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STABLE ISOTOPE RATIOS IN METHANE CONTAINING GASES IN THE UNITED KINGDOM

S P Hitchman, W G Darling and G M Williams

S P Hitchman and G M Williams
Fluid Processes Research Group
Keyworth

W G Darling
Hydrogeology Research Group
Wallingford

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Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

☎ Wallingford (0491) 38800 Telex 849365 HYDROL G
Fax (0491) 25338

Parent Body

Natural Environment Research Council

Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ Swindon (0793) 411500 Telex 444293 ENVRE G
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PREFACE

The gas explosions at Loscoe and Abbeystead have highlighted both the dangers associated with the migration of methane in the subsurface, and the need to quickly and accurately establish its source in order to instigate appropriate control. In order to improve the ability to identify sources, the potential of stable isotope ratios (^{13}C and ^{12}C , ^2H and ^1H) has been investigated as an additional means of characterising methane. Thus a variety of UK sources of methane were analysed to extend the database and assess the potential of stable isotope ratios for source identification.

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EXECUTIVE SUMMARY

The gas explosions at Loscoe and Abbeystead have highlighted the dangers associated with the migration of methane in the subsurface, and the need to quickly and accurately establish the source of the methane in order to instigate appropriate measures for control and remediation. Sources of methane include leaking gas mains, sewers, natural gas reservoirs, gas associated with oil and coal, landfills and the products of anaerobic degradation of organically contaminated groundwater. Although public opinion may demand rapid action following the discovery of methane hasty remedial action which does not consider the source of the gas or its mode of transmission, may at best be a waste of resources, or, at worst, may exacerbate the spread of the gas.

To confirm a methane source three approaches may be used. The source can be identified by comparing the composition of the gas with known source compositions: identifying a migration pathway between the putative source and the point at which methane is observed and confirming the existence of a mechanism (such as diffusion or convection) capable of moving the gas along the pathway (Williams and Hitchman, 1989). In most cases only the first approach is taken: usually by comparing major and trace components with those of known gases, or by determining the ^{14}C content to distinguish 'geological' from recent biogenic methane. Identifying the origin may be very much more complicated if more than one source of methane exists, and, where compositional evidence alone is used, it is important to have a well defined database for the likely composition of possible source gases and to evaluate whether changes in composition may have occurred during gas migration. Stable isotope ratios of carbon and hydrogen (ie $^{13}\text{C}/^{12}\text{C}$, $^2\text{H}/^1\text{H}$) potentially provide an additional means by which methane can be characterised but such data are scant for sources in the United Kingdom.

In order to assess whether stable isotope ratios could be diagnostic of particular sources, methane containing gases from a variety of origins were collected and analysed. These included coal fields, North Sea gas fields, deep biogenic reservoirs, landfills and anaerobic digesters.

Results show that there is some overlap on the $\delta^2\text{H}_{\text{CH}_4}$ versus $\delta^{13}\text{C}_{\text{CH}_4}$ graph, notably between coal and landfill gas, but this was resolved with $\delta^{13}\text{C}_{\text{CO}_2}$ plotted against $\delta^{13}\text{C}_{\text{CH}_4}$.

These results indicate that the determination of stable isotope ratios of carbon and hydrogen in methane and carbon dioxide is a useful additional technique for source characterisation but that isotopic fractionation may occur if the methane is oxidised by microbial processes.

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1 INTRODUCTION

The gas explosions at Loscoe and Abbeystead have highlighted the dangers associated with the migration of methane in the subsurface, and the need to quickly and accurately establish the source of the methane in order to instigate appropriate measures for control and remediation (Williams and Aitkenhead, 1989; HMSO, 1986). In several instances where methane has been detected in the vicinity of landfills, the landfill has not necessarily been the only methane source; leaking gas mains, sewers, indigenous gas from underlying Carboniferous strata, and the products of anaerobic degradation of organically contaminated groundwater are all possible sources of methane. Although public opinion may demand rapid action following the discovery of methane, and certainly after an explosion, hasty remedial action which does not consider the source of the gas nor its mode of transmission, may at best be a waste of resources, or, at worst, may exacerbate the spread of the gas.

To confirm a methane source three approaches may be used. The source can be identified by comparing the composition of the gas with known source compositions; establishing a migration pathway between the putative source and the point at which methane is observed, and confirming the existence of a mechanism (such as diffusion or convection) capable of moving the gas along the pathway (Williams and Hitchman, 1989). In most cases only the first approach is taken: usually by comparing major and trace components with those of known gases, or by determining the ^{14}C content to distinguish 'geological' from recent biogenic methane; identification may be complicated if more than one source of methane exists.

Where compositional evidence alone is used it is important to have a well defined database, and to consider possible changes in composition that may have occurred during migration. For instance the $\text{CH}_4:\text{CO}_2$ ratio is often used in source identification, especially for landfill gas (Emberton, 1984); however, CO_2 may be 'filtered out' during migration (e.g. by sorption onto wet incinerator ash), or may undergo chromatographic separation in moving through a suitable fine grained sediment or soil. Similarly, methane is known to be oxidised to carbon dioxide by bacteria, which makes $\text{CH}_4:\text{CO}_2$ ratios unreliable for source determination.

Where a natural gas or coal gas source is suspected, ^{14}C measurements can be used to

determine the 'age' of the methane. The isotope emits β -radiation at a relatively low energy (156keV) and as natural activities are low, highly efficient sophisticated detection equipment is needed. The methane is first combusted to carbon dioxide, then either (in most cases) synthesised to benzene for liquid scintillation counting, or (when samples are small) purified for gas proportional counting (Bowen, 1988). While this is a very useful technique, it can be expensive and may take considerable time to carry out.

As an alternative, the stable isotope ratios (i.e. $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$) of different methane gases vary according to their formation processes, both primary and secondary. Indeed, the fractionation associated with aerobic methane oxidation has been the subject of a number of laboratory experiments (Zyakun and others, 1986, 1979; Barker and Fritz 1981b; Coleman and others, 1981) and may contribute to the enrichment in ^{13}C of contemporary methane compared to geological biogenic gases. The hydrocarbon exploration industry has long used stable carbon isotope ratios as a tool in recognising oil, gas and oil/gas reservoirs, and while a literature search revealed a substantial body of data on these "geological" methanes, there were few on the stable isotope composition of methane from contemporary sources; data was particularly sparse for sources in the United Kingdom.

In order to assess whether stable isotope ratios could be diagnostic of particular sources, methane-containing gases from a variety of origins were collected and analysed. These included coal fields, North Sea gas fields, landfills, anaerobic digesters, and lake and river muds.

2 THEORY

2.1 Stable isotope ratios

Carbon in the terrestrial environment comprises 98.89% ^{12}C and 1.11% ^{13}C (contrasting with 10^{-10} % ^{14}C), and hydrogen 99.985% ^1H and 0.015% ^2H . Both stable isotope ratios can therefore be determined with a relatively simple mass spectrometer in less time and at a lower cost than ^{14}C measurements.

Stable isotope ratios are defined by the expression (given for carbon):

$$\delta^{13}\text{C}_s = \left[\frac{R_s}{R_{\text{PDB}}} - 1 \right] \times 1000, \text{ where } s \text{ and PDB denote sample and standard respectively,}$$

$$\text{and } R = {}^{13}\text{C} / {}^{12}\text{C}$$

The units for δ are parts per thousand, noted as ‰ and read 'per mil'. The standards used are most commonly the PDB standard for carbon (derived from the rostrum of the calcareous fossil *Belemnitella americana* from the Pee Dee Formation of South Carolina), and 'standard mean ocean water' (SMOW) for hydrogen (Craig, 1953).

The δ notation represents a *differential* measurement of the ${}^{13}\text{C}$ abundance: samples containing more ${}^{13}\text{C}$ than the PDB standard will have $\delta > 0$, and are described as 'enriched' or 'heavier'; those with less will have $\delta < 0$ and are 'depleted' or 'lighter'.

2.2 Stable isotopic characteristics of methane

Methane in the environment is formed either by the chemical reduction of organic matter by micro-organisms (biogenic methane), or abiologically over "geological" periods of time following the burial, compression and heating of organic material (thermogenic methane). It has also been suggested (Gold and Soter, 1980,1982) that methane, trapped deep within the earth when the planet condensed from a cloud of interstellar gases, is presently outgassing, and has given rise to many known hydrocarbon reserves. While this "primordial methane" may well exist in the earth's crust there is at present no evidence to support the view that it could have given rise to the hydrocarbon deposits of the UK (Bath and others, 1984).

It is well known that the character of the gases produced by the different natural pathways (i.e. biogenic and thermogenic) differ in terms of their $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta^2\text{H}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ values. In addition to the primary (i.e. formation) effects, there are potentially secondary (i.e. subsequent to formation) effects which may occasionally become significant. These are associated with movement towards isotopic equilibrium, bacterial degradation, and migration (summarised by Fuex, 1977). Of these, isotopic equilibrium with other hydrocarbons has a negligible effect, and ${}^{13}\text{CH}_4$ equilibration with CO_2 would require a temperature of at least 200°C and a fairly high proportion of CO_2 to be significant. Bacterial oxidation of CH_4 affects the stable isotope ratios, but will only be seen in the near-surface, or where the

atmosphere is able to penetrate to depth (for example in mine workings). Fractionation during migration is also possible, but is generally considered of little importance in hydrocarbon exploration.

Several authors have summarised $\delta^{13}\text{C}_{\text{CH}_4}$ values for natural gases (e.g. Barker and Fritz, 1981a; Fritz, 1980; Deines, 1980) as a basis for differentiation. As a result, a useful "rule-of-thumb" has emerged:

$$\begin{aligned}\delta^{13}\text{C}_{\text{CH}_4} > -60\text{‰} &= \text{thermogenic source} \\ \delta^{13}\text{C}_{\text{CH}_4} < -60\text{‰} &= \text{biogenic source.}\end{aligned}$$

Schoell (1983,1980) compared $\delta^{13}\text{C}_{\text{CH}_4}$ with a number of other characteristics (percentage C_{2+} , $\delta^2\text{H}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$) to produce diagrams separating natural gases into fields according to provenance. As well as differentiating biogenic from thermogenic, subgenetic groupings are also clear. However, because Schoell was primarily interested in commercial gas deposits, data from landfill and other biogenic gas types were not considered.

Laboratory work (Zyakun and others, 1986,1979; Barker and Fritz 1981b; Coleman and others, 1981) and field observations (James and Burns, 1984; Barker and Fritz, 1981b) have shown that aerobic methane oxidation can play a major role in stable isotope fractionation, in one study causing residual methane to be enriched in ^{13}C by up to 50‰ (Coleman and others, 1981). This could easily lead to biogenic methane being construed as thermogenic, though consideration of the $\delta^2\text{H}$ value – itself potentially enriched in $\delta^2\text{H}$ by up to 200‰ (Coleman and others, 1981) – should show otherwise (Barker and Fritz, 1981b). The carbon dioxide formed by microbial oxidation – in laboratory work it has been depleted in ^{13}C relative to residual methane by up to 30‰ (Barker and Fritz, 1981b) – mixed with that produced during formation of the methane, is a possible further complication.

The ranges of $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta^2\text{H}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ values in the literature are collected in Table 1; those with particularly narrow ranges are probably due more to the paucity of data than the presence of well defined limits. The $\delta^{13}\text{C}_{\text{CH}_4}$ range of contemporary methane producers lies within that of thermogenic gases – it remained to be seen whether the $\delta^2\text{H}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ values could characterise these sources.

Table 1 Stable isotope ratio ranges of natural methane gases

gas type	$\delta^{13}\text{C}_{\text{CH}_4, \text{‰}}$		$\delta^2\text{H}_{\text{CH}_4, \text{‰}}$		$\delta^{13}\text{C}_{\text{CO}_2, \text{‰}}$		references ¹
	max	min	max	min	max	min	
<i>thermogenic</i>							
dry gas ²	-21	-76	-136	-177	-7	-11	<i>f g p r u</i>
wet gas ²	-24	-63	-153	-256			<i>g p r u</i>
coal	-12	-71	-133	-155	-10	-30	<i>g o r</i>
<i>biogenic</i>							
glacial drift	-70	-91	-226	-277	+7	-21	<i>f r u</i>
lake mud	-45	-80	-256	-346	-2	-25	<i>b f j k m q w</i>
landfill	-38	-58			+23	-11	<i>a f i j</i>
marsh ³	-49	-76	-207	-374	+2	-21	<i>c h k n r s t v</i>
sewage sludge	-47	-49	-200	-348	+4	-6	<i>j v</i>
deep marine sediment	-40	-109	-168	-261	+11	-32	<i>e v</i>
sea shore sediment	-53	-90	-219	-284	-1	-26	<i>c v</i>
marine reserves	-55	-76	-179	-219			<i>r</i>

¹ in the reference section, marked by *italic* letters

² younger, associated with oil ("wet"); or mature, no oil ("dry")

³ "marsh" also includes locations described as "wetlands" and "peatlands"

3 GAS SAMPLING AND ANALYSIS

Gas samples were collected from existing installations in landfill sites (including the Department of Energy test cells at Shanks & McEwan's Brogborough site), anaerobic waste digesters, marshy ground, peat bogs, deep excavations, coal strata and North Sea gas fields, and their composition and stable isotope ratios determined and compared. Gases were collected by hand pumping into stainless steel gas bombs, teflon lined gas bags or pressurised cylinders (Gresham tubes), and stored at room temperature until analysed.

The samples were analysed using the apparatus shown in Figure 1. Gas from the sample container was carried at a steady rate through the system in a nitrogen stream. It passed first through an ammoniacal barium chloride solution, where CO₂ precipitated out as barium carbonate. This was later filtered and dried for determination of the CO₂ carbon stable isotope ratio. The remaining sample passed through a drying trap where water was removed, then to an 850°C furnace containing copper (II) oxide (cupric oxide); this oxidised the CH₄ to CO₂ and H₂O, which were collected in a liquid nitrogen trap. These components were later separated by dry ice-methanol for stable isotope ratio determination.

Initially some analytical problems were encountered for $\delta^{13}\text{C}_{\text{CH}_4}$ in samples with a high CO₂ content, and for $\delta^2\text{H}$ for samples with a low concentration of CH₄. Most of the $\delta^{13}\text{C}_{\text{CH}_4}$ samples were successfully reanalysed, but for a few only the original data are available. All data are reported, including those of doubtful accuracy.

4 RESULTS AND DISCUSSION

The major gas compositions and stable isotope data of the gases collected are given in Table 2. Those samples from which CO₂ was not completely removed before $\delta^{13}\text{C}_{\text{CH}_4}$ analysis are marked with an asterisk; the $\delta^2\text{H}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ results from them remain valid.

The frequency distribution of stable isotope ratios of biogenic and thermogenic methane (both literature and this study) are shown in Figure 2. This illustrates vividly the distinct groupings resulting from the two formation processes and serves to emphasise the diagnostic value of stable isotope ratios.

Some of the stable isotope ratio ranges found in the literature (and collected in Table 1) are plotted in Figure 3, along with data from this study. Although in most cases the new data fall within the literature-defined boundaries, some points lie outside and serve to extend the database. This is particularly useful where reported data are scarce as, for example, in the case of landfills.

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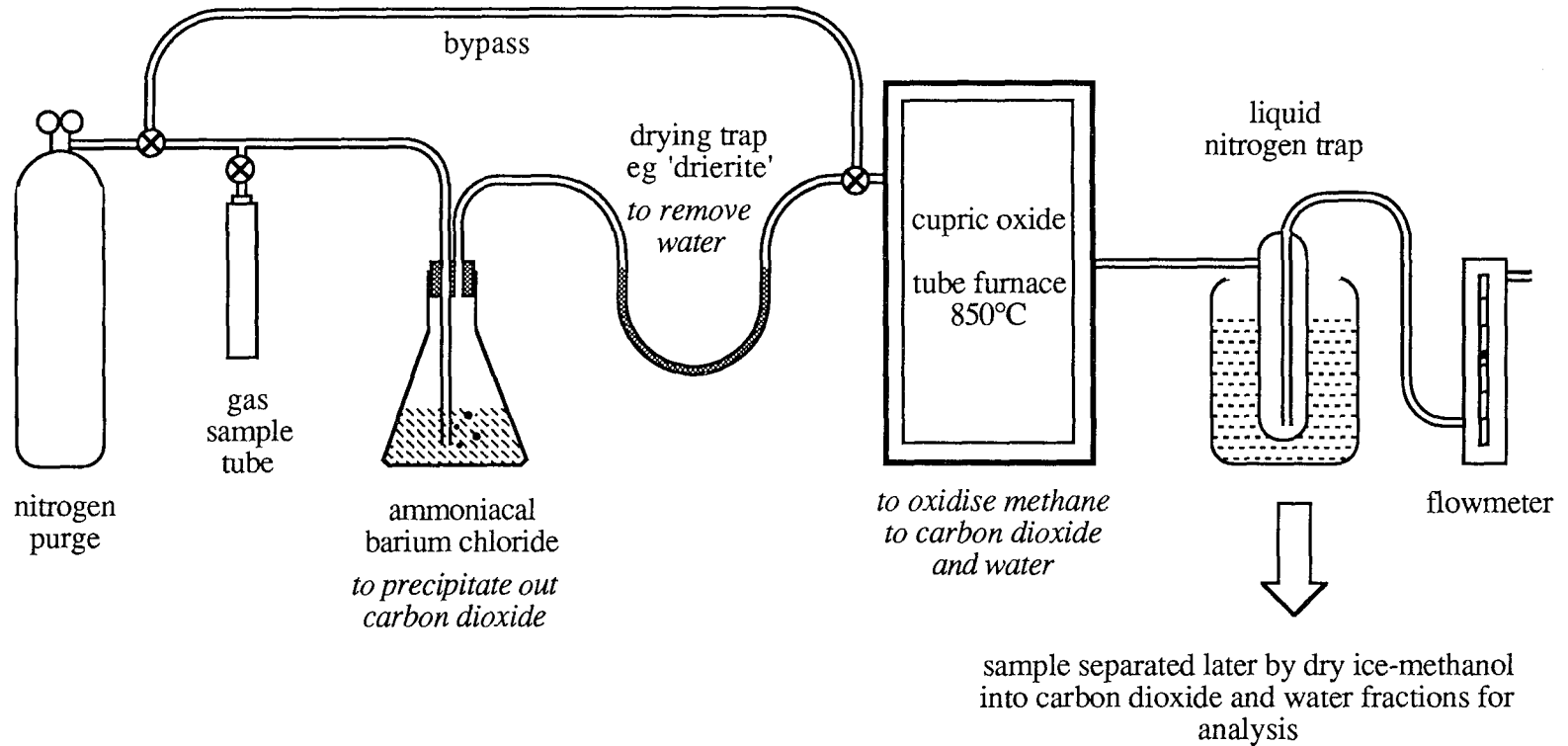


Figure 1 Sample preparation for stable isotope ratio analysis

Table 2 Composition (%) and stable isotope ratios (‰) of methane-containing gases collected in this study

source	N ₂	O ₂ ,Ar	CO ₂	CH ₄	δ ¹³ C _{CH₄}	δ ² H _{CH₄}	δ ¹³ C _{CO₂}	source	N ₂	O ₂ ,Ar	CO ₂	CH ₄	δ ¹³ C _{CH₄}	δ ² H _{CH₄}	δ ¹³ C _{CO₂}
coal															
Notts deep soft seam, drainage (1)	52.7	12.2	1.3	33.0	-47.5	-221		landfill, continued	37	-	28	35	-58.5	-270	+2.1
Notts deep soft seam, drainage (2)	34.9	6.2	1.4	56.0	-53.2	-228		industrial/domestic	34.8	7.5	2.3	55.4	-22.9	-272	
Notts deep soft seam, drainage (3)	60.9	16.0	0.5	22.0	-21.2	-262		*industrial/commercial (1)	55.5	14.1	8.6	21.8	-54.2	-233	-7.7
Notts deep soft seam, drainage (4)	44.6	7.8	5.9	40.0	-42.2	-151	-42.0	industrial/commercial (2)	-	-	60	40	-55.1	-264	+6.9
Barnsley seam, desorbed gas				4.8	-44.1	-146		† Brogborough cell 1	1	-	71	28	-63.9	-254	-12.8
West Leigh field, borehole (1)		15.6	0.9	21.2	-53.8	-265		† Brogborough cell 2	0.5	-	46.5	53	-60.0	-273	+7.4
West Leigh field, borehole (2)		15.2	5.4	15.3	-53.2	-213	-38.1	† Brogborough cell 5	7	-	80	13	-54.5	-108	-12.6
West Leigh field, borehole (3)		1.6	3.6	8.5	-51.0	-199	-54.0	† Brogborough cell 6	19.3	3.4	30.7	46.7	-18.3		-7.0
West Leigh field, borehole (4)					-52.1	-223	-46.4	<i>anaerobic digester</i>	6	-	27	67	-70.2	-342	+10.6
North Sea gas															
Southern basin (1)	4.7	0.9	-	94.0	-34.5	-150		*abattoir waste	6.4	0.9	17.7	75.0	-48.4	-286	-2.5
Southern basin (2)					-44.1	-131		abattoir waste	-	-	39	61	-63.4	-319	+0.5
Southern basin (3)	2.5	-	-	84.6	-43.9	-121		brewery waste	-	-	38	62	-51.6	-265	+2.8
Southern basin (4)	2.8	-	-	87.4	-45.3	-158		dairy herd waste	1	-	39	60	-74.4	-310	+14.4
Southern basin (5)	3.8	0.3	0.4	88.4	-35.3	-158		sewage	70.3	19.9	0.2	9.4	-67.5	-255	
landfill															
*domestic (1)	28.2	-	20.1	50.1	-32.4	-239	+2.6	reservoir excavations (1)	85	-	-	10	-75.6	-347	-16.2
domestic (2)	29	-	43	28	-61.0	-307	+5.3	reservoir excavations (2)	95	-	-	-5	-70.3	-286	-8.5
domestic (3)	1	-	36	63	-58.3	-248	+10.8	deep borehole	42	-	19	39	-64.5	-219	-23.9
domestic/liquid	10.9	2.8	28.9	57.4	-55.4	-224	+0.7	<i>marsh</i>	71	-	17	12	-67.4	-263	-28.5
domestic/commercial	19.5	-	23.5	57	-61.0	-308	-2.3	river mud	79.6	-	0.9	19.5	-68.6	-242	-7.8
domestic/incinerator ash	27	-	16	57	-56.6	-238	+10.5	lake mud							
domestic/industrial	30	-	20	50	-62.3	-275	+12.0	borehole, near river (1)							
dom/industrial/chemical (1a)	24.5	-	29	46.5	-60.5	-236	+10.3	borehole, near river (2)							
dom/industrial/chemical (1b)	24.5	-	31.5	44	-56.4	-248	+6.7	<i>peat</i>							

† The composition of the Brogborough cells is as follows:

- 1: domestic, thin layers, highly compacted 5: as 1 plus 9% wet weight sewage sludge
 2: domestic, standard 2m lift, compacted 6: domestic plus 40% nonhazardous commercial

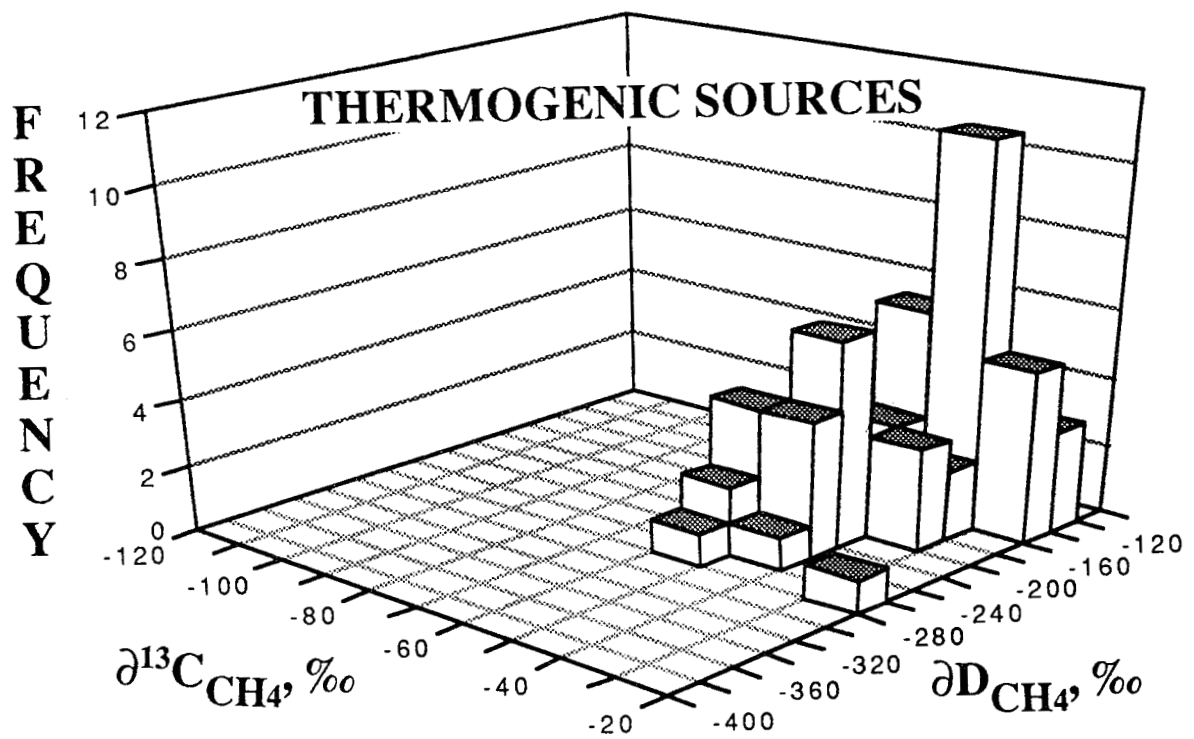
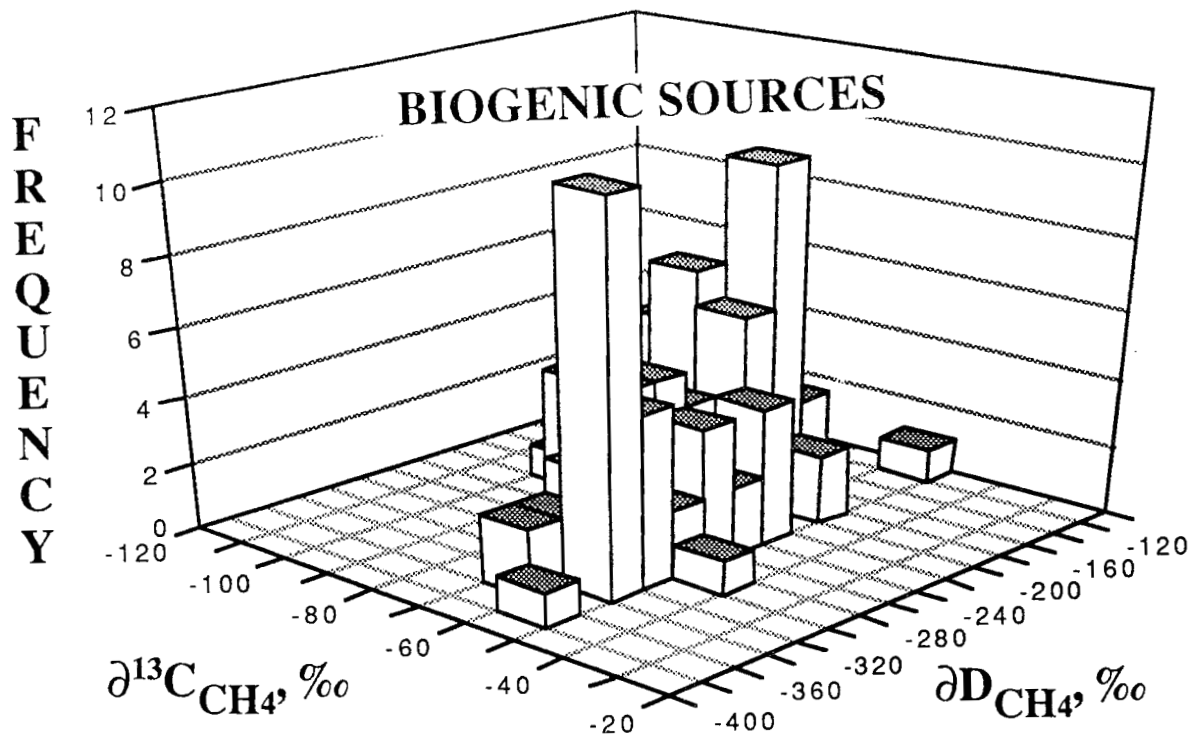


Figure 2 Biogenic and thermogenic methane: frequency distribution of stable isotope ratios

Given the lack of stable isotope data on landfill gas in the literature, the $\delta^{13}\text{C}_{\text{CH}_4}$ values produced by this investigation (-64 to -54‰) are remarkably close to the range quoted (-58 to -38‰). The $\delta^2\text{H}_{\text{CH}_4}$ data are also fairly tightly clustered; the exception is the sample from Brogborough cell 6 (domestic/commercial waste), at -108‰. It is possible that this is a result of microbial oxidation: either due to the rate of filling, or because the nature of the commercial component of the waste – cardboard, wood etc. – might make compaction less efficient and allow air ingress to a greater extent than in other wastes. The composition of the landfilled waste seems otherwise not to affect the stable isotope ratios of the resultant gas.

It is of interest that the two abattoir waste anaerobic digester gas samples are at opposite ends of the $\delta^{13}\text{C}_{\text{CO}_2}$ range found for digesters. These specimens came from the same digester, albeit separated by several months. The heterogeneous nature of the source material (different herds, different diets etc.) may be one explanation; another might be that different stable isotope ratios are produced as degradation progresses, with factors such as time spent in the reactor, mix of older and newer material, temperature etc. governing the output.

Where $\delta^{13}\text{C}_{\text{CH}_4}$ and their corresponding $\delta^2\text{H}_{\text{CH}_4}$ values are given in the literature they are plotted in Figure 4, along with their counterparts from this study. The rough -60‰ division between $\delta^{13}\text{C}_{\text{CH}_4}$ values of biogenic and thermogenic gases can be clearly seen, although contemporary biogenic methane tends to blur the interface, being somewhat heavier than -60‰. The various gas sources are differentiated quite well, although some overlap exists, most notably between landfill gas and the coal gas collected in this study. There is also a degree of association between landfill gas and marsh, wetland, and lake mud gas. The terms "marsh", "wetlands" and, possibly, "lake mud" appear to an extent interchangeable, their usage depending on individual authors' preferences. Other biogenic sources – such as deep marine reserves, deep and shallow marine sediments – are also well defined in Figure 4.

The BGS North Sea samples are identified as dry gas in Figure 3, and in Figure 4 are very close to the literature dry gases, also of North Sea origin (Schoell, 1980), and quite distinct from those associated with oil (wet gas).

Despite the differences in both type of coal gas analysed and the mode of sampling (desorbed from coal samples, collected from boreholes, or from seam drainage) there is a measure of congruity to the BGS coal data points shown in Figures 3 and 4 (the exception is the point on

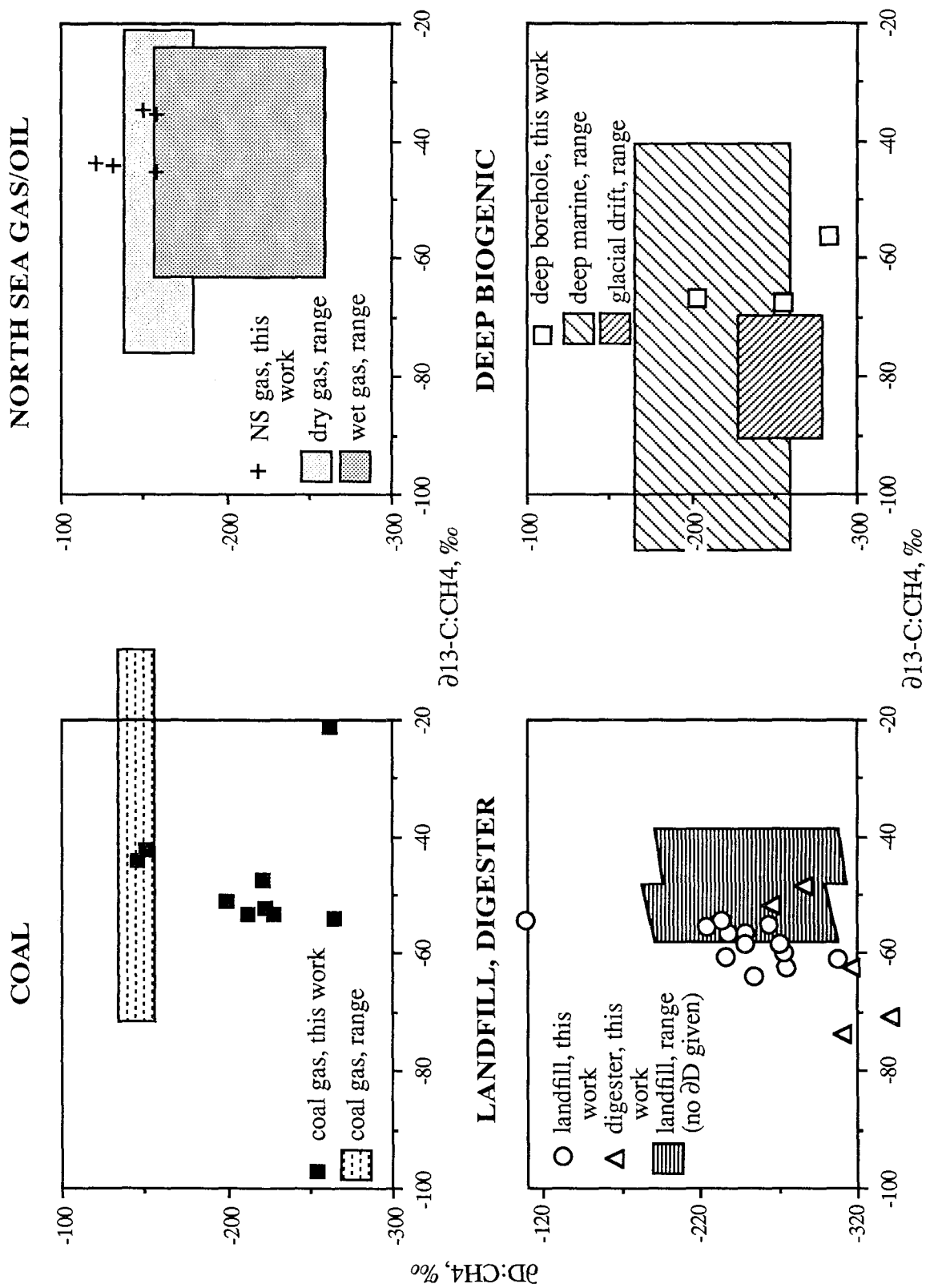


Figure 3 Stable carbon and hydrogen isotope ratios of methane from different sources: data from this study and the literature ranges shown in Table 1

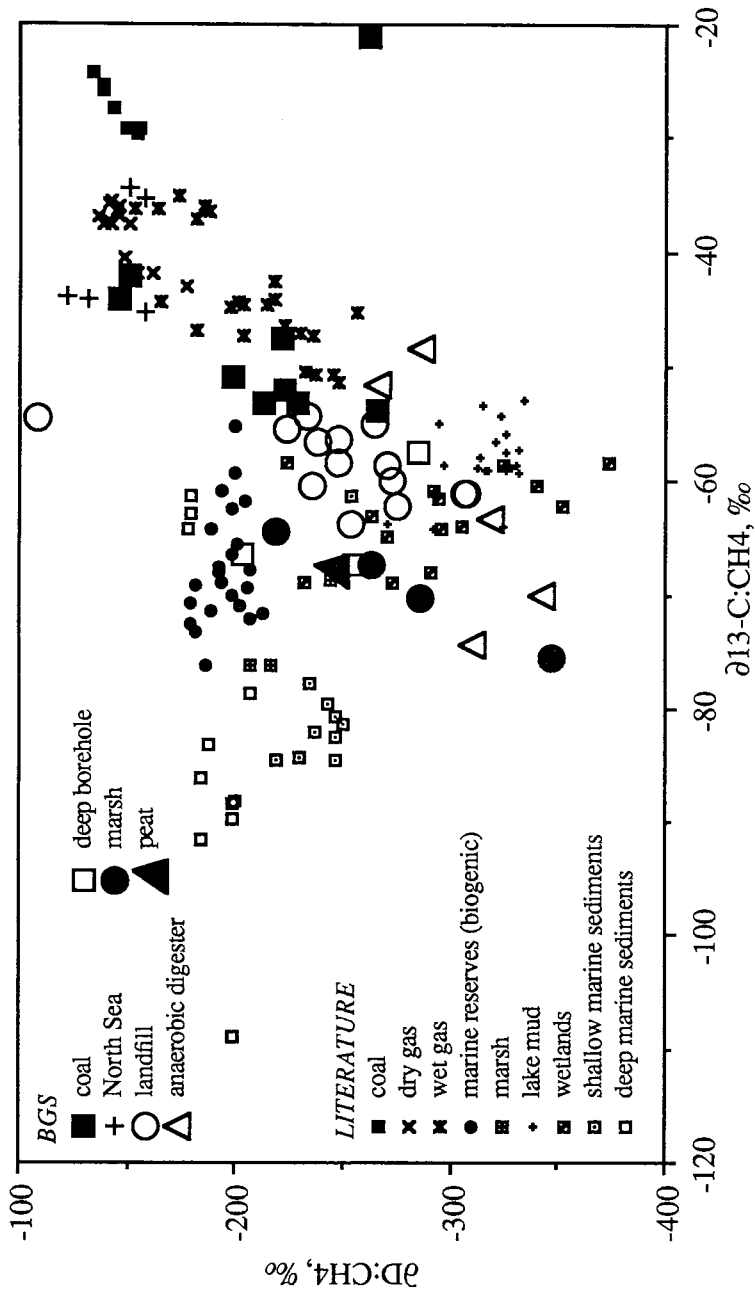


Figure 4 Stable carbon against stable hydrogen isotope ratios of methane from different sources: BGS and literature data

the right of the graph, one of the drainage gas samples from the Deep Soft Seam; the grouping of the remaining coal data points would suggest this to be analytical error). While all BGS samples are within the reported $\delta^{13}\text{C}_{\text{CH}_4}$ range (-12 to -71‰), they are lighter than those shown in Figure 4 (from Schoell, 1980), and most of the $\delta^2\text{H}_{\text{CH}_4}$ values are well outside the anticipated range. The large span (-60 to -265‰) suggests further investigation is needed. Rather than matching Schoell's coal gas points, the BGS coal gases correspond better with wet natural gas (associated with oil). Wet gas is younger than non-associated (dry) gas, and it is possible that the $\delta^{13}\text{C}_{\text{CH}_4}$ value may reflect the maturity of the coal. Alternatively, microbial processes may have caused isotope fractionation, leading to changes in the characteristic coal gas signature; if this were so however, the residual methane would be expected to be enriched in ^{13}C and ^2H rather than depleted.

Where the samples contained sufficient CO_2 , the $\delta^{13}\text{C}_{\text{CO}_2}$ analyses are included in Table 2; these are plotted against $\delta^{13}\text{C}_{\text{CH}_4}$ in Figure 5, along with literature data. The contrast between gases according to source is clear, particularly for coal and landfill gases, and even landfill and marsh/wetland/lake mud gases can be differentiated. In cases where plotting $\delta^2\text{H}_{\text{CH}_4}$ against $\delta^{13}\text{C}_{\text{CH}_4}$ is inconclusive, the $\delta^{13}\text{C}_{\text{CO}_2}$ value provides an additional basis for differentiation.

5 CONCLUSIONS AND FUTURE WORK

The carbon stable isotope ratios (i.e. $^{13}\text{C}/^{12}\text{C}$) of different methane gases vary according to their formation process. This fact has long been used in hydrocarbon exploration to recognise exploitable reservoirs. The hydrogen stable isotope ratio (i.e. $^2\text{H}/^1\text{H}$) of methane and the carbon stable isotope ratio of any associated carbon dioxide also vary, and application of these three factors can lead to identification of the source of methane-containing gases.

The literature provides ranges for values of $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta^2\text{H}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$, but, with a few exceptions, a limited amount of actual data; this is particularly so for those sources potentially hazardous to man-made structures. This study has extended the database considerably with the more probable hazardous sources, notably landfills, emphasised.

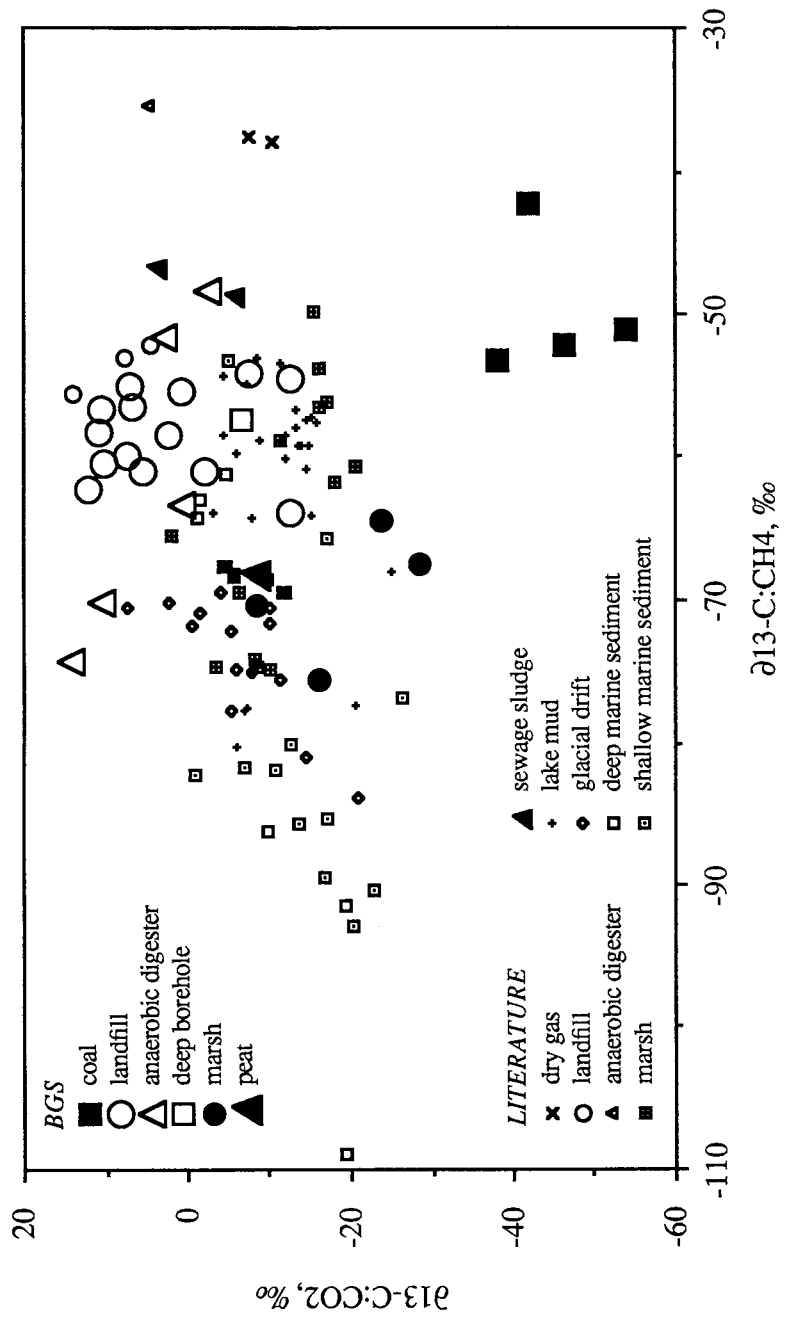


Figure 5 Stable carbon isotope ratios of carbon dioxide against methane in gases from different sources: BGS and literature data

Stable carbon and hydrogen isotope ratios in methane should be sufficient in most cases to identify the source, particularly if samples from rival candidates can be compared. Problems could arise in overlap areas, most notably between coal and landfill gases, but where CO₂ is present the $\delta^{13}\text{C}_{\text{CO}_2}$ should distinguish the two. The use of stable isotope ratios is therefore not proposed as a sole method in all cases, but with other evidence on gas composition will increase the weight of evidence for a particular source.

Work is also underway to assess changes in methane composition during migration, particularly as a result of aerobic and anaerobic methane oxidation (Williams and Hitchman, 1989).

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