Surveillance of Greenhouse Gas Releases

R&D Technical Report E87a

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Statement of Use
This report reviews sources and sinks of the major UK greenhouse gases, their
reduction processes and investigates methods for their measurement. This report will
assist the Agency to achieve its aim that, by the year 2020, greenhouse gas emissions
will be greatly reduced.

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GLOSSARY

Terms

Anthropogenic	produced as a result of human activity
Broiler litter	manure from hens bred for consumption. Excreta mixed with wood shavings
Denitrification	mainly microbial conversion of nitrate to nitrous oxide and di-nitrogen gases
Enteric fermentation	microbiological process of breaking down foodstuffs in the rumen
Emission Factor	rate of gaseous emission, e.g. per animal; per tonne of manure; % of N content
Farm yard manure	mix of dung and urine when dropped on bedding material, e.g. straw
Long-wave radiation	terrestrial radiation as opposed to the short-wave radiation emitted from the sun
Manure	the generic term for all manure types, e.g. slurries and FYMs
Methanotrophs	micro-organisms in soil or else where capable of utilising methane as an substrate
Nitrification	microbial conversion of ammonium to nitrate
Rumen	part of the digestive tract of cattle, sheep etc. responsible for the breakdown of fibrous plant materials
Slurry	intimate mix of animal dung and urine (no bedding material)
System	in the present context refers to the whole farming enterprise and its component parts

Abbreviations

CH_4	Methane: molecular weight 16
DIAL	Differential Absorption Lidar
EF	Emission Factor
EPA	US Environmental Protection Agency
FID	Flame Ionisation Detector
FTIR	Fourier Transform Infrared
FTS	Fourier Transform Spectrometry
FYM	Farm Yard Manure
GC	Gas Chromatography
HDPE	High Density Polyethylene
HFC	Hydrofluorocarbon
IPPC	Integrated Pollution and Prevention Control
IPCC	Intergovernmental Panel on Climate Change
Lidar	Light Detection And Ranging
lu	Livestock unit: 500 kg liveweight
NETCEN	National Environmental Technology Centre
NDIR	Non-Dispersive Infrared
NFFO	Non-Fossil Fuels Obligation
N_2O	Nitrous oxide: molecular weight 44
NO_x	Collective term for nitric oxide (NO) and nitrogen dioxide (NO_2)

NMHC	Non-Methane Hydrocarbon
ppb	parts per billion
ppm	parts per million
SF_6	Sulphur Hexafluoride
TDLS	Tunable Diode Laser Spectroscopy
VOC	Volatile Organic Compound

Units

kt	kilo tonne, 1000 tonnes (= 1 Gg)
Gg	gigagram, grams x 10^9
Tg	teragram, grams x 10^{12}

Conversions

N_2O to N_2O-N	x 0.64
N_2O-N to N_2O	x 1.57
CH_4 to CH_4-C	x 0.75
CH_4-C to CH_4	x 1.33

Note

Most of this report was written in 1999 but due to problems associated with the HyMap system the report was not completed till 2001. The report was then released on a restricted basis.

In making this report publicly available some sections of the report have been updated. In addition a number of Agency R&D projects have been undertaken whose topics relate closely to, or arose from the recommendations of, this study. Summary details follow.

1. A feasibility study into the possibility of developing low cost DIAL or passive imaging systems for monitoring landfill emissions from a light aircraft.
   The research contractor, QinetiQ (formerly DERA, Malvern), concluded that both of these approaches were technically feasible but the cost to take either to the working prototype stage was prohibitive. The project was completed in 2002 and an R&D Technical Report was produced (E1-127/TR).

2. The development of a low-cost, passive, airborne methane detector (see Recommendations, point 2).
   This is a collaborative 30-month project (E1-128) involving Spectra-Map, the main contractor, and Reading University, Shell Research and the NPL. It aims to develop an inexpensive instrument for monitoring landfill gas emissions, principally methane, from a light aircraft. The instrument relies of reflected solar infrared radiation as the source and exploits the detection technique of gas filter correlation spectroscopy. To date (October 2003), a laboratory prototype has been successfully demonstrated.

3. Real-time flux modelling (see Recommendations, point 3).
   Progress was made on this R&D project and the electronic modules were developed by the Agency. However, the project failed to reach a satisfactory conclusion as Siemens Environmental Systems was closed by its parent company before the sensors were fully developed. Nevertheless, it may be possible to take this work further in the future as Advantica (formerly British Gas Research) has since taken over the development of the sensors.

Further, although not an Agency-supported project, the "hand-held laser pointer" (effectively a portable, remote methane detector), mentioned in 4.2.6 of this report, has now reached the working prototype stage and has an operational range of ~12 m.

EXECUTIVE SUMMARY

The purpose of this report is to review sources of the greenhouse gases methane and nitrous oxide in the UK, to place Agency-regulated sources in context of the nation's total greenhouse gas releases including agricultural emissions, and to investigate cost-effective methods of monitoring methane releases to the environment.

Although methane and nitrous oxide are both highly important contributors to the global enhanced greenhouse effect, UK nitrous oxide emissions are less significant, and this report concentrates on methane. The major emission sectors are reviewed, namely landfills, agriculture and fugitive fuel emissions. National emission data are derived from calculations of standard emission factors for an activity multiplied by the national usage of that activity rather than by actual measurements, because of the high cost of national monitoring coverage. This theoretical approach can give rise to serious error, as illustrated by on-going revision of the landfill emissions factor which will result in re-ordering landfills from clearly the highest methane emitting sector to less than agricultural releases. National emissions data do not include emissions from the territorial marine environment, neither is there national monitoring of greenhouse gas sink throughputs, although sinks are arguably as important as are sources to the gas concentrations in air.

A review of presently available methane monitoring methods, which were originally developed for landfill applications, shows that no one method is suitable for all applications and a 'tool kit' approach of the best one for each application is recommended. Unfortunately, none of the existing methods is capable of rapid measurements over wide areas.

However, two developing technologies show high potential for very wide area monitoring and temporal monitoring of large areas. Airborne imaging of methane and carbon dioxide was achieved by this project. As far as is known, this is the first time that these two gases have been imaged and the technique has unique and far reaching potential to map accurately greenhouse gas emissions on a national basis. At the moment, there is no suitable equipment in the UK to make airborne imaging a viable operational technique, but a follow-up R&D project is addressing this. A combination of fixed sensors and computerised flux modelling shows promise for continuous monitoring of whole-site releases, and is also being followed up by a current R&D project.

A review of reduction strategies showed than all sectors other than agricultural ruminant fermentation had viable proposals to reduce methane emissions. In fact, present farming trends are leading to an increase in methane production by moving to maize feed.

1.   INTRODUCTION

The greenhouse effect is a natural process in which the atmosphere allows solar radiation through to warm the Earth's surface, but prevents the re-radiated infrared (i.e. heat) energy from escaping to outer space. This process keeps the Earth's surface at least 20°C warmer than it would otherwise be and is thus essential to sustain the environment.

The major greenhouse gas in the atmosphere is water (strictly speaking a vapour rather than a gas). Other significant greenhouse gases are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and a number of hydrofluorocarbons (HFCs). The first three are formed both naturally and from anthropogenic activities, but HFCs are wholly man-made. There is unease over the enhancement of the greenhouse effect because of the increase in anthropogenic greenhouse gases since the industrial revolution, and it is generally accepted that the Earth's surface has warmed by about 0.6°C in the past 140 years as a result of man-made emissions. Furthermore, there is concern that a further increase in global warming could have serious or possibly catastrophic environmental consequences if remedial action is not taken.

The UK has taken a leading position among industrialised nations in its intent to reduce anthropogenic greenhouse gas emissions, and the Environment Agency is committed to assist in ensuring that the Government's reduction targets are met.

Carbon dioxide is generated predominantly from combustion of fossil fuels, and can be regulated by inspection, tax incentives etc; although a mass monitoring technique would be useful as an audit tool. HFCs are being regulated out of the environment by international action as agreed at the Montreal Convention. This report therefore concentrates on nitrous oxide, and especially methane because its major source is landfill waste decomposition, which is directly under the Agency's regulatory control. The potential of Integrated Pollution Prevention and Control (IPPC) regulated intensive agricultural units to emit methane and nitrous oxide is also reviewed.

The objectives of this report are:
(i)   to review sources of greenhouse gas emissions (other than carbon dioxide) in the UK;
(ii)   to place landfill methane emissions in the context of total greenhouse gas releases;
(iii)   to scope the greenhouse gas emitting potential of intensive agricultural operations; and
(iv)   to review methods of monitoring greenhouse gas emissions, with emphasis on methane from landfills.

2.   BACKGROUND

2.1   Greenhouse Effect

The Earth's atmosphere is transparent to a restricted range of wavelengths of electromagnetic radiation, principally visible light plus some adjacent infrared and ultraviolet radiation. Clouds reflect 17% of this radiation back into space, a further 8% is scattered backwards by air molecules and 6% is reflected back into space by the Earth's surface. Of the remaining 69% of incoming radiation, 19% is absorbed in the stratosphere, clouds in the troposphere absorb 4% and 47% is absorbed by the Earth's surface. During absorption, the Earth's surface is heated and re-radiates the resultant thermal infrared energy. Some 69% of the re-radiated energy is lost to space but certain gases in the atmosphere absorb the remaining 31%, which causes additional heating. These atmospheric gases that absorb infrared radiation, and are warmed up in the process, are known as greenhouse gases.

In summary, the Earth's atmosphere lets incoming solar radiation through where it heats the ground, is re-radiated as heat, and the heat is absorbed by greenhouse gases in the atmosphere. This process is illustrated in the following diagram.
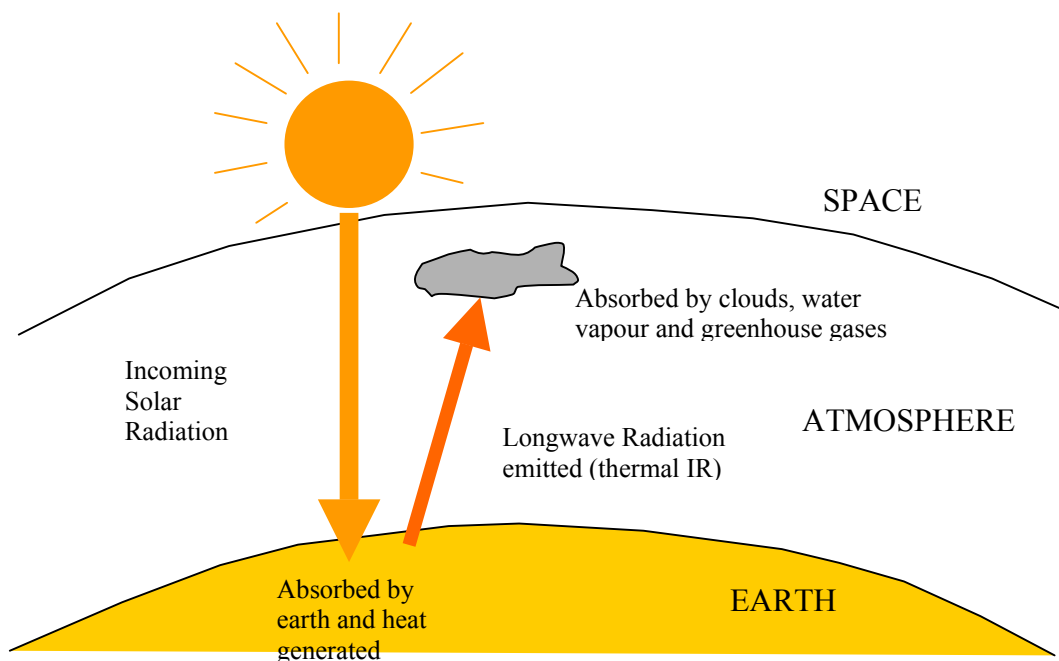
Figure 2.1: The Greenhouse Effect

2.2   Contributing Gases

Table 2.1 gives details of those gases that are considered to contribute to the enhanced greenhouse effect and thus have most impact on climate change.

Table 2.1: Greenhouse Gas Characteristics

Gas	Formula	Concentration (ppm)		Current rate of increase % yr^{-1}	Residence time years	Radiative effect compared with CO_2
		Pre-industrial	Present			
Carbon dioxide	CO_2	280	350	0.4	50-230	1
HFCs	eg $CFCl_3$	0	0.0003	4.0	65-130	>11,000
Methane	CH_4	0.65	1.7	0.9	10-12	30
Nitrous oxide	N_2O	0.28	0.31	0.25	150	200

The major culprit is an increase in carbon dioxide concentration, created largely by the accelerating use of fossil fuels and the removal of important "sinks" as occurs, for example, when tropical forests are felled. Increases in carbon dioxide concentrations are thought to account for some 50% of the currently predicted global warming effects. The major natural sinks for carbon dioxide are photosynthesis and deposition in oceans. HFCs are industrially generated and have been used as aerosol propellants and refrigerants amongst other things; the major sink for their removal is breakdown in the stratosphere. Recent changes in their general use have reduced the potential future impact that this family of gases will have. From Table 2.1, it can be seen that both methane and nitrous oxide have an approximately equal greenhouse effect and, together, account for *c*. 25% of current global warming effects. As seen from Table 2.1, whilst their concentrations are considerably less than that of carbon dioxide, their potency for absorbing long-wave radiation per molecule is substantially greater. The residence time for methane in the atmosphere is around 10 years, whilst that of nitrous oxide is 150 years. The natural sink for methane is chemical removal in the atmosphere by reaction with hydroxide (OH^-) radicals; oxidation in soils is another sink. The major global sink for nitrous oxide is chemical breakdown in the stratosphere. The chemical conversions involved in stratospheric nitrous oxide breakdown also have implications for ozone (O_3) generation in the atmosphere.

2.3   Global Sources of Greenhouse Gases

The sources of nitrous oxide and methane have been reviewed extensively (see Bouwman, 1989; Mosier and Schimel, 1991); in many instances the estimates have been based on relatively few measurements, a synthesis of which has been extrapolated to a global scale. For many of the estimates there are wide ranges of uncertainty; the information shown in Table 2.2, therefore has been, and will be, subject to change over

the next few years as new data become available. Throughout this report, fluxes are expressed on an elemental basis, i.e. either as N_2O-N or as CH_4-C (factors for conversion to a per molecule basis are given in the glossary).

Table 2.2: Major Global Sources of Greenhouse Gas Emissions (from Bouwman, 1989)

Methane (Tg CH_4-C yr^{-1})		Nitrous oxide (Tg N_2O-N yr^{-1})	
Source	Quantity	Source	Quantity
Natural wetlands	30 – 120	Fossil fuel burning	2.0+/- 1
Ruminants	49 – 74	Biomass burning	1.5+/-0.5
Rice production	45 – 105	Oceans & estuaries	2.0+/-1
Biomass burning	41 – 75	Fertilised soils	1.5+/-1
Natural gas exploration	23 – 30	Natural soils	6.0+/-3
Landfills	23 – 53		
Termites	5 – 37		
Coal mining	27		
Oceans & other waters	11 – 27		

3. UK SOURCES OF GREENHOUSE GASES

It has already been noted that the major contributing gas to the enhanced greenhouse effect is carbon dioxide. Within the context of the UK, the majority of the carbon dioxide produced and emitted originates from industrial and energy related activities. Agriculture is considered to be neutral in this respect, with any release generated during farming operations (e.g. from mineralisation of soil organic matter or respiration by animals or plants) being balanced by incorporation into new biomass (via photosynthesis).

This is not the case for methane and nitrous oxide, for which agriculture is considered to be an important and substantial source. Signature of the UN Convention on Climate Change by *c*. 150 nations in 1992 in Rio de Janeiro, indicated widespread recognition that climate change is a major threat to the world's environment and economic development and agreements were set at Kyoto for targets for reductions. As a result of these discussions, nations are required to produce inventories of contributory greenhouse gases in order to establish baseline levels from which the agreed reductions in emissions can be determined. Inventories are already being prepared, and will continue to be so, by each country according to guidelines and protocols defined by the Intergovernmental Panel on Climate Change (IPCC, 1997). The guidelines for inventory preparation allow for either country specific information to be used or, where this is not available, for prescribed defined default values to be adopted. Once inventories have been prepared, these will be the official standard for that particular country. In the meantime, for the purposes of this review, other published reviews and assessments for UK sources of nitrous oxide and methane have been used. Although it is probable that the estimates will change as methodologies and data become more refined and reliable, these provide the most up to date estimates of overall distribution.

Table 3.1: UK Greenhouse Gas Emissions, 1995 (Gg). (Data from National Environmental Technology Centre (NETCEN), 1997)

Source	CH_4-C	N_2O-N
Fuel combustion		
Energy and transportation industries	9.7	5.4
Industry	5.6	1.5
Transport	18.1	5.3
Small combustion	26.3	0.9
Traditional biomass burned for energy	2.5	<0.01
Fugitive emissions from fuels		
Solid fuels	270.7	-
Oil and natural gas	362.3	-
Industrial Processes	-	40.8
Agriculture		
Enteric fermentation	735.7	-
Manure management	92.3	2.2
Agricultural soils	-	4.0
Waste		
Solid waste disposal on land	1312.5	-
Waste water treatment	25.5	-
Waste incineration	1.8	0.3

(With reference to Table 3.1 it should be noted that NETCEN may revise the landfill methane estimate significantly downwards. However, until this is confirmed the above data are taken as correct (ENDS Environment Daily 16/07/99).

Given this constraint, information from NETCEN (1997) shown in Table 3.1 clearly demonstrates the broad distributions of emissions from the major sources in the UK. There will be other contributions of both gases from other sources, but by and large these will be small relative to the overall fluxes. As far as methane is concerned, UK emissions can be divided into four major groupings: fuel combustion, fugitive emissions, agriculture and waste management (which in the main refers to disposal of waste in landfill sites). Figure 3.1, below, indicates the overall distribution of emissions between these sources.
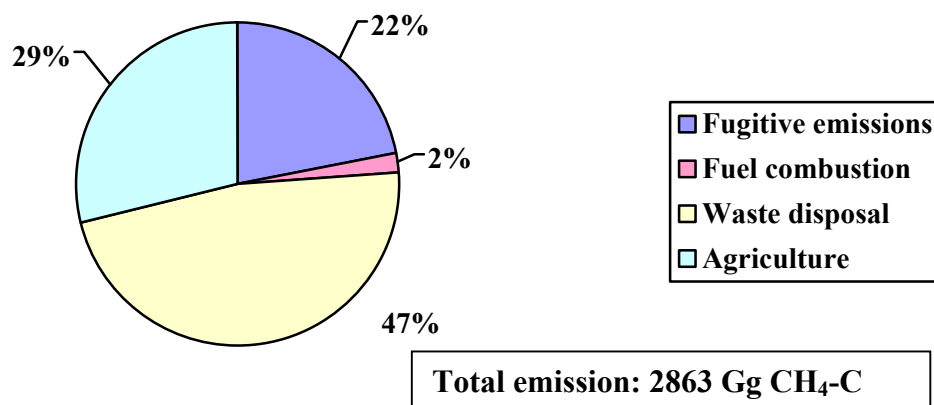
Figure 3.1: Distribution of Major Methane Sources in the UK

There will be other emissions from other components of the landscape, particularly from peats, bogs and wetlands and other natural sources; an earlier review (Williams, 1993) estimated this to be 77 Gg CH_4-C (2.4% of the total emission calculated at that time). Estimates are very uncertain and the methodologies for estimation will be subject to change as ongoing research is completed, but the general pattern shown in Figure 3.1 is similar to that in other estimates (for example, Williams, 1993). The largest emission is that from landfill sites but the information for this is also one of the most uncertain (this will be discussed in Section 3.2). This source is likely to decline as changes in landfill use occur as the result of recent legislative requirements to restrict filling and to implement methane recovery systems. Furthermore, the national estimate from this source is presently under review by NETCEN and may be revised downwards.

Soils can act as a sink for methane when they are in an oxidative state, and a range of consumption values of 0.0751-5.18 mg CH_4-C m^{-2} d^{-1} has been suggested (Tyler *et al.*, 1994; Goldman *et al.*, 1995; Boeckx *et al.*, 1997). If the entire managed land surface of the UK removed methane at the suggested upper rate, this would account for 377 Gg yr^1, i.e. nearly 10% of the national budget (NETCEN, 1997). At the lower rate, the sink

would be 5.5 Gg, i.e. less than 0.2% of the total emission. Further, many soils can also act as a source under anaerobic conditions and this would lessen the national impact further. It therefore seems likely that the net effect of agricultural soils is to play only a minor role in the overall budget of emissions in the UK.

There is an even greater level of uncertainty attached to the estimates of nitrous oxide emissions: there are many small sources, both natural and anthropogenic, which have not been quantified. The main sources shown in Table 3.1 indicate the current domination of emissions from adipic acid manufacture (a feedstock for nylon) and the production of nitric acid which together contribute 67% of the UK total in 1995. Agricultural sources of nitrogen are substantial and, proportionately, will become more important as the industrial sources are reduced.

Agricultural management provides by far the greatest emissions of nitrous oxide from UK land surfaces: there is also a background low emission from natural ecosystems which are in unpolluted areas (i.e. those not subjected to major depositions of anthropogenically derived combined nitrogen). As an example, those for upland grassland/moorland areas are of the order of 0.06 to 0.31 kg N_2O-N ha^{-1} yr^{-1} with a total estimated UK emission of 0.6 Gg N_2O-N yr^{-1} from unmanaged, compared with 15.2 Gg from managed, grasslands (Fowler *et al.*, 1997).

3.1   UK Sources in Global Context

The global picture (Tables 2.1 and 2.2) shows methane and nitrous oxide to have an approximately similar greenhouse impact and collectively to contribute about one third as much as carbon dioxide does to the enhanced greenhouse effect. The major global sources of methane are wetlands, ricefields and ruminants; and the major global sources of nitrous oxide are natural soils, fuel burning and eutrophic estuaries and oceans. Furthermore, since both carbon dioxide and methane arguably have greater potential for reduction by constraining anthropogenic generation, nitrous oxide may one day become the major enhanced greenhouse gas. The UK picture is very different from the global one. Nitrous oxide is a less important greenhouse gas because of the UK's small land area and lack of eutrophic estuaries (cf global). Its chief UK source is industrial emission, which is in the process of regulation, with fuel combustion and agriculture as the other significant sources. UK-generated methane is an important greenhouse gas but, in contrast with the global picture, its major sources are landfills, agriculture and fugitive fuel emissions (i.e. coal mines and natural gas leakage).

3.2   Landfill Sources

Landfill gas is generated from the bio-degradation of the organic fraction of landfilled waste. Under the conditions prevalent in most modern landfill sites these bio-degradation processes are predominantly anaerobic and give rise to landfill gas; this gas contains between 40% and 60% methane with the balance being predominantly carbon dioxide, plus trace concentrations of various non-methane hydrocarbons (NMHC).

There is now significant concern about the environmental impact of methane and NMHC emissions from landfill in addition to the greenhouse effect enhancement, as follows:

- Possible carcinogenic effects of some NMHCs. Some studies of the trace components of landfill gas have identified low concentrations of carcinogenic compounds such as benzene (Scott, 1988; Milton, 1996).

- Unpleasant odour of some NMHCs and sulphur-containing compounds in landfill gas.

- Formation of asphyxiant atmospheres as a result of the very low oxygen content of landfill gas.

- Production of tropospheric ozone from reactions between NMHCs and nitrogen oxides (largely emitted from vehicles). Although the photochemical generation of ozone is a slow process which is not usually associated with local sources, emission of NMHCs from landfill make a contribution to national emissions.

A recent trend in landfill site management has been to exploit the energy potential of landfill gas through electricity generation schemes. Such schemes have been selected for support by the Government's NFFO (Non-Fossil Fuels Obligation) programme. The development of sites for their methane potential has changed the way that sites are operated. This raises the possibility that sites designed to maximise methane combustion may give rise to more fugitive emissions. Further discussions of this important issue are outside the objectives of this report.

Modern landfill practice is that industrial, commercial and domestic waste is placed together in a void and compacted. The compacted waste is then covered with layers of soil or clay or other materials, usually at the end of each day. The process continues until the available space is full at which time the waste is capped with an impermeable layer of either natural material (clay) or artificial textile (HDPE).

Studies of the biological decay processes within a landfill site show that a series of different processes occur involving different bacteria. Initially, the waste decays anaerobically as a result of bacteria which hydrolyse complex biological polymers into smaller molecules. The products of hydrolysis then decay by the action of acetenogenic bacteria into acetic and other fatty acids. In the anaerobic conditions within a landfill, these acids accumulate within the leachate and then decay through the action of methanogenic bacteria to form methane.

It may take several years before the decay processes reach the stage of methanogenesis. After a further period of time, the increase in the decay processes will become limited by the supply of suitable material, at which point the rate of generation of methane will decay exponentially for between 5 and 50 years.

3.3 Agricultural Sources

Because of the current activities in generating national inventories for nitrous oxide and methane, information and data synthesis for both these gases is under a constant process of change and update. A number of new research projects have recently started which will supply new and more reliable information from which more confident estimates may be made. For the present purposes so that future comparisons may be made, the current divisions and definitions as specified by the current IPCC protocols (IPCC, 1997) are used. The following is a brief description of the specific sources for each of the two gases and the mechanisms and controls over their generation.

3.3.1 Agricultural methane sources

Enteric fermentation

By far the greatest source of agricultural methane is enteric fermentation in the rumen of ruminant animals. Ruminants ingest large amounts of fibrous carbohydrate plant material, which is subjected to intensive digestive breakdown processes into simpler carbohydrate products for absorption and utilisation by the animal. This process is conducted by a large and complex microbial population, with the rumen acting as a large fermentation vessel. The pathways of carbohydrate breakdown (shown below in Figure 3.2) result in the generation of, amongst other things, considerable volumes of methane which are emitted from the animal via eructation or in breath. Published data indicate the large amounts that may be emitted through this mechanism, i.e. 75 and 6 kg CH_4-C per head per year from for dairy cows and sheep, respectively (IPCC, 1997). Although this process is a particular feature of ruminant digestion so that they can utilise the large quantities of cellulose that they ingest, some non-ruminant animals (e.g. horses, pigs) also produce methane, but the volumes are small compared with that generated by the ruminant population of the UK.
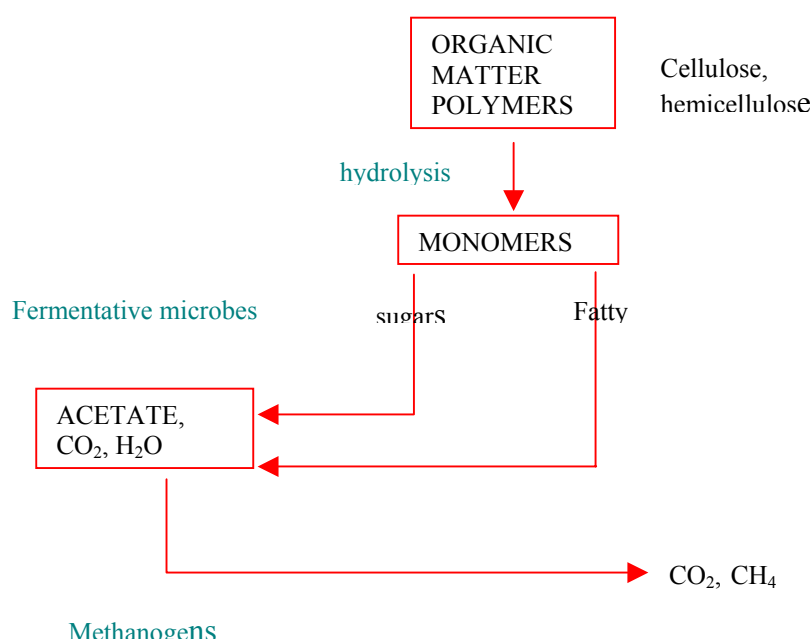
Figure 3.2: Methane Generation by Ruminants

The quantity of methane that is released depends on the type, age and weight of the animal, the quality and quantity of the feed, and the energy expenditure of the animal. Because of their numbers, the dairy and sheep herds of the UK provide the majority of the methane emitted by agriculture. Using the IPCC default emission values of 75, 36 and 6 kg CH_4-C per head per year for diary and non-dairy cattle and sheep, respectively, this gives a total value of nearly 771.9 Gg for the 2.5, 9.1 and 42.8 million herds, respectively. This accounts for the majority of the rumen emissions in Table 3.1 (These are simple calculations, based on IPCC 'Tier 1' methodology: for the purposes of the calculations at the farm scale, we have used a more comprehensive approach that takes account of animal size, intake and quality). A number of recent studies (e.g. Lockyer and Jarvis, 1995) have placed effort in obtaining measurements from grazing animals where feed availability, quality and intake patterns may be sufficiently different to influence the production of methane. Figure 3.3 shows the measurement system that provides an integrated spatial measurement of complete grazed sward system with a fine time resolution (this system has applications for other measurements of methane where there is spatial and temporal variability, for example landfill sites).

Figure 3.3: IGER Tunnel System for Providing Integrated Methane Measurements over the Larger Scale

Manure management

Methane is also generated from the more volatile components of animal manures as these decompose under anaerobic conditions: microbial activities are again responsible for the generation of methane from this source. The circumstances under which this can occur are particularly when animals are in confined conditions and where their excreta are accumulated or stored. Manure stored under anaerobic conditions has a high potential for loss. Biogas production from agriculture is increasing in Europe with an increasing interest in co-fermentation of organic wastes. Co-fermentation of organic wastes and animal manures increases gas yield and offers an environmentally friendly alternative to landfilling of organic wastes. However, amounts and quality of the added organic wastes have to be carefully monitored to guarantee a safe operation and good quality biogas. Addition of 850 kg of pure fat to 600 t of fermentation substrate (80%

cattle slurry; 20% food waste) resulted in an increase of the methane yield from 31.3 to 54.0 m^3 h^{-1} (Amon *et al.*, 1998).

The principal factors affecting methane generation from manures are the amounts produced and that part that decomposes anaerobically (in the absence of oxygen) by methanogenic bacteria which will be part of interrelated populations of micro-organisms. The component that may decompose anaerobically is dependent on how the manure is collected and stored. Manures stored as a liquid slurry (e.g. in lagoons, ponds or storage tanks) are assumed to have a greater potential to decompose anaerobically and produce a significant amount of methane than when they are collected and stored as a solid (e.g. farmyard manure (FYM)), although recent work (Chadwick, personal communication) indicates that the difference may be small. Dung deposited in the field while animals graze also has some potential for methane generation as does spreading manure on land, but in practice the amounts emitted are very small (Jarvis *et al.,* 1995; Chadwick and Pain, 1997, respectively). A simple emission factor (EF) has been given by IPCC for default calculations. The IPCC Tier 2 methodology relies on estimates of volatile solids excreted: this information is usually not available so this factor is generally calculated from a knowledge of intake levels for each animal type. For our discussions of a typical intensive pig production unit (Chapter 4) we have used recently obtained data (Chadwick, personal communication) from recent experimental measurements to construct a more comprehensive picture of the impact of livestock manures and their management on methane emissions.

Other sources and sinks

As noted in Chapter 2, soil can act as a sink for methane when aerobic conditions prevail but this is likely to have only a relatively small impact on the overall national budget. In fact, many managed soils can act as both sinks and sources (Figure 3.4), so any generalised sink effect is likely to be smaller rather than greater than the rate suggested above. Additionally, the impact of ammonia-based fertilizer leads to a reduction in methane oxidation capacity through competitive effects within the soil microbial biomass (Hutsch *et al.,* 1994; Steudler *et al.*, 1989).
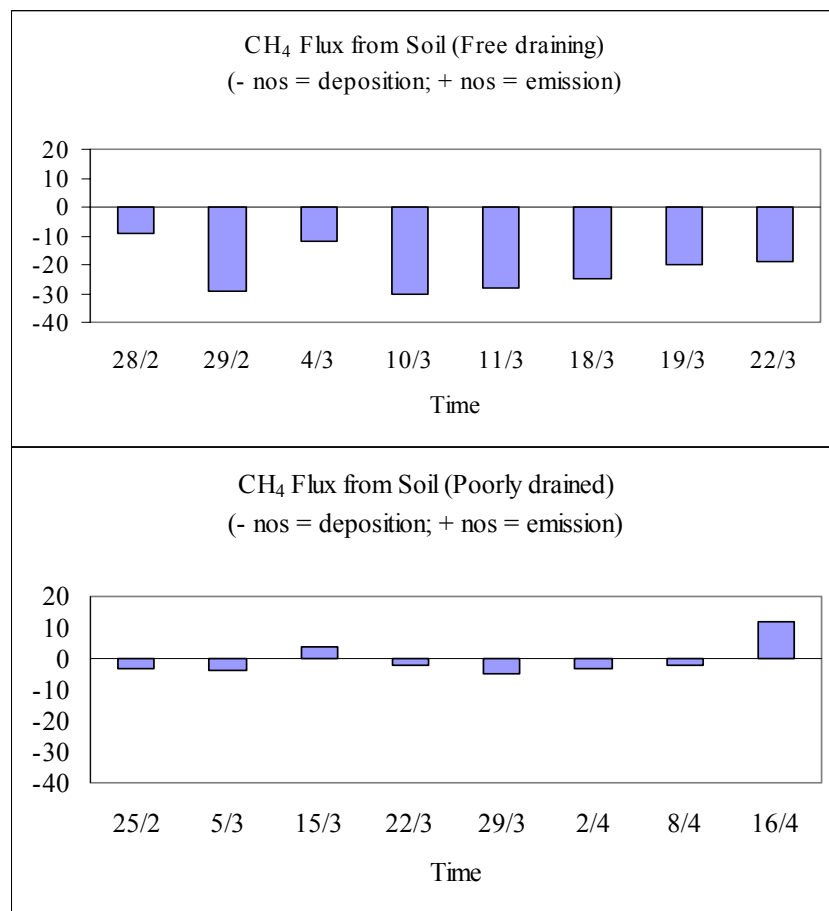
Figure 3.4: Methane Exchanges with Grassland Soils, μg CH_4-C m^{-2} h^{-1}

3.3.2 Nitrous oxide sources

Microbial generation

Nitrous oxide is also generated by microbial processes. IPCC identifies three major sources within an agricultural context, (i) direct emission from soils, (ii) from animal production (which also includes emissions from their housing) and (iii) emission indirectly induced by agricultural activities. Anthropogenic impact on the increase in nitrous oxide emission from agriculture has come about through enhanced rates of biogenic processes in soil. This arises primarily through two microbial processes, those of nitrification and denitrification. These are shown below (Figure 3.5) and are important components of nitrogen cycling, transforming inorganic ionic forms of nitrogen into gaseous compounds. Denitrification is an important global process, returning 'fixed' forms of nitrogen back to the atmospheric nitrogen pool.

NITRIFICATION

$$\text{mineralization, excreta, fertilizers, deposition} \Big\} \longrightarrow NH_4^+ \quad \nearrow N_2O + NO_x \quad NO_2^- \quad \nearrow \quad NO_3^-$$

Soil colloids

DENITRIFICATION

$$\text{nitrification, fertilizers, deposition} \Big\} \longrightarrow NO_3^- \longrightarrow NO_2^- \longrightarrow N_2O \longrightarrow N_2$$

Figure 3.5: Nitrous Oxide Generation Processes in Soil

In brief (for a more comprehensive description of nitrification and denitrification see Blackmer and Bremner, 1978 and Anderson and Levine, 1985, respectively), nitrification is the aerobic oxidation of ammonium (NH_4^+) (supplied from soil mineralisation processes, additions of excreta, fertilizer inputs and atmospheric deposition) to nitrate with the evolution of nitrous oxide (and small volumes of NO_x gases) as the result of some of the intermediary biochemical processes conducted by the microbial populations involved. Denitrification is the anaerobic reduction of nitrate (NO_3^-), ultimately to nitrogen (N_2) gas, but with nitrous oxide as an intermediate product (Figure 3.5). The ratio of $N_2:N_2O$ emitted is highly variable and depends upon a range of factors. Major regulators of both processes are temperature, pH and soil moisture (dry soils = aerobic conditions and nitrification; wet soils = anaerobic conditions and denitrification). Both processes are highly variable under field conditions and although there is a vast literature on both processes, prediction of emissions is difficult and has a high degree of uncertainty. Less is known about nitrous oxide emissions from nitrification, but this is usually considered to be a lesser source. Some chemical denitrification can occur un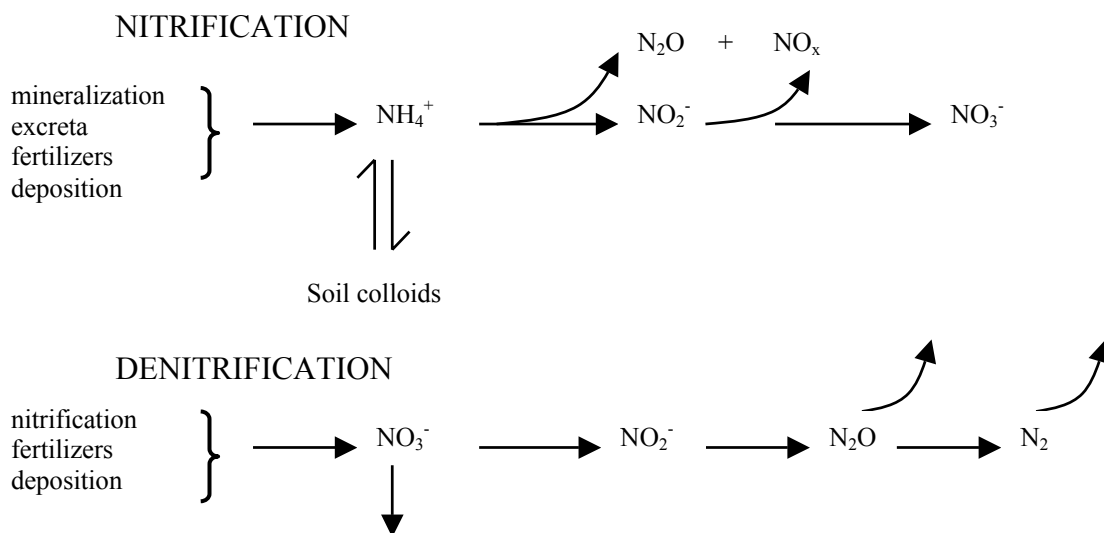der specific conditions but in most circumstances this makes a minor contribution. Most denitrification occurs in the top soil, but there is potential for denitrification to occur at depth in the profile (Jarvis and Hatch, 1994). If this generates nitrous oxide, then this will contribute to the indirect agriculturally derived sources (see below).

Nitrous oxide generation takes place in all soils, but is enhanced by an increase in available mineral nitrogen, which in turn increases nitrification and denitrification rates. Addition of fertilizers therefore increases this potential. There has been a large volume recently of published literature on this and many other aspects of effects on emissions of N_2O; viz. fertilizers (Yamulki *et al.*, 1998), manures and slurries (Chadwick, 1997; Sommer *et al.*, 1996, Comfort *et al.*, 1990; Paul *et al.*, 1993), spatial variability (Velthof *et al.*, 1996) measuring techniques (Jarvis, 1998) as well as the close examination of process controls (Scholefield *et al.,* 1997).

As well as fertilizer and manurial effects, increases in production that depend upon enhanced levels of biological fixation (via legumes) also supply additional nitrogen to agricultural systems which increase the potential to denitrify.

IPCC direct sources from agricultural soils

The following have a direct effect on nitrous oxide emissions and contribute to the calculation for this sector of the IPCC methodology.

(i)   Synthetic fertilizers, climate, soil, fertilizer placement, fertilizer type and other background management effects all influence the rate of emission. An overall emission factor (EF) of 1.25% is used by IPCC as the default value, although the range encountered in UK soils is very large (Brown *et al*., personal communication).

(ii)   Animal excreta used as manure. Estimates are made of emissions using the same EF as for synthetic fertilizers after taking into account the large prior loss of ammonia that will take place from manures.

(iii)   As well as applied manures, excreta is deposited onto fields whilst animals are grazing. Dung and urine patches provide powerful sources of nitrous oxide (Allen *et al*., 1996; Yamulki *et al*., 1998). IPCC calculates these effects separately but includes this estimate in with the total direct soil emissions.

(iv)   Biological fixation. As currently defined, this component is considered not to have much relevance to UK conditions: relatively small areas of land are involved in growing crops (pulses etc). This section does not include nitrous oxide produced in legume based pastures which is considered to at least be partially accounted for within the grazing calculation.

(v)   Glasshouse crops receive high fertilizer additions, but there are few data from which to generate an EF. IPCC does not consider these emissions separately, but includes them within the total fertilizer usage within each country.

(vi)   Large emissions can occur as the result of the cultivation of organic soils. The range suggested for the EFs is from 2-15 kg N_2O-N ha^{-1} yr^{-1}. For UK conditions, the suggested default value is 5 kg N_2O-N ha^{-1} yr^{-1}. Again in the UK, the overall effect is likely to be small because of the relatively small areas of organic soils.

(vii)   Crop residues and sewage sludges applied to agricultural land are also included within the direct soil category.

Nitrous oxide from animal production

The impact of excreta deposited during grazing and that which results from manure application to land has already been discussed and is included in the direct sources from soils category. Production of nitrous oxide during storage and treatment of animal wastes can occur via both nitrification and denitrification of ammoniacal nitrogen contained within the wastes. The extent of this will depend upon the ammonium content of the excreta (and this is dependent upon the return of excretal nitrogen in urine: the partitioning of excess nitrogen to urine increases as the nitrogen intake in the diet increases). As the first step in the generation of nitrous oxide is nitrification, this process forms a rate-limiting step to the generation of nitrous oxide. Increased aeration therefore enhances the potential for nitrous oxide to be emitted by removal of nitrous oxide before conversion to nitrate. Because of the lack of data the values for EFs

suggested by IPCC are listed as tentative and range from 0 for daily spreading systems to 0.02% of nitrogen excreted for solid storage systems (Table 3.2). These compare with more recent data obtained by Chadwick *et al*. (1999a). Emission factors for slurry stores were also zero but an average of 0.53 g N_2O-N was emitted per cubic metre of solid manure per day. Assuming an 85-day storage period and a total nitrogen content of 5 kg m^{-3}, the total emission rate could represent 1.25% of the total nitrogen.

Table 3.2: Default IPCC Emission Factors for Key Agricultural Sources of Nitrous Oxide in UK (from IPCC, 1997)

Sector reporting	Source	Efs
Direct soil emissions	Fertilizers Manures	EF_1= 0.0125 kg N_2O-N kg^{-1} N applied
	Cultivation of organic soils	EF_2 = 5 kg N_2O-N ha^{-1} yr^{-1}
	Grazing	EF_3 = 0.02 kg N_2O-N kg^{-1} excreted
Indirect Agricultural Sources	Deposited NH_3/NH_4^+	EF_4 = 0.011 kg N_2O-N per kg^{-1} NH_3-N and NO_x emitted
	Leached and runoff nitrogen	EF_5 = 0.025 kg N_2O-N kg^{-1} N leached (considered to be 30% of N applied)
Manure (waste) management		EF_3=
	Anaerobic lagoons	0.001kg N_2O–N per kg^{-1} N excreted
	Liquid systems	0.001 "
	Daily spread	0
	Solid storage	0.020 "

Nitrous oxide from indirect agricultural sources

Nitrogen derived from agricultural sources and transferred from the farm is also considered to be an important source of nitrous oxide that is assigned to the agricultural sector. Recent calculations (Brown *et al.,* personal communication) indicate that, for the UK, this provides an apparent large emission (over 30% of the total agricultural emission), but which has a very high degree of uncertainty (unquantified) attached to it. The main contributing sources for this are firstly the ammonia (and NO_x) originating from agricultural activities and then deposited onto soil and the re-entering the nitrogen nitrification and denitrification sequence. Secondly, the nitrogen leached from

agricultural management can enter groundwaters, riparian areas and wetlands, lakes and oceans. This may then be denitrified with a consequent emission of nitrous oxide. There are few data available for both of these sources with which to add some assurance to emission factors.

There have been several recent estimates of agricultural nitrous oxide emissions from the UK, all using slightly different approaches. These are summarised in Table 3.3 and indicate the wide range of uncertainty that is attached to these estimates. Current projects conducted by IGER and collaborators are seeking to develop an improved, more robust methodology to estimate nitrous oxide emissions over a range of scales.

Table 3.3: Estimates of UK N$_2$O-N Emissions from Agriculture

Reference	Estimate per year	Comments
NETCEN (1997)	6.2 Gg	Total UK emissions 61 Gg
HMSO (1994)	10.7 Gg	Omits outdoor and indoor livestock, manure stores
Chadwick *et al.*(1999a)	24.5-30.9 Gg (±50%)	Direct emissions from farmed livestock (including fertilizers and grazing)
Armstrong *et al.* (1996)	65.9 Gg	From farmed livestock
Fowler *et al.*(1997)	16.2 Gg	From grassland only
Brown *et al.* (personal communication)	*c.* > 64 Gg	Uses IPCC default methodology

3.4   Fugitive Emissions From Fuels

3.4.1   Solid fuels

Globally, coal is thought to be responsible for some 10% of anthropogenic methane emissions. Table 3.1 estimates that in the UK fugitive emissions from solid fuels equated to 270.7 Gg in 1997. Major sources are deep coal mines, open cast coal mines and coal storage depots. For example, in 1997 deep mined coal generated 278 Gg methane, coal storage and transport generated 35 Gg, domestic coal use generated 21 Gg and open cast mining generated 6 Gg (source: NETCEN website). This is consistent with reports from CISRO Australia that methane emission is greatest in deep mine seams, but that up to 40% of the methane may still reside within the micropores of coal at the crushing and cleaning stage.

3.4.2 Oil and natural gas

Table 3.1 estimates that 362.3 Gg methane was emitted from oil and natural gas sources in the UK in 1997. The Health and Safety Executive publishes annual offshore hydrocarbon releases statistics (such releases are notifiable under Health and Safety regulations), and they indicate offshore drilling releases to be low. However, the NETCEN website estimates offshore flaring to have generated 22 Gg methane in 1997, offshore gas and oil releases total 70 Gg, whereas gas leakage from installations and pipework generates 348 Gg.

3.5 Fuel Combustion

Table 3.1 gives a breakdown of methane and nitrous oxide emissions from fuel combustion, broken down into the following categories: energy and transportation, industry, transport, small combustion and biomass burning. The totals of 63 Gg of methane and 13 Gg of nitrous oxide for 1997 are relatively minor. However, it is worth noting that vehicles fitted with catalytic converters to reduce the higher nitrogen oxide emissions produce significant amounts of nitrous oxide emissions through incomplete catalytic reduction.

3.6 Integrated Pollution and Prevention Control (IPPC) Implications

3.6.1 IPPC requirements

The pig and poultry (P&P) sector of intensive livestock units will be brought into IPPC regulation in 2003/04. Also, the Acid Emissions Protocol will require information on ammonia emissions from all sources, with no sectoral restriction. The principal gaseous pollutants to air from P&P farms are methane, nitrous oxide and ammonia. Methane emissions from grassland are excluded from IPPC reporting, but all agricultural sources of ammonia are relevant to the Acid Emissions requirement.

3.6.2 Agricultural systems approach to estimate emissions

It is essential, in order to aid the assessment of policy requirements and their future developments, to provide emissions national budgets. However, the operational managerial unit for agricultural function is the farm, and in order to provide measures of effectiveness of current or future management, analysis and synthesis at this scale is very important. Once this has been done, the information provides a valuable tool for comparison with other sources at the local scale. For this reason, in this review we have synthesised information at the farm scale using, as far as possible, EFs for the relevant components of the system which have been obtained recently and which are relevant to UK conditions. These are compared wherever appropriate with estimates based on IPCC default values.

For the present review, we have chosen three defined farming types, an intensive dairy unit, an intensive pig production unit, and an arable/tillage farm to make estimates of methane and nitrous oxide emissions. This approach has been used previously to assess effects for a typical dairy farm (Jarvis and Pain, 1994) for nitrous oxide and methane,

and to examine the impact of some managerial changes (Jarvis *et al.,* 1996) for nitrous oxide and methane and specifically for methane (Jarvis and Moss, 1994).

3.6.3 The intensive dairy farm

Intensive animal production systems have been identified as important sources of pollutants. Previous desk studies have made estimates of their likely impact on emissions both as nitrate and the other N losses (Jarvis, 1993) and also for specific emissions of methane and nitrous oxide (Jarvis and Pain, 1994; Jarvis and Moss, 1994). Managed grassland is an important component of the UK landscape (see Figure 3.6) and represents an important emission source of greenhouse gases. We, for the purposes of this review, present information from these sources and also provide an updated estimate using recently obtained local emission factors appropriate to this system. We have used the same ''model'' farm description as described by (Jarvis, 1993) and used by Jarvis and Pain (1994). Table 3.4 shows some characteristics of the farm and its management. This dairy farm represents a relatively intensively managed farming system under conditions that are typical for this agricultural type.
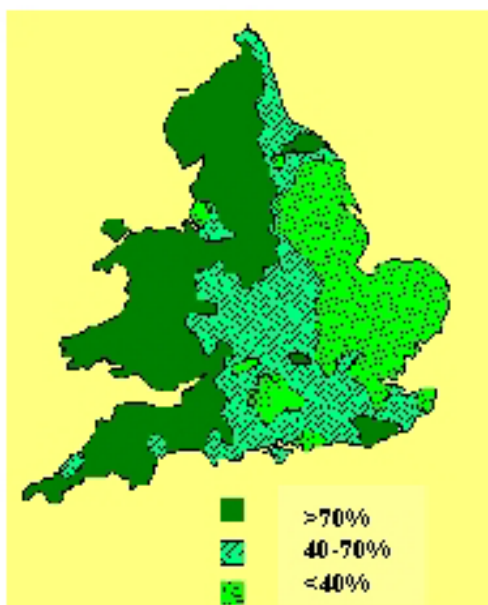
Figure 3.6: The Proportion of Agricultural Land under Grass

Desk study/systems analyses have to rely on a number of broad assumptions because of the nature of the processes involved and the uncertainty attached to the available data. Jarvis and Pain (1994) considered only two major sources for nitrous oxide on this farm, i.e. from (i) fertilized grazed swards with denitrification in the soil resulting from fertilizer and dung/urine deposition and (ii) slurry returned to land. They assumed that a fixed proportion of denitrification products would be nitrous oxide. This simple approach provided an average emission of 14 kg N_2O-N ha^{-1} over the whole farm on an annual basis (Table 3.5). Using the emission factors given in Table 3.2, and including indirect as well as direct sources, gives an overall farm loss of N_2O-N of 813 kg, or 11 kg ha^{-1}. As noted earlier, the degree of uncertainty attached to these numbers is large.

Table 3.4: Characteristics of Typical Dairy Farm (from Jarvis, 1993)

Land use	76 ha grazed and cut swards
Soil type	Loam/clay loam
N fertilizer	250 kg N ha^{-1}
Total annual N input to the farm	25.6 t
Cattle	102 cows ⎫ 165 LU*
	110 other cattle ⎭ total
Feed: Silage	393.5 t
Concentrates	129.4 t
Milk yield	5554 l per cow
Wastes:	
Slurry	1693 m^3
Dirty water	670 m^3
Silage effluent	198 m^3

* Livestock Unit

Table 3.5: N_2O-N and CH_4-C Emissions for Dairy Farms (from Jarvis and Pain, 1994)

Source of loss	Kg N or C ha^{-1}	Total farm N or C, kg
(a) Nitrous oxide		
Fertilizer + grazing excreta	11	844
Slurry application	3	205
Total	**14**	**1,049**
(b) Methane		
Ruminant enteric fermentation	89	6,775
Stored slurry	30	2,285
Silage effluent	34	2,596
Dirty water	4	332
Total	**158**	**11,988**

A similar simplistic approach was taken for methane, in this case four major sources were recognised: enteric fermentation; stored slurry; silage effluent and dirty water. The total farm emission in this case was nearly 12,000 kg C (equivalent to *c*. 158 kg C ha^{-1}) (Table 3.5). An up-dating of the estimate for methane was carried out by Jarvis and Moss (1994) which included some amended emission factors as well as consideration of some additional features. The latter, i.e. dung excreted in the field (see Jarvis *et al,* 1993) and the exchanges with the soil (see Figure 3.5) both had only a

minor impact on the overall total for the system. The updated estimate by Jarvis and Moss indicated that the total CH_4-C emission from the farm was 18,012 kg (equivalent to 237 CH_4-C ha^{-1}). Using the default IPCC values for enteric and manure emissions for this farm resulted in a very similar overall total emission from the farm of 18,561 kg CH_4-C (equivalent to 244 kg C ha^{-1}).

Another recent desk exercise examined the impact of changing on-farm nitrogen management on various emissions, including nitrous oxide and methane. The prime objective of the managerial changes were to reduce nitrate produced (Table 3.6), but effects on other pollutants were also considered.

Table 3.6: Impact of Changes in Nitrogen Management on N$_2$O-N Emissions from a Dairy Farm (from Jarvis *et al.*, 1996)

Management	kg N$_2$O-N			
	Per ha	Per lu*	Total	% reduction
1. As in Table 3.5	13.8	6.4	1049	-
2. Improved tactical fertilizer use + injected slurry	7.9	3.7	600	43
3. Fertilizer N replaced with biologically fixed N (clover)	6.8	3.9	520	50
4. Grass silage substituted with maize silage	3.9	2.3	300	71
2 and 4 combined	6.3	2.9	480	54
3 and 4 combined	5.7	3.3	430	41

* livestock unit

3.6.4   The intensive arable farm.

The emissions from an arable system based only on cereal production are much more straightforward. Under most circumstances, there will be no significant methane sources on the farm, unless manures are brought into the system. We have indicated earlier that aerated soils can act as a sink for methane: using the range of values quoted this means that a cereal farm of 300 ha on a freely draining soil, in the eastern part of the country, could remove between <0.3 to 18.9 kg CH_4-C yr^{-1} from the atmosphere. The potential to meet this capacity would be determined by temperature, soil moisture status, soil nitrogen status as well as other factors.

Nitrous oxide emitted from this farming system would largely be determined by the fertilizer inputs. Using the IPCC default value, and an assumed fertilizer application rate of 180 kg ha^{-1} (as would be typical for winter wheat production), there would be a

direct annual loss of 675 kg and an indirect loss (ascribed in this case to only that leached from the farm) of 405 kg N_2O-N from the farm, i.e. equivalent to 3.6 kg N_2O-N ha^{-1}). This compares with the loss of 11 kg N_2O-N ha^{-1} from the dairy farm.

3.6.5 The intensive pig unit

The model pig enterprise falls under the EU Directive (No. 96/61/EC) on Integrated Pollution Prevention and Control (IPPC) which was formally introduced on 24th September 1996. Implementation of the Directive was due to start in all member states by 30 October 1999 for all new installations. It aims to reduce polluting emissions to air, water and land from industrial processes in the EU, including installations for intensive rearing of pigs with more than 2000 places for production pigs (> 30 kg), or 750 places for sows. The model pig unit is described in Table 3.7 The pig unit comprised 240 sows with all progeny produced for bacon.

Table 3.7: Pig Numbers and Manure Output as Slurry and Farm Yard Manure (FYM) (data from MAFF, 1997)

Type	No.	Average animal weight (kg)	Fraction on slurry	Fraction on straw	Slurry output per animal t/animal/year	FYM output per animal t/animal/year
Lactating sows	40	250	0.66	0.33	2.00	3.00
Dry sows	200	250	0.50	0.50	2.00	3.00
Piglets	450	5	0.66	0.33	0.40	0.60
Weaners	400	15	0.95	0.05	0.55	0.82
Growers	600	30	0.85	0.15	1.46	2.19
Finishers	1200	65	0.85	0.15	1.46	2.19
Maiden Gilts	40	120	0.10	0.90	1.97	2.95

We have used emission factors for nitrous oxide and methane as recently measured under UK conditions (Chadwick, 1998; Chadwick *et al.*, 1999b). Manure storage times were based on farming practice. The EFs were those measured from manure spreading for pig slurry and pig FYM applied to grassland at 50 m^3 ha^{-1} (slurry) or 50 t ha^{-1} (FYM), respectively. We have assumed that EFs for the spread manure are the same for arable land as they are for grassland.

Total direct losses of methane and nitrous oxide from the pig farm were 15.7 t yr^{-1} and 102 kg yr^{-1} for CH_4-C and N_2O-N, respectively (Table 3.8). No nitrous oxide emissions due to nitrogen fertilizer applications or methane oxidation have been included.

Table 3.8: Losses of CH$_4$-C and N$_2$O-N from a Model Pig Unit

	Methane				Nitrous oxide			
Buildings	Slurry EF g lu^{-1} d^{-1}	FYM EF g lu^{-1} d^{-1}	Slurry loss kg	FYM loss kg	Slurry EF G lu^{-1} d^{-1}	FYM EF g lu^{-1} d^{-1}	Slurry loss kg	FYM loss kg
	125	9-66	10985	1565	0.26	0.26	22.6	9.0
Stores	Slurry EF g m^{-3} d^{-1}	FYM EF g m^{-3} d^{-1}	Slurry loss kg	FYM loss kg	Slurry EF G m^{-3} d^{-1}	FYM EF g m^{-3} d^{-1}	Slurry loss kg	FYM loss kg
Assuming 76 d slurry 85 d FYM	27	7.5	2345	728	0	0.16	0	15.5
Spreading	Slurry EF g m^{-3} d^{-1}	FYM EF g t^{-1} d^{-1}	Slurry loss kg	FYM loss kg	Slurry EF g m^{-3}d^{-1}	FYM EF g t^{-1} d^{-1}	Slurry loss kg	FYM loss kg
50 m^3 ha^{-1}	4.2	36.7	11.9	42	17.7	4.6	50.0	5.2
Sub-total			13342	32335			72.6	29.8
TOTAL	kg yr^{-1}			**15677**				**102**

4   METHODS OF REDUCING EMISSIONS

4.1   Landfill

Preventing the escape of landfill gas is one of the most complex challenges in effective site design. Following its generation in areas within the site where bio-degradation is underway, landfill gas migrates through the site until it reaches the capping layer or the sides. It will then escape through any flaws in the cap or the sealing at the edge of the site. In the absence of any gas control system, any positive pressure that builds up will be relieved in this way. On sites where particular hazards due to gas migration have been identified, passive gas migration controls are often installed. These may consist of trenches or vent holes that limit migration in particular directions.

Since the early 1980s it has usually been a licence condition that landfill site operators install some form of gas collection system. This usually consists of wells sunk into the waste connected through pumps to a flare. In some cases methane is used to generate electricity; in these cases any surplus gas, or any gas collected when the generation system is not in operation, will also be flared.

Assessing the relative influence of different escape routes for landfill gas from a site is one of the most difficult aspects to monitoring emissions. As is highlighted in the review of different methods, some methods only measure gas escaping by a particular route. If such methods are used to estimate emissions from the site as a whole, they may give an unrepresentative picture.

As noted earlier, landfill sites are an important source of methane generation. There seem to be two major options where landfill is the mechanism of disposal, either (a) to encourage the production of the gas and then to devise mechanisms of containment and entrapment as a fuel source, or (b) to encourage oxidation as it diffuses to the soil surface. Aerobic soil provides the medium by which this oxidation can take place and this is influenced by soil type with rates in finer soils being up to three times less than in coarser soils (Boeckx *et al*., 1997). Therefore selection of coarser soils for capping materials would in theory increase potential methane reductions. Others (Goldman *et al*., 1994) have reported greater rates of oxidation and that increased nitrogen availability reduced methane oxidation. Previous land-use affects methane oxidation with greatest rates from forests and lowest from grasslands (reflecting nitrogen availability) (Boeckx *et al*., 1997). Therefore selection of soil with low nitrogen status may be advantageous. Cultivation, i.e. aeration of the soil, may maintain the oxidation capacity of the soil at a higher rate. Taking the highest oxidation rate, 6.9 mg CH_4-C m^{-2} d^{-1}, the soil could potentially reduce methane emissions by 250 kg per year from a 10 ha landfill site. This calculation assumes no effect of soil depth although it may make a significant contribution as the gas percolates to the surface. Methane oxidation in landfill cover soils has been estimated to reduce emissions by about 35% (Reeburgh, 1996; Williams, 1993). Nitrifying bacteria and some fungi are able to oxidise methane. Obligate methanotrophs are probably the most important oxidising organisms in methane–rich environments because of their stronger ability to convert large amounts of methane and their shorter generation times (Conrad, 1995). Three landfill sites were studied: (a) with a mineral soil cover, (b) with a new sewage sludge covering mixed with mineral soil and (c), with one year old sewage sludge cover mixed with mineral

soil. The study showed that emissions were higher from the mineral soil cover, and completely mitigated at the landfill site with old sewage sludge (probably by providing an inoculum). Use of a coarse mineral soil as base mix for the old sewage sludge is also thought to increase oxidation capacity as methanotrophs thrive better on particles of >0.5 mm diameter (Bender and Conrad, 1994). Results suggest that the older sewage sludge cover had had a longer time for methanotrophs to develop; laboratory experiments suggested that it took at least one month for steady-state conditions needed for growing methanotrophs in a soil column. Outdoors this may take longer and cultivation may therefore disturb the stability required. There is current research activity in developing methods of investigating microbial activity and diversity (Borjesson *et al*., 1998). However, when fine-grained clays are in caps to control water ingress, you do not tend to get laminar flow of escaping methane. Rather, the tendency is towards fissure flow. The ability of soils to oxidise methane is not dependent upon the average oxygen concentration of methane concentration, but rather on the concentration at a multitude of discrete points. Fissure flow is therefore not conducive to methane oxidation. Estimates of landfill methane oxidised in cover material which assume consistent laminar flow are likely to be well off the mark (Sauer, personal communication).

4.2   Agriculture and IPPC Implications

4.2.1   Manure management

Traditionally, the choice of manure management system has been made with convenience and cost-efficiency in mind. In recent times, intensification of animal production has led to an increased number of animals being housed. This has resulted in a greater volume of manure being collected during the housing period, which consequently requires suitable management during storage and land spreading.

Table 4.1: Amount of Manure Applied to Land in the UK (1997 data from MAFF)

Animal category	Type of manure	Manure applied to land t x 1000
Cattle	Slurry	38 225
	Solid manure	32 574
Pigs	Slurry	4 891
	Solid manure	4 365
Poultry	Solid manure	3 823
Sheep	Solid manure	1 759
Deer	Solid manure	0

Slurry-based systems

Slurry is an intimate mix of dung and urine (with no bedding material) and its dry matter content can vary between 2% and 8%. Slurry based systems have the advantage that the waste can be automatically scraped from buildings and pumped into, and stored in, tanks and lagoons for later dispersal from spreaders onto the land. Once stirred, it is a fairly homogeneous material that can be tested for nutrient contents and can be spread evenly on the land surface. Slurries are anaerobic in nature because of their high water content and have great potential therefore for methane generation.

Straw-based systems

In contrast to slurries, solid manure (FYM) is the product of the dung and urine being dropped onto some form of bedding material, usually straw. It is a much more solid material than slurry, often having a dry matter content of between 25% (pig and cattle) and 60% (broiler hen litter). The FYM has to be removed from buildings after the animals have been turned out. It is then stored in heaps prior to spreading by machine. Fresh FYM is a fairly heterogeneous material with dung and non-degraded straw clearly visible. It is, therefore, difficult to determine an accurate estimate of its nutrient content and to spread it evenly across the soil surface. By its nature, FYM has both aerobic and anaerobic micro-sites within its matrix with potential, therefore, for both oxidative and reductive processes to generate gases.

Emissions from manures

For their recent inventory, Chadwick *et al.,* (1999a) measured nitrous oxide and methane emissions from both slurry and straw based buildings, from slurry and FYM stores, and following applications of slurries and FYMs to land. Taking nitrous oxide first, low emissions were detected from the buildings for a number of animal types based on slurry. This was because of the anaerobic nature of the slurry maintaining the inorganic nitrogen as ammonium, i.e. inhibiting nitrification to nitrate (which is the first step in nitrous oxide production – see Chapter 3). The small amounts of nitrous oxide detected were thought to come from dried slurry not cleared through regular scraping. However, no nitrous oxide was emitted from the slurry stores. Larger nitrous oxide emissions were detected from houses where animals were kept on bedding material, particularly poultry houses, because nitrification of ammonium in manure can take place in the more aerobic bedding material. Housing emission factors ranged from 0.26 g N_2O-N lu^{-1} d^{-1} (pigs – slurry based) to 16.6 g N_2O-N lu^{-1} d^{-1} (poultry – broiler litter). Storage emission factors for nitrous oxide ranged from 0 g m^{-3} d^{-1} (slurry stores) to 0.7 g m^{-3} d^{-1} for cattle FYM heaps. Spreading manures to land has impact on nitrous oxide emission; emissions were generally greater after applications of slurry than FYM to land because of the greater proportion of inorganic nitrogen present in slurries (Chadwick *et al*., 1999b).

Methane emissions are similar for both slurry and straw based systems. The majority (90%) of methane emitted is the product of enteric fermentation with only 5% of the UK's total methane emission from livestock farming coming from manures stores and

<1% being emitted following manure spreading (Chadwick, 1998). Although some methane is emitted from manure and slurry management the on-farm impact of change is unlikely to be large in most instances. However, because of the potential for methane and other hydrocarbon production in anaerobic wastes, one potential option is to enhance the conditions for this to occur and collect the gases for energy use.

Influence of methods to reduce ammonia emissions

A recent ammonia emissions inventory has shown that nearly 35% of all ammonia emitted from UK agriculture is as a result of slurry spreading (Pain *et al.*, 1998). Therefore, alternative slurry spreading technology is being developed and evaluated to reduce these emissions. This new breed of slurry spreaders has one common thread and that is to reduce the amount of the emitting surface area of slurry in contact with the air. This can be achieved through placing slurry in discrete bands on the soil surface or by injecting slurry into the soil; ammonia emissions can be reduced by up to 60-70% using this technology. However, by placing high concentrations of slurry NH_4^+-N in areas of low oxygen concentration with a large available pool of carbon, conditions become favourable for denitrification and nitrous oxide production is increased (Thompson *et al.*, 1987). Recent research at IGER has shown that nitrous oxide emissions can be increased by up to three times when slurry is injected rather than surface spread (Table 4.2).

Table 4.2: Net total N_2O-N and NH_3-N Emissions Following Slurry Spreading by Surface Broadcasting and Injection

Month	Soil type	Method	Rate m^3 ha^{-1}	N content kg m^{-3}	Net N_2O loss kg N ha^{-1}	N_2O loss % of N added	NH_3 loss kg N ha^{-1}	NH_3 loss % of N added
Mar	Clay loam	Injection	31	2.1	0.05	0.08	4.1	16.6
		Surface	34	2.1	0.01	0.01	16.4	62.5
Jun	Sandy loam	Injection	29	2.2	0.36	0.56	1.7	5.1
		Surface	21	2.2	0.07	0.15	13.2	57.4
Aug	Clay loam	Injection	30	1.7	3.14	6.16	3.2	10.7
		Surface	30	1.7	1.00	1.96	22.3	71.8
Sept	Sandy loam	Injection	34	2.0	0.07	0.10	0.5	1.4
		Surface	32	2.0	0.03	0.05	10.9	31.9

Another management option to control ammonia emissions is to increase straw usage in animal houses. Straw is thought to immobilise ammonium in the bedding and therefore prevent emission during the housing phase. Taking this to its extreme, some farmers may move from slurry based systems to straw based systems, resulting in lower ammonia emissions but increased nitrous oxide emissions. Table 4.3 illustrates the impact of changing from slurry-based to straw-based cattle and pig enterprises.

Table 4.3: Effect of Changing from Slurry-Based to Straw-Based Production Systems on Annual N_2O-N (Gg yr^{-1}) Emissions from Cattle & Pigs (Chadwick , 1999a)

% animals		Dairy cows		Beef cattle		Pigs	
Slurry	Straw	Storage	Land spreading	Storage	Land spreading	Storage	Land spreading
100	0	0.00	0.13	0.00	0.13	0.01	0.13
85[a]	15[a]	0.65	0.18	0.39	0.18	0.01	0.12
75	25	1.09	0.21	0.64	0.22	0.02	0.11
55[b]	45[b]	1.97	0.27	1.18	0.28	0.03	0.09
50	50	2.40	0.31	1.44	0.32	0.04	0.08
40[c]	60[c]	2.62	0.23	1.57	0.33	0.05	0.08
25	75	3.68	0.37	1.96	0.39	0.05	0.06
0	100	4.37	0.45	2.61	0.47	0.06	0.04

a the current situation for dairy cattle
b the current situation for pigs
c the current situation for beef cattle

Potential abatement practices to reduce nitrous oxide emissions from housing and storage facilities could therefore involve moves from straw based to slurry based systems. The anaerobic nature of slurry should reduce nitrous oxide emissions considerably, but possibly at the expense of increased methane emissions unless preventative actions were taken. There is a trade-off in the greenhouse effect to be considered.

A further 'upstream' management strategy would be to reduce nitrogen excretion by feeding animals diets more closely related to their nutritional requirements. This hypothesis was tested and proved by Hobbs *et al.* (1996). When the resulting slurry from pigs fed a modified diet (reduced crude protein content with supplementary amino acids) was spread onto grassland, significantly reduced emissions of ammonia, methane and denitrification losses, and better utilisation of slurry NH_4^+-N resulted (Misselbrook *et al.*, 1998).

4.2.2   Options for reducing emissions from ruminants

Methane emissions from rumens of cattle can also be influenced by diet. Recent work at IGER has demonstrated significantly greater CH_4 emissions from beef cattle fed maize silage (168 kg CH_4-C lu^{-1} d^{-1}) than cattle fed grass silage or hay-based diets (131 kg CH_4-C lu^{-1} d^{-1}) (unpublished data – MAFF report WA0618). A number of other options

have been considered in the past: these have been particularly directed at cattle production and can be separated broadly into four main groups of approaches:

- Dietary changes: either as a continuing process of conventional dietary improvements or by utilisation of supplementary additives;

- Manipulating the rumen microflora, possibilities include: supplying probiotics to eliminate protozoa; supplying methane oxidisers or acetogens; genetic manipulation of the microflora and developing immunogenic approaches;

- Systematic changes including improved genetic potential for dairy cows, providing BST (Bovine Somatotropin) or anabolic steroids etc.;

- Changing animal manure/waste management as noted above.

4.2.3   Improved fertilizer management to reduce nitrous oxide

In general, all attempts to reduce fertilizer inputs to the farm and increase the overall nitrogen use efficiency within the system will reduce nitrous oxide emissions. This is well illustrated in the dairy farm example shown in Table 3.6. Restrictions on time and application rate offer the potential for further reducing nitrous oxide emissions following fertilizer nitrogen and manure applications. Soil mineral nitrogen levels should be kept at an optimum level for crop requirements and reduced to a minimum at times of low crop demand, e.g. in autumn and early spring when soil conditions are favourable for denitrification. Other options to reduce emissions include:

- Changes in grazing and other rotational patterns. Reductions in nitrous oxide emissions from grazed pasture would arise from increasing the productivity per animal with a concurrent decease in animal numbers, dietary control of nitrogen excretion and restricted grazing (i.e. promote a best practice for grazing with respect to nitrous oxide reduction rather than yield alone);

- Develop a fertilizer tax as an economic instrument;

- Improved fertilizer and manure application methods;

- Use catch crops to reduce excess nitrate in soil;

- Reduce water tables;

- Make better use of natural fixation processes;

- Switch to organic and less intensive systems;

- Reduce nitrogen in animal diets and improve management of nitrogen in excreta and manures.

4.3   Fugitive Emissions

A literature search provided little published information on methods for the reduction of methane from solid, oil or gas fuel fugitive emissions. Verbal discussion with instrument manufacturers indicated that at least some deep coal mines trapped methane and used it to generate power, and discussions with British Gas established that they (i.e. BG Technology) were active in researching new methods to detect and address fugitive emissions from natural gas installations. In fact, BG Technology seems to be to be more than willing to share expertise in technical aspects of methane sensing. Moreover, technical literature shows that there is a wide range of commercial systems for detecting fugitive gas emissions. This project was not planned to address the complex technical issues of fugitive fuel emissions and is limited to noting the magnitude of the topic.

4.4   Fuel Combustion

Little information was found on methods to reduce methane and nitrous oxide emissions from industry, small combustion and traditional biomass burning. In contrast, there is a large and expanding database on commercial pressures for, and methods of, reducing vehicle exhaust emissions in total (although the methane contribution was not discussed separately). This item was not investigated further.

4.5   Comparison of Impacts

Landfills are (unless revised) the highest category source of methane emission; but their long term impact has to be balanced against the (conceptual) ease of application of their principal reduction technique, trapping and combustion. There is also potential for further reduction by increasing the rate of microbial oxidation of methane during its diffusion through the capping soil. However, this would involve highly visible and aesthetically unpleasing changes, for example replacing grass cover with bare rotivated soil seeded with sewage sludge as inoculum for nitrifying bacteria. This and other practical problems precluded following up this approach.

Enteric fermentation by ruminants is the second largest methane source (and indeed may possibly be revised to be the highest category source.) Unfortunately, the simplest reduction strategy of replacing a high fibre (e.g. maize) diet with hay runs counter to the present trend of a change from hay to maize feed for economic reasons. Other reduction strategies of manipulating rumen microbiology genetically, use of anabolic steroids etc, are radical and unlikely to gain acceptance, and ruminant fermentation therefore appears to remain a serious long-term problem.

Fugitive emissions from fuels also appear to be long-term problems, not least because of the lack of published data on them. It may well be that the considerable in-house research by the gas industry will reduce emissions from that sector, but at present leakage from natural gas installations remains high. The continuing decline in deep coal mining will cause a marked reduction in methane emission. However, in view of the increase in open cast mining it may be worthwhile reviewing its emission factor calculation.

Anaerobic manure digestion (e.g. farm slurry production) is likely to favour methane and ammonia generation at the expense of nitrous oxide. Slurry spreading is a major source of ammonia emission, and soil injection techniques are being developed to reduce the ammonia yield by encouraging microbial denitrification. As would be expected, this process increases nitrous oxide generation.

Emission of nitrous oxide from soil is a significant, but not major, fraction of the UK greenhouse gas budget. Reduction of nitrous oxide from soil is best addressed by reducing nitrogen fertilizer usage. This is in step with best practice to reduce eutrophication, and nitrous oxide emission from soil will decrease if the use of nitrogen fertilizer is restricted in order to protect groundwater or for other environmental reasons.

5.   METHODS OF MONITORING METHANE EMISSION

Methane is always present in the atmosphere at a concentration that varies between 1.6 and 2 ppm. The higher concentrations are usually found in developed areas where there are a large number of methane emission sources. Since the atmospheric background is not constant, even at a fixed location, any methane emitted from a landfill site must be measured in the presence of these variations in the natural background. Hence, there is no benefit in using instruments that have a sensitivity of less than 1% of the expected background to measure the concentration of atmospheric methane. (This does not apply to the eddy correlation method, which requires greater sensitivity as well as a faster response).

Section 5.1 reviews methods of measuring methane concentration in air. However, it is usual to measure not just the concentration of methane, but also its flux defined by:

$$\text{Flux } [\text{kg s}^{-1}] = \text{concentration } [\text{kg m}^{-3}] \text{ x flow rate } [\text{m}^3 \text{ s}^{-1}]$$

Section 5.2 discusses commonly used methods that combine a measure of concentration with a measure of flow in order to estimate flux.   Section 5.3 discusses the application of airborne and satellite surveillance techniques and Section 5.4 summarises techniques of methane measurement under development.

5.1   Methane Concentration Measurement

This Section describes some of the methods that are used when measurements of methane concentration are required without any reference to the flux. The most important of these is the Flame Ionisation Detector (FID). Additionally, dispersive and non-dispersive optical methods are reviewed.

5.1.1   Flame ionisation detection

The FID is probably the commonest device used for making measurements of methane at concentrations below 100 µg m^{-3}. It works by passing the sample gas through a hydrogen flame mounted between two plates of an electrode. The volatile organic component of the gas is ionised which results in a potential across the electrodes. The size of this potential is proportional to the concentration of covalent carbon in the sample gas. Therefore, the FID itself measures total organic carbon (TOC) and has no capability to speciate different VOCs in a sample. Consequently, the FID is often used with gas chromatography which is able to separate different gases as they flow through a densely packed column of inert material. Lower cost FID-based instruments use a chemical filter to remove all VOCs apart from methane and are able to record the specific methane concentration.

FID systems have little or no cross-sensitivity to water, carbon dioxide or carbon monoxide, although some older instruments show some response to oxygen. The measurement time is typically tens of seconds, and a calibrated system can have an accuracy of a few per cent (at ambient methane concentration levels).

5.1.2 Dispersive and non-dispersive infrared

Non-dispersive infrared (NDIR) monitors use optical filtering to select a particular wavelength band, which is then directed through the sample gas and the transmitted energy measured. This type of monitor is generally simple and robust, but does not suffer from cross-sensitivity particularly from water vapour. There are a number of different versions of the NDIR technique, including single beam, dual beam (signal and reference) and rotating filter. However, the sensitivity to methane is poor – even for the more sensitive versions the methane detection limit is typically 0.5 ppm. Therefore, the NDIR method is only suitable for applications where the methane level is at least an order of magnitude above the ambient.

Dispersive optical monitors use some form of optical interferometer to separate light at different wavelengths. This enables them to distinguish those parts of the spectrum that are absorbed by methane from those that are not. The concentration of methane can then be calculated using standard values for the absorption coefficient of methane. Fourier Transform Spectrometers (FTS) are an example of this type of instrument. They have the capacity to measure a very wide range of species at ambient concentrations, including methane.

An alternative optical method with much greater sensitivity is direct optical absorption. An example of this type of instrument is the tunable-diode laser spectrometer (TDLS). It is capable of carrying out measurements sufficiently rapidly to be used in the eddy-correlation method.

5.2 Present Landfill Methane Monitoring Methods

5.2.1 Static and dynamic flux chambers

The flux chamber (or "flux box") captures gas escaping from the surface of a landfill site and measures the consequent increases in concentration within the chamber. The flux (E) can then be calculated from (Czepiel *et al*, 1996):

$$E = \frac{V}{A} p \frac{\Delta C}{\Delta t}$$

Where V is the volume of the chamber, A is the enclosed surface area, ρ is the gas density within the chamber, and $\Delta C / \Delta t$ is the rate of increase of concentration within the chamber. This is the simplest approach which is referred to as a static chamber since there is no flow of gas through the chamber apart from the small flux from the surface being measured. If measurements of methane are required, the concentration within the chamber can either be measured by taking a series of samples for analysis by GC-FID or FID alone. Alternatively, the concentration within the chamber can be monitored continuously using a FID, in which case some method must be used to ensure that the pressure within the chamber is not reduced by the removal of sample gas.

A more sophisticated version of the flux chamber uses a continuous flow to sweep gas through the chamber at a rate significantly larger than the emission rate from the surface. This is known as a dynamic chamber.

Review of applications of flux chambers to landfill methane measurement

Flux chambers have been used extensively for measurements of surface fluxes of methane and NMHC (Ekland, 1992). As the equation above shows, the measured change in concentration is proportional to the area and inversely proportional to the volume, hence, the minimum detectable flux is only proportional to the height of the chamber. Generally, a cylindrical geometry is preferred over rectangular ones because mixing within the chamber is enhanced. Flux chambers should be constructed from metal rather than plastics, some of which emit hydrocarbons and even methane. Accurate measurements require gas-tight seal between the chamber and the ground in order to prevent leakage or ventilation by wind.

The design developed by NPL (Figure 5.1) (Milton, 1996) has the edges of the cylindrical chamber sharpened so that the chamber can be forced into the surface of the site to a depth of at least four centimetres. Of the different designs that have been discussed, the most frequently used in the US (Reinhart and Cooper, 1992) consists of a stainless-steel dome 71 cm in diameter placed on top of a cylinder 30 cm high.

A novel design for a flux chamber that does not require clean sweep gas and does not disturb the surface being monitored has been patented [US Patent 5,33,739], but no applications have been reported yet.

**Figure 5.1: Cylindrical Flux Chamber (Developed for Monitoring Methane
           Emissions from the Surface of Landfill Sites)**

Difficulties for all designs of flux chamber which give rise to uncertainties in the results include the following:

- The need to mix gas within the chamber because emission will not be homogeneous over the area being sampled. This is easily achieved in a dynamic chamber by the sweep gas; alternatively it can be achieved by the use of a mechanical stirrer.
- Changes in the temperature, pressure and humidity at the surface being sampled because of the presence of the chamber.
- False negative fluxes being recorded as a result of high concentrations of ambient methane trapped in the chamber when it is placed on the site.

The largest single source of uncertainty associated with the flux chamber method is the sampling strategy used to ensure that the measured flux at selected points is averaged, to give a representative estimate of emissions rates from the site as a whole. The strategy is dependent on the size and nature of the emissions and the objectives of the measurements themselves. The usual procedure (Ekland, 1992) is divide the site into areas that can be expected to be approximately uniform in their emission characteristics (for example they have the same capping material or surface vegetation and a constant depth of waste of similar age). Each area can then be divided into a grid that can be sampled randomly, ideally with at least six surface flux measurements at each point. Since eight to ten measurements can usually be achieved during a day, two or three days work with each chamber may be required to measure each area of a site. Even a well conceived statistical design will not be able to deal accurately with a site for which emissions are dominated by gas escaping from the site through cracks or local sources (e.g. around wells) which, from Section 4.1, may well be commonplace.

Recommended applications

Since the flux chamber method is very labour intensive when used to measure total site fluxes, it can only be recommended for use in the measurement of small areas of a site. It is well suited to studies of different types of capping since it is capable of measuring the very low fluxes expected through the cap. It might also be used for studies of long-term variations of emissions from a site in which repeated measurements are made at exactly the same location. It is unsuitable for monitoring in any situation where the emissions are inhomogeneous or where the surface is not uniform enough to form a gas-tight seal against the chamber. Again, from Section 4.1, many landfill surfaces are inhomogeneous and this is a limiting factor in the application of this technique.

5.2.2   Flux survey method

Principle of method

The flux survey method works by measuring the concentration of methane in the atmosphere at a fixed height above the site along a series of paths both upwind and downwind of the emissions. The recorded concentrations are then processed to calculate the average concentration along each path. The flux is then calculated by reference to the wind speed and direction (measured simultaneously) and a model calculates the expected profile of the plume at any distance from an area source.

Applications of flux survey methods to landfill methane measurement

The most detailed applications of the flux survey method have been developed by NPL (ref NPL Report QM 134). This implementation of the method uses an accurately calibrated portable FID (see Section 5.1.1) with automatic data logging, which is carried along the site at a constant height above the ground (Figure 5.2). Simultaneous measurements of the wind field are made with automated anemometers. The method also requires an estimate of the atmospheric stability, which is straightforward to obtain from standard meteorological observations. The wind and methane data are then combined with an estimate of the height (derived from the atmospheric stability) of the plume of methane above the site to give the flux. The method has the major advantage that it measures methane from a wide area of the site so it does not have the problem that flux chambers have with cap variability.

Figure 5.2: Portable Flux Survey Equipment (Developed for cost-effective emissions monitoring)

The flux survey is similar in its implementation to published reports of methods used to fulfil the requirements of the US EPA's "Municipal Solid Waste Landfill New Source Performance Standard". This standard imposes the requirement on operators to measure the concentration of methane around the perimeter of sites and along a grid of lines spaced 30 metres apart. Published examples of work to fulfil this standard in Canada (Eade, 1997) and the USA (Huitric and Banaji, 1996) are based on transportable FIDs either carried on a vehicle or manually. Neither of these methods involves combining the point concentration measurements with the wind profile to calculate the flux.

The use of a flux survey method called "Integrated Surface Sampling" (ISS) has been reported by California Air Resources Board, but no detailed information is provided about how the results are calculated from the measured data.

Recommended applications

The flux survey is the quickest and lowest cost method reviewed here. The equipment is straightforward to obtain commercially and costs less than £5,000. In general, processing of the measurement data to produce results is not too difficult. Consequently, the flux survey method is recommended for rapid estimation of total site emissions and for screening sites to quantify the effectiveness of gas control systems. It is not suitable for estimating emissions from sites with highly complex topographies, for example, it might be difficult to achieve good results from a steep-sided land raising site.

5.2.3 Tracer gas methods

Principle of method

Tracer gas methods work on the basis that, if a tracer gas can be mixed into the plume of emitted gas from a landfill surface, then measurements of the flux of the tracer gas (from its release points) can be used to calculate the flux of landfill gas from the surface using the equation:

$$ Q_m = Q_t \frac{C_m}{C_t} $$

where Q_m is the flux of the gas being measured, Q_t is the flux of tracer gas, C_t is the concentration of the tracer and C_m is the concentration of the gas being measured (Figure 5.2). This equation is only accurate when the dispersion of the tracer gas in the atmosphere is the same as that of the surface emissions being measured. Hence tracer gas methods have principally been developed for the measurement of fluxes from point sources such as stacks. Their application to the measurement of large area emissions which are likely to be highly inhomogeneous is more difficult.
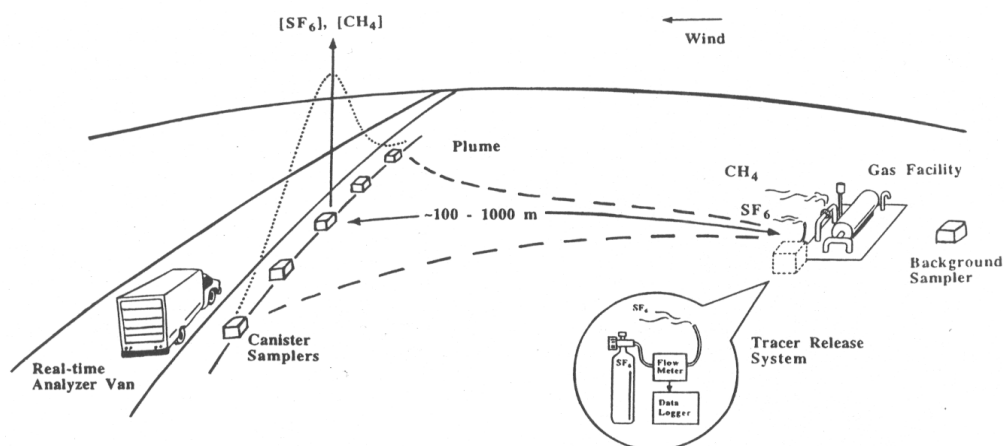

Figure 5.3: Schematic Illustration of Tracer Gas Method - in this example it is used to measure methane emissions from a "Gas Facility"

The method is restricted to situations where there is no "natural" emission of the tracer gas. Consequently, species such as sulphur hexaflouride (SF_6) which have very low ambient atmospheric concentrations are used as tracers. However, sulphur hexafluoride is a strong greenhouse gas and an alternative should be sought if this technique is to be considered seriously.

Applications of tracer gas methods to landfill methane measurement

Tracer gas methods have been used by various researchers to study methane fluxes from a range of different sources (Howard and Lamb, 1992; Moriizumi *et al*, 1996). The main attraction of tracer methods is that it is theoretically possible to determine the methane flux from a single downwind measurement of the methane and tracer concentration. However, this principle only holds for a point emission source of methane with no interference from neighbouring sources. To apply the tracer technique to a diffuse source such, as a landfill site, a number of assumptions have to be made about the source distribution and the atmospheric conditions.

Czepiel *et al.* (1996) describe the use of the tracer gas method to determine the methane emissions from a 60 hectare landfill site in the US. The tracer gas, sulphur hexafluoride was released from three points along the upwind edge of the landfill. The tracer and methane plume distributions were measured 1.2 to 3.5 km downwind of the landfill. The plumes were located using a vehicle fitted with fast response analysers which made repeated traverses across the plumes. Once a suitably mixed plume had been located, a series of static gas-samples were taken across the plume and then analysed for methane and SF_6. The methane flux estimated from the tracer measurement results was 17750 litres per minute, which correlated well with the flux of 15800 litres per minute determined from a series of 139 enclosure measurements. The agreement between the two results was improved when the effect of atmospheric pressure on the emission rate was taken into account.

A similar intercomparison of techniques was carried out by Savanne *et al.* (1997). Two tracer methods were employed: one assumed a simple point source for the emissions and the other made an attempt to reconstruct the source distribution. The two methods gave methane emission flux results of 67 ml m^{-2} min^{-1} and 55 ml m^{-2} min^{-1} respectively, which compared to flux chamber results of approximately 90 ml m^{-2} min^{-1}. Landfill measurements are also reported by Tregoures and Gonze. (1997). This work includes a number of modifications to the tracer technique which aim to improve the accuracy of the method when applied to diffuse inhomogeneous sources. However, most of these add significantly to the complexity of the method.

The review of the various tracer measurements has shown that, although the principle is relatively simple, the actual implementation of the technique can be complex and time consuming. In addition, the requirements for homogeneous emissions, no interfering sources and particular dispersion conditions means that accurate results can only be obtained under very limited circumstances. However, the area where tracer measurements are useful is when they are combined with one of the other measurement techniques that requires dispersion modelling. The tracer measurements can be used to give accurate information about the dispersion conditions at the time of the

measurement thereby improving the quality of the dispersion model, as demonstrated by Piccot *et al.* (1996).

Recommended applications

Tracer gas methods are best suited to research studies that are aimed at characterising the dispersion conditions at a site. Consequently, they are recommended for applications that involve quantifying the extent of dispersion from a site. Well planned tracer gas studies can be used to locate the origin of odorous or hazardous emissions and in most cases should be able to provide quantitative data for estimating environmental impacts. They could be used to do this many hundreds of metres from the source of the emissions but are ultimately limited by a lack of detection sensitivity. The tracer gas should, of course, not be a greenhouse gas.

5.2.4 Optical integrated-path methods

Principle of method

In the optical integrated-path method a collimated infrared beam is directed at a retro-reflecting mirror placed a suitable distance away (typically around 100 metres). The reflected beam is collected by a small telescope and the optical absorption is measured. The integral amount of target gas along the beam path is determined from the level of absorption of the infrared beam. This enables the integrated path concentration to be calculated from:

$$CL = \int c\,dl = \frac{1}{\alpha}\frac{I(l)}{I(0)}$$

where CL is the integrated path concentration c over a distance l , I is the light intensity and α is the absorption coefficient.

Measurements are then made at different heights to determine the distribution of the gas in a vertical plane upwind and downwind of the site. These concentration measurements are combined with the wind velocity to determine the gas flux through the measurement plane.

Applications of optical integrated-path methods to landfill methane measurements

The wide spatial coverage of open-path techniques means that they are often used in the measurement of emissions from large-scale diffuse sources such as landfill sites. The most common approach is to use Fourier Transform Spectrometry (FTS) to carry out the measurement. Weber *et al.* (1996) report FTS measurements of methane across a clay-capped landfill site. A site survey was performed in which concentrations were measured along a series of ground-level lines of sight. The maximum methane path-averaged concentration observed was 27 ppm. However, the results were not used to calculate emission fluxes.

One of the main advantages of the FTS technique is that many species can be monitored simultaneously. Haus *et al.* (1995) have made measurements at a variety of different

sites, including landfill, of numerous species such as methane, carbon dioxide, carbon monoxide, ammonia, nitrous oxide and formaldehyde. Their measurements at a landfill included a site survey that showed methane concentrations varying between 4 and 20 ppm. They also measured the site flux along a 500 metre path 50 m downwind of the site boundary. The measured emission rate was 0.36 mg m^{-2} s^{-1}. This rate was inferred from the path-averaged concentration along a single horizontal line-of-sight. A simple plume-dispersion model was used to extrapolate this measurement to give the integrated plume concentration.

The validity of using simple plume dispersion models to predict total emission rates from integrated path measurements has been studied by Piccot *et al.* (1996). They set up a simulated diffuse methane source (30 metres by 7.5 metres) combined with a point source of tracer gas (SF$_6$). Open-path FTS measurements were made in a vertical 'pie-slice' approximately 50 metres downwind of the source using four retro-reflectors mounted at different heights up to a maximum of 20 metres elevation. A plume dispersion model was used to predict the fraction of the emitted plume passing through the measurement area. The wind vector was measured at two heights (2 metres and 10 metres) and the results used to estimate the vertical wind profile. The two data sets were then combined to give the flux.

Compared to a landfill site, the experimental arrangement described by Piccot represents a relatively simple and small-scale source, used for an extensive set of measurements. Despite this, the measured flux was consistently 20-40% lower than the known value. The authors trace this discrepancy to the calculation of the Pasquill stability class used in the dispersion model. At the simplest level, the stability class can be determined through observation of the meteorological conditions at the time of the measurement. However, this method is somewhat subjective. A more prescriptive method relates the stability class to the standard deviation of the horizontal wind direction, and this method was used in the initial dispersion model runs. It was found that the agreement between the measured and actual fluxes improved dramatically (2% variation) if a 'synthetic' stability class was used. In this case, the results of the simultaneous tracer measurements were used to determine the most suitable stability class on a run-by-run basis. The authors stress that this synthetic stability class does not represent the actual class, but instead the class that gives the best results in a dispersion model of a particular measurement. This work highlights the crucial importance of the dispersion model if the entire plume is not measured, and shows that simpler forms of the model can lead to significant errors in the flux calculation.

An alternative open-path measurement technique is described by Milton *et al.*(1995) based on earlier work with an experimental system (Partridge and Curtis, 1986). This system used a broad-band light source and an oscillating optical filter to measure the IR absorption of various atmospheric gases, including methane, over open-paths up to 400 metres long (Figure 5.4). In order to simplify the mechanics of carrying out elevated measurements, a vertical slant path to a retro-reflector mounted on a portable mast (30 m maximum elevation) was used. Where possible, measurements are made at high enough slant path angles to ensure that the entire vertical extent of the plume is measured, eliminating the dependence on the plume dispersion models discussed above. Model calculations show that with neutral stability (typical of over-cast UK conditions) 99% of the plume from a 600 metre site will be below 30 metres at the site edge.

Measurements were performed at a landfill site using this technique resulting in a measured methane flux of 1.7 mg m^{-2} s^{-1}.

Figure 5.4: Optical Integrated-Path Monitoring Using a HAWK Infrared Monitor Along One Side of a Landfill Site

Recommended applications

The different implementations of the optical integrated-path method are capable of giving accurate results, if carried out correctly. Under favourable wind conditions, they are cost-effective methods for producing accurate measurements of total site emissions. Unlike the other methods, they are not able to provide information about the distribution of high-emission points on the site. Since they are not straightforward to implement, they can be recommended for verifying the accuracy of lower-cost and more convenient methods. Current developments in diode laser technology offer the potential for lower-cost implementations with greater sensitivity.

5.2.5 Eddy correlation methods

Principle of method

The eddy correlation method is a micro-meteorological method that is based on the fundamental assumption that the emitted gas is transported away from the surface by the vertical eddying motion of the atmosphere. This vertical transport can be measured by correlating the instantaneous concentration at a point with the instantaneous vertical wind velocity at the same location. Fast response detectors are required to carry out this

type of measurement since the natural frequency of the atmospheric eddies can be as high as 10 Hz.

The mean flux density F over any given measurement period is given by the mean of the product of instantaneous vertical wind speed w and gas density ρ_g. This can be written as:

$$F = \overline{w}.\overline{\rho}_g + \overline{\Delta w.\Delta \rho_g}$$

where the bars denote the mean value over the measurement period and Δw and $\Delta \rho_g$ are the fluctuations about the mean wind speed and mean gas density respectively. In the simplest case the mean vertical wind speed is assumed to be zero, so the flux is given by the second term only. More detailed calculations can be used which take into account the effects of the net heat and water vapour flux.

Related methods

Relaxed eddy correlation

If fast response monitors are not available for use in the standard eddy correlation technique described above, then the "relaxed" eddy correlation method can be used. In this method, gas concentrations are measured at one point, and the flux is estimated using the following relationship:

$$F = \beta(C_u - C_d)\sigma_w$$

where β is a dimensionless constant, C_u and C_d are the mean concentrations associated with upwards and downwards eddies, and σ_w is the standard deviation of the wind speed.

Gradient diffusion

An alternative micro-meteorological method enables the vertical flux F from a surface to be determined by measuring the gas density ρ_g at different heights, z, to determine the vertical gradient of the gas. The flux is then given by:

$$F = -K_g \partial \overline{\rho}_g / \partial z$$

where K_g is the eddy diffusivity of the gas which depends on the meteorological conditions, the measurement height, and the surface roughness. The determination of K_g is the key factor in the application of this method and requires a number of meteorological and local site factors to be considered.

Applications of eddy correlation methods to landfill methane measurement

The key advantage of the eddy correlation technique is that it enables emissions from a wide area to be monitored from a single point. A number of authors have reported methane flux measurements using the eddy correlation technique, either on landfill sites or on other terrain types. Hovde et al (1995) reports the use of a near-infrared diode

laser sensor to make 10 Hz methane concentration measurements at a clay-capped sanitary landfill site (with no gas recovery system). Rapid response measurements were also made of the 3-D wind vector, water vapour concentration and carbon dioxide concentration. A high level of correlation was observed among the four data sets. The average methane emission rate over a combined period of three hours was 0.076 mg m^{-2} s^{-1}. Some comparisons were made with other methane flux measurements (Fan et al, 1992) but the results cover a very limited data set in terms of spatial and temporal coverage.

Relatively sophisticated equipment is required for the fast response measurements of methane and the 3-D wind velocity, but this equipment is becoming more generally available. Once the equipment is set up at a site it will generally not need to be moved and can be left to run automatically, reducing staffing requirements. Once the relevant procedures have been automated, the analysis of the results is relatively straightforward and the equipment does not require frequent calibration (Oonk and Boom, 1995).

In their review of different measurement techniques for measuring landfill methane Savanne *et al.*, (1997) highlight one of the main issues with the interpretation of eddy correlation measurements. They quote an average emission density of 0.019 mg m^{-2} s^{-1}, in a comparative study approximately 40 times lower than the other techniques reviewed. Savanne attributes this discrepancy to the position of the eddy correlation sensor which was located downwind of an area of the site known to have low emissions. The location of the sensor and the ground 'footprint' from which emissions are detected need to be monitored carefully. Fan *et al.*, (1992) show how this footprint can be estimated using simple plume dispersion models. In this work the methane flux from sub-Arctic tundra was measured using an eddy correlation sensor at the top of a 12 m tower. The calculations of the footprint area show that the upwind footprint depends upon the atmospheric stability, varying from 200 to 300 metres for unstable conditions to more than 1000 metres for stable conditions. In comparison the cross-wind footprint is small - typically only 15% of the upwind footprint. Therefore, the location of the measurement footprint is strongly dependent on the wind direction, and this needs to be taken into account when analysing eddy correlation data.

One benefit of eddy correlation over the flux chamber or flux survey is that it is less affected by the micro-topography of the site. Clement and Verma (1995) conducted a long-term inter-comparison of methane flux measurements from an area of peatland using the eddy correlation and flux chamber techniques. For the first eighteen months of the inter-comparison the flux chamber technique gave results approximately 30% higher than the eddy correlation, and then 20% lower for the last six months (the latter period associated with a high water table level). The correlation between the results improved significantly when the flux chamber results were corrected for the effects of the micro-topographical spatial variations in the locations of the flux chamber measurements.

Recommended applications

Eddy correlation methods have the potential to measure very low fluxes, but their accuracy is limited by the uniformity of the surrounding terrain and the uniformity of emissions. Since it is difficult to use and the data are difficult to process into measured flux results, it cannot be recommended for routine measurements of landfill methane emissions. It can be

recommended for long-term studies of emissions from a single site with reasonably uniform emissions over an extended period of time.

5.2.6   Differential absorption lidar (DIAL)

Principle of method

The Differential Absorption Lidar (DIAL) technique is a development of the optical integrated-path method described in Section 5.2.4. It works by measuring the small amount of light scattered by particles in the atmosphere when an intense pulse of radiation is transmitted through the measurement region. The exact distance to the scattering volume can be determined by timing the flight of the pulse from the transmitter to the scattering point and back. The measured signal energy is given by the Lidar (light detection and ranging) equation which in simplified form gives the returned power $P_x(r)$ from a range r as:

$$P_x(r) = E_x \frac{D_x}{r^2} B_x(r) \exp\{-2 \int_0^r [A_x(r') + \alpha_x C(r')]dr' \}$$

where C(r) is the concentration of an absorber with absorption coefficient α_x and $A_x(r')$ is the absorption coefficient due to all other atmospheric absorption, E_x is the transmitted energy and B_x is the backscatter coefficient for the atmosphere at wavelength x. D_x is a range-independent constant.

Measurement of the differential Lidar signal at two wavelengths allows the range-resolved concentration to be calculated independently of the other parameters. This is the DIAL method. Concentration measurements along different lines-of-sight are combined to generate a concentration profile across a vertical plane. The emitted flux is then calculated by combining the profiles of methane concentration in the atmosphere upwind and downwind of the measurement volume with the wind profile through the volume.

Applications of DIAL to landfill methane measurements

The DIAL method combines the wide spatial coverage of the open-path method with the fine detail of the point-sampling methods. The DIAL systems can measure range-resolved methane concentrations at distances of up to one kilometre in any direction from the system. As a result, the entire plume distribution can be measured in almost all wind conditions, removing the need for any dispersion modelling and greatly simplifying the calculation of the emitted flux. In addition, the speed of the measurement means that the entire site flux can be measured in a few minutes. The fine scale range resolution also shows the structure of the plume, which can give useful information on the emission distribution across the site.

Since a DIAL system is single-ended there is no requirement for carefully aligned retro-reflectors, leading to a considerable manpower saving over the open-path techniques. However, the main disadvantage of the DIAL method is that the equipment is large and expensive, and requires experienced operators.

Although there are a large number of DIAL systems operating around the world, measurements of methane emissions require the use of laser transmitter sources that operate in the infrared spectral region. The number of such DIAL systems is extremely limited. Robinson *et al.* (1995) describes the mobile DIAL system developed by NPL that has been used to measure hydrocarbon emissions (including methane) from a wide range of industrial sources. As part of the system calibration DIAL measurements have been made of the methane fluxes from a controlled emission source. The agreement between the measured and actual fluxes was within ±15%. Diffuse industrial sources have also been measured, indicating that the technique can be applied to large-scale sites with inhomogeneous emissions.

Recommended applications

The combination of wide area coverage and range-resolved measurements means that the DIAL method is well suited to carrying out detailed studies of site emissions; for instance, in the assessment of the quality of gas control measures. Since the DIAL method measures the entire emission distribution, flux calculations can be made without reference to dispersion models. This removes one source of uncertainty from flux results and means that DIAL can be used to measure emissions when topography or meteorological conditions would lead to unreliable dispersion modelling.

Another application area is in the measurement of emissions from sites where access is difficult or hazardous. Since the DIAL method is single-ended and has a range of up to one km, the measurement locations can be several hundred metres from the site.

5.2.7   Other methods

Satellite measurements

There are a number of instruments operating on earth remote sensing satellites that are able to measure methane in the free troposphere and above. However, such instruments are not capable of measuring methane concentrations at distances corresponding to the typical plume height from a landfill site (typically no more than 50 m). Developments in satellite imagery are reviewed in Section 5.3.

Infrared imaging

Infrared images of landfill sites obtained using hand-held or airborne imagers are often used to provide information about the surface of sites. The images produced in the infrared spectral region highlight variations in the temperature of objects as well as variations in their infrared emission characteristics. Although methane has a complex spectral signature in the infrared, thermal imagers do not have sufficient spectral resolution to discriminate between variations due to the presence of methane in the atmosphere and variations due to the difference in the infrared emission characteristics of different surfaces. This subject is reviewed in detail in Section 5.3.2.

Sub-surface gradient methods

Measurements of the gradient of the concentration of gases below the soil surface have been used extensively to study diffusion processes within the soil. These measurements are of particular interest in quantifying the influence of biological processes on the diffusion of gas through the subsoil. They can be time consuming to carry out, particularly if the soil is difficult to penetrate. Also, they must be repeated a large number of times in order to develop a statistically representative result. Their accuracy depends upon the extent to which any concentration gradient measured can be interpreted by use of a simple diffusion law. These difficulties effectively limit the scope of applications of sub-soil gradient methods to scientific investigations of processes in cover soils. Also fissure flow would limit the accuracy of this technique.

Gas borehole or extraction measurements

It is routine operational procedure to measure the concentration of landfill gas (particularly the carbon dioxide and methane concentrations) in boreholes and gas extracted from all managed landfill sites. This information is primarily used to monitor whether subsoil conditions are anaerobic (leading to efficient methane generation) and the extent of methane migration from the site. Such "static" measurements of methane concentration do not readily give information about methane flux from the site as a whole. Even when they are combined with measurements of gas flow rates through the extraction system, they do not yield information about total methane emissions because they do not provide any measure of the amount of gas escaping through the surface or through defects in the surface or any pipework.

5.2.8   Comparison of methods

Measurement principles

It is difficult to make a true comparison of the methods reviewed in Section 5.2 because they all attempt to estimate the same quantity (landfill methane emissions), but achieve this through monitoring different parameters that are combined on a different basis. The parameters measured by each of the methods are listed in Table 5.1 together with the principle used to combine them to calculate the flux. Each of the methods uses measurements made over a different length scale so that they yield results that are associated with different length scales. These vary from typically 1 to 2 metres for flux chambers to many hundreds of meters for the optical open-path methods. Since the total amount of methane emitted along a 100 metre path is larger than that along a 1 metre path, there is a tendency for the methods that measure over larger distances (or areas) to be more sensitive.

Table 5.1: Basis for Flux Measurement for Each Method

Method	Parameters Measured	Basis of Flux Calculation
Flux Chamber	Rate of change of concentration within enclosure	Direct measurement of emission rate within enclosed area at a number of locations around the site
Flux Survey	Point concentrations around perimeter of site (up- and down-wind)	Combination of measured concentrations and wind speed with estimated plume and wind profiles
Tracer Gas	Concentration of methane and tracer in plume downwind of source. Release rate of tracer	Relate measured tracer and methane concentrations to known tracer release rate, assuming that tracer release and dispersion is representative of methane emission
Open-path Monitoring	Integrated-path concentrations up- and down-wind of site	As for flux survey, except plume profile can be measured directly
Eddy-correlation	Short timescale fluctuations in methane concentration and vertical wind speed	Correlation between vertical wind speed and methane concentration
DIAL	Range-resolved methane concentration measurements in vertical planes upwind and downwind of source	Combines measured concentration profile with measured (horizontal) wind speeds

Minimum detectable flux

This section calculates the minimum detectable flux and the measurement uncertainty of the six methods under typical conditions. Since five of the methods are based on measurements of the concentration of methane above the surface of the site, it is convenient to compare them using a common set of assumptions about the dispersion of methane from the site surface. These assumptions are used solely as the basis for a comparison in this report. They do not relate to any limit on the applicability of the methods themselves.

Baseline conditions

The UK-ADMS atmospheric dispersion model has been used to model the profile of methane above a site (Milton *et al*, 1995). These calculations are a very straightforward application of dispersion modelling which characterises the atmospheric stability conditions according to Pasquill stability classes. The concentration of methane can be calculated at any point along the edge of a site emitting methane uniformly at a rate of 1 unit m^{-2} s^{-1} under Pasquill C conditions, which are typical of the UK. The measurement point is chosen to be on the upwind side of a site stretching 400 metres in the upwind direction, and the wind speed is measured. If the data are scaled appropriately, then the

surface emission rate needed to give an observed excess concentration of methane over the atmospheric background at a height of 1.5 metres (i.e. measurement height) can be calculated. This calculated relationship between the excess ambient concentration and the surface emission flux forms the basis for calculating the minimum flux detectable by the different methods. This is applicable to the benchmark conditions of a 4 m s^{-1} wind on a site reaching 400 metres in the up wind direction. If the wind is lower, then the minimum detectable flux will be smaller. Similarly, if the site is larger, the minimum flux detectable will also be smaller.

Optical integrated-path, eddy correlation, flux survey and DIAL

For the optical integrated-path method, a typical minimum detectable point concentration for an optical instrument is 0.2 ppm. Hence it would be expected to be able to measure the baseline flux of 50 μg m^{-2} s^{-1} under the conditions discussed in the previous paragraph's calculation. Taking account of a realistic range of site sizes from 200 to 600 metres, the associated range of minimum detectable fluxes would be 20 to 100 μg m^{-2} s^{-1}. The DIAL method is capable of measuring point concentrations of 0.05 ppm, hence the minimum detectable flux is four times lower. An estimated minimum detectable flux for the eddy-correlation methods can be made on the basis of using instrumentation capable of measuring correlated changes of methane concentration of 1 μg m^{-3} and changes in wind speed of 0.1 m s^{-1}. Allowing for a small range in each of these numbers leads to a minimum detectable flux in the range 0.1 to 0.5 μg m^{-2} s^{-1}.

Flux chamber

The flux chamber method involves direct measurement of the methane that has been emitted through an enclosed area of the site, and the calculation is not based on the same assumptions as the other methods. If the instrument measuring the increase in methane concentration within the chamber is (a) capable of monitoring a change of methane of the order of 7 mg m^{-3} s^{-1} (0.1 ppm per minute), (b) has a volume of the order 1 m^3, and (c) an area of the order 0.5 m^2, then its minimum detectable flux is of the order 50 μg m^{-2}s^{-1}.

The minimum detectable fluxes for each of the five methods are plotted in Figure 5.5. This illustrates that each of the methods has a different limit of detection. In general, the methods can all be used to measure fluxes that are significantly larger than these minimum values.
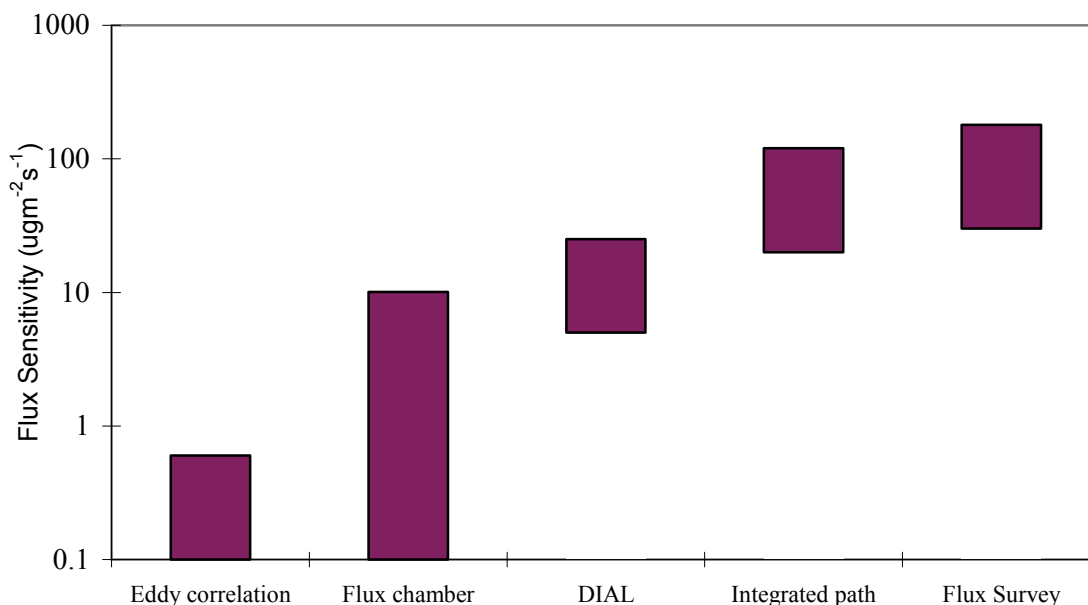
Figure 5.5: **Flux Sensitivities of the Different Measurement Techniques (The range indicates the extent of variation of the sensitivity according to site and meteorological conditions)**

5.2.9 Selection of most appropriate methods

Costs and availability

It is not straightforward to compare the costs of the five presently available methods reviewed here, because they would be used to study different qualities of problem and would yield different qualities of data. For example, one day of operation with a DIAL facility would generate many tens of thousands of accurate methane concentration measurements, but one day of operation with a flux chamber would produce no more than ten measurements of surface flux. Consequently, the following estimates of cost should be interpreted with care.

Typical implementation of the flux survey and flux chamber methods would involve two people working on a site for one day using a portable monitor, calibration gases, meteorological equipment (for the flux survey) and flux chambers (for the flux chamber method). The total cost of this equipment would not exceed £5,000 and is available from a number of UK suppliers. The results from such one-day measurements would be an estimate of total site emission flux (by the flux survey method), or several tens of surface emission measurements (using the flux chamber). Additionally the flux survey method produces detailed information about the distribution of high emission points across the site.

The eddy correlation and optical integrated-path methods would typically require a team of two people working for a week on a single average-sized site. The capital cost of the equipment would be in the range £10,000 to £30,000 for optical integrated-path. Both

of these methods would yield a representative estimate of total site emissions at the end of such a survey.

The DIAL method is uniquely able to characterise a complete site within one day, including locating high emission points and producing a representative estimate of total site emissions. Such a survey would cost between £5,000 and £10,000.

Presently available technology

A recommendation to use one of the methods reviewed in this study can only be made when considering a particular application. In Table 5.2, the major advantages and disadvantages of each of the methods is summarised, together with some of the applications for which the method may be most suitable.

Future technology developments

The flux chamber and flux survey methods both rely upon an FID instrument. This is a very well developed technology that would not be expected to change in performance or cost in coming years. Hence, the costs or availability of these methods is not expected to change significantly in the future.

The two optically-based methods (DIAL and optical integrated path) are likely to reduce in cost as laser and optoelectronic systems become more sophisticated and compact. The eddy-correlation method relies upon fast-response anemometers and methane monitors and might also benefit from advances in optical-based methane measurement instruments.

**Table 5.2: Advantages, Disadvantages and Applications for Six Different Methods
of Measuring Fluxes of Methane from Landfill Sites**

Method	Advantages	Disadvantages	Applications
Flux Chamber	- accurate measurement over small area. - high sensitivity if required (with long averaging time) - can measure NMHC as well as methane	- labour intensive - time consuming - requires large number of samples to give representative results - intrusive measurement technique - requires full access to site	- landfill cover studies - localised emission measurements - long-term studies
Flux Survey	- cost-effective - simple equipment - locates significant emission sources around site	- inaccurate on complex terrain or in difficult wind conditions - requires dispersion modelling to give total site flux - no measurement of vertical plume profile	- rapid, cost-effective estimation of total site emissions - screening of sites for quality of gas control installations
Tracer Gas	- no assumptions about wind profile required	- assumes point release of tracer is equivalent to diffuse methane emission - large number of sophisticated sample collection and release systems required	- confirming dispersion characteristics - source identification for odour/hazard impacts at downwind locations
Optical Integrated-path	- wide coverage (up to 500 m) - vertical plume profile can be measured - good accuracy - limited dependence on dispersion modelling	- time consuming installation of equipment (future advances may improve this)	- verification of other methods
Eddy correlation	- single point measurement with large area coverage - long-term (automatic) operation possible - measurements have high sensitivity	- initial installation complex. - complex data processing - accurate results require numerous parameters to be measured. - accuracy depends on surface conditions	- long-term monitoring of site emissions
DIAL	- wide coverage (up to 1 km) - measurement of complete plume distribution - rapid flux measurements - localised sources can be identified - no requirement for dispersion modelling - no site access required	- large, complex equipment - reasonable road access required	- detailed studies of sites - screening sites for quality of gas control installations (particularly where site access is not possible)

Combined integrated path/flux survey

Siemens Environmental and Shell Global Solutions have collaborated to develop an
improved flux survey technique, in which the computerised air dispersion model is

validated by open-path methane data derived from a Siemens Hawk System. The greater capacity to monitor methane profiles (compared with point source meters in conventional flux survey) and refinement of the dispersion model to open-path data validation, has resulted in a robust monitoring system for petrochemical site surveillance. Shell evaluated the system by monitoring a controlled release of sulphur hexafluoride in a processing plant on the east coast of Scotland. Comparison with reference tracer gas analyses showed that the dispersion model predicted the plume location within 15 m of its true position, and the emission rate (i.e. methane flux) within 30% of its true value. These impressive data were obtained from a site where wind flow characteristics were strongly modified by the process plant structures, and it can be assumed to be a more challenging test site than that of a typical landfill.

Further trials were carried out, and the system is now installed in a number of shell petrochemical plants throughout the world, principally those sited adjacent to populated urban areas.

Shell Global Solutions have indicated their willingness to externalise the technique and supporting knowledge on a commercial basis.

5.3 Application of Remote Sensing Techniques

5.3.1 Theoretical considerations for remote detection of methane

The detection of methane over landfill sites by ground-based methods has developed into a mature technology. However, significant improvements in the time-cost factor for landfill monitoring could be made if remote sensing systems on airborne or satellite platforms were made available to scan large areas for methane leaks. Airborne and spaceborne sensors gather data in the electromagnetic spectrum, and therefore can only sense methane if it shows a characteristic spectral property that can be detected in the presence of other atmospheric effects. This section reviews the current spectral detection methods for methane, and looks ahead to emerging technologies that may achieve the aim of remote detection of methane from aircraft, such as the HyMap hyperspectral imaging scanner, and (less-likely) satellite platforms.

Spectral properties of methane

Methane gas has a rich infrared absorbance spectrum with a number of vibration-rotation bands that make up its spectral fingerprint. The remote detection of methane requires the spectral recognition of one or more of these vibration bands, which are shown in Figure 5.6.
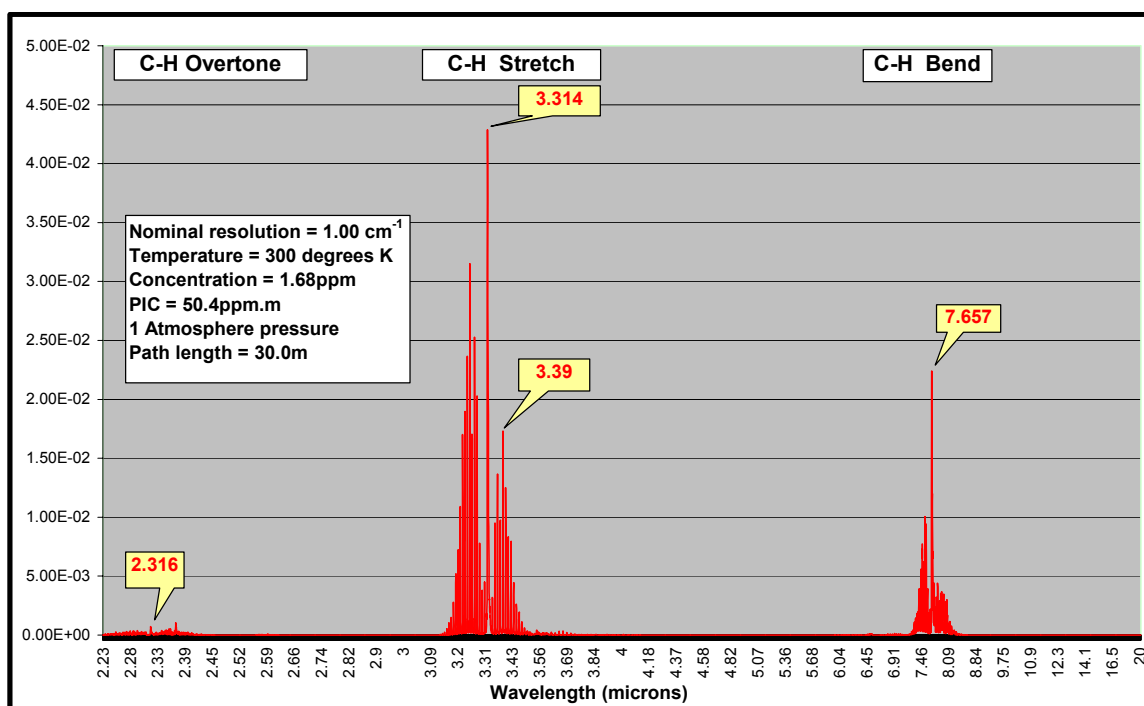
Figure 5.6: Infrared Absorbance Spectrum of Methane

Methane's spectral fingerprint can be clearly identified in two regions of the infrared spectrum. The strongest fundamental vibrations – formed by stretching vibrations of the C-H molecule - are seen in the 3.2 to 3.5 µm range, which corresponds to the mid infrared (MIR) part of the infrared spectrum. Slightly weaker C-H bending vibrations are seen in the 7.3 to 8.0 µm region, the long wave infrared region (LWIR). Much weaker combination tones of these fundamental vibrations are seen at short wave infrared (SWIR) wavelengths around 2.32 µm (and 1.65 µm - not shown on graph). The most prominent and regularly used vibrations for electro-optical monitoring of methane are flagged in yellow.

Electro-optical detection methods for methane

Monitoring of methane over a large area like a landfill site - through the detection of its characteristic vibrations - requires an open-path style of measurement. Here the characteristic spectral signature of methane can be detected using electro-optical remote sensing instruments sited tens to hundreds of metres away from the plume. Two styles of remote detection can be used - active and passive measurements.

Active methods

In active remote sensing measurements the infrared light at a selected wavelength is emitted by an artificial infrared source. This light is received by a separate spectrometer placed either at the opposite side of the gas plume to the source, or retro-reflected by critically aligned mirrors to a combined source and spectrometer instrument. In this style of measurement methane's signature always appears as absorption bands within the spectrum of the high-temperature element used as the source of the infrared beam.

Because all active open-path methods, except those that measure the backscatter of very intense infrared laser light from a gas cloud (see "Passive Infrared" section below), need carefully positioned mirrors or a distal infrared source or both, the active detection of methane is impractical from remote sensing aircraft or satellites.

Passive methods

Passive methods measure the ambient infrared emitted radiation from the target itself instead of the light from an artificial infrared source. This results in the tremendous advantage of mobile and fast operation systems, able to detect remotely a gas plume (depending on its concentration) up to several kilometres. Passive methods therefore, unlike most active systems, offer great potential for remote sensing of methane from the air. However, despite the increased mobility and 'stand-off' capability of passive instruments they are still ground-based. Nonetheless, several opportunities exist for passive remote sensing of methane from the air, especially now that new and improved detection technologies have become available. These involve passive instruments that measure methane's characteristic absorption features either as reflectance (ρ) or emittance (ε) spectra. Figure 5.7 schematically illustrates how these different spectral parameters of a methane plume over a landfill site can be detected by passive remote sensing methods.

Passive emittance measurements

The emittance mode of measurement ($\varepsilon_{g\,(\lambda)}$) is the most common (ground-based) passive detection method used for gases. This is because some of the stronger absorption lines of methane ($\alpha_{g\,(\lambda)}$) are found in the LWIR spectral region, where objects at terrestrial temperatures (300 K) have maximum emittance ($\varepsilon_{T\,(\lambda)}$). These absorption bands or lines become emission peaks in the LWIR region when the temperature of the background scene is cooler than the temperature of the cloud or plume being monitored. In ideal conditions where a methane plume from a landfill site is several degrees warmer than the background, an LWIR measurement from a thermal camera, for example, will show the plume emitting more energy (appearing warmer) at methane's absorption wavelengths than the landfill surface.

Phenomenology model for passive remote sensing of solids and gases

Atmospheric Transmittance

Sky Rad (Ts)

$\rho_{g(\lambda)}$

$\varepsilon_{g(\lambda)}$

$\rho_{T(\lambda)}$

CH_4 (Tgas)

$\alpha_{g(\lambda)}$

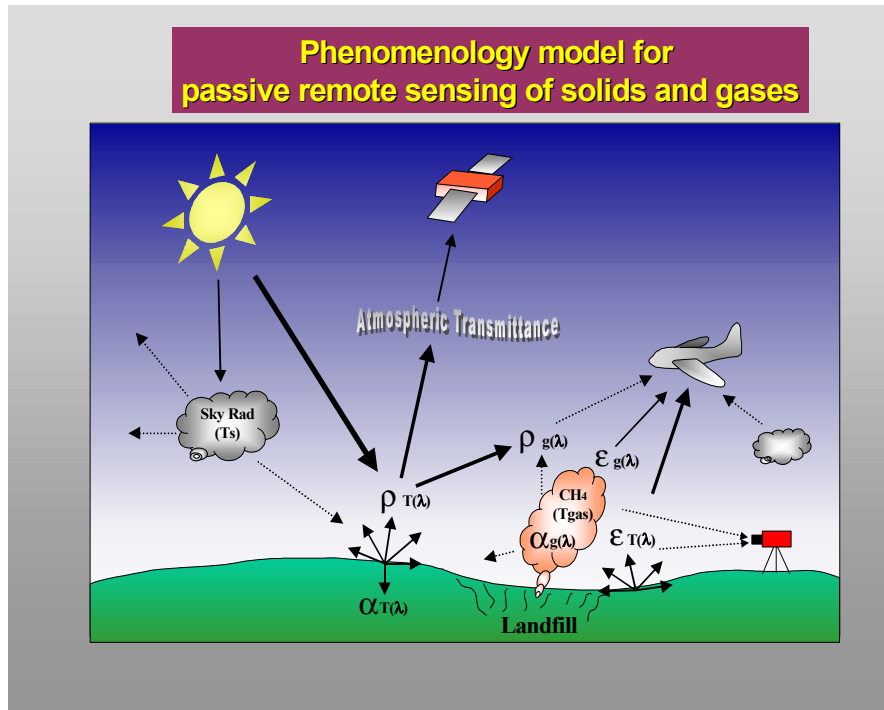$\varepsilon_{T(\lambda)}$

$\alpha_{T(\lambda)}$

Landfill

Figure 5.7: Phenomenology Model for Passive Remote Sensing of a Methane Plume over a Landfill Site (Description of the various terms illustrated in this schematic diagram is given below).

Unfortunately the remote detection of methane by passive emittance (thermal) methods has been quite difficult. Decomposing waste products in the landfill are also emitting LWIR radiation ($\varepsilon_{T\ (\lambda)}$) that can mask or impede the passive measurement of the methane plume. Indeed, passive methods are less sensitive to gas concentrations than active methods, because sensitivity decreases with decreasing temperature difference between the background and the target gas. Where the temperature difference between the gas plume and the ambient background is less than the minimum detectable temperature (sensitivity) of the instrument itself (defined by Near Equivalent Delta T (NEΔT) the detector) then no gas will be detected.

However, in the last 2 years or so the NEΔT of MIR and LWIR cameras has come down considerably – from 0.1 K to 0.0025 K - leading to a dramatic increase in their sensitivities to gas absorption bands. It is this recent improvement in camera technology and introduction of rapid selective filters that provides a new impetus to using emittance measuring technology for methane detection from the air. This will be discussed later in the review.

Passive reflectance measurements

The reflectance mode of measurement uses the naturally occurring energy peak of solar radiation that occurs at much shorter wavelengths in the visible and SWIR regions of the spectrum. This natural illumination is of course used by multispectral and hyperspectral sensors, onboard remote sensing satellite and aircraft respectively, for Earth observations.

As shall be discussed in Section 5.4 it is feasible that hyperspectral airborne scanners, such as HyMap, could be used to detect a change in reflectance ($\rho_{g\,(\lambda)}$) at wavelengths where methane's absorption bands occur, i.e., at 2.3 µm. Therefore, in theory at least, passive remote detection of methane gas plumes over landfill sites, using the reflectance style of measurement, is possible from the air.

Atmospheric windows and methane detection considerations

The main impediment to either reflectance or emittance passive remote sensing measurements along or above the ground is the atmosphere. Infrared light absorption by atmospheric water vapour and carbon dioxide overlaps much of the characteristic fingerprint signatures of many target types, including methane. Increasing the concentration of these infrared-absorbing gases by increasing the atmospheric column reduces the infrared energy available for detection. In many cases these two gases effectively reduce the frequency or wavelength range usable for remote sensing to a small number of windows, or spectral regions, where they do not absorb strongly. These regions or atmospheric windows are shown in Figure 5.8 below, with the wavelength position of the main methane vibrational bands superimposed.
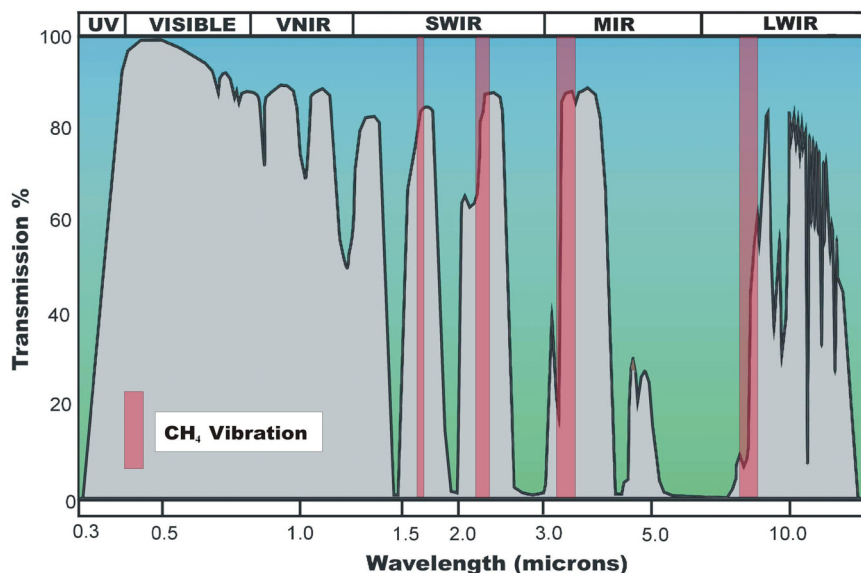
Figure 5.8: Atmospheric Windows of Transmittance for Infrared Remote Sensing. Approximate positions of the methane vibrations are superimposed

It is fortuitous that methane's characteristic SWIR overtone, MIR stretch and LWIR bend vibrations occur at wavelengths where these atmospheric windows have maximum transmittance and, spectrally speaking, they are ideally placed for airborne remote sensing.

However, even in spectral regions where methane has maximum transmittance, the atmosphere still creates difficulties for remote sensing systems. This is especially true for sensors on board orbiting satellites that have an atmospheric column of 100 km to see through, compared with atmospheric columns of only 100-300 m below low flying aircraft.

The main problem in landfill methane detection is that naturally occuring methane (around 1.65 ppm) is large. Nonetheless, many landfill sites are known to emit methane in percentage terms (>2%), which makes its passive detection from the air a feasible option.

Other considerations for the remote detection of methane include the problem of selecting the appropriate wavelengths inside the atmospheric windows that are diagnostic of methane, and the sampling interval of its spectrum. The latter may involve a simple 2 or 3 channel ratioing instrument, or a much more complicated hyperspectral instrument that has many contiguously spaced, but narrow-bandwidth channels across its fingerprint region.

Unfortunately, regardless of how well the methane's absorption features can be sampled, these features can be partially or fully masked by the overlapping spectral effects of other objects. For example, Figure 5.9 shows a MIR single-beam absorbance spectra ("Field Spectrum") collected by a ground-based passive Fourier Transform Infrared (FTIR) instrument at an agri-chemical plant - using the warm wall of a cooling tower as an on-site source of infrared energy. The three spectra below this field spectrum are the three pollutants recognised at the industrial site: methane, nitrous oxide, and ammonia. The methane signature is largely obscured by the nitrous oxide signature in the field spectrum, but becomes much more apparent once the nitrous oxide signature is stripped out of the field spectrum with spectral analysis software.
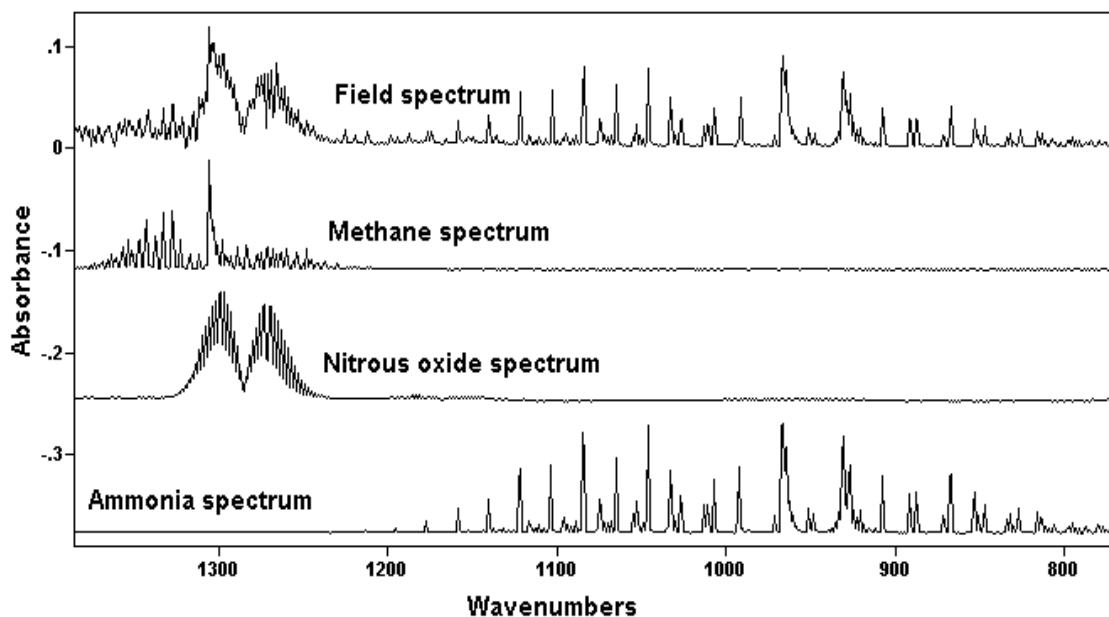
Figure 5.9: Spectral Extraction of Methane from a MIR Single-Beam Absorbance 'Field Spectrum' (Collected by a ground-based passive Fourier Transform Infrared (FTIR) instrument)

Related with the above is the spectral detection performance of the sensors themselves. Given that the right wavelengths or spectral region have been selected to maximise methane detection in the first place, then the amount of methane able to be detected is dependent upon the instrument performance itself. This is usually defined by its Signal to Noise Ratio (SNR) or its NEΔT. Both performance measures can be up to an order of magnitude lower in satellite systems – where the intervening effects of the

atmosphere are at their greatest – compared with low-flying aircraft. However, one of the critical milestones for both satellite or aircraft remote sensing systems is to be able to detect methane below its lower explosive limit (LEL%) in air which is 5% (50000 ppm).

5.3.2 Airborne surveillance

At the moment the only sensors collecting hyperspectral image data of the Earth's surface are flown on board airborne platforms. These instruments typically measure reflected light in the Very Near Infrared (VNIR) and SWIR atmospheric windows. They have between 90 to 256 narrow-band (10-40 nm) channels across this spectral region, depending on the imaging spectrometer's spectral configuration. Because the deleterious effects of the atmospheric column are at minimum, low-flying sensors, such as HyMap, Hydice and AVIRIS, are able to collect reflectance data where solar transmission flux rates are high, and therefore obtain image data with high SNR, typically over 600:1.

The only examples of atmospheric trace gas mapping come from several studies using NASA's AVIRIS hyperspectral imaging scanner. It, like HyMap, has contiguous channels which sample the overtone vibrations (absorption lines) for carbon dioxide, water vapour and ozone, and other gases including methane (see Figure 5.6). Because the scanner has a relatively high spectral resolution, ie. many narrow channels, there are several sensor channels that are located within the bands or absorption lines of these gases. Figure 5.10 illustrates the concept of hyperspectral imaging with a 3D AVIRIS image cube.
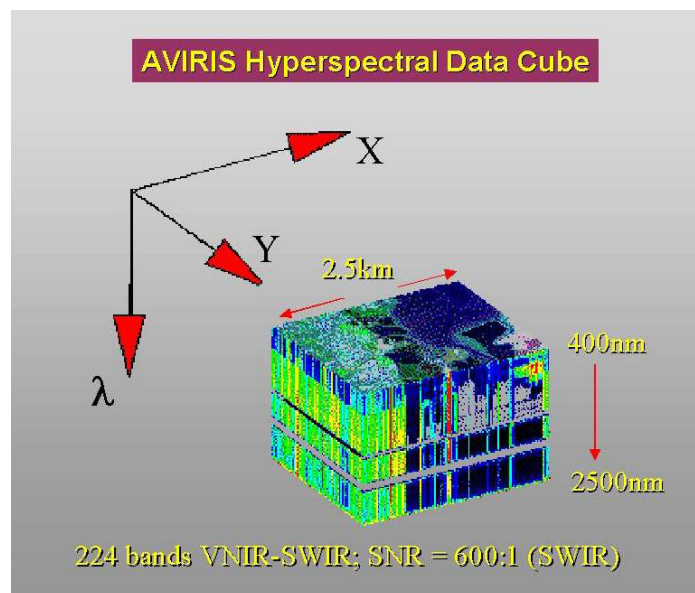
Figure 5.10: Illustration to Show the Concept of Hyperspectral Imaging with a 3D AVIRIS Image Cube

By performing a ratio between influenced channels within the absorption band (measurement channels) to non-influenced channels besides the band (reference channels), it is possible to get an optical measurement of these atmospheric trace gases. These optical measurements are calibrated to the total trace gas columns at standard

ground reflectance spectra - applying the radiative transfer code MODTRAN - to provide quantitative values within 6% accuracy for water vapour. Carbon dioxide and ozone quantitative image maps have also been created in a similar fashion. An example of an AVIRIS water vapour image is shown on the right side of Figure 5.11.
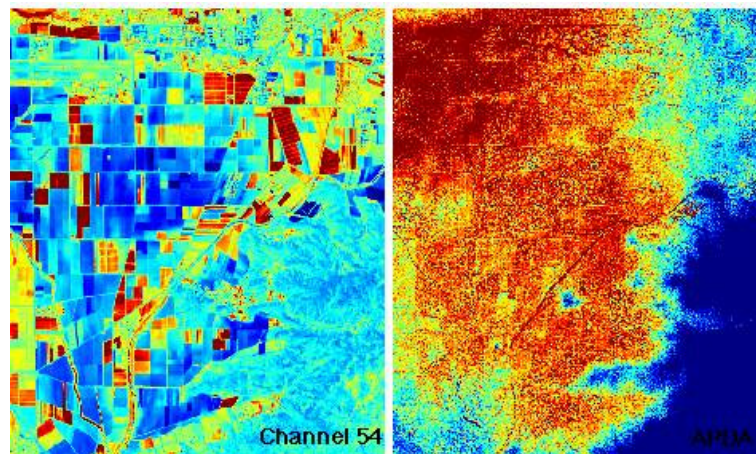

Figure 5.11: An AVIRIS Water Vapour Image. (The original image (left) has been colour coded (on the right) so that pixels with high water vapour values are red and the lowest values are blue).

Why this or similar techniques have not been applied to AVIRIS data for methane mapping is not clear. Possibly it may be that the restriction that airborne sensors prior to HyMap, such as AVIRIS, have lacked the spectral resolution and high SNR to sense through the relatively narrow atmospheric window. Alternatively, it may be that no-one has expressed a need to carry out such work or recognised that it could be done from airborne hyperspectral imaging systems. What has been done however - and shall be shown in the HyMap section below – is that methane and other atmospheric gases are continually being modelled out (discarded) from airborne hyperspectral SWIR (reflectance) data as part of the calibration process to convert radiance to reflectance. Thus, in theory it should be feasible to keep the atmospheric information, including methane, whilst discarding the rest.

The Environment Agency has two imaging sensors used in one aircraft, a CASI (Compact Airborne Spectrographic Imager) captures electromagnetic radiation in the visible and infra-red spectrum as separate wavebands, and a digital thermal sensor records emitted far infrared radiation as a broad waveband. The CASI data are configured as 15 channels of radiance recorded in a selection of wavelengths between 420-920 nm. An overview flight of the Foxhall site was flown at 3000 m with a narrow-width lens giving a spatial resolution of 5 m.

True colour CASI composite images that resemble those seen by the human eye can be generated by combining channels from blue, green and red visible wavelengths. However, the real strength of CASI imagery is that the range of wavelength spectra comprising these visible images contain a wealth of information on the composition of the land surface and the condition of the vegetation growing on it. The true potential of the system is seen when these hidden trends are interpreted by computer and visualised in false colour or selectively enhanced using channel ratios. Vegetation can be

highlighted on the composite image in shades of red by using a near infrared band in the red display, and red and green visible wavebands in the green and blue display. A commonly used procedure used for visualising stressed vegetation uses a false colour composite with an infrared wavelength in the red display. This enhances healthy vegetation in red and sparse/senescent/unhealthy vegetation in orange and yellows. Another procedure uses a band radio known as NDVI (Normalised Difference Vegetation Index) to intensify the difference in reflectance between NIR and red parts of the spectrum:

NDVI = (NIR – Red) / (NIR + Red) *n

where n is an empirical factor for appropriate colour scale

Plate 1 is a true colour CASI image of the landfill site. Plate 2 is the same view but processed to visualise stressed vegetation by reduced infrared scatter, and Plate 3 visualises vegetation stress by the NDVI technique. It can be seen that none of these approaches identified vegetation stress where methane emission would be expected, and this approach was abandoned.

The thermal sensor measures emitted infrared radiation from land surface as a broad band in the 1000 – 12000 nm wavelength range. It can remotely sense temperature differences of 0.1°C but must be calibrated with reference to an external thermometer to give absolute temperature data.

Plate 4 is a thermal image of the landfill site taken in the early morning, and it shows warm areas, and by implication the presence of methane, at the working and recently capped areas. This was followed up by a site visit using a hand-held thermal infrared imager (a Sony ISG Thermo View). An area of methane emission was located using a methane FID sensor, and it the thermal imager confirmed it was co-incident with a 2°C increase in temperature. However Plate 5, a hand-held thermal image of the ground, shows the presence of a large number of localised hot spots due to unevenness and debris.

5.3.3   Satellite surveillance (thermal)

A satellite orbit can observe a large swath of the Earth's surface on a regular basis and, provided that the satellite's sensors can detect the property of interest, spaceborne surveillance of large areas of land is highly cost-effective.

Thermal imaging is an established technique for detecting methane emissions from landfills. It is usual to image the target sites at night time or at dawn in order to maximise the temperature difference between emitted methane and the landfill surface. It has long been assumed that landfill gases in the plant root zone causes vegetation stress, and vegetation stress can be visualised by a number of image processing techniques.

The Foxhall (Ipswich) landfill site which was the subject of a recent R&D project to site test flux chamber monitoring (R&D Project, Landfill Methane Measurement Protocol), was therefore chosen for satellite sensing evaluation. The Landsat 5 satellite, with a

repeat cycle of sixteen days, was selected as an appropriate spaceborne sensor, and thermal infrared and multispectral images of the Foxhall site were purchased. Plate 6 is a true colour composite image of the Ipswich area with the site outlined, and Plate 7 is a thermal image of the area. Plate 8 shows an expanded true colour image of the site. It is clear that there is not sufficient spatial resolution to attempt vegetation stress processing. Plate 9 has warm areas identified by thermal infrared sensor superimposed on to an expanded true colour image. There is some evidence of warm ground where methane would be expected but, again, the resolution is not sufficient to be useful. The total cost of the satellite imagery for Foxhall was £1746.

5.3.4 "HyMap" hyperspectral scanner

The HyMap airborne imaging spectrometer passively collects hyperspectral (radiance) image data across the wavelength interval that methane is infrared active. It represents the state-of-the-art in scanner technology, with its 128 bands of almost continuous spectral coverage in the VNIR-SWIR wavelength range $0.45 - 2.5 \ \mu m$.

As previously mentioned HyMap collects a reflectance style of measurement of the Earth's surface. However, atmospheric gases, including methane, also contribute to this reflected signal, by completely or partially reducing the transmission of solar energy that reaches the Earth's surface at wavelengths at which these gases absorb. Figure 5.12 shows calculated transmission spectra of methane and six other gases found in the VNIR-SWIR region which HyMap measures radiant data. Peak absorption or maximum transmittance of methane is modelled at approximately 20% for its absorption band around 2.3 μm. This can be compared with 80% and 100% transmittance for carbon dioxide (2.0 μm absorption band) and water vapour (1.4 μm and 1.9 μm) bands, respectively. The same radiant transfer processes (as they are known) also operate when the solar energy is reflected off the Earth's surface, and the intervening atmospheric particles, back to the sensor (see Figure 5.7 for a schematic review).
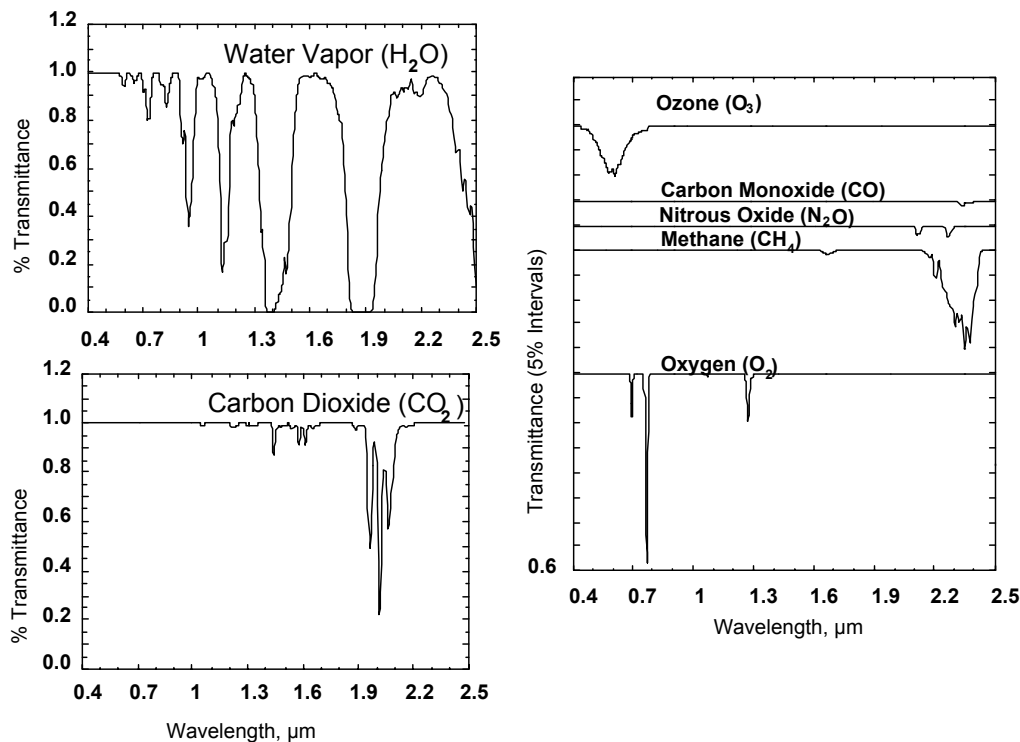
Figure 5.12: Calculated Transmission Spectra of the Seven Atmospheric Gases, Including Methane, Found in the 0.4-2.5 μm Region. These have been modelled at 10 nm resolution for an observer looking straight down through the atmosphere and for a solar zenith angle of 45 degrees using the Tropical Model of LOWTRAN7.

The reduced transmission of solar energy around 2.3 μm – due to methane absorbing at this wavelength – should be detectable in HyMap hyperspectral imagery. Pixels in the imagery that represent areas of the landfill where a methane plume exists will have subtly different radiance values in the methane channel compared with other pixels that are not affected by the methane plume. This assumes of course that there are no significant variations in the landfills surface reflectance properties due to differences in local topographic/illumination or even vegetation type, and other atmospheric parameters across the image swath, such as water vapour, are constant.

Future operational considerations for the remote detection of methane by HyMap include that the sensor be flown at a height that maximises the SNR of the detector and the radiant energy being sensed from a methane plume over a landfill surface. Maximum SNR for the SWIR detector are achieved with pixel sizes greater than 5 m. This equates to a minimum flying height of 2000 m, where a 5 metre-pixel resolution produces a swath width of around 2.3 km and an average flight line length of 10 km. However, pixel sizes, and hence flying heights, that are too large compound the dilution effect of an increasing atmospheric column by reducing the radiance contribution a methane plume will make to the instantaneous field of view within a pixel.

The HyMap system was scheduled to be in the UK in August 1999 for a series of contracted flights, and the Agency secured a 10-km flight from Basildon, Essex, to Tilbury, East London. This flight took in Pitsea (a poorly-controlled landfill site, and

Mucking Flats (a well controlled landfill site). It also included an oil refinery, a power station and mixed industry and housing in East London. Unfortunately, the system malfunctioned at the last minute and the flight was cancelled. However, the instrument returned to the UK in July 2000 and the selected path was overflown and imaged. There was then an additional six months delay in collating and despatching imaging data, clearly indicating the impracticality of this equipment for routine work.

The images were processed by Hunt Spectral Consultancy using specialised ENVI hyperspectral software to identify and isolate the methane and carbon dioxide absorptions, as arbitrary scales, and they were geo-referenced to 1:10,000 OS map background. Further work will be required to calibrate the image data and model the total column gas concentrations quantitatively (say, ppm.m).

Plate 10 is a true colour image of the flight line from Basildon at the top right to Tilbury at the bottom left. Plates 11 and 12 are methane and carbon dioxide emissions images for Pitsea landfill site and Plates 13 and 14 are the corresponding images for Mucking landfill site. These sites were selected because Pitsea is known to be "gassy" and Mucking is better managed. It should be noted that the intensity colour scales are arbitrary and can be used to compare the same gas from different sites but not to compare methane and carbon dioxide concentrations. The Agency regulators for these sites confirmed that the methane images are an accurate representation of the site emissions, as far as is known. Plates 15 and 16 are expanded methane images of the Pitsea and Mucking sites, to illustrate the level of detail available for regulation by ground level inspection. It can be seen that the practical limit is 5m of ground resolution for each pixel.

Plate 17 is a methane image of the oil refinery, and clearly illustrates leakage or venting from some containers. It may be that the absorptions are due to higher hydrocarbons than methane, that also absorb in the same infrared region, and so contributing to these signals. Plate 18 is a carbon dioxide image of Tilbury power station, and the downwind plumes from its two stacks are evident.

Plate 19 is a carbon dioxide image of Tilbury Docks, the River Thames and Northfleet, and dramatically illustrates the complex and high level of emissions in a city environment (the solid red line marks the limit of the airborne image scan). Plate 20 is an expanded image of the dockside and shows the technique's potential to audit greenhouse gas emissions from individual buildings.

Plates 21 and 22 are methane and carbon dioxide emission images of farmland near West Tilbury. Methane emissions in Plate 21 are infrequent and sparsely distributed. They can tentatively be put down to emissions from ruminant animals and/or manure heaps, but there is not sufficient image resolution to confirm these suppositions. Plate 22 shows significant and strongly-clustered carbon dioxide emissions from farmland. Plate 23 superimposes the carbon dioxide emissions on the true colour image as background. Surprisingly, the clustering is on smooth (i.e. not ploughed) bare earth fields. The Institute for Grassland Environmental Research (IGER) comments that there may well be a strong positive flux of carbon from bare arable fields in warm weather, in the order of 10 - 150 kg CO_2/ha/day depending on temperature, soil water content, aerobicity and previous cropping history. Plate 23 also shows that the main methane cluster in Plate 21 is located in a field with alternate strips of crop and earth

areas. Possibly, this may suggest methane emitted from sludge or slurry spread onto a seeded field but confirmation is not possible.

5.4   Techniques Under Development

5.4.1   Future remote surveillance developments

Gas detection sensors on board aircraft have the technological edge over proposed satellite systems, primarily because of the shorter atmospheric columns that these sensors have to see through and hence less deleterious effects on the detector performance. A significant improvement in current instrument technology is required, in terms of spectral resolution and SNR, before the same achievements in airborne hyperspectral sensing can be matched by satellite images. Indeed, it is likely that methane remote detection technology designed for airborne platforms will always be 'one-step ahead' of satellite systems. Instrumentation on aircraft can be larger, more powerful, and importantly, more sensitive because of the shorter atmospheric column.

Notwithstanding these technological limitations, there are several satellite sensors planned for the future that may shorten the technological gap between the potential of airborne and satellite based systems. However, the earliest anticipated benefits for the remote detection of methane over landfill sites are likely to come from the application of new or improved methane sensors on board airborne platforms. Interestingly, many of the new sensors being developed for the research community are designed to look at the MIR and LWIR fingerprint region.

5.4.2   Infrared camera developments

Imaging spectrometers like HyMap use a grating to provide a dispersive element, usually combined with line arrays and some sort of scanning, to split the incoming radiance into discrete wavelengths to form an image cube (see HyMap description). For many instruments the motion of the instrument platform, such as an aircraft or satellite, provides the scanning motion itself. Such technology can be expensive in terms of instrument build time, calibration and maintenance, and is restricted to a handful of specialist instrument makers (and data processors) around the world.

However, new imaging spectrometer technology is available for wavelength dispersion that is relatively cheap, becoming increasingly common and easy to buy off the shelf, and has low maintenance. These use 2D staring array cameras to detect the passive emitted or reflected energies of the object of interest, and an electronically tuneable optical filter to provide wavelength selection. The infrared cameras are similar to everyday video cameras in concept if not design. They use new quantum photodetectors that have peak sensitivities in any of the atmospheric windows that methane has its absorption or emission bands. For example, recent developments at NASA's Jet Propulsion Laboratory have culminated in a particularly sensitive (NEΔT of 0.004 K) yet affordable hand-held camera that operates in the 8-12 μm window. Its remarkable sensitivity is demonstrated by its ability to image passively invisible acetone fumes leaking out of a bottle several tens of metre away - acetone strongly absorbs the 8.8 μm radiation from its surroundings.

The acousto-optical tuneable filter (ATOF) can be rapidly tuned to acquire random or sequential wavelengths (bandpasses) of light and can be used to filter light to methane-specific wavelengths within microseconds, which is faster than the scan speed of a camera. They are solid-state with no moving parts and can be easily mounted on the front or behind any camera lens. By combining the relatively simple, variable field of view, cryogenically cooled and cheap camera technology with AOTFs it should be possible to collect video images from low flying aircraft that show methane emissions from landfill sites.

5.4.3   Airborne gas sensors

Although gas sniffing technology is confined to ground-based operations, both FIDs and infrared instruments have been modified to provide sub-second sampling rates so that they can be used successfully on moving vehicles. In theory these same instruments should be capable of installation in drones or manned aircraft. An overview of relevant sensor developments is given below.

5.4.4 Imaging FTIR

The high spectral resolution and optimum signal-to-noise ratios derived by Fourier transform spectroscopy is now being used for terrestrial imaging. The Lawrence Livermore National Laboratory is currently operating a hyperspectral imager, the Livermore Imaging Fourier Transform Infrared Spectrometer (LIFTIRS), from an airborne platform. Like all imaging spectrometers the LIFTIRS acquires a 3D "data cube" consisting of two spatial and one spectral dimension. It acquires a full 2D image per frame, with successive frames associated with different positions of a moving mirror in a Michelson interferometer. The Fourier transform of this interferogram yields the spectrum. A camera looking through the interferometer completes the imaging spectrometer.

This instrument is capable of operating throughout the infrared spectrum from 3 to 12.5μm with controllable spectral resolution. Thus methane's characteristic absorption features found in both the MIR and LWIR atmospheric windows are available for sensing. Indeed, it has been developed for the identification and mapping of gaseous effluent, amongst other things. However, as it is a military research instrument, no further information on its successes in this application are available, except that high SNRs between 500 and 800 for 25 to 30 bands were achieved in the LWIR. The commercial availability of this or similar instruments is not known.

5.4.5 Satellite sensors

Several passive-style gas sensors onboard satellite platforms are planned for launch in the near future. They represent the first steps of a technological transfer of high spectral and spatial resolution imaging spectrometers from low-flying aircraft to orbiting satellite platforms. The reason why the concept of hyperspectral imaging has not been possible from space until now was due to poor detector technology, in terms of low SNR or NEΔT; no useable reflected or emitted measurements through the atmosphere

could be made. However, it is still not clear whether these new technological advances can still overcome the mitigating effects of the atmosphere to detect methane from landfill sites.

Flying Falcon

An experiment named the 'Flying Falcon' will use a passive quantum photodetector Hyperspectral Imaging System – similar to the infrared camera and AOTF system described above – to detect gas absorption bands, including methane, from the Earth's surface. This instrument represents the state of the art in SWIR, MIR and LWIR infrared detectors. It is expected to have exceptionally high SNR and NEΔT (0.001K) sensitivity, and was due to be launched on-board the space shuttle at the end 2001.

However, to detect photon energy emitted from a methane plume at 300 K by a detector in orbit 242 km above the plume, a pixel size greater than 300 m is required. Moreover this minimum size is designed for remote detection of a methane plume over water, i.e., for offshore natural gas seeps, leaking gas wells and leaking pipelines, which are a much easier proposition for plume detection than over land. Models of detector sensitivity from space suggest that the minimum methane concentration detectable over water and with a 300 m minimum pixel size is 1.6% (16000 ppm).

SCIAMACHY – ENVISAT

The SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY (SCIAMACHY) – due to be launched on board ESA's ENVISAT satellite in 2000 – will passively measure UV, visible and IR spectra of the upper atmosphere. Channel 8 covering the wavelength range 2265 – 2380 nm will allow the global determination of concentrations of methane, amongst other greenhouse gases.

Several space orbiting VNIR – SWIR hyperspectral imaging spectrometers are planned for launch in the next 2 to 3 years, including ARIES and Orbview 4. These will be able to collect image swaths up to 60 km wide and pixel sizes of 30 m over the entire globe. Although they have been designed to identify surface biophysical properties and compositions of geological materials, they will also have narrow channels that cover the 2.3 μm methane absorption band. However, the modelled SNR over this range is anticipated to be too low (ARIES SNR ~ 300:1) for it to be of use to detect surface methane emissions.

SEBASS

The Spatially-Enhanced Broadband Array Spectrograph System (SEBASS) is intended to explore the utility of hyperspectral infrared sensors for remotely identifying solids, liquids, gases and chemical vapours in the 2 to 14 μm 'chemical fingerprint' spectral region. The instrument, which is an extension of an existing non-imaging spectrometer, uses two spherical-faced prisms to operate simultaneously in the MIR and LWIR atmospheric transmission windows. The sensor has already been used from the ground and in aircraft, but the results in terms of its effectiveness to map gases in the fingerprint region are not known.

5.4.6   Passive infrared spectrometry

Section 5.2.4 outlined commercial open-path spectrometers for methane measurement, and pointed out the major disadvantage of having to align source and reflector units prior to measurement, which limits the rate at which large areas can be surveyed.

A passive infrared system (the Optigas GasCam) is being developed which utilises the temperature difference between air and a remote background rather than an infrared source, and consists of a detector unit only.   A pre-production prototype GasCam system was obtained on loan and evaluated on an Environment Agency site using bottled methane gas as a surrogate landfill with a "controllable" methane leak.

The instrument consists of a self-powered detection system, weighing 7 kg, mounted on a tripod and designed to be used by and untrained operator. It is pointed in the desired direction, left one minute to process the signal, and then displays the methane concentration for that particular line of sight. The test demonstrated that methane could be sensed, but not to a suitably low level of detection. It should be emphasised that the test instrument was a development unit, and a final unit is planned with a more sensitive detector.

Hand-held laser pointer

A consortium comprising St. Andrews University, Siemens plc and British Gas submitted a proposal for Foresight LINK funding to develop a hand-held remote methane sensor based on low cost laser diodes. Conceptually, the proposed sensor will consist of a laser pointer with three lasers: a visible laser to indicate where it is pointing, a pulsed laser at methane's maximising infrared absorption wavelength, and a pulsed laser set at a baseline wavelength. When the operator points the device at a solid surface (ground, wall etc.) the reflected energy will be sensed, converted to a methane concentration value, and displayed on a screen. It is estimated that the "wand" will have a measurement range in order of 5–10 metres.

5.4.7   Solid state sensor research

Several UK universities are, or have recently been, engaged in research into novel solid-state sensors for methane. Topics under study include thick and thin films of doped metal oxides, solid electrolytes and advanced catalytic devices such as mesoporous films etc. A number of commercial organisations are, or have been, supporting this work. Details of prevailing R&D can be found in a recent review, published by the UK Gas Analysis & Sensing Group (Bogue, 2003).

5.4.8   Optical sensor research

As with the above, a number of UK university groups are engaged in research into optical methane sensors. Topics include a variety of point, distributed and multiplexed optical fibre-based techniques, a range of spectroscopic methods, interferometry and novel optical sources such as LEDs and laser diodes. As with the solid-state research, some of this work is being supported by industrial organisations and details can also be found in Bogue (2003).

6   DISCUSSION

6.1   Global/National Picture

The Earth's natural greenhouse effect has been enhanced since the start of the industrial revolution by man-made greenhouse gases, principally carbon dioxide, methane, nitrous oxide and hydrofluorocarbons. The rate at which the enhanced effect is growing is of concern and targets for the reduction of anthropogenic greenhouse gas emissions were set by international agreement at Kyoto. In global terms, methane and nitrous oxide together are responsible for some 25% of the enhanced greenhouse effect. Methane is particularly important in that it is second only to carbon dioxide in its global warming effect, it is increasing faster than carbon dioxide, its reduction strategies are more complex than those for carbon dioxide, and possibly it may eventually become the dominant man-made greenhouse gas. Whereas carbon dioxide and HFCs have straightforward origins (biomass and fossil fuel combustion, and refrigerant and aerosol propellant respectively), methane and nitrous oxide are formed in a number of ways. These include widespread natural processes and staple crop growing practices, and consequently viable strategies for their reduction are more difficult to implement.

In global terms, the main sources of nitrous oxide are soil, river and estuarine microbiological reactions. As these effects are predominantly in Asia and Africa, nitrous oxide is not an important UK greenhouse gas in comparison with methane. At present the major UK sectoral source of nitrous oxide emission is industrial processes, followed by fuel combustion and agriculture. UK methane emissions are primarily from three sources: landfill waste, agriculture, and fugitive emissions from fuel; whereas in global terms the principal sources are wetlands, rice production, ruminants and biomass combustion.

Landfill contribution to the UK's methane release is currently estimated to be some 47% of the total, although that value is now questioned as an overestimate. Agriculture contributes 29%, mostly from enteric fermentation by ruminant animals but also from manure management. Fugitive emissions from coal, oil and gas account for 22% with the remaining 2% contributed by combustion processes.

6.2   Reduction Strategies

Reduction strategies for UK methane emissions depend on the generation process. Landfill emissions are being minimised by a regulatory framework that includes capping with impermeable material and recovering and burning methane to generate power. Agricultural researchers indicate the potential for developing a microbiological methane reducing soil cap, but fissure flow emissions may make this impractical.

Agricultural reduction strategies are based on best practice guidelines. Manure management strategies involve improved composting to maximise aerobic oxidation (the accompanying increase in nitrous oxide generation has to be assessed as a trade-off). There appears to be no significant move in the UK towards capturing and combusting manure methane. The principal agricultural methane source, i.e. ruminant enteric fermentation, does not lend itself to a straightforward best practice reduction

strategy. Three approaches to reduce rumen fermentation yields are possible: namely dietary change, altering the rumen microflora, or improving the genetic potential through (for example) anabolic steroids. Unfortunately actual dietary trends are tending to increase rather than decrease ruminant methane production. Specifically, the trend to move from grass silage or hay to maize feed increases ruminant methane production by some 25%.

Emissions from coal mining are declining as deep mines continue to shut down in the UK, but as open cast coal mining is increasing and it may be worth revisiting the emission factor calculation for open cast mining. Estimates of methane leakage from natural gas piping and installation are high. Initial contact has been made with British Gas's technical unit, BG Technology (now Advantica) to collaborate on instrument developments.

Releases from nitrogen-fertilised farmland are a significant source of UK nitrous oxide emissions. Fortuitously, on-going initiatives to better manage fertiliser usage for drinking water protection or as part of the eutrophication strategy should also reduce nitrous oxide emission.

The principal UK sources of nitrous oxide are industrial processes (adipic acid, nylon, nitric acid) and the principal reduction strategy lies with process industry regulation. In terms of soil production, the best reduction strategy is more efficient nitrogen fertilizer usage to reduce unnecessary application in spring and autumn when crop demand is low.

The points discussed above consider reduction strategies from the viewpoint of reducing inputs to the environment. The complementary approach of reduction by increasing the processes of removal of greenhouse gases is, arguably, an equally valid route to reduction of greenhouse gases in the atmosphere. At the least, there may be scope to review the "health" of the dependent factors in the natural removal processes (sinks). Obvious examples are relative efficiencies of land cover types in photosynthesising carbon dioxide to biomass carbon; the relative balance of emission and sequestration of carbon by agricultural practices; and the degree of land drainage as a criterion of soil's methane oxidising capacity. All can be estimated on a broad scale by established remote surveillance and GIS techniques.

6.3   Surveillance Techniques

The flux chamber method is accurate and gives a direct measurement of methane flux but is labour intensive and slow, and thus not amenable to extensive spatial coverage. Of the other techniques, flux survey appears the most promising, but its reliance on computerised dispersion modelling that has to be validated specifically for each site can give rise to measurement uncertainty. Nonetheless, its speed and wide spatial coverage make it a useful complement to the flux chamber process.

Shell Research has developed the flux survey technique further by using optical integrated path monitoring instead of discrete methane measurements (i.e. linear rather than point measurements) to calibrate the computerised methane dispersion model. It has been validated and is widely used on overseas petrochemical plants sited in urban

areas, and Siemens and Shell who developed the technique jointly are interested in marketing it commercially. British Gas has also developed a computerised dispersion model for locating fugitive emissions based on a mobile point source sensor.

Portable sensors for methane are commercially available but there is no low cost hand held sensor (other than the flame ionisation detector described in Section 5.1.1) to promote mass monitoring by ground inspection. However, a large number of researchers are developing small hand-held sensors for methane (twelve programmes in Northern Europe were identified by a rapid literature research, no doubt there are more on a global basis). The main driver for this burgeoning research area appears to be health and safety.

In addition to hand-held application, these sensors can be deployed in two other ways: mounted in an unmanned aircraft (drone) for rapid aerial survey, or distributed around a site to feed a computerised methane dispersion model of a site in real time. One hand-held sensor research project is of particular application to field inspection in that it proposes to develop a laser pointer/sensor for methane that can sweep areas of 2-5 m radius.

Airborne imaging of methane and carbon dioxide was successfully demonstrated in this project. As far as is known, this is the first time that these gases have been imaged from the air. The technique has great potential for cost effective and widespread monitoring of these gases, but at present the equipment is experimental and not available on a routine basis.

Present spaceborne systems have no application to ground level methane measurement. A number of future satellites which will be able to image in the infrared region are planned for launch in the next 3-4 years, notably Flying Falcon, SCIAMACHY and SEBASS. Their capability to detect ground level methane emissions remains to be proven.

In addition to the techniques discussed above, there is an exceptionally wide range of methane sensing systems under development, for example infrared cameras, passive infrared sensors, selective semiconductor devices. It is reasonable to assume that a review of methane measuring techniques carried out in (say) two years time would identify a proven suite of new technology monitoring options.

7   CONCLUSIONS

Methane and nitrous oxide are highly important contributors to the enhanced greenhouse effect globally, but from the UK emissions perspective nitrous oxide is of minor significance. The principal sources of UK methane are landfills at 47% of the total (that value is now under review), agriculture at 29% (predominantly ruminant enteric fermentation), and fugitive emissions from coal, oil and gas at 22%. The remaining 2% are assigned to combustion process emissions.

These data are based on emission factor calculations rather than monitoring and have a high degree of uncertainty, as evidenced by landfill methane's estimate's recent revision. Little, if any, actual monitoring of the major greenhouse gas releases (i.e. carbon dioxide, methane, nitrous oxide and halofluorocarbons) is carried out. Moreover, the processes that remove greenhouse gases from the atmosphere do not appear to be monitored or audited despite their fundamental importance in fixing equilibrium concentrations of the gases in air.

Methane generation by ruminant (i.e. cattle and sheep) fermentation is high and there appears to be no viable reduction strategy other than reducing the number of animals. Moreover, the current trend of moving from grass to maize feed is exacerbating the problem in that it can cause a 25% increase in methane generation. Also, radical approaches to ruminant methane reduction such as genetic modification are unlikely to obtain public support. Other sectoral sources of methane and nitrous oxide seem to offer scope for viable reduction strategies.

The marine coastal margin appears not to have been considered in UK greenhouse gas releases or sinks estimation, despite the acknowledged importance of the seas as a carbon dioxide sink and a nitrous oxide source. In particular, the effect of eutrophication of estuarine and coastal waters on nitrous oxide emission (and possibly as an enhanced photosynthetic sink for carbon dioxide) is worth consideration.

Present methane monitoring methods were developed for investigating landfill capping characteristics and are not suitable for wide area monitoring of the whole environment, or even of a whole landfill site. Two developing techniques, airborne infrared imagery and real-time flux modelling, show potential for wide area monitoring and temporal monitoring respectively.

Airborne infrared imaging of methane and carbon dioxide was demonstrated successfully in this project, but the equipment is expensive and based overseas, and is therefore not practicable for routine use. Some commercial companies such as British Gas and Shell use real time flux monitoring of hydrocarbon gases but their systems are not openly available. Both airborne imaging and flux modelling are being taken forward by future R&D projects.

Carbon dioxide reduction is being addressed by Government Initiatives arising from the Kyoto conference. At present its emission is being estimated from fuel usage, but airborne carbon dioxide imaging will present an opportunity to audit these data.

8   RECOMMENDATIONS

1. No presently available greenhouse gas monitoring method is suitable for wide area or wide temporal monitoring of the whole environment. Present methods for landfill applications have limited value for landfill capping condition monitoring but are too labour intensive for wider applications. The flux survey method appears to be the most applicable for wide scale use.

2. This project has demonstrated that methane and carbon dioxide can be imaged by an airborne spectrometer that was brought in from overseas for the purpose. The system is too expensive to be considered for routine use but an R&D project will be initiated to develop a low-cost instrument in the UK. Airborne imaging is effectively limited to carbon dioxide and methane greenhouse gases. It is unlikely to become sensitive enough to measure nitrous oxide and the other less concentrated greenhouse gases.

3. Real-time flux modelling has application to measuring the total methane flux from large area sites continually. An R&D project is in progress to develop a suitable system for methane emissions from landfills or agricultural units. As part of this a new technology sensor, based on an infrared laser, is being developed in partnership with Siemens Environmental Systems and British Gas.

4. The emission of methane from open-cast coal mines appears not to have been monitored in the UK. It would be worthwhile confirming that these emissions are in fact, as low as they are claimed to be.

5. Liaison with the Institute of Grassland Environmental Research (IGER) should continue, to maintain an awareness of manure management and best management practice for nitrogen fertilizer usage, and remain up to date with any developments in the ruminant fermentation issue.

6. Some questions remain unanswered: namely whether the natural and agricultural environments are neutral with respect to carbon dioxide emission/sequestration, and whether eutrophication of marine waters increases or reduces the net effect by emission of nitrous oxide or photosynthesis of carbon dioxide.

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LIST OF PLATES

Plate 1. CASI true colour image of Foxhall landfill site, nr Ipswich

Flown on the 13th June 1999

Environment Agency 1999
National Centre for Environmental Data & Surveillance

Plate 2. Vegetation Stress visualised by IR Scatter

Plate 3. Normalised Difference Vegetation Index (NDVI) Image

Areas of high vegetation cover shown in red
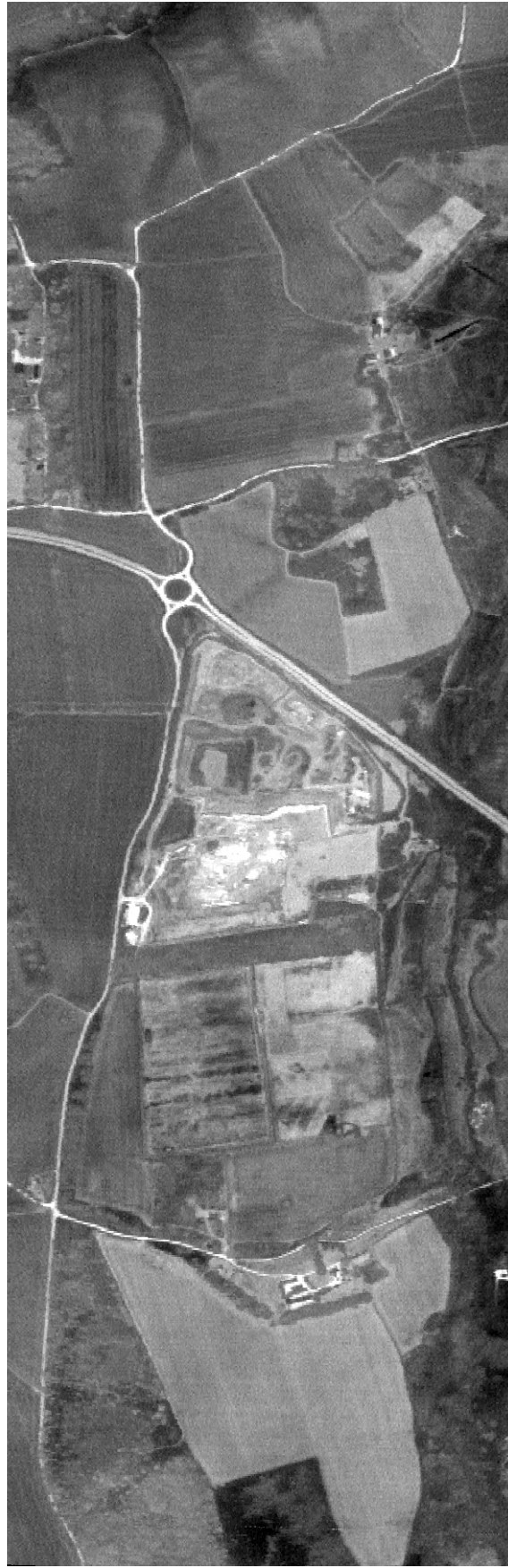
Plate 4. Airborne thermal image of Foxhall landfill site

Flown on the 8th July 1999 at 04:00 GMT

The warmest areas are highlighted in red.
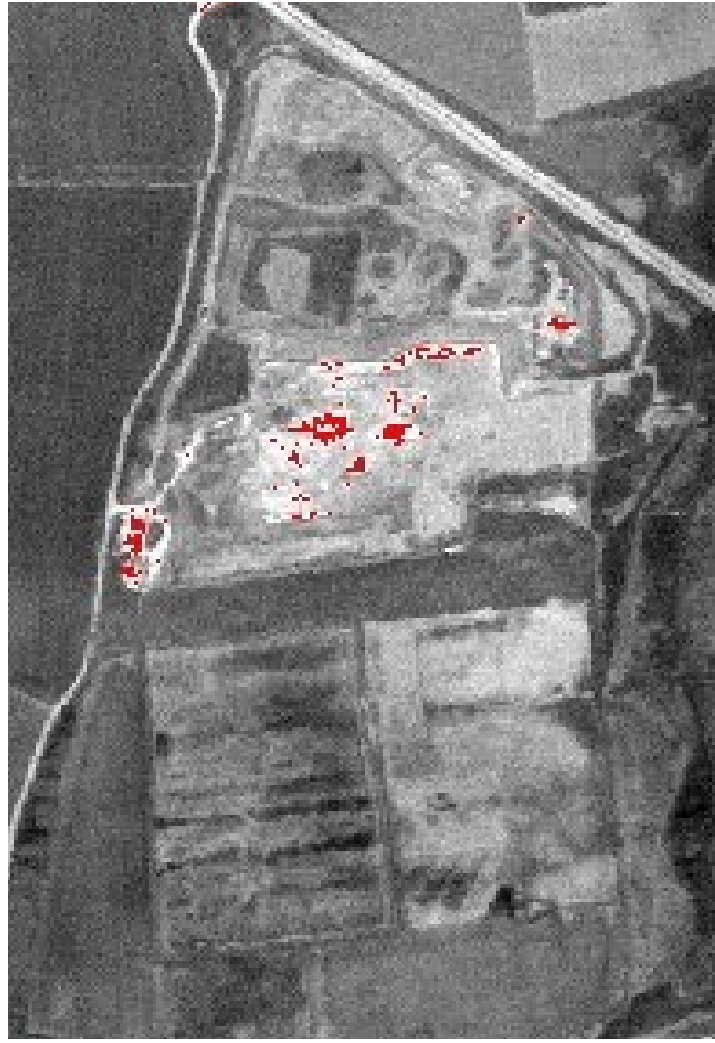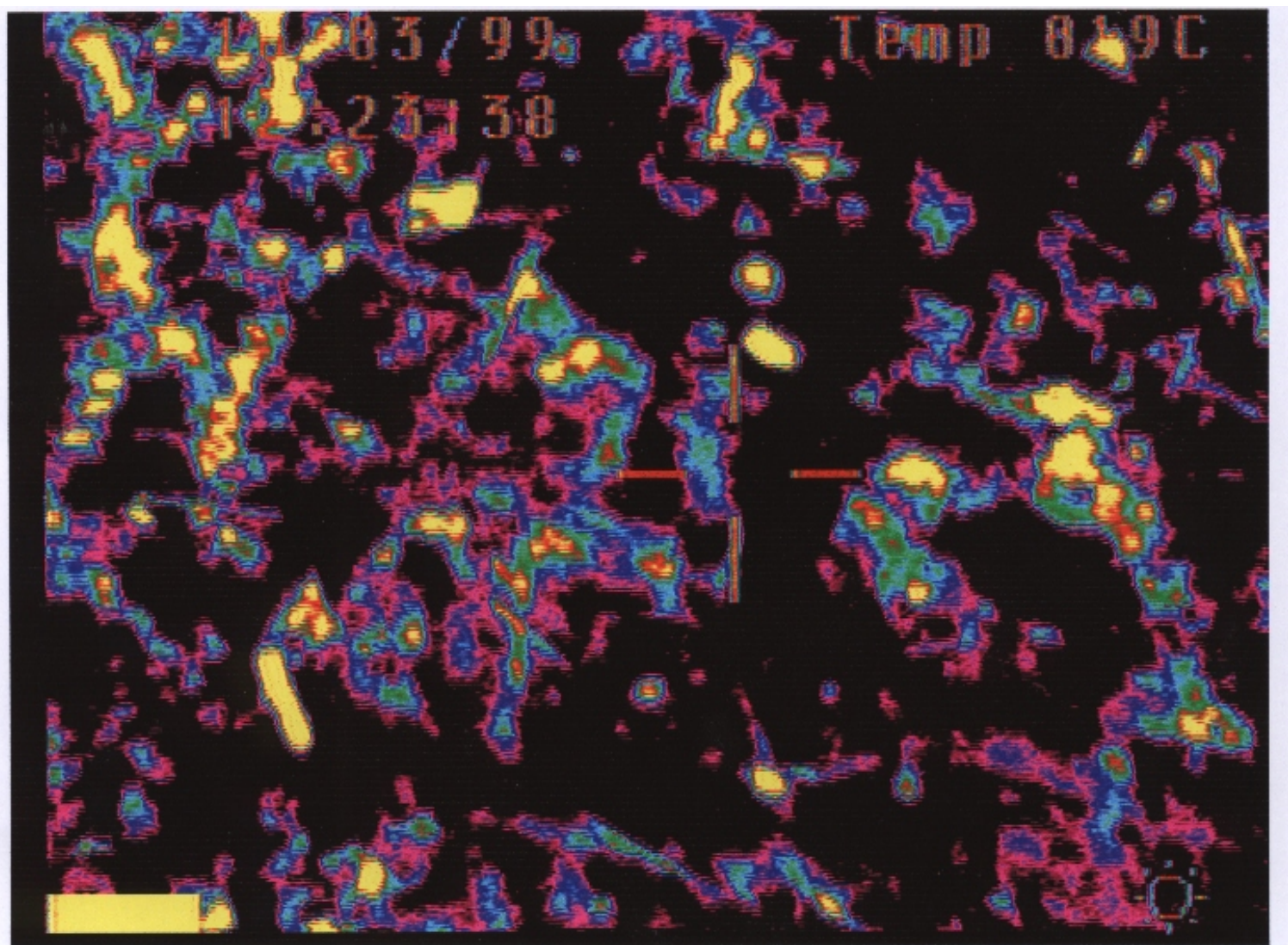
Plate 5. Hand-held thermal Image of Landfill Cap

Plate 6. Landsat TM satellite image of the Landfill site.

Foxhall Landfill site is outlined in red
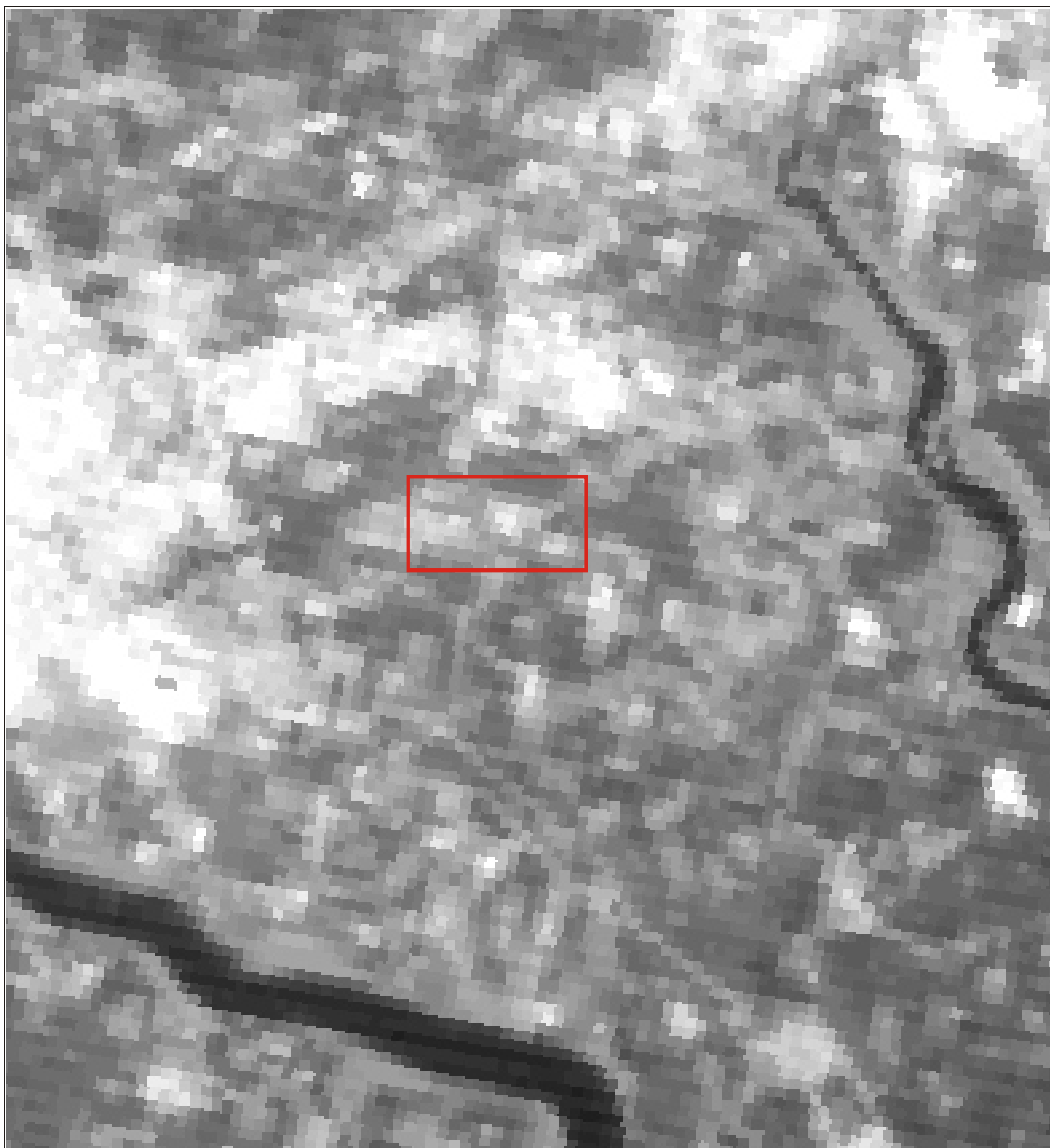
Plate 7. Landsat TM thermal image of the Ipswich area.

White = hot, Black = cold

Environment Agency 1999
National Centre for Environmental Data & Surveillance

Plate 8. Landsat TM image of Foxhall Landfill Site

Plate 9. Landsat TM image of Foxhall Landfill Site with warm areas coloured in red.

Plate 10: True colour image of the Hymap flight path over South East London

Plate 11: Pitsea landfill: methane emissions

Plate 12: Pitsea landfill: carbon dioxide emissions
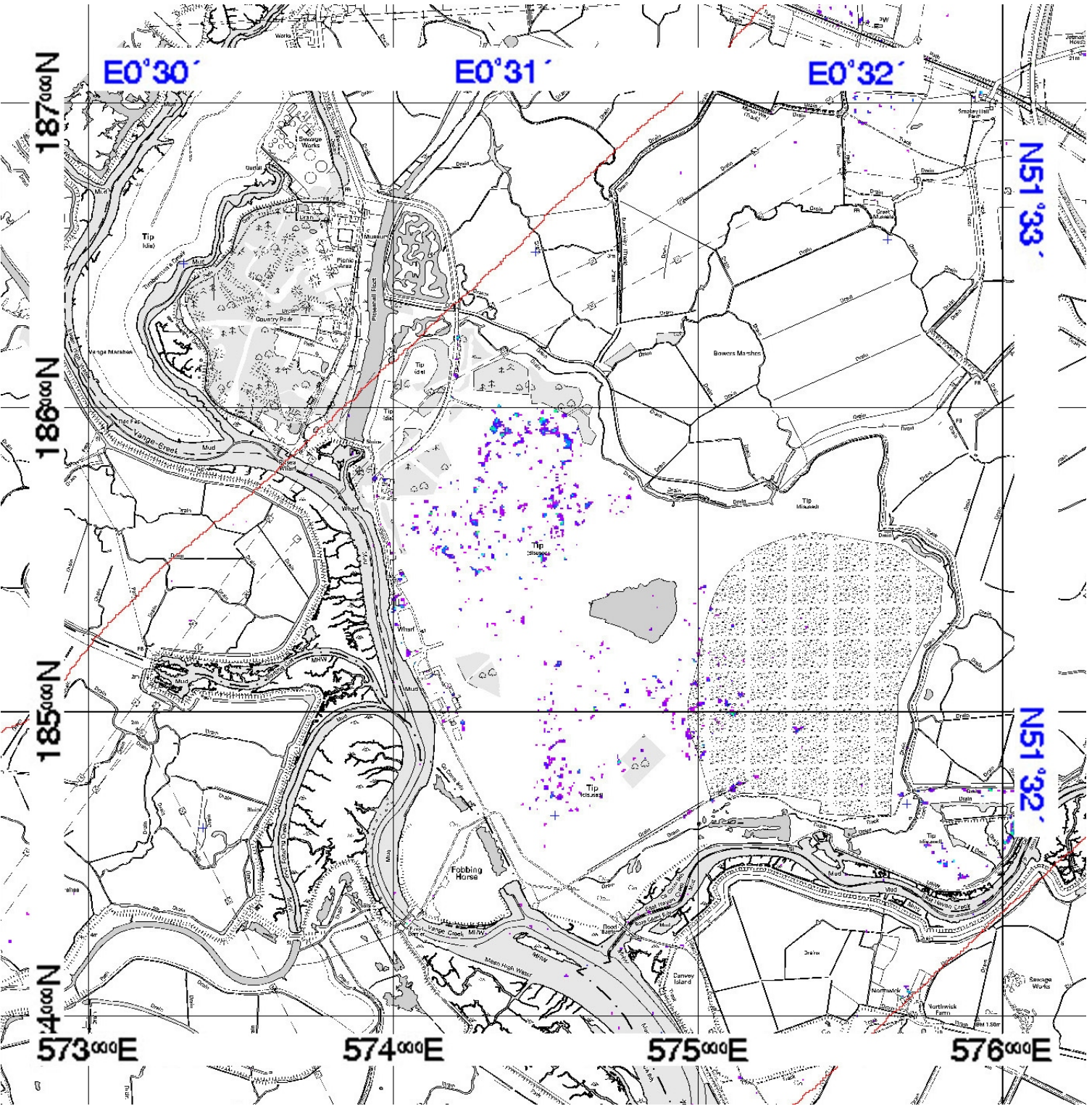
E0°30′ E0°31′ E0°32′

N51°33′

N51°32′

187000N 186000N 185000N 184000N

573000E 574000E 575000E 576000E

Plate 13: Mucking landfill: methane emissions

E0°25´ E0°26´ E0°27´

N51°29´

567₀₀₀E 568₀₀₀E 569₀₀₀E 570₀₀₀E

Walton's Hall
Turner's Farm
Sutton's Farm
Merrie Loots Farm
Linford
Recreation Ground
George and Tregon Pit
East Tilbury
Thames Industrial Park
Sports Ground
Sand and Gravel Pit
Sand and Gravel Pit
Sewage Works (disused)
Mucking Marshes
River Thames
Travelling Crane
Mud
Jetty
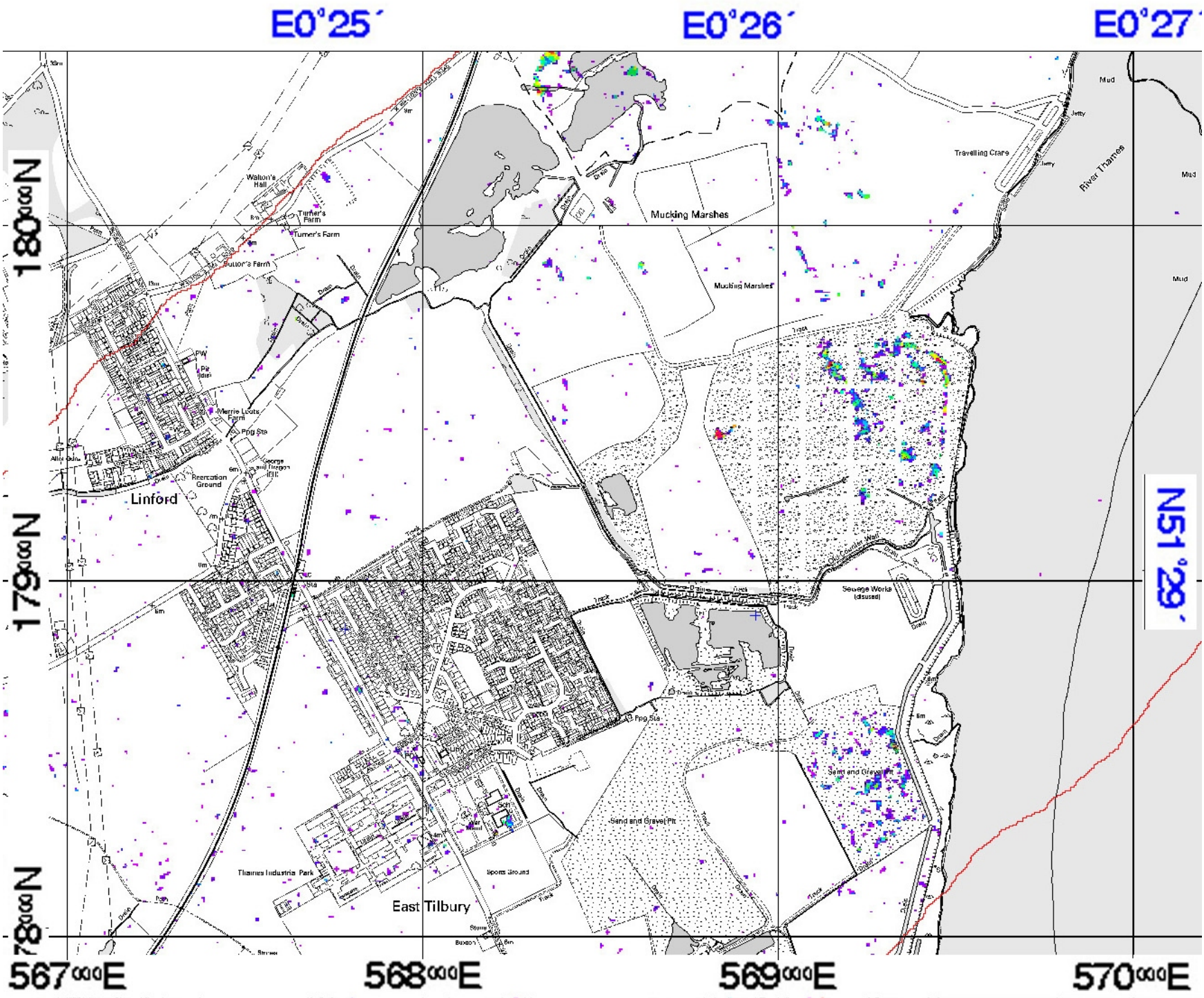
Plate 14: Mucking landfill: carbon dioxide emissions
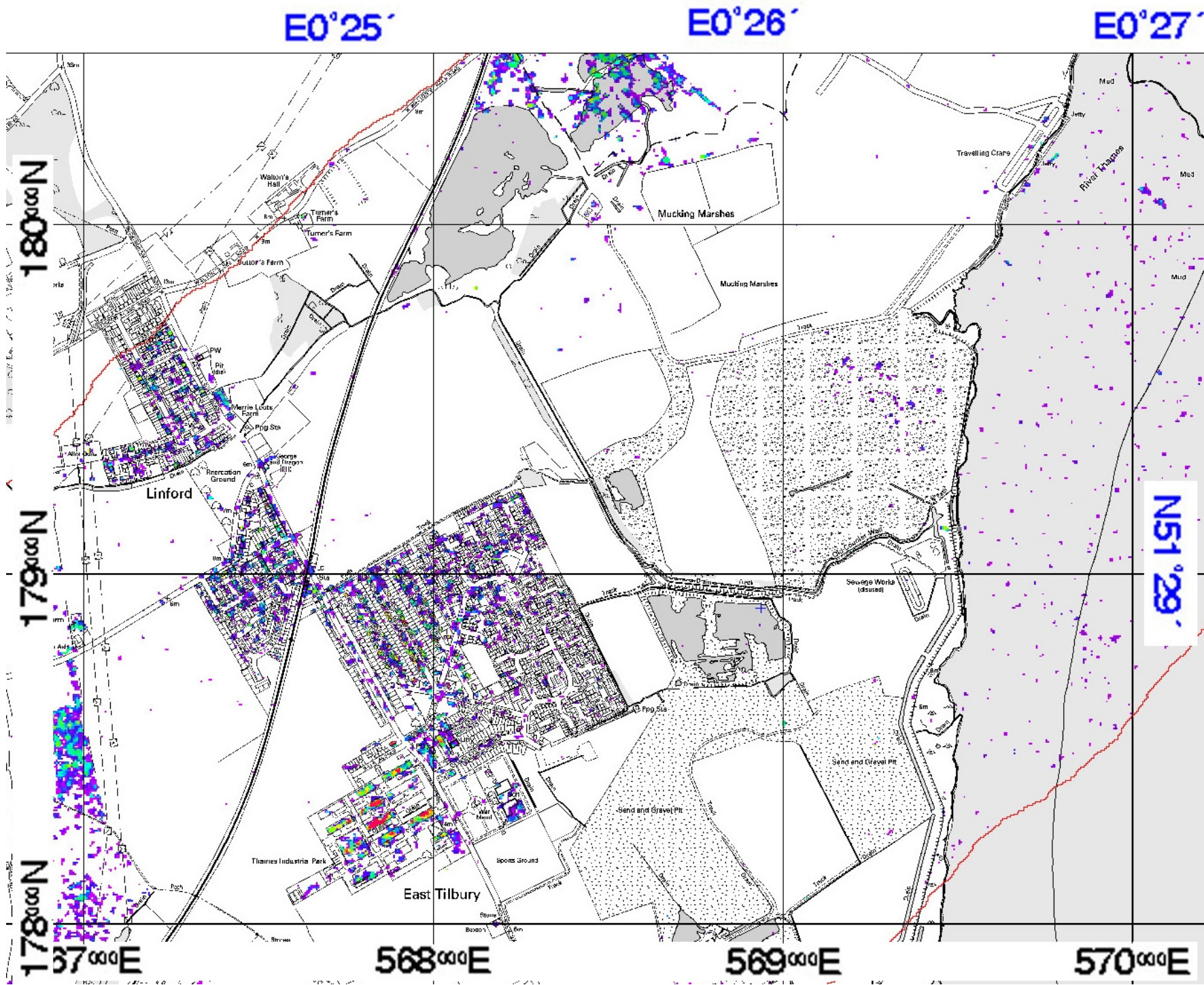
E0°25′ E0°26′ E0°27′

N51°29′

567°°°E 568°°°E 569°°°E 570°°°E

180°°°N 179°°°N 178°°°N

Walton's Hall
Turner's Farm
Turner's Farm
Sutton's Farm
PW
Pit (dis)
Merrie Loots Farm
Png Sta
George and Dragon
Recreation Ground
Linford
Mucking Marshes
Mucking Marshes
River Thames
Travelling Crane
Jetty
Jetty
Mud
Mud
Mud
Counter Wall
Sewage Works (disused)
Png Sta
Sand and Gravel Pit
Sand and Gravel Pit
Sand and Gravel Pit
Thames Industria Park
Sports Ground
East Tilbury

Plate 15: Pitsea landfill: methane emissions - showing pixels

180**N

569**E

Marshes
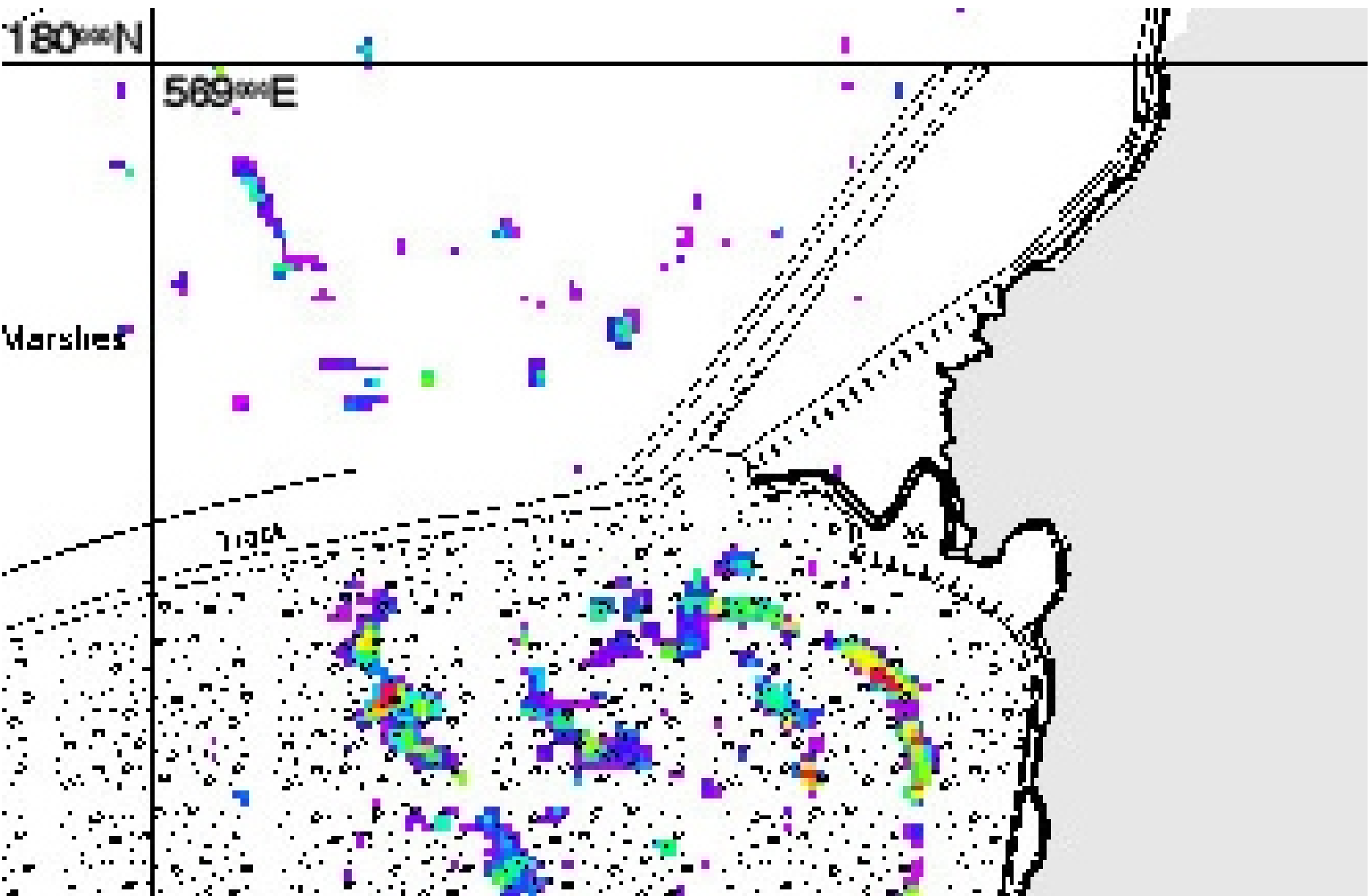
Plate 17: Thames Haven oil refinery: methane emissions

Oil Storage Depot

182⁰⁰⁰N

572⁰⁰⁰E

176ᵒᵒᵒN

566ᵒᵒᵒE
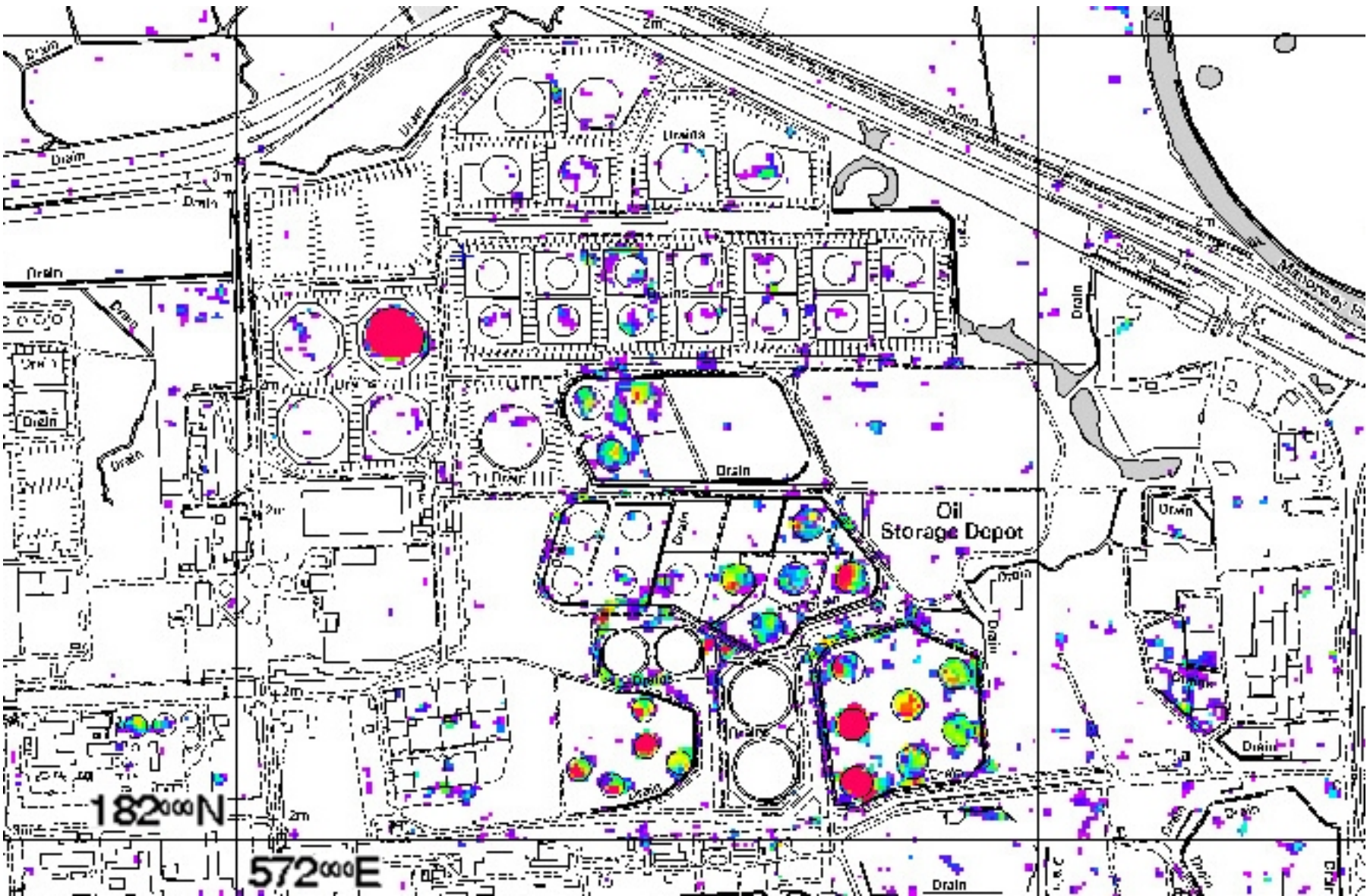
Tilbury Power Station
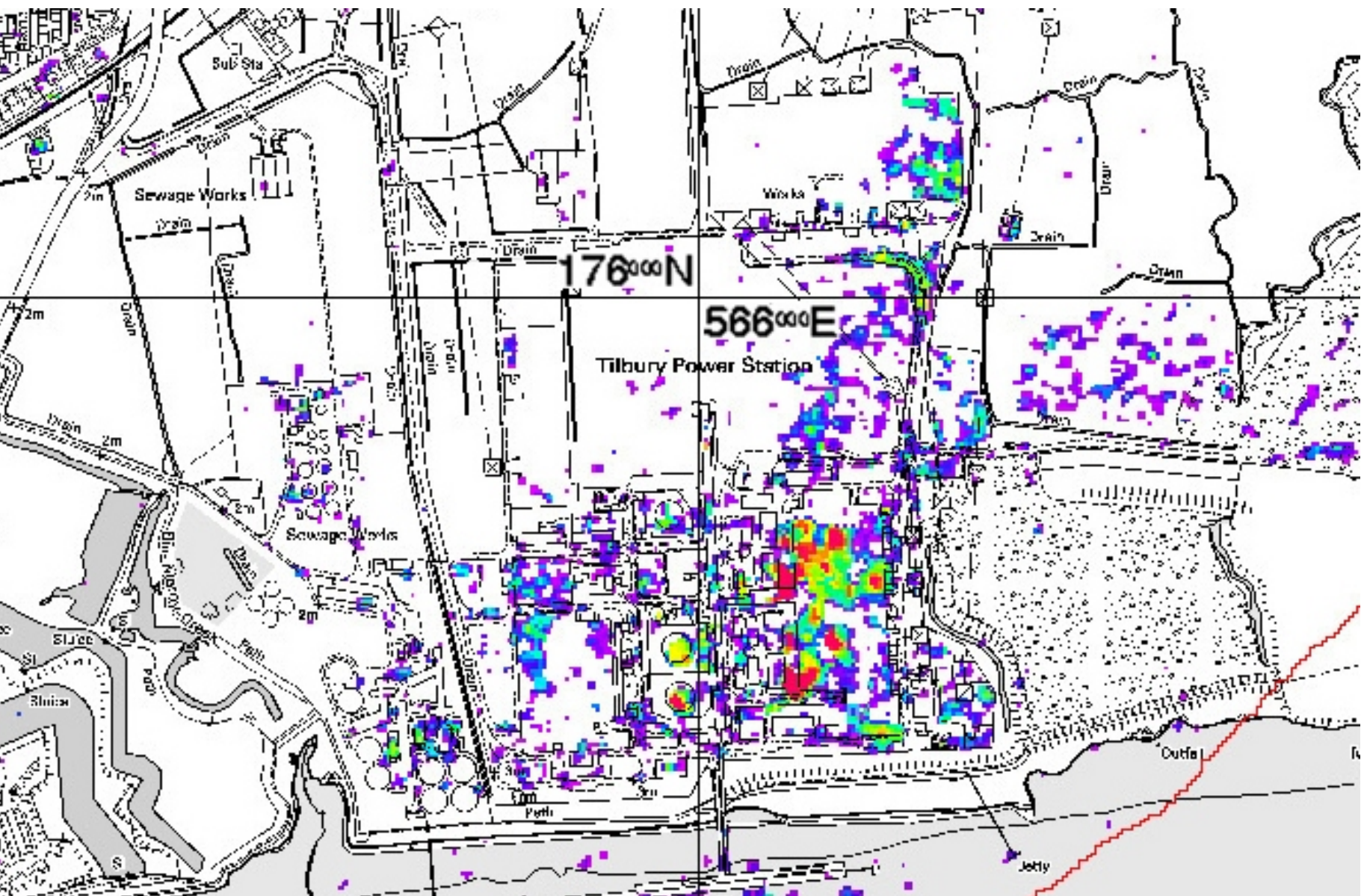
Plate 19: Tilbury docks, the River Thames and Northfleet: carbon dioxide emissions
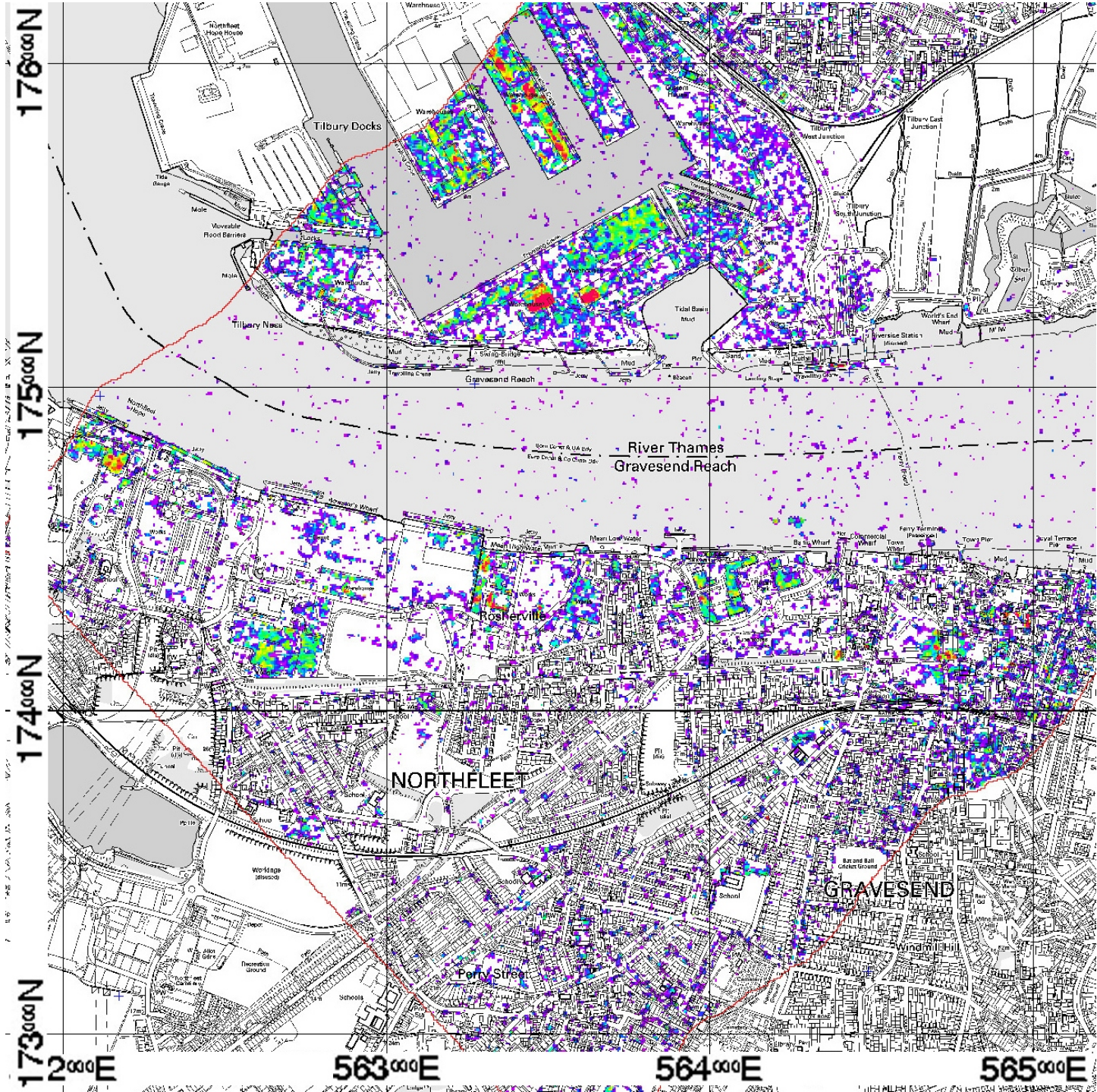
Mill House Farm

Beckaland

Ashlco Farm

High Ash

Blue Anchor Cottage

Halford Farm

Halford House

Coal Road Track

178 000 N

566 000 E
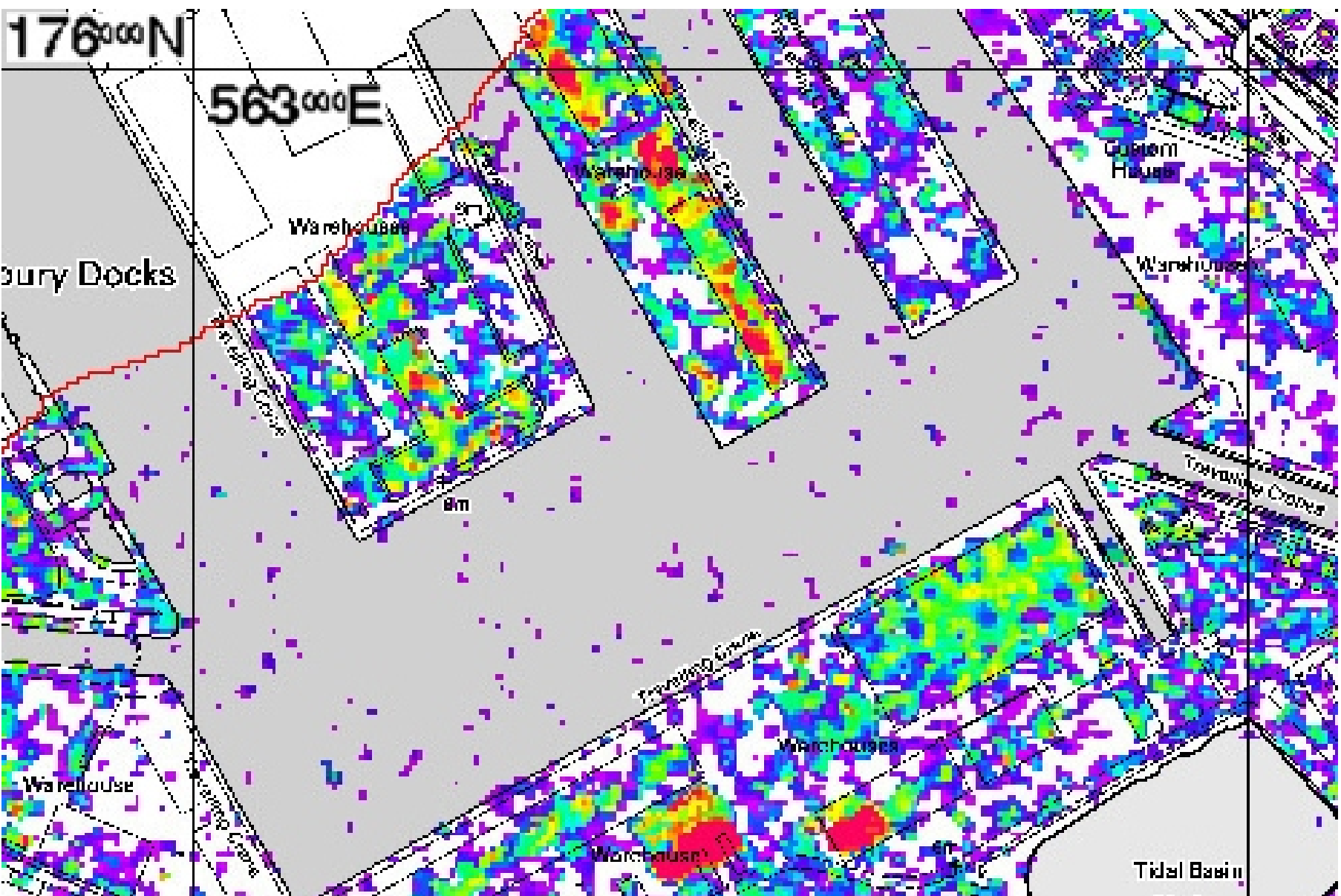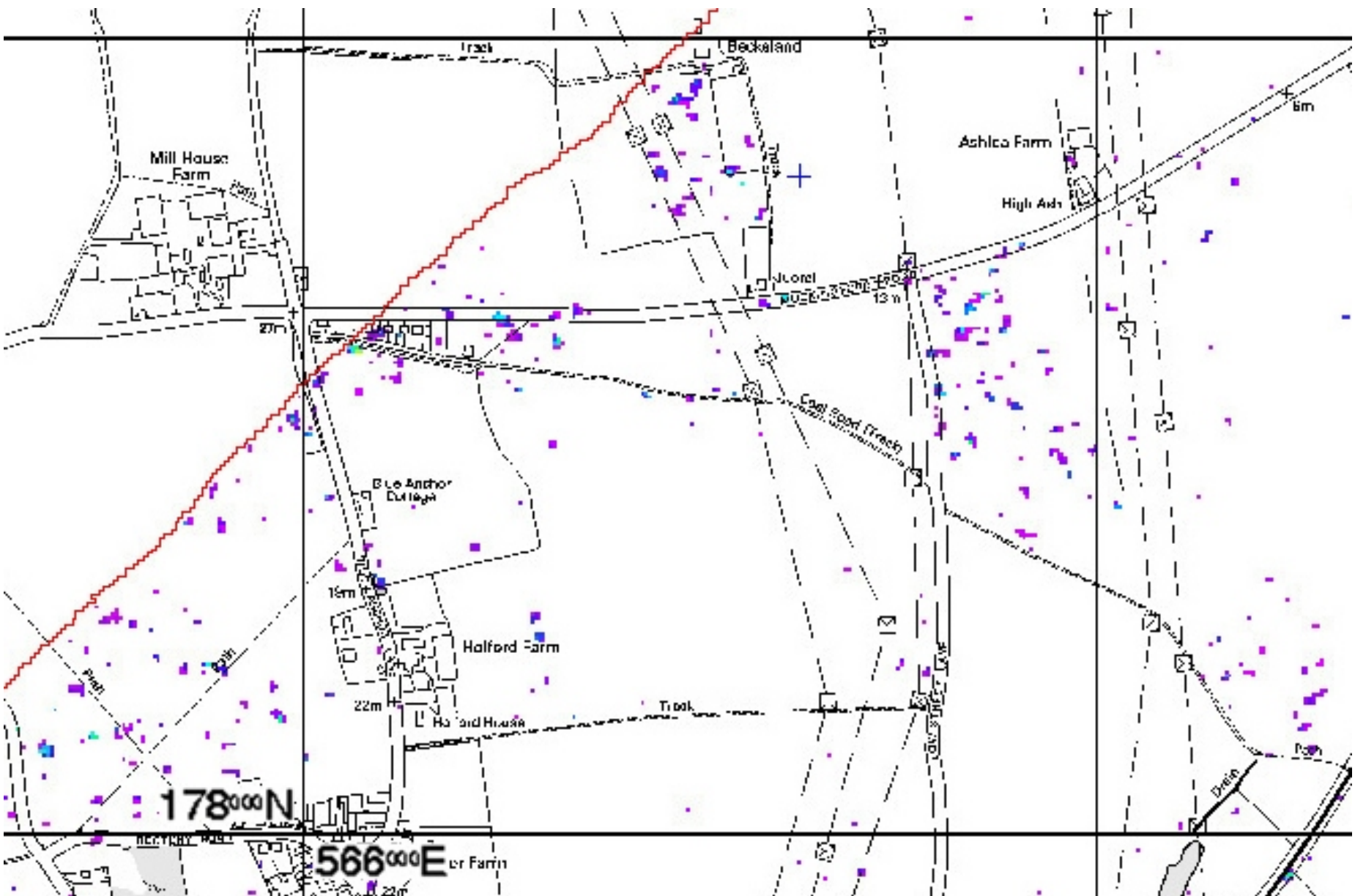
Plate 22: Farmland near West Tilbury: carbon dioxide emissions