill gas combustion (PM₁₀ , Benzene, NO_x , N₂O, CO, CH₄ , VOC)
- sewage gas combustion (PM₁₀ , Benzene, NO_x , N₂O, CO, CH₄ , VOC)
- pesticide use (POPs)
- manufacture of pressure sensitive tapes (VOC)
- tyre manufacture (VOC)
- chlorinated solvent manufacture (HCB)
- malting (VOC)
- creosote use (VOC)
- wood products manufacture (PM₁₀)
- alumina production

In addition, a briefing note on fireworks emissions was prepared. Further minor but worthwhile tasks have included obtaining copies of BREF reports, other publications such as company environmental reports, and miscellaneous background data (e.g. for identification and positioning of point sources) via the internet.

Finally, we had identified a need to obtain more up-to-date activity data for the incineration of sewage sludge, chemical waste, and clinical waste. However new data are likely to be available through work being undertaken by Entec Ltd for DEFRA (Chemicals & GM Policy Division) and so this area has not been investigated further.

Progress in each of the areas is summarised in the following sections.

3 Results and recommendations

3.1 GLASS PRODUCTION

Data on the UK glass industry has been purchased from UK Glass Ltd. These data include locations and production capacities of UK glass producers, estimates of energy use and emissions of NO_x and SO₂, and details of use of metals in the production of glass by type of product.

These data can be fed directly into the NAEI (e.g. the SO₂ and NO_x estimates and the location/capacity data which will be used to generate new point source data). In addition, they will help to identify priority areas for further research especially in the case of metal & dust emissions, which are areas of great uncertainty.

Two specific areas of interest with regard to metals have already been investigated: emissions of selenium and other metals from flat glass production, and emissions of chromium from continuous filament glass fibre. Both emissions were identified as subject to high uncertainties but in both cases the emission was from processes run by a single operator. The two operators were contacted and further information provided which has allowed the emission estimates for flat glass to be revised in the 2001 version of the NAEI, and has provided the necessary background information on the emission estimates for continuous filament glass fibre for these estimates to be regarded with greater confidence. The revisions are summarised in the following table.

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Glass (flat)	Glass (flat)	Zinc		0.0138	Source removed
Glass (flat)	Glass (flat)	Nickel		0.00239	Source removed
Glass (flat)	Glass (flat)	Mercury		6.28E-05	Source removed
Glass (flat)	Glass (flat)	Chromium		0.00301	Source removed
Glass (flat)	Glass (flat)	Copper		0.000753	Source removed
Glass (flat)	Glass (flat)	Cadmium		0.000188	Source removed
Glass (flat)	Glass (flat)	Arsenic		0.000151	Source removed
Glass (flat)	Glass (flat)	Lead		0.0151	Source removed
Glass (flat)	Glass (flat)	Selenium	0.0010	0.0226	Data acquired
Glass (continuous filament glass fibre)	Glass (glass fibre)	Chromium	0.00316	0.00293	Quality checked

3.2 NON-AEROSOL CONSUMER PRODUCTS

Two areas of uncertainty have been addressed in this study :

- emissions from methanol based antifreeze
- emissions from windscreen wash & de-icer.

Following contact with suppliers of the chemicals used in these products, revisions have been made to the estimates for antifreeze in the 2001 version of the NAEI. The information provided has established that current estimates are reliable and our assessment of the uncertainty of these estimates can be revised. Species profiles for windscreen washes and de-icers will be revised based on information on the chemical make-up of these products.

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Non-aerosol products (automotive products)	Carcare products	VOC	26.8	31.9	Data acquired

3.3 ADHESIVES USE

Market data has been purchased for the UK adhesives sector. This has been necessary because of the dearth of publicly available data sets for this sector, for example the lack of consistent data on sales of adhesives. We have therefore purchased a report on the UK Adhesives sector to provide background data on trends in adhesives sales, trends in types of adhesives used by sector and information on the types of industries using

adhesives and finally, to help with identification of major UK manufacturers of adhesives by type of adhesive.

As a result, we have made some revisions to the estimates of emissions from adhesives use in the 2002 version of the NAEI. Further work is needed however, and the market information provides useful background data for future research.

Summary of revisions to NAEI for adhesives use

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Industrial adhesives	Adhesives and sealants	VOC	29.9	29.7	Data acquired

3.4 PESTICIDE USAGE

Various reports of UK pesticide usage and a database of selected pesticides have been purchased. These will be used to update the activity data used in the NAEI to estimate emissions of various POPs released when certain pesticides are used. Other research (Task 5 of the emission factor programme) will address uncertainty in emission factors for these sources.

3.5 WHISKY MANUFACTURE

The industry's trade association has been contacted and some information received on the practice of drying spent grains. As a result, a revision will be made to the NAEI estimates for this source. At the same time, further information was sought on the emission factor used for maturation emissions and we have confirmed that this emission factor is reasonable. As a result our assessment of uncertainty for this source will be revised. Activity statistics for spent grain drying were also updated (reduced) which will improve the emission estimate for this activity

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Spirit manufacture: maturation	Whisky in storage	VOC	46.7	46.7	Quality checked
Spirit manufacture: maturation	Grain drying	VOC			Data acquired

3.6 COMBUSTION OF SEWAGE GAS & LANDFILL GAS

Data used to generate point source data for landfill gas combustion in the 2001 version of the NAEI were quite old, but no updated information was available from the source of the data used for those estimates (DUKES). Up to date information was obtained from various sources including Ofgem. This information covered both landfill gas engines and those running on sewage gas and, as a result, more accurate and up-to-date point source data were included in the 2002 version of the NAEI.

The Environment Agency has commissioned ENTEC and **netcen** to undertake emission research at landfill gas engines and landfill gas flares (to support development of

emission measurement protocols) and, when published, this data should allow improvement to emission factors.

3.7 CHEMICAL WASTE INCINERATION

Previously, the NAEI only included estimates for persistent organic pollutants from this source. Emission estimates have been generated for this source based on data reported to the Pollution Inventory, covering carbon, CO, NO_x, SO₂, VOC, PM₁₀, metals & HCl.

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Incineration (Chemical Waste)	Chemical waste	Arsenic	1.71E-04		New Source
Incineration (Chemical Waste)	Chemical waste	Carbon	311		New Source
Incineration (Chemical Waste)	Chemical waste	Cadmium	9.92E-06		New Source
Incineration (Chemical Waste)	Chemical waste	Carbon monoxide	9.89E-02		New Source
Incineration (Chemical Waste)	Chemical waste	Chromium	9.11E-05		New Source
Incineration (Chemical Waste)	Chemical waste	Copper	1.24E-04		New Source
Incineration (Chemical Waste)	Chemical waste	Hydrogen chloride	3.44E-02		New Source
Incineration (Chemical Waste)	Chemical waste	Mercury	2.27E-05		New Source
Incineration (Chemical Waste)	Chemical waste	Manganese	1.09E-04		New Source
Incineration (Chemical Waste)	Chemical waste	Nickel	2.16E-04		New Source
Incineration (Chemical Waste)	Chemical waste	Oxides of nitrogen	0.325		New Source
Incineration (Chemical Waste)	Chemical waste	Lead	3.80E-04		New Source
Incineration (Chemical Waste)	Chemical waste	PM10	7.76E-02		New Source
Incineration (Chemical Waste)	Chemical waste	Tin	5.62E-05		New Source
Incineration (Chemical Waste)	Chemical waste	Sulphur dioxide	0.322		New Source
Incineration (Chemical Waste)	Chemical waste	VOC	0.249		New Source
Incineration (Chemical Waste)	Chemical waste	Zinc	7.51E-06		New Source

3.8 ANIMAL CARCASE INCINERATORS

Animal carcase incineration: previously omitted from the NAEI, emission estimates have now been included for CO, NO_x, SO₂, HCl, VOC & PM₁₀. The data are from research undertaken by **netcen** on behalf of the DEFRA Farm Wastes Research programme.

Animal carcase incineration NAEI modifications

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Incineration (animal carcasses)	Non-fuel combustion	Carbon monoxide	3.3		New Source
Incineration (animal carcasses)	Non-fuel combustion	Hydrogen chloride	0.0007		New Source
Incineration (animal carcasses)	Non-fuel combustion	Oxides of nitrogen	0.245		New Source
Incineration (animal carcasses)	Non-fuel combustion	PM10	0.31		New Source
Incineration (animal carcasses)	Non-fuel combustion	Sulphur dioxide	0.165		New Source
Incineration (animal carcasses)	Non-fuel combustion	VOC	2		New Source

3.9 PETROL DISTRIBUTION

New data was obtained both from the Institute of Petroleum (IoP) and from the United Kingdom Petroleum Industries Association (UKPIA). The data obtained covered various areas including petrol volatility, petrol composition, the extent of controls at petrol terminals & petrol stations, and the structure of the UK petrol supply market. The contact with UKPIA also resulted in another area of improvement being identified - the temperature data used in the calculation of emissions. As a result of these contacts, estimates of emissions of benzene, 1,3-butadiene, and non-methane volatile organic compounds (NMVOC) have all been revised in the 2001 version of the NAEI.

Petrol distribution – VOC inventory

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Petrol stations (petrol delivery)	Petrol (leaded)	VOC	0.439	0.514	Data acquired
Petrol stations (petrol delivery)	Petrol (unleaded)	VOC	5.86	6.79	Data acquired
Petrol stations (spillages)	Petrol (leaded)	VOC	0.168	0.252	Data acquired
Petrol stations (spillages)	Petrol (unleaded)	VOC	2.24	3.32	Data acquired
Petrol stations (storage tanks)	Petrol (leaded)	VOC	0.252	0.378	Data acquired
Petrol stations (storage tanks)	Petrol (unleaded)	VOC	3.36	4.98	Data acquired
Petrol stations (vehicle refuelling)	Petrol (leaded)	VOC	2.75	3.95	Data acquired
Petrol stations (vehicle refuelling)	Petrol (unleaded)	VOC	36.7	52.0	Data acquired
Petrol terminals (storage)	Petrol (leaded)	VOC	0.250	0.286	Data acquired
Petrol terminals (storage)	Petrol (unleaded)	VOC	3.46	3.90	Data acquired
Petrol terminals (tanker loading)	Petrol (leaded)	VOC	9.38E-02	0.108	Data acquired
Petrol terminals (tanker loading)	Petrol (unleaded)	VOC	1.25	1.42	Data acquired

Petrol distribution – benzene and 1,3 butadiene inventory

Source	Fuel	Pollutant	Inventory, kg		Comment
			2001	Old (2000)	
Petrol stations (petrol delivery)	Petrol (leaded)	Benzene	0.000658	0.00200	Data acquired
Petrol stations (spillages)	Petrol (leaded)	Benzene	0.000376	0.00098	Data acquired
Petrol stations (storage tanks)	Petrol (leaded)	Benzene	0.000564	0.00147	Data acquired
Petrol stations (vehicle refuelling)	Petrol (leaded)	Benzene	0.00578	0.0154	Data acquired
Petrol terminals (storage)	Petrol (leaded)	Benzene	0.000563	0.00111	Data acquired
Petrol terminals (tanker loading)	Petrol (leaded)	Benzene	0.000176	0.000419	Data acquired
Refineries (road/rail loading)	Petrol (leaded)	Benzene	0.000128	0.000311	Data acquired
Petrol stations (petrol delivery)	Petrol (unleaded)	Benzene	0.0209	0.0364	Data acquired
Petrol stations (spillages)	Petrol (unleaded)	Benzene	0.0119	0.0178	Data acquired
Petrol stations (storage tanks)	Petrol (unleaded)	Benzene	0.0179	0.0267	Data acquired
Petrol stations (vehicle refuelling)	Petrol (unleaded)	Benzene	0.184	0.279	Data acquired
Petrol terminals (storage)	Petrol (unleaded)	Benzene	0.0185	0.0210	Data acquired
Petrol terminals (tanker loading)	Petrol (unleaded)	Benzene	0.00561	0.00764	Data acquired
Refineries (road/rail loading)	Petrol (unleaded)	Benzene	0.00406	0.00567	Data acquired
Petrol stations (petrol delivery)	Petrol (leaded)	1,3-butadiene	0.000274	0.000834	Data acquired
Petrol stations (spillages)	Petrol (leaded)	1,3-butadiene	0.000157	0.000409	Data acquired
Petrol stations (storage tanks)	Petrol (leaded)	1,3-butadiene	0.000235	0.000613	Data acquired
Petrol stations (vehicle refuelling)	Petrol (leaded)	1,3-butadiene	0.00241	0.00641	Data acquired
Petrol terminals (storage)	Petrol (leaded)	1,3-butadiene	0.000235	0.000465	Data acquired
Petrol terminals (tanker loading)	Petrol (leaded)	1,3-butadiene	7.36E-05	0.000175	Data acquired
Refineries (road/rail loading)	Petrol (leaded)	1,3-butadiene	5.33E-05	0.00013	Data acquired
Petrol stations (petrol delivery)	Petrol (unleaded)	1,3-butadiene	0.000512	0.000893	Data acquired
Petrol stations (spillages)	Petrol (unleaded)	1,3-butadiene	0.000293	0.000437	Data acquired
Petrol stations (storage tanks)	Petrol (unleaded)	1,3-butadiene	0.000439	0.000655	Data acquired
Petrol stations (vehicle refuelling)	Petrol (unleaded)	1,3-butadiene	0.00450	0.00684	Data acquired
Petrol terminals (storage)	Petrol (unleaded)	1,3-butadiene	0.000455	0.000514	Data acquired
Petrol terminals (tanker loading)	Petrol (unleaded)	1,3-butadiene	0.000138	0.000187	Data acquired
Refineries (road/rail loading)	Petrol (unleaded)	1,3-butadiene	9.96E-05	0.000139	Data acquired

3.10 CRUDE OIL REFINERIES

Results of research carried out by the IoP into speciation of refinery emissions were obtained. This research has been used to revise the species profile for refinery emissions used in the 2001 version of the NAEI.

3.11 CHEMICALS MANUFACTURE

Data on emissions from various Scottish chemical processes has been obtained, both from the Scottish Environment Protection Agency (SEPA), and from process operators. The estimates of emissions of NMVOC, benzene and 1,3-butadiene have been revised in the 2001 version of the NAEI as a result. A review of the Pollution Inventory has provided a new source for carbon monoxide. One further impact of this work has been to provide additional information on the emissions of carbon tetrachloride from one Scottish chemical plant. Emission estimates for carbon tetrachloride will be improved in the 2002 inventory as a result of this work.

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Chemical industry	Chemicals and manmade fibres	VOC	70.8	71.1	Data acquired
Chemical industry (titanium dioxide)	Titanium dioxide	Carbon monoxide	55.9		New Source
Chemical industry	Chemicals and manmade fibres	Benzene	Inventory, kg		Data acquired
			0.527	0.506	
Chemical industry	Chemicals and manmade fibres	1,3-butadiene	0.264	0.270	Data acquired

3.12 MANUFACTURE OF PRESSURE SENSITIVE TAPES

Emission estimates for processes located in Northern Ireland were very uncertain. Regulators responsible for these processes were contacted to try to obtain further data on the scale of the processes and emissions. As a result, estimates of NMVOC emissions from this source were revised in the 2001 version of the NAEI.

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			Proposed (2002)	Current (2001)	
Industrial adhesives (pressure sensitive tapes)	Solvent use	VOC	1.23	1.37	Data acquired

3.13 TYRE MANUFACTURE

An emission estimate for the one process located in Northern Ireland were very uncertain. The regulator responsible for this process was contacted and provided data on solvent emissions. In addition, up-to-date information was also obtained on emissions

from two of the largest English plants. As a result, estimates of NMVOC emissions from this source were revised in the 2002 version of the NAEI.

Tyre manufacture inventory revision

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Tyre manufacture	Rubber and plastic products	VOC	1.75	1.71	Data acquired

3.14 CHROMIUM CHEMICALS MANUFACTURE

Details of the derivation of chromium emissions data reported in the Pollution Inventory were sought from the operator. Although the information received has not led to any revisions to the NAEI it has allowed revision of the uncertainty which is important in establishing the reliability of the emission data used in the NAEI for this major chromium source.

3.15 NICKEL REFINING

Details of the derivation of nickel emissions data reported in the Pollution Inventory were sought from the operator. Although the information received has not led to any revisions to the NAEI it is important in establishing the reliability of the emission data used in the NAEI for this important source of nickel.

The operator confirmed that emissions data reported in the Pollution Inventory for 1998 and 1999 (but rejected by **netcen** for the purposes of deriving NAEI data) were indeed unreliable. The operator had reported 50 kg in 1998 and over 5 tonnes for 2000.

This highlights an area of concern with significant parts of the PI. Use of the point source data in the PI potentially improves the NAEI. However, although the PI is improving as operators develop more robust reporting systems, there are many examples of similar anomalous data in this important reference database.

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Non-ferrous metals (nickel production)	Nickel production	Nickel	0.00529	0.00509	Quality checked

3.16 CHLORINATED SOLVENT MANUFACTURE

Information on production and/or consumption of major chlorinated solvents was obtained from the major UK producer. As a result, revisions were made to the estimates of NMVOC from solvent use and hexachlorobenzene (HCB) from solvent production were revised in the 2001 version of the NAEI.

Revised Chlorinated solvent manufacture emissions

Source	Fuel/activity	Pollutant	Inventory, kg		Comment
			2001	Old (2000)	
Chemical industry (Trichloroethylene Prod)	Process emission	HCB	23.9	54.1	Data acquired
Chemical industry (Tetrachloroethylene Prod)	Process emission	HCB	20.7	32.6	Data acquired
Chemical industry (Prod Carbon Tetrachloride)	Process emission	HCB	0	144	Data acquired

3.17 MALTING

A species profile was developed for NMVOC emissions from production of brewers' and distillers' malts, based on data published on the composition of odours from malting processes. The new profile is subject to considerable uncertainty but is an improvement on the previous situation where emissions from these sources were left unspecified.

3.18 CREOSOTE USE

A species profile was developed for NMVOC emissions from use of creosote, based on data available on the internet on the composition of creosote. The new profile is subject to considerable uncertainty but is an improvement on the previous situation where emissions from these sources were left unspecified.

3.19 LIME PRODUCTION

The British Lime Association were asked for information on the likely composition of dust emissions from lime plant. This composition data is used in the calculation of emission estimates for calcium. As a result of information provided, a revision will need to be made to the 2002 version of the NAEI.

3.20 WOOD PRODUCTS MANUFACTURE

Contact was made with the local authority leading the link authority activity for PG 6/4 'Manufacture of particleboard etc.'. The authority was able to confirm the accuracy of existing NAEI point sources and also helped to identify one further process. Finally, information was provided on typical abatement systems used for these processes and this information may be used to help identify improved NMVOC and PM₁₀ emission factors for this sector.

Source	Fuel/activity	Pollutant	Inventory, ktonnes		Comment
			2001	Old (2000)	
Wood products manufacture	Wood product production	PM10	1.41		Data acquired

3.21 ALUMINA PRODUCTION

Contact was made with SEPA in order to obtain better information on the level of control at this plant although no data has been obtained to date.

3.22 OTHER ACTIVITIES

A briefing note on fireworks and other munitions use was prepared for DEFRA. The note is attached at appendix 1. Currently, the NAEI does not include any estimates of emissions from any of these sources. First estimates of copper and base cation emissions have been derived and these are proposed for inclusion in the 2002 inventory.

Further data are required on the usage of fireworks and other pyrotechnics and the use of metals and other chemicals in these products. In particular, research needs to concentrate on the use of copper fireworks, and the use of metals generally in pyrotechnics. First estimates are required for emissions of dioxins and PCBs from fireworks and other pyrotechnics and explosives.

Emissions from bonfires associated with celebrations on November 5th and other festival dates should be estimated.

4 Conclusions

This task has allowed significant improvements to the NAEI and has also allowed response to 'ad hoc' enquiries from DEFRA. The number of work items undertaken was increased over the original work programme.

Improved estimates of emissions were determined for several pollutants across a range of industry sectors. These have resulted in identification of several new sources, revised inventories for several industrial activities or have allowed confirmation of existing estimates. In addition, improved speciation (of VOCs) data were obtained for several activities.

The simple studies task format is recommended for years two and three of the project.

Appendices

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Appendix 1 Fireworks briefing note

Appendix 1

Fireworks briefing note

Briefing note on potential for emissions from use of fireworks and other explosives

1. Introduction

This note presents the available information on the potential for, and scale of, emissions to air resulting from the use of fireworks and other explosive products. Although the use of fireworks is the main topic addressed, the use of other related products including other pyrotechnic devices such as safety flares, as well as explosives such as those used for mining/quarrying and the military, are also discussed. Currently, the National Atmospheric Emissions Inventory (NAEI) does not include any estimates of emissions from any of these sources. Estimates of UK consumption of fireworks and other products are provided in Section 2, while Section 3 considers what pollutants might be released through use of these products. Provisional estimates of emissions of the most significant pollutants are given in Section 4. Section 5 gives conclusions and recommendations for further research.

2. Scale of use of fireworks and other explosives

Some data are available from the Office of National Statistics although, in the case of fireworks, these data are very limited. Table 1 gives details of the figures for fireworks.

Table 1. UK manufacturers' sales of fireworks

Period	Sales (£)
1998 Q4	507,000
1999 Q1	36,000
1999 Q2	nd
1999 Q3	nd
1999 Q4	nd
2000 Q1	na
2000 Q2	na
2000 Q3	379,000
2000 Q4	408,000
2001 Q1	11,000
2001 Q2	nd
2001 Q3	nd
2001 Q4	nd

na = publication not available/obtained

nd = no data given in publications

The data are for value of sales and it is difficult to translate this into a more useful measure - the mass of fireworks consumed. A further difficulty is that the figures relate to sales of fireworks by UK manufacturers and so include exports of fireworks and exclude imports of fireworks into the UK. One notable

feature of the data is that sales of fireworks are very seasonal - this is to be expected since use of fireworks is concentrated on a limited number of days, especially around 5 November and, to a lesser extent, public holidays such as 31 December. This may have important ramifications for the significance of emissions from fireworks. In particular it is possible that, although fireworks might not be major sources of pollution when considered over the whole year, they might still emit some pollutants over a period of a few hours or few days in sufficient quantities to breach health-related, short-term exposure limits.

Manufacture of fireworks in the UK is limited to a small number of specialist producers manufacturing devices at the higher end of the market (e.g. devices for professional use rather than the general consumer). The vast majority of fireworks sold in the UK are imported, mainly from China, although some imports come from Germany. UK sales of fireworks including imports has been estimated by various sources in industry and regulatory bodies as follow:

- value: £40 million, £70-80 million (both estimates for consumer market only)
- no of fireworks: 100 million for consumer market
- tonnage: 1500 tonnes explosives in imports (total weight of fireworks is 7,500 - 10,000 tonnes)

These estimates are compared by converting all to a mass basis. The figures for the value of the UK consumer market (i.e. excluding professional users) range from £40 million to £80 million and a mean estimate of £60 million will be used here. Sales of fireworks to professional users are not known although one contact has estimated that two thirds of sales are to the consumer market. Overall therefore, the UK market for fireworks might be worth £90 million. Prices for fireworks seem to vary enormously with the cheap end of the market probably about 50p per firework while the highest quality 'DIY' sets of fireworks seem to work out at more than £10 per firework (note that these are also likely to be more powerful and contain more explosives. I will assume a price of between £1 to £2 per 'typical' firework. This gives a estimate of the number of fireworks sold of between 30 million and 60 million. The number of fireworks sold to the consumer market has also independently been estimated at about 100 million, giving an overall range of 30 million to 100 million fireworks for the consumer market only. According to an industry source, a typical firework for the consumer sector might contain between 10g and 20g of explosive, although the weight of other materials such as paper, plastic, clay would be greater - typically fireworks are 15% to 20% explosives. The very largest fireworks for professional use can contain as much as a kilogramme of explosive and a total weight of 10 kg (i.e. 10 times the weight of explosives). By combination with the figures above for numbers of fireworks for the consumer sector, we obtain the following range for the mass of explosives in fireworks for that sector:

Number of fireworks	30 - 100 million
Explosive per typical firework	10 - 20 g
Total weight of typical firework explosives)	50 g - 130 g (assume 15-20% explosives)

This gives overall estimates of between 300 and 2000 tonnes of explosives and 1500 and 13,000 tonnes total weight of fireworks but with best estimates of 975 tonnes and 5525 tonnes respectively.

Assuming half as much again for professional fireworks (based on one third of value of the market) gives a range of 450 to 3000 tonnes of explosives and 2250 to 19,500 tonnes of fireworks but with best estimates for explosives and fireworks of 1460 and 8,300 tonnes respectively.

The estimate of tonnage of fireworks imported will obviously exclude UK manufacture. As a rough estimate, I have assumed that UK manufacturers supply only 5% of the UK market for fireworks so the estimate for imported fireworks is increased accordingly to give an estimate of 1580 tonnes of explosives and 9,200 tonnes of fireworks.

A final alternative estimate of the total mass of fireworks has been obtained using an estimate of 4500 tonnes of fireworks consumed in Denmark from an article written by Allan Andersen of the Danish Association for the Conservation of Nature (available at <http://www.chemical-awareness.com/news.php?nid=2&aid=98>). Extrapolation on the basis of population gives an estimate of 30,000 tonnes of fireworks which is 50% above the maximum of the range calculated from UK market data above and more than three times as high as the best estimates calculated this way. This number will, however be used as a 'worst case' figure, as will a figure of 6,000 tonnes of explosives (20% of 30,000 tonnes).

For the purposes of calculating emissions, I will assume a range of 2250 to 30,000 tonnes of fireworks with a best estimate of 8,750 tonnes and a range of 450 to 6,000 tonnes of explosives with a best estimate of 1520 tonnes.

Table 2 shows data on UK manufacturers' sales of other explosive products.

Table 2 UK manufacturer sales of other explosive products (various units)

Product type	Units	2001 Q1	2001 Q2	2001 Q3	2001 Q4
Propellant powders	tonnes	na	na	68.8	89.1
Prepared explosives	tonnes	9411	9057	9409	12557
Safety & detonating fuses	km	669	532	573	772
Percussion & detonating caps etc	items	538,000	na	na	526,000
Signalling flares, rain rockets, fog signals etc.	tonnes	2323	4603	2769	2144

na = not available

As with data for fireworks, there are significant gaps. Overall, the UK manufacturer sales of each type of product may be estimated as:

Propellant powders	320 tonnes
Prepared explosives	40000 tonnes
Safety & detonating fuses	2500 km
Percussion & detonating caps	2.1 million items
Signalling flares etc.	12000 tonnes

As with fireworks, the data are for sales by UK manufacturers only and thus include exports and exclude imports. In addition, sales data will presumably overestimate the consumption of at least some products such as signalling flares which are purchased but, presumably, rarely used.

At the moment, insufficient data are available to derive robust estimates of UK consumption (i.e use rather than just ownership) for the products listed above. However for the purposes of evaluating the potential for air pollution it will be assumed, arbitrarily, that UK consumption of prepared explosives and propellants is the same as UK production and that consumption of signalling flares is 10% of production. For fuses and caps, I do not have any information on the characteristics of these items and cannot estimate the weight of UK production and so have not estimated UK consumption. I would assume though that it is small compared with the prepared explosives figure. Available estimates are then:

Propellant powders	320 tonnes
Prepared explosives	40000 tonnes
Signalling flares etc.	1200 tonnes

It is not certain whether these figures include other products such as military devices (e.g. smoke screens) or children's caps. Military products may be used in large quantities while children's cap will certainly not be.

3. Potential for pollution from fireworks and other explosives

The use of fireworks and other explosives is likely to cause emissions of practically every pollutant covered by the NAEI, although the quantities involved are likely to be trivial in many or possibly all cases. The potential for pollution is considered below for four categories of pollutant: gaseous combustion by-products; particulate matter; metals; toxic or persistent organic pollutants.

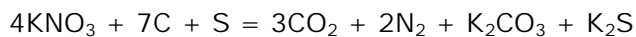
Gaseous combustion by-products

This category includes those gaseous pollutants released from all combustion processes:

- carbon dioxide
- methane
- carbon monoxide

- oxides of nitrogen (N₂O, NO, NO₂)
- sulphur dioxide
- volatile organic compounds (VOC)
- hydrogen chloride

Emissions of methane and VOC occur mainly from industrial and other 'processes' whilst the remaining pollutants occur almost exclusively due to the burning of fuels. During combustion, all of these pollutants are released due to reactions between the components of the fuel (or explosive) and air. Fireworks use gunpowder which burns roughly according to the following equation:



This equation can be used to derive a reasonable estimate of CO₂ emissions from fireworks. Presumably other minor by-products could include as methane, carbon monoxide and volatile organic compounds as well as oxides of nitrogen. Other explosives would also 'burn' to form carbon dioxide and small quantities of other by-products such as methane, carbon monoxide and volatile organic compounds, while any nitrogen or sulphur in the explosive might be oxidised to oxides of nitrogen or sulphur dioxide. Annual UK releases of each of these pollutants are very large, ranging from about 540 million tonnes for carbon dioxide to 80,000 tonnes for hydrogen chloride. In each case, I believe that it is extremely unlikely that releases from fireworks, fuses, caps, propellants and flares would contribute enough to UK emissions to warrant inclusion in the inventory, although it would be relatively easy to include figures for carbon dioxide. In the case of prepared explosives, emissions of some pollutants (NO_x?, SO₂?) might not be trivial and some further investigation is recommended.

Particulate matter

The NAEI includes estimates for various sizes of particulate matter including PM₁₀ (particulate matter of less than 10 microns). PM₁₀ emissions occur both from fuel combustion and from industrial processes and UK emissions during 2000 totalled 170,000 tonnes. Fireworks and other explosives will cause emissions of particulate matter during use. I believe that it is unlikely that these emissions from fireworks will be very significant when considered on an annual basis. However, fireworks could have a significant impact on short-term levels of atmospheric particulate matter could be high and the releases of particulate matter from fireworks should therefore be assessed. It should be noted that monitoring of atmospheric emissions have shown elevated levels of atmospheric particulate matter on days around the 5th of November. Fireworks would have contributed to these high levels, however bonfires would also have done so and could have been the more significant source. Emissions of particulate matter from explosives could be worth investigation given that large quantity are likely to be used in quarries (although much more particulate matter would presumably be formed from the material being blasted).

Metals

The NAEI includes emission estimates for arsenic, beryllium, cadmium, calcium, chromium, copper, lead, magnesium, manganese, mercury, nickel, potassium, selenium, sodium, tin, vanadium and zinc. Some metals are included in the NAEI because of concerns about toxicity, others because of their involvement in reducing the impact of acid deposition (so-called 'base cations'). Metal releases occur when fuels containing metals are burnt, although other sources are also important. Annual UK releases range from a few tonnes to several thousand tonnes as shown in Table 3.

Table 3. UK emissions of metals during 2000 (tonnes)

Metal	Emission	Notes	Metal	Emission	Notes
Arsenic	35	hazardous	Mercury	8.5	hazardous
Beryllium	16	hazardous	Nickel	115	hazardous
Cadmium	5.2	hazardous	Potassium	1080	base cation
Calcium	6600	base cation	Selenium	50	hazardous
Chromium	63	hazardous	Sodium	1080	base cation
Copper	46	hazardous	Tin	74	hazardous
Lead	496	hazardous	Vanadium	157	hazardous
Magnesium	960	base cation	Zinc	336	hazardous
Manganese	303	hazardous			

Fireworks and possibly other products such as flares certainly can contain metals and these metals would then be emitted. The information available on the internet (including that at Alternet.org) suggests that the NAEI pollutants arsenic, cadmium, calcium, chromium, copper, lead, magnesium, mercury, potassium, sodium, zinc can be used, as well as other metals including aluminium, barium, rubidium, strontium, titanium and non-metals such as lithium and boron. Based on discussion with UK manufacturers and importers, it seems extremely unlikely that some of these metals are now used. Table 4 summarises use of metals in fireworks

Table 4. Potential for use of metals and other elements in fireworks

Metal	Uses & compounds
Copper	Used for blue colours (not a common colour). Copper oxide.
Lead	Historically used to produce crackling effects but no longer - phased out in last five years. Lead chromate?
Chromium	Historical use in lead chromate (see above)? Traces of chromium compounds still used in very small number of fireworks.
Sodium	Used for yellow colours. Sodium oxalate
Potassium	Use as oxidant in the forms potassium perchlorate & potassium nitrate.
Arsenic	Historical use for blue colours in copper acetoarsenite (Paris Green), $Cu_3As_2O_3Cu(C_2H_3O_2)_2$
Magnesium	Used for white/silver colours. Used as metal, commonly alloyed with aluminium
Aluminium	Used for white/silver colours. Used as metal, commonly alloyed with magnesium
Calcium	Used for orange colours (rare). Calcium carbonate
Barium	Used for green colours. Barium nitrate, barium carbonate
Strontium	Used for red colours (most common colour). Strontium carbonate, strontium nitrate, strontium oxalate
Antimony	Historically used as oxidant in form of antimony sulphide.
Iron	Used for gold colours. Added as fine metal powder
Bismuth	Used for crackling effects. Bismuth oxide
Titanium	Used for silver colours. Added as the metal

Other metals including cadmium, mercury, vanadium, selenium, tin, zinc, manganese, nickel, and beryllium are not used although mercury has been used in the distant past. Zinc and manganese are both used in military smoke products.

From the above, it is clear that only in the case of copper, potassium, sodium and magnesium is there much likelihood of significant emissions from fireworks of metallic pollutants covered by the NAEI. It is also possible that emissions from fireworks, particularly of copper, could have a significant impact on short-term levels in the atmosphere. Historically, other metals such as lead, arsenic and mercury would have been emitted and could have been significant. Further work is recommended to better quantify current and historical emissions.

An area of possible interest is other pyrotechnics such as those for marine safety, special effects, and military uses. These could contain metals (military smoke products contain manganese and zinc) but no further details are known.

Previous work had estimated an upper limit of 170 kg of mercury in children's caps but this figure is very uncertain.

Toxic and persistent organic pollutants

These pollutants include the following:

- benzene
- 1,3-butadiene
- dioxins
- polycyclic aromatic hydrocarbons (PAH)
- polychlorinated biphenyls (PCB)

The first two pollutants are toxic and are emitted from combustion and chemical processes. The remaining three pollutants are both toxic and persistent and are released from both combustion and other processes. Fireworks and other explosives could cause emissions of these pollutants. In the case of benzene and 1,3-butadiene, I do not believe that they would be a significant source since the inventories of these pollutants are dominated by sources such as road transport which emit large quantities of the pollutant (i.e. thousands of tonnes).

In the case of persistent organic pollutants, since chlorine is present in some of the chemicals used in fireworks, formation of dioxins and polychlorinated biphenyls (PCBs) is possible. Metals such as copper are also present and help to catalyse the formation of dioxins. Monitoring of emissions of dioxins and PCB during the bonfire night period of 2000 show that elevations in levels of these pollutants occurred at that time. Since levels of other pollutants such as CO and NO_x, which would not be emitted in large quantities from fireworks, did not show similar elevations, the elevated levels of the dioxins and PCBs was concluded not to be due to an episode of generally high pollution levels. Dioxins and PCBs could also be formed during use of other pyrotechnics and explosives.

Other issues

Although, fireworks may emit significant quantities of some pollutants, it is important to recognise that bonfires may contribute as much or more to emissions on November 5th and other celebrations. I recommend that any further research on fireworks also include assessment of the potential for emissions from bonfires.

4. Emission estimates

Two approaches are available for estimating metal emissions from fireworks. Some emission factors, expressed in terms of emissions per tonne of fireworks are available from an article written by Allan Andersen of the Danish Association for the Conservation of Nature (available at <http://www.chemical-awareness.com/news.php?nid=2&aid=98>). The basis of the assumptions in the article are unknown but the following emission factors are given:

lead	0.6667	kg metal / tonne firework
copper	0.4444	kg metal / tonne firework
chromium	0.01556	kg metal / tonne firework
arsenic	1.333	g metal / tonne firework
cadmium	0.6667	g metal / tonne firework

Given, what is known about use of metals in UK fireworks, the factors for arsenic and cadmium seem unreliable, since neither metal is used in UK fireworks. The factor for lead is also likely to be obsolete, however emissions will be calculated in order to give information on the potential for emissions in previous years.

Estimated use of fireworks = 2250 to 30,000 tonnes (best estimate of 8,750 tonnes)

Emission of copper	1 - 13.3 tonnes (best estimate of 3.9 tonnes)
Emission of lead	1.5 - 20 tonnes (best estimate of 5.8 tonnes)
Emissions of chromium	35 - 470 kg (best estimate of 140 kg)

Of the three estimates, that for lead is applicable only to historical emissions (probably 5 or more years ago), when emissions of lead from all sources were at least 900 tonnes per year - the best estimate would add 0.6% more to the inventory in 1998. The best estimates for copper and chromium above are equivalent to increases of 0.2% and 8.5% in the 2000 chromium and copper inventories respectively.

A second approach is based on some estimates of the quantities of the various chemicals used in fireworks. Starting from the estimates of consumption of explosives (450 to 6,000 tonnes with a best estimate of 1520 tonnes), the approach is as follows:

- explosives for each firework comprise 50% black powder ejection charge & 50% effects charge
- blue colours are used for 2.5% of fireworks
- blue effects contain 18% copper oxide

Overall this suggests a copper use of 1.81 kg per tonne of explosives. The proportion of the copper which would be emitted is not know - at least some solids are left in spent fireworks and could include some of the copper. As a worst case, however, we will assume all of the copper is emitted. This gives the following:

Emissions of copper	0.82 - 10.9 tonnes (best estimate of 2.8 tonnes)
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This is fairly good agreement with the estimate derived from the Danish emission factor and suggests that fireworks might add 6% to the UK copper inventory in 2000. This emission estimate is considered the most reliable available and it is recommended that it should be used in the NAEI.

Emissions of sodium, potassium, magnesium and other metals can be calculated in a similar way using estimates of the use of other effects and their composition.

Emissions of potassium	30 - 400 tonnes (best estimate of 100 tonnes)
Emissions of sodium	1.6 - 22 tonnes (best estimate of 5.5 tonnes)
Emissions of magnesium	22 - 290 tonnes (best estimate of 73 tonnes)
Emissions of barium	19 - 260 tonnes (best estimate of 65 tonnes)
Emissions of strontium	2.9 - 39 tonnes (best estimate of 9.9 tonnes)
Emissions of aluminium	26 - 340 tonnes (best estimate of 86 tonnes)
Emissions of titanium	1.6 - 21 tonnes (best estimate of 5.3 tonnes)

Emissions of potassium, sodium and magnesium would add 9.3%, 0.5% and 7.6% to the 2000 inventories for each cation respectively. It is recommended that these estimates are included in the NAEI.

Emissions of carbon dioxide and carbon monoxide are trivial but can be calculated from the equation given in section 3, again based on the estimate that 50% of the explosive charge is gunpowder:

Emission of carbon dioxide	47 - 620 tonnes (best estimate of 160 tonnes)
Emission of carbon monoxide	36 - 480 tonnes (best estimate of 120 tonnes)

With no emission factors for other pollutants and for other explosives, no emission estimates can be derived. However, given the potential for dioxin & PCB formation from fireworks and the fact that emissions of all pollutants will occur over a very limited period of days possibly leading to significantly elevated levels of some pollutants such as PM₁₀ it is recommended that work be carried out to estimate emissions for these three pollutants. Emissions of other pollutants such as VOC, SO₂ & NO_x are likely to be trivial and no further investigation is recommended.

In the case of other explosives, there is a potential for emissions of metals, dioxins, and PCBs from signalling flares and similar products, special effects pyrotechnics, and military pyrotechnics and the potential for some emissions of PM₁₀ and gaseous pollutants from explosives. Table 5 summarises our assessment of the potential for significant emissions from fireworks and other explosives.

Table 5 Significant emissions from fireworks and other explosive products

Pollutants	Fireworks	Explosives, fuses, detonators etc.	Flares, pyrotechnics, military	Caps
CO ₂	Trivial	Possible	Trivial	None
CO	Trivial	Possible	Trivial	None
Other gases	Trivial	Possible	Trivial	None
PM ₁₀	Possible short-term significance	Possible	Trivial?	None
Metals	Yes (Cu) Historical (Pb, As) Trivial (Cr)	Trivial?	Possible	Possible (Hg)
POPs	Possible (PCDD, PCB)	Possible	Possible	None
Base cations	Yes (Na, K, Mg)	Possible	Possible	None

I recommend that those emissions highlighted above as possibly significant should be investigated further. The emission estimates given here for cations and copper from fireworks should be included in the NAEI until better numbers are available.

5. Conclusions & recommendations

Best estimates of emissions of air pollutants from use of fireworks are as follows:

Copper	2.8 tonnes (6% of emissions in 2000)
Potassium	100 tonnes (9.3% of emissions in 2000)
Sodium	5.5 tonnes (0.5% of emissions in 2000)
Magnesium	73 tonnes (7.6% of emissions in 2000)
Barium	65 tonnes
Strontium	9.9 tonnes
Aluminium	86 tonnes
Titanium	5.3 tonnes
Carbon dioxide	160 tonnes (trivial)
Carbon monoxide	120 tonnes (trivial)

In addition, historical emissions of lead could have been about 5.8 tonnes, equal to 0.6% of emissions in 1998 but emissions are likely to be zero now.

Other metals including cadmium, mercury, vanadium, selenium, tin, zinc, manganese, nickel, and beryllium are not used in fireworks and no emissions are expected.

Emissions of dioxins and PCBs might be significant from fireworks. Emissions of PM₁₀, gaseous pollutants, dioxins and PCBs might be significant from use of explosives. Emissions of metals, dioxins and PCBs might be significant from distress flares, special effects pyrotechnics and military devices.

Emissions from bonfires of all these pollutants might also be important and in some cases might dominate emissions on November 5th and other celebrations.

It is recommended that:

- 1) Estimates for emissions of copper, potassium, magnesium and sodium presented here are included in the NAEI until better data are available.
- 2) Further data be obtained so that the quantities of fireworks and other pyrotechnic and explosive devices sold and used in the UK can be estimated with greater confidence. For fireworks, distress flares and other pyrotechnics information is also needed on the types of device used (e.g. for fireworks information on colours & sizes would be useful).
- 3) Further data are required on the usage of metals and other chemicals in fireworks and other pyrotechnics. In particular, research needs to concentrate on the use of copper and lead (historically) in fireworks, and the use of metals generally in distress flares and other pyrotechnics.
- 4) First estimates are required for emissions of PM₁₀, dioxins and PCBs from fireworks and other pyrotechnics and gaseous pollutants, PM₁₀, dioxins and PCBs from explosives.
- 5) Further investigation of the potential for mercury from childrens cap's could be combined with the investigation of fireworks and other explosives.
- 6) Emissions from bonfires associated with celebrations on November 5th and other dates should be estimated.

Neil Passant
28 February 2003