Potential hazards resulting from the presence of methane dissolved in groundwater.

By **J.S.EDWARDS**[1] .

[1]Department of Mining Engineering,
University of Nottingham,
University Park, Nottingham, United Kingdom.

ABSTRACT

The occurrence of methane in solution in groundwater is a common phenomenon worldwide and has resulted in several serious incidents. This paper discusses the scale of the hazard that can result from the presence of methane in water and describes the factors which control the quantity of gas that can be dissolved and the mechanisms of gas release. The various methods available for the collection and analysis of groundwater for dissolved methane determination are described and a number of predictive tools are presented which can aid in the assessment of risk.

INTRODUCTION

In many parts of the world methane is a common constituent of local groundwater, either as a result of bacterial activity in near-surface sediments or as the result of an association with natural gas or petroleum. Groundwater movement is an important mechanism by which methane migrates from its source, in solution, and accumulates in suitable traps.

Gas in solution in an aquifer will be released when water is pumped to the surface and brought to atmospheric pressure. Also, under certain hydrogeologic conditions, the concentration of gas in groundwater can exceed the limit of saturation resulting in the formation of a gas phase which, being mobile, can accumulate in geological traps

The presence of methane in solution in water can present a serious risk of explosion if the gas comes out of solution and accumulates in spaces which are not ventilated. The risk of explosion is dependent upon the concentration of methane in solution and the relative volumes of water and air.

SOURCES AND DISTRIBUTION OF METHANE IN GROUNDWATER

Origins of methane

Methane may be biogenic in origin, having been derived from organic matter, or abiogenic as a result of inorganic reactions (1). Biogenic methane may be subdivided into 'bacterial' ('microbial') methane which is produced by the action of bacteria on organic matter, and 'thermogenic' methane which results from the thermal degradation of organic matter with increasing depth of burial.

Anaerobic conditions in the subsurface provide an environment in which microbial methane can be produced from the decomposition of buried organic matter such as peats and paleosols. Whilst most such methane occurrences are associated with Recent sediments and glacial deposits there are cases where microbial decomposition of organic matter has taken place in Palaeozoic sediments. Where groundwater is moving down through the sediments, microbial methane is frequently found well below the original source material.

Worldwide distribution of dissolved methane

In the USA microbial methane is present in groundwaters throughout much of the midwestern part of the country and, in some circumstances, occurs in sufficient quantity to provide gas for home heating(2). Similar occurrences of dissolved methane of microbial origin are found in Canada(3), Japan(4) and Hungary(5) although in the latter case dissolved gases in the deeper groundwaters are considered to be of thermogenic origin associated with petroleum-bearing rocks.

In South Africa many of the gold mines encounter methane in solution in fissure water under great pressure(6). The source of the gas, which is commonly accompanied by hydrogen, is the coal-bearing sequences of the Karoo formation which overly many of the gold fields. Both methane and hydrogen are dissolved in the meteoric waters percolating down through shears, fractures and contacts into underlying strata. The amount of gas that can be held in solution at the water pressure in these fissures is considerable and whenever water is encountered the drop in pressure releases methane to the atmosphere with the resultant risk of ignition.

Methane has been encountered while dewatering flooded timbered mine workings in Canada and the USA(7). The presence of the gas is almost certainly due to the decomposition of timber under water. Similar methane emissions were encountered during construction of the Channel Tunnel when the pilot tunnel intercepted the old 'Beaumont' workings which had also been timber lined. In this case the origin of the methane was confirmed by the accompanying aroma of creosote which had presumably been applied to the timber for protection.

In the United Kingdom methane has been found in groundwater infiltrating the Wyresdale aqueduct tunnel(8), which forms part of the Lancashire Conjunctive Use Scheme for water-transfer between the rivers Lune and Wyre. Dissolved methane occurrences have also been observed in a similar project at Carsington in Derbyshire(9). The methane encountered in the Wyresdale and Carsington aqueduct tunnels is almost certainly from similar sources. In the case of the Carsington project historical evidence from old lead mining in the vicinity of these tunnels points to methane having been encountered on many occasions, sometimes with disastrous results. In this context the methane was invariably associated with shale sequences between the Carboniferous Limestone (Visean) and the overlying Millstone Grit (Namurian).

An unusual example of groundwater-derived methane has been reported at the Outokompu Zinc-Tara mines Ltd in County Meath, Ireland(10). This mine is the world's fourth largest underground lead/zinc mine extracting some 330,000 tonnes of zinc and 60,000 tonnes of lead concentrate *per annum*. The main orebodies are contained within the lower units of a Lower Carboniferous marine transgressive sequence which unconformably overlies the Ordovician/Silurian basement. Mining activity, which began in 1973, has caused a wide and deep cone of depression to develop in the water table around the mine (up to 3 km wide and 400 m deep). Dewatering of the strata has been particularly extensive through the 'B' fault conduit system. Exploration boreholes to the south-west of the mine, along the strike of the 'B' fault have been found to be emitting hydrocarbon gases, principally methane.

Two types of groundwater are generally recognised in and around the mine. The water that enters the mine from the north is termed 'NW type' water and, close to its recharge area, is high in calcium and bicarbonate. Owing to its interaction with the sulphide orebody it is also high in sulphate. Analyses for the presence of dissolved methane in this water have proved negative.

The groundwater to the south-west of the mine is termed 'B fault type' water since it is eventually drained to the mine by the 'B' fault. This water has a longer residence time than the 'NW type' water and calcium is partly replaced by sodium; the water also has a low redox potential. Methane has been shown to be present dissolved in the water and active methanogenic bacteria have been positively identified. Other evidence for a microbial origin of the dissolved gas is provided by the low sulphate content of the water as a result of the activity of sulphate reducing bacteria (which are natural precursors to methanogenic activity) and the presence of hydrogen sulphide, a by-product of the sulphate- reduction process.

BEHAVIOUR OF METHANE IN SOLUTION IN WATER

Factors affecting solubility

All gases dissolve in water to some extent and therefore most naturally occurring waters will contain dissolved gases, the most abundant of which are nitrogen, oxygen, carbon dioxide, methane and hydrogen sulphide.

At a given temperature the solubilities of gases that do not react with the solvent are directly proportional to the partial pressure of the gas above the solution. This relationship is known as Henry's law which may be expressed mathematically in the form:

$$p=Hx \qquad (1)$$

where,

p = partial pressure of the gas (mmHg)
x = mole fraction of the gas in the liquid
H = Henry's constant (mmHg/mole fraction)

Henry's law is exact only in the infinitely diluted state but is a good approximation in dilute solutions. If the solubility of the gas is known for one pressure the Henry's law constant may be calculated and used to calculate the solubility at any other gas pressure.

The solubility of some of the more common unreactive gases are shown in Table 1:

Table 1. Solubility of gases (mg/l) at 1 atm pressure and 25°C.

nitrogen	oxygen	hydrogen	methane
17.9	40.4	1.58	21.5

The solubility of methane in water is dependent on several factors: temperature, pressure, and salinity. The solubilities of most gases usually decrease with increasing temperature but methane shows a decrease with temperature up to about 80°C with an increase in solubility at higher temperatures. At 80°C the solubility of methane is only half that at 25°C.

The solubilities of gases also show a marked increase with increasing pressure, the solubilities of many gases being approximately linear functions of pressure. The solubility of methane in water may therefore be predicted from one experimentally determined value - that at atmospheric pressure. This relationship may be expressed by the relation:

$$V = kp \qquad (2)$$

where V, the volume of the gas dissolved, is measured at atmospheric temperature and pressure (25°C and 760 mmHg). If p is the pressure in atmospheres absolute, k becomes equal to the atmospheric solubility. Table 2 gives some typical values:

Table 2. Effect of pressure on the solubility of methane in water.

Pressure (atm)	1	20	40	60	80	100
Solubility (mg/l)	21.5	429	859	1288	1717	2147

Solubilities of gases are normally quoted with respect to fresh water although, in reality, natural waters contain varying amounts of dissolved salts. Solubility values should be adjusted accordingly - the effect of increasing salinity is to cause a decrease in solubility of 5% per 1% increase in dissolved mineral matter.

Of the three effects on the solubility of methane in water: temperature, pressure and salinity - the effect of pressure is dominant.

Safe limits

The concentration of dissolved methane that would be required to create a given concentration of methane in the headspace above a body of water can be calculated using the equation(11):

$$\% \ CH_4 \text{ in air at equilibrium} = 3.417 \times 10^2 \ Q/P \tag{3}$$

where,

Q = dissolved methane concentration (mg/l)
and , P = absolute pressure (kPa).

An important question is: what are the safe limits for dissolved methane?

For a concentration of 5% methane in air by volume, i.e. a concentration equal to the lower explosive limit, and assuming that water containing dissolved methane flows through an unventilated airtight chamber at atmospheric pressure, a 5% mixture would build up if the water contained as little as 1.5 mg/l (ppm) dissolved methane. Using a methane concentration in air of only 0.5% (the mines limit) the methane concentration would need to be only 0.15 mg/l. The limit of safety is so low for an unventilated chamber that it would be difficult to attain in practice without a combination of methane removal and ventilation.

In many instances both methane and nitrogen may be dissolved in the water and therefore the combined effect of both gases should be considered, especially in circumstances where groundwater is brought to atmospheric pressure from depth, or a decrease in barometric pressure occurs.

Adopting a standard temperature of 15°C, the solubilities of methane and nitrogen are 27.3 and 22.1 mg/l respectively. If the gas dissolved in water is 100% methane and the total gas content is greater than 27.3 mg/l the reduction in pressure to atmospheric will release the supersaturated gas as small bubbles within the body of the water which may then be emitted as a free gas into the surrounding atmosphere.

The saturation relationship for mixtures of methane and nitrogen dissolved in water is given by :

$$a = \frac{100 a_m a_n}{a_n y + a_m (100 - y)/y} \tag{4}$$

where, a = dissolved gas volume (methane + nitrogen) (mg/l)
y = % methane in the dissolved gas
a_m = solubility of methane (mg/l)
a_n = solubility of nitrogen (mg/l)

Equation (4) is shown as the curve CF in Fig 1.

Release to atmosphere in cases of supersaturation is dependent upon barometric pressure rather than on the slow diffusion of gas through the liquid and liquid film. A fall in barometric pressure can make an under-saturated solution supersaturated and release the gas within the liquid, thus allowing it to rise rapidly to the surface.

If the dissolved nitrogen concentration is sufficiently high relative to methane, it is possible that no dilution of the released supersaturated gas with air can produce a flammable mixture. In the presence of excess nitrogen, oxygen must be present at least to the extent of 12.8% and no nitrogen-methane mixture can form a flammable mixture on dilution with air. These values are derived from the work of the US Bureau of Mines(12) on the limits of flammability of gases and vapours.

No supersaturated gas solution can form a methane-nitrogen vapour of 14.3% (the limiting value of methane concentration for the formation of explosive mixtures) if the dissolved methane percentage is less than that given by the curve BE in Fig 1 which represents the locus of all solutions which, when reduced to one atmosphere, will release a gas of composition:14.3% methane in nitrogen.

Figure 1 can be used to define the extent of the hazard due to the presence of dissolved methane and nitrogen in water: definitely hazardous gases are those having a greater total gas content than the values indicated by the line EF in the diagram and greater methane percentages than than the values indicated by the line BE.

Consideration also has to be given to the concentration of methane that can be produced above the surface of a body of water in which methane is dissolved. Assuming a condition of no ventilation and the presence of a source of ignition, the limiting methane concentration in the airspace above the water is 5% - the lower limit of flammability.

In Fig 1 the curve ADG represents the locus of all liquid compositions whose methane partial pressure is 0.05 atm or 5% in air. The ultimate limit for methane concentration in water, as noted earlier, is 1.5 mg/l which represents a special condition where an unlimited quantity of aerated water is sprayed into an unventilated chamber. Such a condition is unlikely to be encoutered in practise.

The quantity of water exposed to a volume of air is an important factor to be considered. Assuming that as much methane as possible leaves the water and that no air becomes dissolved in the water the following relationships can be derived:

Assuming that venting of the chamber occurs, and therefore constant pressure is maintained, the quantity of water, W (l), required to form an explosive mixture when the methane concentration in the water is Q mg/l is given by an equation of the form:

$$W = \frac{(Q + a)}{a^2} \ln \left[\frac{Q}{Q - a p_m} \right] - \frac{p_m}{a} \qquad (5)$$

This relationship is shown in Fig 2. which gives the minimum quantities of water which would be necessary to produce an explosive methane-air mixture.

The rate of transfer of methane from water to air is a process which is heavily dependent on the rate of gas transfer from the liquid to the air and the extent of the water surface in contact with air. Particular conditions of interest are those where large volumes of water (in effect infinite) come into contact with small volumes of air. Examples include wells, storage reservoirs, tunnels and small unventilated rooms with constantly flowing water.

WATER SAMPLE COLLECTION AND ANALYSIS

Sampling methods

Several techniques may be used for the collection of water samples for dissolved gas analysis, the choice being governed by the nature of the contaminant (i.e gas) and the type of water source - surface water (shallow or deep), or from boreholes(13,14,15).

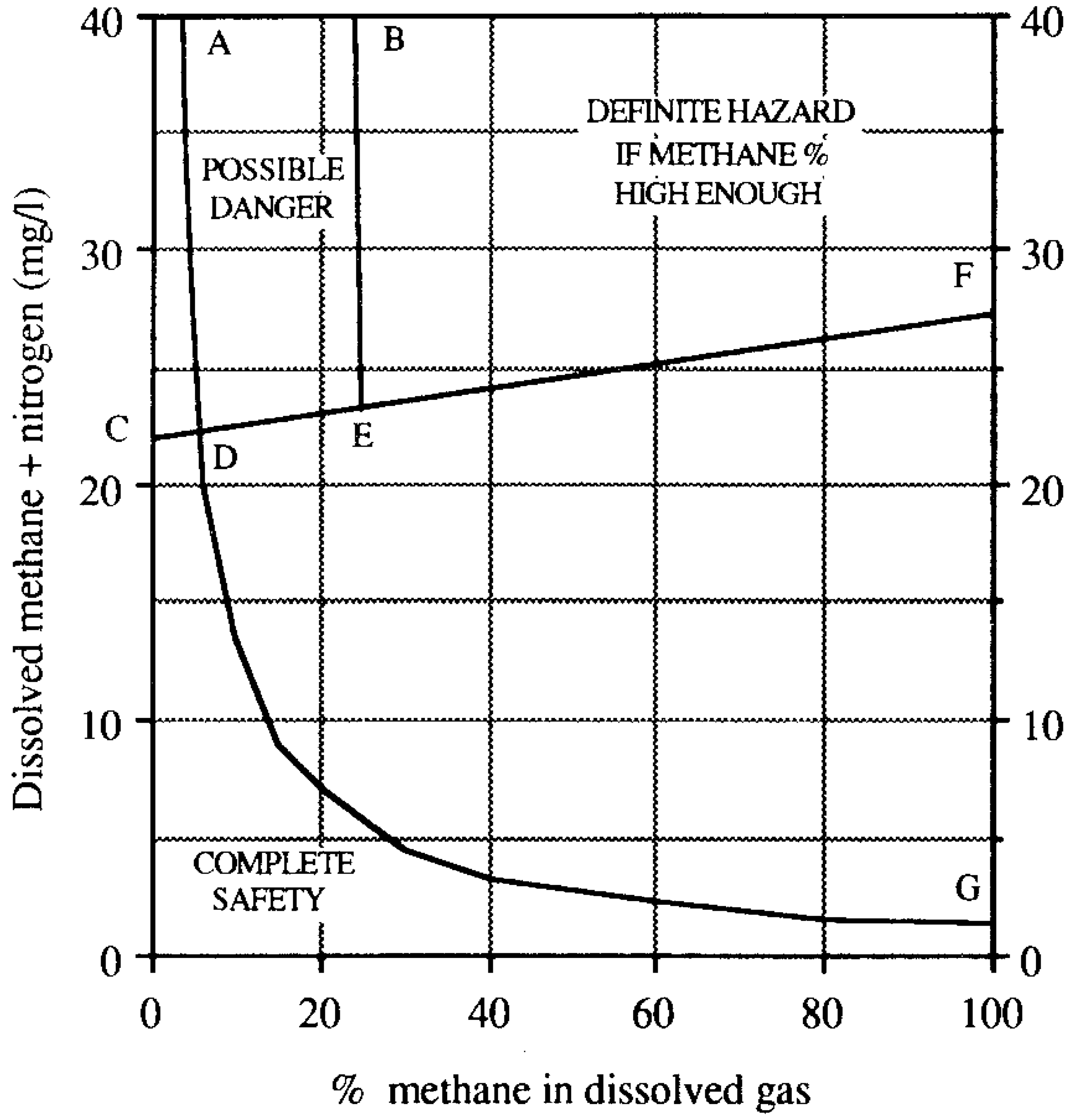

Fig 1 Solubility of methane and nitrogen mixtures in water

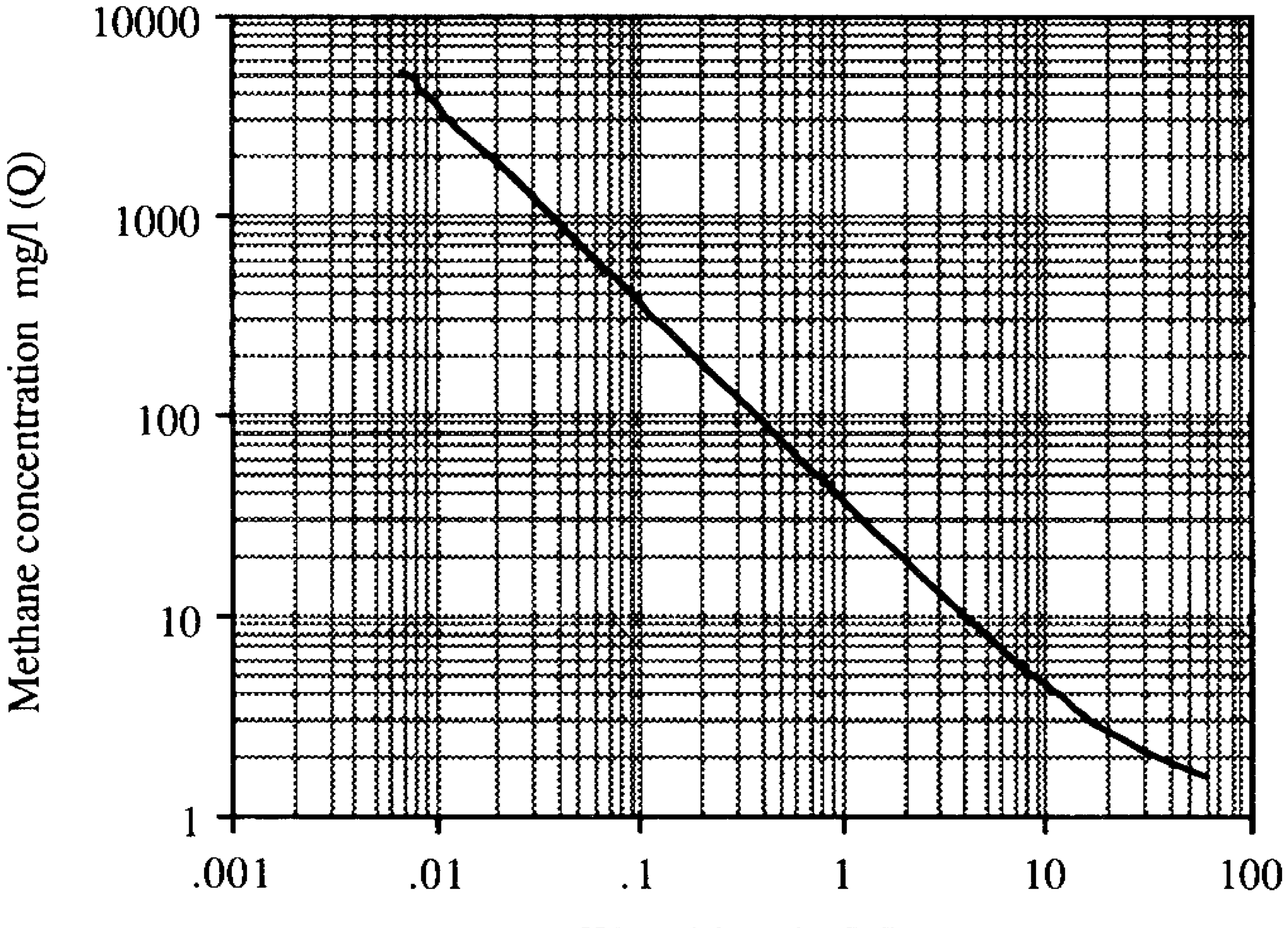

Fig 2. Minimum quantities of water to produce
an explosive methane - air mixture

The proper collection and storage of water samples for analysis is often more difficult than appreciated. In the case of dissolved gases, especially the more volatile ones such as methane, it is essential to collect water samples in such a manner that will clearly reflect the concentrations that actually exist.

It is important to consider the materials from which pumps, samplers, discharge lines, storage containers etc are constructed; materials should be selected which have the least potential for affecting the sample either as a result of contamination or through loss of sample. In the case of gases it is important to appreciate that there may be substantial loss of gas by diffusion through the walls of tubing and containers, especially if the gas is in a supersaturated condition. Rapid analysis of samples with minimum of storage time is therefore desirable.

Grab samples of groundwater from shallow depth (< 10 m) are readily obtained using simple bailers, the water sample being carefully poured from the bailer into clean septum bottles or screw cap vials. Alternatively, a sample may be obtained by withdrawing water through Teflon tube into a sample bottle by means of a peristaltic pump.

For sampling at greater depths non-contaminating submersible high-lift pumps may be used to pump the water directly into the sample container. In recent years continuous-discharge submersible pumps, having all components made from glass or Teflon, have been designed.

Particular problems arise in sampling from wells as great care is needed to ensure that the water to be sampled is representative of the aquifer. This is usually accomplished by purging of monitoring wells prior to sampling either in total or, where samples are required from a particular horizon, in part using packers to isolate the section of the well of interest.

Two basic types of samplers are employed in wells: "dedicated" samplers which are devices that can be permanently installed in the well, and "single-event" samplers which are placed in the well only at the time of sampling and collect one sample at a time. A single-event sampler may be used as the storage vessel, a strategy which eliminates many of the sample handling difficulties.

Many types of samplers can be used in either mode, including: bailers; gas-driven devices; positive-displacement devices; suction-lift devices; syringes etc.

Laboratory techniques.

Methane and other hydrocarbon gases (ethane, ethylene, propane, propylene and the butanes) are readily measured in the laboratory using gas chromatographic (GC) techniques(16). Two basic methods are used:

(a) direct aqueous injection into a GC fitted with a packed column and a flame-ionisation detector (FID).

The range of application of this technique is 0-8 mg/l but the method can be extended to 20 mg/l. The limit of detection is of the order of 0.1 mg/l. There are no known interfering compounds and typical times for analysis are 2-5 samples per hour depending on the type of standard (aqueous or gaseous) employed.

(b) vacuum degassing using purpose-made equipment and a GC fitted with a gas-sampling valve, packed column and FID as in (a).

The range of application of this method is 0-20 mg/l with a limit of detection of 0.4 ppm in the headspace (equivalent to 0.057μg/l aqueous methane). Sampling times are approximately 2 per hour.

Field methods

A convenient method for estimating the dissolved methane content of water in the field is the 'combustible-gas indicater method'(17). The principle of the technique is based upon the equilibrium which, according to Henry's law, is established between the methane gas in solution and the partial pressure of methane in the gas phase above the water.

A sample of the water to be tested is placed in a suitable container to between 1/2 and 3/4 full. The container is fitted with a stopper through which pass two tubes, the external ends of which are connected by flexible tubing and which terminate inside the container at different heights above the water surface. The container is then shaken vigorously for about one minute to force the gas out of solution and then left to stand for two hours to enable equilibrium to be established between the gas remaining in solution and that in the headspace above the water. The concentration of methane in the headspace is easily measured by means of an combustible-gas indicator (methanometer, explosimeter) using an aspirator or pump to withdraw a sample.

To calculate the methane concentration C in the water in mg/l units use is made of equation (7) below:

$$C = V_f P\,[0.257(V_g/TV_s) + (890/H)] \qquad (7)$$

where,

V_f = volume fraction of methane in the vapour phase (%CH_4)
p = system pressure (760 mmHg at sea level)
V_g = volume of the vapour phase (l)
T = system temperature (°K)
V_s = volume of sample (l)
H = Henry's law constant (mmHg/mole fraction).

CONCLUSIONS

Methane may be found as a dissolved gas in many hydrologic environments, often accompanied by other gases. In many cases the gas will be present as a trace contaminant only but occasionally large volumes of the gas may be in solution as a result of high hydrostatic pressure. The release of the gas from solution in these circumstances can give rise to a serious risk of ignition. In order to assess the risk the mechanism governing release of the gas from solution, and the factors controlling it's concentration in atmospheres in contact with the water, should be appreciated.

Selection of the most appropriate techniques for sampling and analysis of water is an important consideration in the examination of waters for the presence of dissolved volatile gases such as methane.

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