# Division of Coal and Energy Technology

## INVESTIGATION REPORT CET/IR575R (Expanded)

DIEBACK AND GAS EMISSIONS IN THE CATARACT RIVER GORGE

by

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Report to BHP

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#### **SUMMARY**

Measurements have been made of gas emissions associated with the areas of dead vegetation in the Cataract River Gorge. The results showed that the maximum gas emission rate through the sandy vegetated area (where temperature sensors have been inserted) occurred in the region with the warmest sub-surface temperature. The gas composition is reasonably consistent with that emanating from the Bulga Sandstone after allowance for oxidation of a portion of the methane in the upper 0.5m of the soil. It is believed that the two dieback areas lie on top of fractures emitting gas from the Bulga Sandstone. Other similar areas of vegetation growing on sandbanks next to the river could be similarly affected if subsidence occurs underneath. Recent measurements have confirmed this, emphasising the need for further monitoring.

An estimate of the overall flux of gas has been made, using air pollution techniques, leading to a value of ~ 20 l/s. This is consistent with peak gas concentrations encountered in the Gorge, which are unlikely to be hazardous unless there is a particularly large vent, a well-known one being at the most northerly box weir.

#### 1. INTRODUCTION

Gas is bubbling up through the Cataract River above a goaf area where coal has been extracted by longwall mining. There are two areas of vegetation on the banks of the river, where the vegetation has died off. One of these areas has been instrumented by BHP with temperature probes which have demonstrated the presence of warm ground under the dead vegetation. CSIRO Division of Coal and Energy Technology (DCET) was invited to assess whether the dead vegetation was associated with the gas emissions. The work was subsequently extended to include other areas that might be potentially affected as well as an assessment of the overall flux of gas and the peak gas concentrations that might be encountered. The measurements, reported here, took place between May 7 and July 22, 1997.

The approach taken by DCET has been based on extensive experience in measuring air pollution fluxes, the absorption off pollution by vegetation, a process known as dry deposition, and emissions from landfills.

#### 2. METHODOLOGY

#### 2.1 Gas Emission Rates

Because of the presence of warm ground indicating possible oxidation of carbonaceous material and also because of the difficult access, it was decided to concentrate on CO<sub>2</sub> emissions. The principle was to place a chamber over a selected area (0.21 m<sup>2</sup>) of ground. The chamber was fitted with a solar powered stirrer and the accumulation rate of CO<sub>2</sub> in the chamber was measured. If the emission rate was too high for this to be measured accurately, then the chamber was diluted with ambient air at a known rate and the steady state value determined. The CO<sub>2</sub> concentration in the chamber was continuously monitored by sampling the chamber air, passing the sample through a Nafion<sup>®</sup> drier into an infra-red CO<sub>2</sub> analyser (Rosemount Binos 100). The pumps and CO<sub>2</sub> monitor were powered by lead acid batteries and an inverter.

#### 2.2 Gas Sampling for Analysis

Shallow metal chambers, formed from garbage can lids, were placed on the ground for periods of ½ h to ¾ h. The chambers were fitted with a 6 mm pipe to which wine bladders could be attached via a hand-operated rubber pipette-filler. Approximately 200 ml of gas were pumped into the bladder, then subsequently analysed by GLC using both TCD and FID detectors. Surface soil temperatures were also noted at most of the sites.

In a second set of experiments performed on a downstream area, gas was collected from the chamber used to determine the gas emission rates

#### 2.3 Soil Oxygen Profile

A gas sampling probe consisted of a 6mm dia stainless steel tube with its lower end screwed on to the 6mm dia base of an inverted brass cone. A horizontal hole was drilled

across the cone and connected to a vertical hole drilled in from the base. This was attached via a hypodermic needle to 1.6mm dia teflon tubing inserted along the length of the steel housing. The top of the teflon tube was sealed with a rubber septum into which a syringe could be inserted to withdraw gas samples for subsequent analysis. A piece of pipe cleaner was inserted into the horizontal hole to prevent clogging when being driven into the ground.

#### 2.4 Gas emission flux determination.

The overall gas emission flux was estimated using an air pollution technique, which requires a knowledge of the vertical CH<sub>4</sub> concentration and air speed profiles within the gorge under certain meteorological conditions, viz existence of valley drainage flows which can occur during clear calm conditions during the night and early morning, particulally in the colder part of the year. Difficulties of finding suitable access meant that the measurements were in the Nepean Gorge about 5 km downstream of the mouth of the Cataract River. A flying fox was strung from the top of the gorge to the river side, along which a moveable 13 mm polythene sampling tube was suspended. Air was pumped up the tube at ~ 10 L/min and supplied to a sampling manifold inside the DCET instrumented vehicle. CH<sub>4</sub> concentrations were measured using an Horiba Alpha 150E hydrocarbon analyser. Wind speed in the gorge were estimated from observing the drift behaviour of neutral buoyancy balloons. the cross-sectional dimensions of the gorge were determined with a laser range gun.

Recently, another access was arranged from Morrison's Dairy and another flying fox system set up on the Cataract River downstream of the emissions. Its location is indicated in Figure 222. To date, meteorological conditions have not allowed any further measurements to be made.

#### 2.5 Peak gas concentrations.

Gas samples were collected in 'wine' bladders in the early morning during conditions of minimal dispersion at a number of locations and a different heights along the affected part of the Cataract River. These locations are indicated on Figure 222 which depicts the portion of the river system afflicted by gas emission and 'quantified' subjectively into regions of low, medium and high emission rates on the basis of degree of bubbling. The location of the sites ranged from just outside the northern limit of gas emission to just north of the patches of dead vegetation. Gas samples were collected at heights ranging from 1 to 9m above the river surface. The samples were taken back to the instrumented vehicle for subsequent analysis the same day.

#### 3. RESULTS

The locations of the sampling sites are shown in Figure 1. The temperature sensors put in by BHP formed the backbone of the sites, the gas analysis sites being extended a little outside the areas of the dead vegetation. Very recently, extra measurements of surface gas emission rates were made further downstream near the last box weir. The locations of these sites are indicated in Figure 2.

## **LOCATION OF SITES**

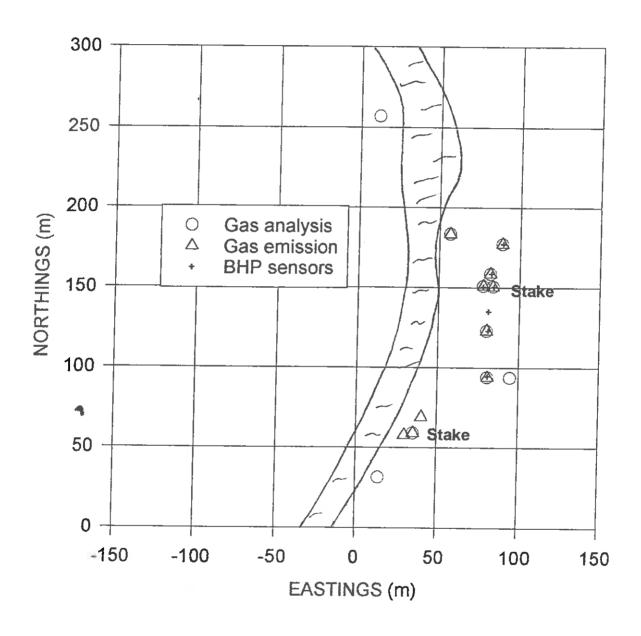


Figure 1. Location of sites

## **IDENTIFICATION OF GAS EMISSION SITES**

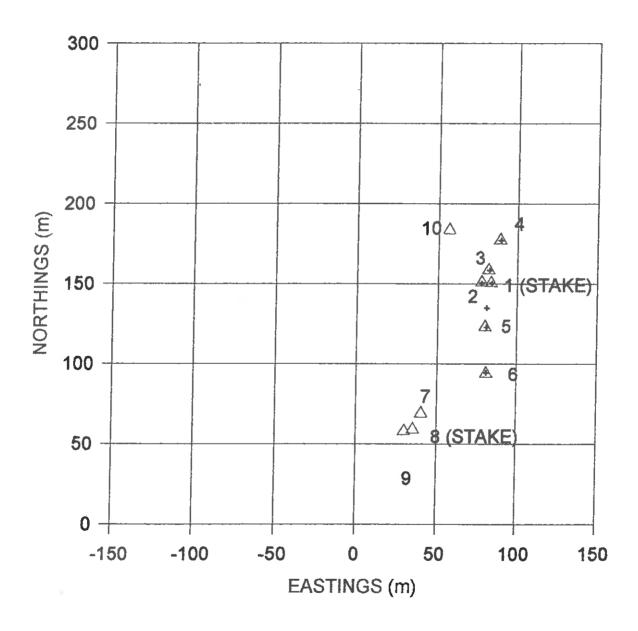


Figure 2 Identification of gas emission rate sites

#### 3.1 Surface Gas Emissions

#### 3.1.1 Dead Vegetation Zones

Table 1 presents the CO<sub>2</sub> emission rates made at ten which are identified in Figure 2. Also shown are some of the sites of the BHP temperature probes. All but sites 9 and 10 were within the overall area of dead vegetation.

Table 1. CO<sub>2</sub> emission rates from selected sites

Site id	CO <sub>2</sub> Emission Rate
	(l/m²/min)
1	0.22
2	0.14
3	0.08
4	0.09
5	0.19
6	0.08
7	0.20
8	0.05
9	0.04
10	0.05

By assuming that gas emission rates were low around the boundaries of the dead vegetation, it is possible to provide a contour of emission rates as shown in Figure 3.

#### 3.1.1.1 Gas Emission Analysis

The identity of the sampling locations are shown in Figure 4, again with the BHP sensors shown for comparison. Table 2 presents data on an air-free and nitrogen-free basis. There was always going to be large amounts of air within the sample due to the methodology, and although there is evidence of  $N_2$  emissions, the loss of oxygen in the soil gases plus the large air content means that such emissions can not be quantified, hence the basis for the data presentation. The gases were wet ie ethane and propane were detected when overall  $CH_4 + CO_2$  was at high enough concentration. Also listed in Table 2 is the soil surface temperature, ambient being  $\sim 16.8$  °C. The ratio of  $CO_2$  to  $CH_4$  varies from 0.2 to 2.25. As it is believed that this is a function of both gas emission rate (assuming  $CH_4$  is the bulk gas) and the presence of microbial oxidisers, it is hard to draw a conclusion, but the highest values tend to be associated with the locations at the edges of the dead vegetation where emission rates were lower, although the coldest location, 7, which was up slope on non-sandy ground, was a notable exception.

# CO<sub>2</sub> EMISSION RATES litres/m<sup>2</sup>/min

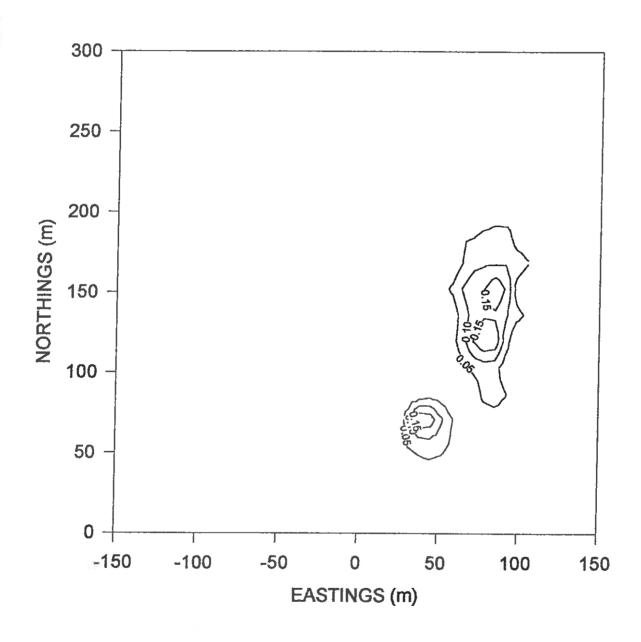


Figure 3. Contours of CO<sub>2</sub> emission rate (1/m<sup>2</sup>/min)

## **IDENTIFICATION OF GAS ANALYSIS SITES**

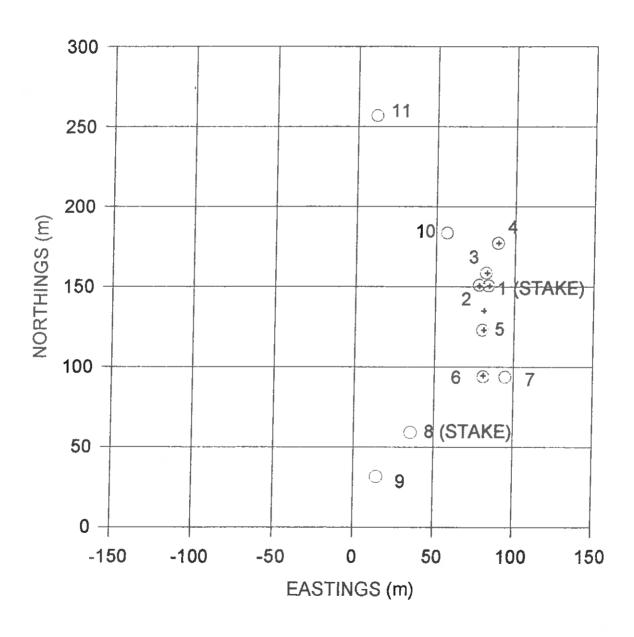


Figure 4. Identification of sites for surface gas sampling and analysis

Table 2. Analysis of gas emissions from soil surface

Site id	Surface	CO2	CH4	Ethane	Propane
	temp (°C)	(%)	(%)	(%)	(%)
			-	-	
1	20.8	33.7	66.1	0.1	0.1
2	25.2	39.5	60.3	0.1	0.1
3		61.9	38.1	0.0	0.0
4		63.6	36.4	0.0	0.0
5		41.4	58.5	0.1	0.0
6	21.7	54.5	45.4	0.1	0.0
7	15.8	18.0	77.1	0.5	0.3
8	18.8	53.8	46.1	0.1	0.0
9	17.7	57.0	42.8	0.1	0.1
10	17.4	69.2	30.8	0.0	0.0
11	17.1	66.6	33.3	0.1	0.0

The data are also shown in abbreviated form to give a spatial impression in Figure 5, which gives the percentage CO<sub>2</sub> and soil surface temperature.

#### 3.1.1.2 Soil Oxygen Profile

The results of gas sampling down to 50 cm are shown in Table 3. The salient features are the rapid drop in oxygen concentration to  $\sim$  10% at 30 cm and the corresponding decrease in the  $\rm CO_2$  /CH<sub>4</sub> ratios. The wetness of the gas is more apparent in these analyses, compared to the surface gas analysis, due to higher gas concentrations.

Table 3. Soil gas composition depth profile

Probe Dept	h Temp*	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	Ethane	Propane	$N_2$	$O_2$
(cm)	(°C)	(%)	(%)	/CH <sub>4</sub>	(%)	(%)	(%)	(%)
						-		
0	20.8	-	-	-	-	-	-	-
10	27.1	1.1	6.9	0.159	0.014	0.009	74.5	17.5
20	30.9	1.3	12.6	0.103	0.022	0.013	71.1	15
30	34.7	2.3	23.8	0.097	0.051	0.018	63.9	10
40	36.9	1.7	27.3	0.062	0.075	0.026	61.2	9.8
50	37.4	1.8	28.1	0.064	0.085	0.028	59.9	10.2
60	37.8	-	-	*		1,50	-	_
70	38.0	52	1.00	2		**	-	2
80	37.9			-		(2)	_	5
90	37.8	-	52	-	_	27	2	-
100	37.7	-5	:=	-	=	-	*	_

<sup>\*</sup>Temperature profile determined with a separate probe

The decrease in oxygen concentration with depth, in conjunction with the temperature profile is consistent with the oxidation of carbonaceous material such as methane. This

# $%CO_2$ AND SOIL SURFACE TEMP. (Ambient temp. ~ 16.8°)

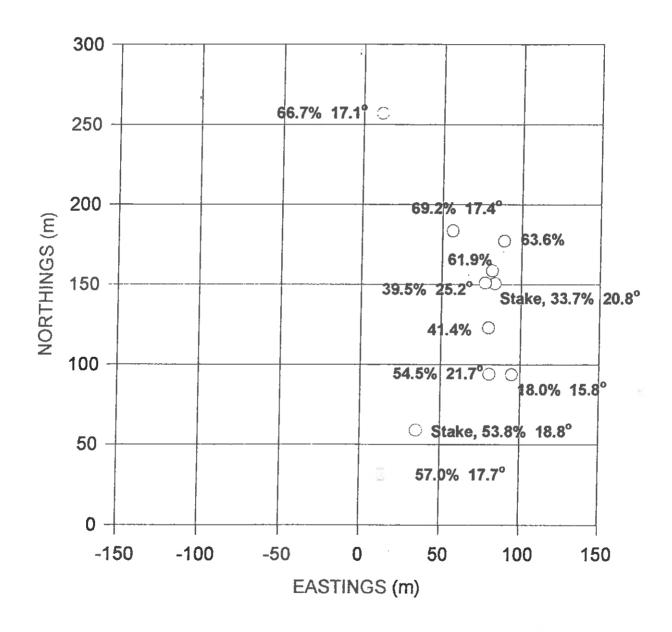


Figure 5. Percentage CO<sub>2</sub> in surface emitted gas and soil surface temperature

assessment assumes that the sandy soil has a void ratio of 0.3, which determines the rate of ingress of air, and its thermal conductivity is 0.2 W/cm/s. Further it is assumed that the  $O_2$  is consumed, solely, by such an oxidation process. It is estimated that the heat release is  $\sim 1 \times 10^4$  J/g  $O_2$  or  $3.2 \times 10^5$  J/g-mol  $O_2$ , very similar to values found in the low temperature oxidation of coal (Carras and Young,1994). CH<sub>4</sub> oxidation appears to occur throughout the upper soil layers.

#### 3.1.2 Downstream Surface Emissions

Table 4 presents the gas emission rates measured further downstream and on the other side of the river to the dieback areas. The values are an order of magnitude lower than those found for the dieback areas. Sub-soil temperatures were measured at depths of 0.25, 0.5 and 1.0 m and the values are shown in Table 5. No signs of heating are apparent. The trees here exhibit no significant adverse impacts, although there is some dead bracken in the undergrowth, which is not uncommon for bracken. This is an area

Table 4. Analysis of gas emissions from soil surface

Site id	CO <sub>2</sub> Emission	CO2	CH4
	Rate	(%)	(%)
	(cc/min/m <sup>2</sup> )		
1	3	33.7	66.1
2	2	39.5	60.3
3	2	61.9	38.1
4	2	63.6	36.4

Table 5. Soil Temperature Profiles

Site id	Temperature		
	0.25	0.5	1.0
1	9.8	11.3	14.0
2	9.4	11.5	13.6
3	9.0	10.6	13.3
4	11.4	11.9	13.9

for which the survey needs extending and periodically monitored to see if the emission rates change as subsidence matures. If emission rates do increase it may be possible to implement a drainage system, similar to that used in landfills to ameliorate the effects of up-welling gas.

#### 3.2 Gas Emission Fluxes

The results from the 'flying fox' experiment in the Nepean Gorge are summarised in Figure 1, with the air-mass in the Gorge being divided into three layers. The excess CH<sub>4</sub> concentrations are those after subtracting a background of 2 ppm from the measured values.

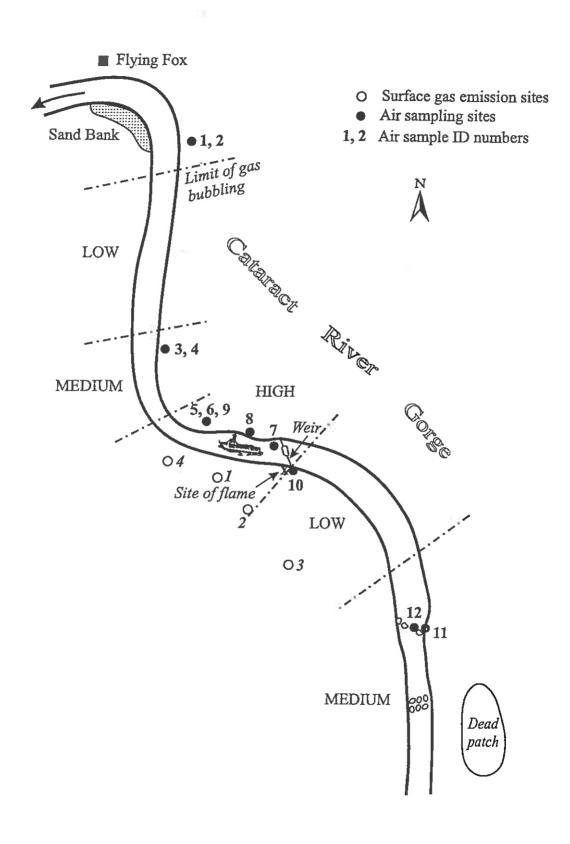


Figure 6. Schematic of Sampling Sites in the Cataract River Gorge.

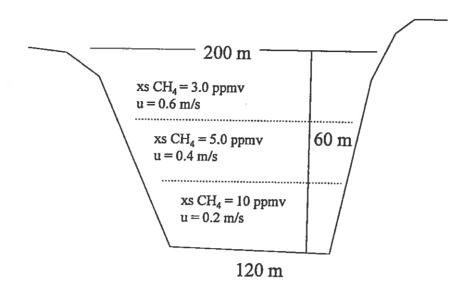


Figure 7. Schematic of cross-section of Nepean Gorge with layer CH<sub>4</sub> concentrations and wind speeds.

Multiplying the  $CH_4$  concentrations by the cross sectional dimensions of the respective layer and the wind speed leads to an overall  $CH_4$  flux of  $\sim 20$  l/s. This value would not be inconsistent with subjective assessment of bubbling rates. However, it must be stressed that this is not an easy measurement to make and needs repeating a few times to reduce the uncertainty. It has been assumed that there is no escape of gas out of the top of the Gorge.  $CH_4$  is lighter than air and there will be some initial rise from the water surface due to density buoyancy. We believe the flux is likely to be in the range 10 - 50 l/s.

One can use the value for the flux to provide a very approximate and lower estimate of the duration of gas emission, provided the source of the gas is known. This, however, is not necessarily the case. The only known significant gas reservoirs first occur at depths of ~ 180-200 m in the Bulgo Sandstone. The gas in the Bulgo Sandstone is wet ie contains higher hydrocarbons, (Battino, 1987) with the highest gas flows in surface boreholes coming from the upper part of the stratum. The Cataract River gas and the soil emissions also are wet. Boreholes sunk for water in Douglas Park encountered gas at 180 m (Williams, personal communication). There may be sources of gas at lower depths, which are ignored or go undetected during drilling. Despite this uncertainty, one can provide 'ballpark' estimates of duration.

Assuming (1) the lateral dimensions of the fracture network that intercept the gas reservoir are of the same sort of size as the width of the bottom of the gorge and the long-wall panel ie  $100 \, \mathrm{m} \times 200 \, \mathrm{m}$ , (2) the sandstone reservoir is  $20 \, \mathrm{m}$  thick with  $10 \, \mathrm{m}$  porosity and an excess gas pressure of 1 atmosphere above ambient, and (3) the gas containing sandstone has low permeability, then the total volume of accessible gas is  $4 \, \mathrm{m}^3$ . At a constant release rate of  $20 \, \mathrm{l/s}$ , the emission would last for  $\sim 3$  weeks for each panel. A reservoir at this pressure would be very close to the bottom of the Gorge. At the depths typical of the Bulgo Sandstone, reservoir pressures might be in the region of  $10 \, \mathrm{atmospheres}$ , so that gas emission would then persist for  $6 \, \mathrm{months}$ . This value is

comparable with the results of Battino (1987) who showed that high gas flows, induced by mining, into drill holes above longwall panels from the Bulgo Sandstone last for about 3 months.

#### 3.3 Peak gas concentrations

Measurements of CH<sub>4</sub> and non-methane hydrocarbon (HC) concentrations were made on Friday, July 11<sup>th</sup> at a number of locations within the Cataract River Gorge. They were made in the early morning when conditions of minimal dispersion might be expected. The locations are shown in Figure 2,. The details are listed in Table 6, together with the CH<sub>4</sub> and HC concentrations.

Table 6. Details of gas concentration measurements

Sample	Sample	Comment	CH <sub>4</sub>	HC	% C
ID	Ht (m)				wetness
1	3	N'most site -	53	7	11
		downstream drift			
2	5	66 66	44	6	12
3	3	By first	106	12	10
		significant			
		bubbling - no drift			
4	9	66 66	171	21	11
5	7	High gas- no drift	102	20	17
6	3	High gas - no drift	189	39	17
9	1	High gas - no drift	269	56	17
7	1	High gas-rock by	229	47	17
		weir - no drift			
8	1	High gas - at boat	254	53	17
		mooring - no drift			••
10	1	1m S of flame site	899	237	21
		- upstream drift		,	~-
11	1	by river side -	52	8	13
		upstream drift		•	10
12	1	on midstream	12	2	15
		rock - upstream		_	10
		drift			

The first two samples were measured between 0725h and 0800h when the air was drifting slowly (< 1m/s) down stream. There was no obvious directional movement of the air for samples 3 to 9 (between 0815h and 0845h), whilst the air appeared to be drifting slightly upstream for the remaining samples (0845h-0915h).

The highest concentration of CH<sub>4</sub> was measured close to the readily ignitable site on the southern side of the weir. Concentrations about a quarter of this level were encountered on the other side near where the survey boat/punt is tied up.

The final column in Table 1 is the volumetric ratio of HC (as  $CH_4$ ) to  $HC+CH_4$  ie a measure of wetness but on a relative carbon basis. As the HC is unspeciated and determined as equivalent  $CH_4$ , then the presence of 2% by vol of ethane and 1% by volume of propane would result in a % C wetness = (2\*2+1\*3)/(98+2\*2+1\*3)\*100 or 6.7%.

In general, the intermittent nature of the gas emissions bubbling up through the water means that a flame cannot be sustained. However, at the south end of the weir, a combination of high emissions and a rocks forming a trapping volume or reservoir allows a substantial flame to be sustained. It is possible that a flame could occasionally be sustained elsewhere, if emission rates are high enough in a contiguous area. The other side of the weir could be a possibility, in this regard, but it would probably only sustain combustion for short periods.

The ultimate accumulated concentration in the Cataract River Gorge can be estimated from the flux measurements. If we assume that the cross-sectional area of the Cataract River Gorge is 1/3rd that of the Nepean, then allowing for dilution by air flowing down the Nepean river,  $CH_4$  concentrations reaching  $\sim 40$  ppmv in the Cataract Gorge might have been expected.

It maybe that there are occasions when ventilation rates are even lower within the Cataract River Gorge, perhaps under calm but slightly less stable conditions, when drainage flows are not properly established. It is unlikely that dispersion will be equivalent to less than 0.1 m/s, averaged throughout the Cataract River Gorge cross-section. On the basis of a flux of 20 l/s, this would give rise to an average value  $\sim 60$  ppmv CH<sub>4</sub>. This estimate can be compared with the value of  $\sim 50$  ppmv found at the northernmost sampling site, which suggests that the emission flux may be higher than 20 l/s

#### 4. CONCLUSIONS

The above data are consistent with the following scenario, although other explanations may well be possible.

Mining has caused subsidence at the area of investigation. The Cataract Gorge intercepts the fracture network which reaches down to a reservoir of 'wet' gas. Consequently, gas is venting into the bottom of the gorge and bubbling up through the river water. The Bulga Sandstone is known to contain wet gas, (Battino, 1987) with the highest gas flows in surface boreholes coming from the upper part of the stratum. This is the shallowest stratum known to contain significant quantities of gas.

Along some parts of the gorge sandbanks occur, some of which are well vegetated. The two dieback areas are examples of such occurrences. It is likely that they each sit over gas vents, with gas permeating throughout the sandbank causing anoxic conditions resulting in dieback. The warm ground is likely to be the result of partial oxidation of the up-welling gas, probably through microbial processes. This situation may repeat itself at other similar vegetated sand banks if affected by subsidence. Preliminary

measurements have confirmed that gas is indeed emanating from other vegetated areas. This needs further examination and monitoring to see if possible remediation is either needed or indeed can be applied before dieback occurs.

The flux of  $CH_4$  is estimated to lie in the range 10 - 50 l/s. Local peak concentrations can be high enough to ignite providing the local emission rate is high enough and a ballasting volume is available to overcome the intermittent nature of the emissions. Short-term combustion without much of a ballasting volume may be possible

#### 5. ACKNOWLEDGEMENTS

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