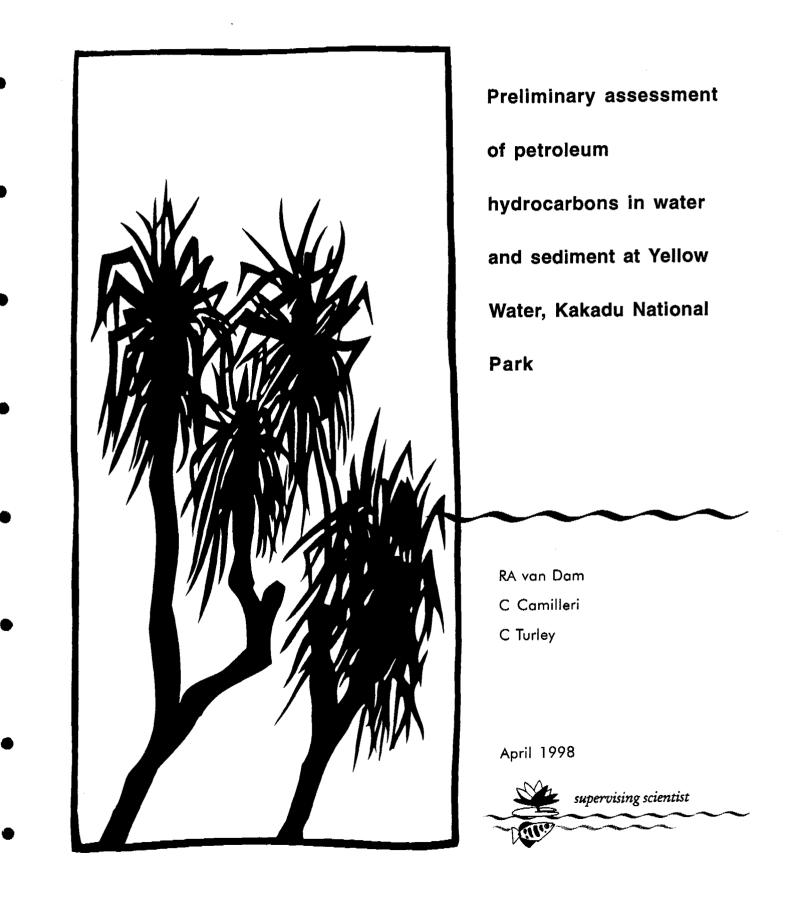
internal report





Preliminary assessment of petroleum hydrocarbons in water and sediment at Yellow Water, Kakadu National Park

1

Rick A van Dam, Caroline Camilleri & Catriona Turley

Wetland Protection and Management Environmental Research Institute of the Supervising Scientist (*eriss*) Locked Bag 2, Jabiru, NT, 0886

Summary

In 1996, the environmental impacts of a commercial tour boat operation at Yellow Water, a highly valued wetland ecosystem within the World Heritage listed Kakadu National Park were assessed. While not specifically addressing pollutant-related issues associated with boating, the report did recognise the potential for pollution from outboard motors to impact upon the Yellow Water environment.

Leaking fuel and oil from outboard motors results in the contamination of waterways with petroleum hydrocarbons. The period of high boating activity at Yellow Water coincides with that of low water levels and no freshwater input, suggesting that petroleum hydrocarbons could accumulate to potentially toxic concentrations. Therefore, the present study aimed to provide a preliminary assessment of outboard motor-derived petroleum hydrocarbon levels in water and sediment during the late-dry season (ie a worst-case-scenario). In the event of petroleum hydrocarbons being detected, an assessment was to be made regarding the potential impacts on the Yellow Water environment, and the requirement for further monitoring/toxicity/risk assessment programs.

Water and sediment samples were collected from three sites at Yellow Water on December 16, 1997. The sampling sites were chosen according to where boating activity was considered to be greatest. Samples were analysed for benzene, toluene, ethyl-benzene and xylene (BTEX), and total petroleum hydrocarbons (TPH).

Petroleum hydrocarbons were detected in water samples from one of the three sites, at a concentration of 200 μ g/L. Analysis revealed that the hydrocarbons were relatively high molecular weight compounds, possessing carbon numbers of between 15 and 28. Petroleum hydrocarbons were not detected above the Practical Quantitation Limit in any of the sediment samples.

For the contaminated site, the fact that no low molecular weight, highly volatile hydrocarbons were detected indicated that i) the contaminant event was not particularly recent, and ii) the source was oil, not gasoline (ie unleaded petrol).

Based on previous literature on the aquatic toxicity of petroleum hydrocarbons, it appears unlikely that acute toxicity would be observed for the plant and animal species inhabiting Yellow Water. However, at the concentration detected, there appears to be a possibility of sub-lethal effects to aquatic organisms.

The present study did not represent the 'worst-case-scenario' situation initially anticipated. Boating activity in December is much lower compared to the July – September peak, while Yellow Water had already received significant freshwater input prior to sample collection, potentially diluting hydrocarbon concentrations in the water.

As a result of the potential for sub-lethal toxicity to aquatic organisms, and also for the presence of higher hydrocarbon concentrations during peak boating periods, the implementation of a more comprehensive monitoring program, incorporating sampling periods before, during, and after the peak boating activity, is recommended. Such a program will better characterise the input of petroleum hydrocarbons to Yellow Water throughout the dry season. In addition, more specific chemical analyses, and potentially, toxicity assessments, will assist in the prediction of adverse environmental effects associated with boating activities at Yellow Water.

Contents

Sumn	hary	ii
Ackno	owledgments	v
1 Intr	oduction	1
Air	ns	2
2 Mat	erials and Methods	2
2.1	Sampling sites	2
2.2	Sample collection	2
2.3	Sample analysis	4
3 Res	sults	4
3.1	Water samples	4
3.2	Sediment samples	5
4 Dis	cussion	4
4.1	Source of petroleum hydrocarbons at Yellow Water	5
4.2	Aquatic toxicity of petroleum hydrocarbons	6
4.3	Implications for the Yellow Water environment	7
5 Cor	clusions and Recommendations	8
Refer	ences	8
Apper	ndixes	
Α	Copy of permit to carry out research at Yellow Water	11
В	Quality assurance/quality control report for chemical analyses	13
С	Analysis report for all samples	19

Figures

Figure 1	Aerial photograph of Yellow Water during the dry season,	
	showing the three sampling sites	3

1

Tables

Table 1	Sampling sites, and type and number of samples to be collected from Yellow Water	2
Table 2	Levels of BTEX and TPH in water at three sites at Yellow Water, Kakadu National Park	5

Acknowledgments

We are very grateful to Parks Australia North, in particular Miss Georgianna Fien, Mr Pat Shaughnessy and Mr Manfred Haala, and traditional owners for approving this preliminary research at Yellow Water. Dr Chris leGras is thanked for providing constructive comments on the manuscript. Thanks must also go to Dr Max Finlayson and Dr Arthur Johnston (*eriss*) for supporting the research.

1 Introduction

Yellow Water is a biologically diverse freshwater wetland situated within Kakadu National Park. Along with all wetland habitats in Kakadu, it is listed under the Convention on Wetlands of International Importance Especially as Waterfowl Habitat. Yellow Water possesses many environmental and cultural values, and as a result, has become a major tourist destination in northern Australia. The wetlands of, and surrounding, Yellow Water are a highly important habitat for waterfowl, with over 60 species, including up to a million magpie geese (*Anseranus semipalmata*) inhabiting the region at various stages during the annual seasonal cycle (Morton & Brennan 1991, Whitehead & Chatto 1996). A large tour boat operation allows visitors to view the abundant wildlife, including the birdlife and estuarine crocodiles, while also learning about the region's cultural history (Braithwaite et al 1996). In addition to its appeal as a sightseeing destination, Yellow Water is also a popular destination for recreational fishermen, in search of the sport fish, barramundi (*Lates calcarifer*).

In 1995, an extensive environmental, social and economic assessment of tour boat operations at Yellow Water was undertaken (Braithwaite et al 1996). While the study assessed environmental factors such as animal behaviour in response to tour boat operations, it did not assess the environmental effects of pollutant impacts arising from boating operations (ie pollution from outboard motors). However, Braithwaite et al (1996) did recognise that pollution, in the form of leaking fuel and oil from outboard motors, particularly two-stroke engines, was visible, and represented a potential environmental concern.

Fuel (gasoline) and oil (petroleum) contain a large number of different types of hydrocarbons, known collectively as petroleum hydrocarbons. Petroleum hydrocarbons can enter aquatic systems either as components of uncombusted petroleum and petroleum products (eg fuel, lubricating oils), or as products of incomplete combustion in exhaust emissions (Müller 1987). They have been shown to be quite toxic to a variety of aquatic fauna and flora (see reviews by Müller 1987 and Shales et al 1989), while they have also been found to accumulate in fresh and marine waters and sediments at elevated concentrations as a result of boating activities (Montz et al 1982, Mastran et al 1994, Trapido & Veldre 1996). The majority of the hydrocarbons in gasoline (eg unleaded petrol) are of low molecular weight and highly volatile (Müller 1987, Budavari 1996). While being quite toxic, such compounds evaporate from water quite rapidly (Robotham & Gill 1989, Mastran et al 1994), and hence do not usually represent great concern to the aquatic environment. In contrast, many hydrocarbons found in oil are of higher molecular weight and less volatile, and thus tend to persist in the water or deposit in the sediments (Mastran et al 1994). Twostroke engines, used by most recreational boaters at Yellow Water are of particular concern as they contain considerable quantities of oil. It has been estimated that up to 56% of fuel used in two-stroke engines may be discharged directly into the water column, although an average of 10--20% is considered more realistic (Muratori 1968, Jackivicz & Kuzminski 1973). In addition, it has been estimated that the total discharge of hydrocarbons from an outboard two-stroke motor operating for one day would be equivalent to the sewage produced by a population of 400 people (Jackivicz & Kuzminski 1973). The above points emphasised the need for initial concern over the levels of petroleum hydrocarbons in both water and sediment at Yellow Water.

Yellow Water experiences the same seasonal hydrological conditions as most other waterbodies in the wet-dry tropics of Australia (see Taylor & Tulloch 1985, Finlayson et al

1989). Large amounts of rainfall during December to March (~1500-2000 mm) result in extremely large volumes of water at high flow rates passing into and through Yellow Water, as it connects with the main body of the nearby South Alligator River. During the Dry season, from May to approximately October, the water level declines, and flow ceases. If hydrocarbon levels do accumulate in the water and sediment at Yellow Water, it is likely that their concentrations would peak in the late Dry season, with the water at its lowest, the area having received little or no freshwater input for several months, and boating pressure having been maintained throughout the dry season. Samples taken during this period would most likely represent a 'worst-case-scenario' assessment of hydrocarbon levels at Yellow Water, and would assist in determining whether more extensive monitoring/toxicity/risk assessment programs were warranted.

Aims

The aims of the study were:

i) to determine whether petroleum hydrocarbons could be detected in water and sediment at Yellow Water during the late dry season, as a result of both recreational and tourism boating operations,

and if so;

ii) to assess the requirements for further research on the potential ecological risks of petroleum hydrocarbons at Yellow Water.

2 Materials and Methods

2.1 Sampling sites

Approval for carrying out research at Yellow Water was granted by Parks Australia North and traditional owners on 12 December 1997 (a copy of the research permit is shown in Appendix A).

Water and sediment samples were collected between 1330 and 1530 on 16 December 1997, from three sites at Yellow Water. As financial constraints limited the size of the sampling program, the sites were selected according to where boating activity/pressure was considered to be greatest. The three sampling sites, all of which were located within Yellow Water billabong, are shown in figure 1. The type and number of samples collected from each site are outlined below, in table 1.

Table 1 S	Sampling sites,	and type and number	of samples to be	e collected from Yellow Water
-----------	-----------------	---------------------	------------------	-------------------------------

	Number of samples					
Sampling site	surface water	sediment	Total			
A: public boat launching area	2	2	4			
B: tour boat embarkation area	2	2	4			
C: Yellow Water billabong - South Alligator River junction	2	2	4			
			12			

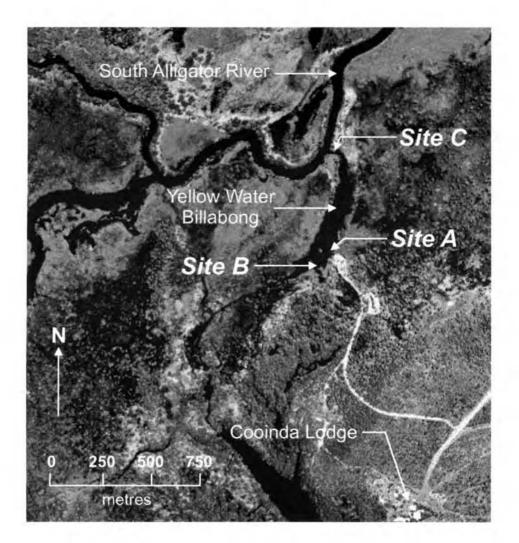


Figure 1 Aerial photograph of Yellow Water during the dry season, showing the three sampling sites. Site A: public boat launching area; Site B: tour boat embarkation area; Site C: Yellow Water billabong -South Alligator River junction (Photograph supplied by G. Lindner, Parks Australia North)

2.2 Sample collection

Samples were collected from a boat powered by a four-stroke outboard motor. Care was taken to switch off the motor well before reaching the sampling site to avoid the chance of contamination from the motor. Water was collected in 500 ml Schott bottles that had been washed in 5% HNO_3 and dried the day before sampling. Two surface water samples were taken at each site. Sediment was collected using a long PVC rod with an aluminium scoop fastened to one end. Sediment was placed in 250 ml Schott bottles prepared as described above. Two sediment samples were collected at each site. A clean water blank (Milli-Q water) and sediment blank (empty bottle) were also included for analysis.

For all samples, care was taken to minimise the air space in the neck of the bottle, so as to avoid evaporation of the more volatile hydrocarbons. Gloves were worn during all sample collections. Aluminium foil liners were placed over the openings of the bottles and the screw-cap tightly fastened. Due to the unavailability of teflon-lined screw caps, the water samples were not acidified upon collection. Following labelling, the samples were placed on ice in the dark until transportation to the laboratory, where they were placed in the dark at 4°C, overnight. A separate water sample was also taken from within Yellow Water Billabong for measurement of pH and conductivity.

2.3 Sample analysis

On 17 December the samples were sent by air to a NATA-registered analytical chemistry laboratory in Sydney (AMDEL) for analysis. Due to flight delays, the samples arrived at the laboratory on the morning of 19 December, approximately 24 h later than expected. All samples were analysed for benzene, toluene, ethylbenzene and xylene (BTEX), and total petroleum hydrocarbons (TPH), using gas chromatography (AMDEL Methods: E084, Total Petroleum Hydrocarbons in Soil; E083, Total Petroleum Hydrocarbons in Water; E054, Benzene, Toluene, Ethylbenzene & Xylene in Soil; E052, Benzene, Toluene, Ethylbenzene & Xylene in Water).

3 Results

3.1 Water samples

The QA/QC report for the analyses is presented in Appendix B. The pH and conductivity of Yellow Water billabong water at the time of sampling were 7.6 and 50.5 μ S/cm, respectively.

Petroleum hydrocarbons (BTEX or TPH) were not detected above the Practical Quantitation Limits $(PQL)^1$ in water samples collected from the boat launching area (Site A), the tour boat embarkation area (Site B) (table 2), or in the clean water blank. However, petroleum hydrocarbons were detected in both water samples taken from the Yellow Water billabong-South Alligator River junction (Site C) (table 2). Analysis revealed the hydrocarbons possessed carbon numbers of between 15–28 (table 2). The analysis report for all the water samples is presented in Appendix C.

¹ The PQL is typically $2-10\times$ the method detection limit.

			Si	te*			
	Α			3	с		
	Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2	
Benzene	nd	nd	nd	nd	nd	nd	
Toluene	nd	nd	nd	nd	nd	nd	
Ethylbenzene	nd	nd	nd	nd	nd	nd	
Xylene	nd	nd	nd	nd	nd	nd	
TPH:							
C ₆ -C ₉	nd	nd	nd	nd	nd	nd	
C ₁₀ -C ₁₄	nd	nd	nd	nd	nď	nd	
C ₁₅ -C ₂₈	nd	nd	nd	nd	200	200	
C ₆ -C ₉ C ₁₀ -C ₁₄ C ₁₅ -C ₂₈ C ₂₉ -C ₃₆	nd	nd	nd	nd	nd	nd	
Total (C6-C36)		-		-	200	200	

 Table 2
 Levels of BTEX and TPH in water at three sites at Yellow Water, Kakadu National Park.

 Measurements are in µg/L (parts per billion; ppb)

* Site A: private boat launching area; Site B: tour boat embarkation area; Site C: Yellow Water billabong - South Alligator River junction

nd: not detected

3.2 Sediment samples

No petroleum hydrocarbons (BTEX or TPH) were detected above the PQL in any of the sediment samples, including the sediment blank. The analysis report for the sediment samples is presented in Appendix C.

4 Discussion

4.1 Source of petroleum hydrocarbons at Yellow Water

As stated in section 2.1, the Yellow Water sampling sites were chosen because they represented the areas of greatest boating activity. Of the three sites, the private boat launching area and the tour boat embarkation area (sites A and B, respectively) were considered most likely to be contaminated. However, it was the water samples from site C, the Yellow Water billabong – South Alligator River junction that revealed the presence of petroleum hydrocarbons, at a concentration of 200 μ g/L. The junction is a narrow entrance into the South Alligator River, through which the majority of vessels travelling throughout Yellow Water pass. The chemical analyses provided some information on the potential source of the hydrocarbons. The fact that no lower molecular weight, highly volatile hydrocarbons (eg BTEX) were detected in the sample suggested that the contamination event was not particularly recent. This effectively eliminated the contaminant source being the outboard motor of the sampling boat. In addition, that only large carbon chain hydrocarbons were detected (ie $C_{15} - C_{28}$), indicated that the source was oil, and not gasoline (ie unleaded petrol), which characteristically contains a mixture of C_4 to C_{12} hydrocarbons (Müller 1987, Budavari 1996).

The fact that higher molecular weight hydrocarbons were detected in surface water but not in sediment was somewhat unusual, as such compounds tend to deposit in sediments as a result of their hydrophobicity and high octanol-water partition coefficient ($Log K_{ow}$) (Mastran et al 1994). Illustrating this property, Mastran et al (1994) reported total concentrations of polycyclic aromatic hydrocarbons (PAHs) in surface water and sediment of the Occoquan reservoir in Virginia of up to 18 μ g/L (ppb) and 1319 μ g/kg (ppb), respectively, a difference of approximately two orders of magnitude. However, most pollutants also have a tendency to concentrate in the surface microlaver (ie top 200 μ m) of a water body (Mullins 1977), thus potentially explaining the presence of hydrocarbons in surface water but not sediment. While multiple depth sampling would have resolved this, the budget of the sampling program did not allow for it. It should also be noted that increased water temperatures, high dissolved organic matter (DOM) content, and low salinity, all common characteristics at Yellow Water, serve to increase the solubility of hydrocarbons (Müller 1987). Alternatively, the hydrocarbons may not have been dissolved in the water column, but adsorbed to suspended sediment/particulates within the water column. Supporting this, a recent study reported that total PAHs in marine water were mostly bound to particulates than dissolved in the water column (Zeng & Vista 1997). Filtration of Yellow Water water samples prior to analysis would reveal whether the above hypothesis was correct.

4.2 Aquatic toxicity of petroleum hydrocarbons

The toxicity of petroleum products to aquatic organisms varies enormously. For example, Tsvetnenko (in press) compiled toxicity data for marine species on different petroleum products including crude oils, diesel oils and bunker fuels, with LC50 values (based on μg petroleum hydrocarbons/L) ranging from 190 $\mu g/L$ for the ghost crab, *Ocypode quadrata*, to 2620 $\mu g/L$ for the alga, *Isochrysis* sp. The advisable water quality criterion (AWQC) derived from the toxicity values (based on US EPA Guidelines) was 7 $\mu g/L$ (Tsvetnenko in press), well below the level of petroleum hydrocarbons found at Yellow Water. However, this value was derived for marine waters only, and thus does not necessarily apply to freshwater ecosystems. Müller (1987) and Shales et al (1989) reviewed the toxicity of oils and petroleum products to freshwater organisms. However, much of the data are difficult to compare to the levels detected at Yellow Water because they involved crude oils with complex, and often uncharacterised compositions. In addition, the hydrocarbon content, and potentially toxicity, of petroleum products such as two-stroke outboard motor fuel does not necessarily reflect that of the parent crude oil (Gill & Robotham 1989). Nevertheless, a summary of the aquatic toxicity of petroleum and petroleum products is presented below.

Apparently, microorganisms in freshwater environments exhibit no wide-scale toxicity to petroleum hydrocarbons, with many responses actually involving increases in microbial populations (Shales et al 1989). Kauss et al (1973, as cited by Shales et al 1989) reported a 40% decrease in algal cell number compared to controls for the green alga, *Chlorella vulgaris*, two days following exposure to a 90% extract of outboard motor oil, indicating some toxic effect. However, cell number had returned to normal after four days' exposure. King & Coley (1985) exposed three species of duckweeds (*Lemna* spp.) to water soluble fractions (WSF) of various oils. Toxicity varied enormously depending on the oil type and the species of *Lemna*, from no effect at 100% WSF of oil, to 100% growth inhibition at 10% WSF of oil. The 48 h LC50 of the WSF of a crude oil to the freshwater invertebrate, *Asellus aquaticus*, was reported to be 11.58 mg/L (Ramusino & Zanzottera 1986). However, the ephemeropterans, *Baetis rhodani* and *Ecdyonurus helyeticus*, were more sensitive, with 100% mortality occurring at 10 mg/L WSF (Ramusino & Zanzottera 1986). Woodward et al

(1987) reported up to 90% mortality for the invertebrate genera, *Baetis* and *Isoperla*, at 0.5–0.7 mg/L WSF of several crude shale oils. In addition, the 96 h LC50s of the same WSFs to the cut-throat salmon, *Salmo clarki*, ranged from 1.3–2.1 mg/L (Woodward et al 1987). Müller (1987) summarised the literature on low level, sub-lethal toxicity of hydrocarbons to freshwater species. Effects of various individual hydrocarbons on fish and crustaceans were reported at concentrations of 0.1–20 μ g/L and 10 - 80 μ g/L, respectively. In addition, toxic effects of a crude oil WSF to the brown alga, *Fucus edentatus*, have been reported at 0.2 μ g/L (as reviewed by Müller 1987).

In addition to aquatic animals, birds may also be at risk from waters contaminated with petroleum hydrocarbons. In the case of chronic hydrocarbon pollution, such as that arising from boating activity (excluding large spills), birds could be exposed directly, by drinking contaminated water (Shales et al 1987), or via biomagnification, having eaten contaminated food (ie fish, invertebrates, plant matter) (Roper et al 1996). Brunström (1991) investigated the toxicity of various PAHs to avian embryos. A 200 μ g/kg (ppb) dose of benzo[k]fluoranthene, a PAH known to be present in many crude oils (Müller 1987), resulted in 100, 65 and 44% mortality of domestic duck (*Anas platyrhynchos*), turkey (*Meleagris gallopavo*), and eider (*Somateria mollissima*) embryos, respectively (Brunström 1991). A 2000 μ g/kg mixture of 18 PAHs was also highly toxic, resulting in 100, 83 and 94% mortality of embryos of the above three species, respectively (Brunström 1991). These results confirm the susceptibility of avian early life stages to petroleum hydrocarbons.

When considering the toxicity of petroleum hydrocarbons, two additional factors deserve recognition: i) the production of highly toxic metabolites of hydrocarbons, and ii) the high carcinogenicity of certain PAHs known to be present in oil and exhaust emissions. Highly toxic metabolites of PAHs are known to be produced as a result of their exposure to light (photooxidation; Müller 1987, McConkey et al 1997), while the metabolism of many PAHs by the mixed function oxidase enzyme system within living organisms results in the formation of highly carcinogenic metabolites (Ahokas 1991). Depending on the nature of the hydrocarbons present at Yellow Water, the above two factors could be of concern.

4.3 Implications for the Yellow Water environment

While it is difficult to predict potential impacts on the Yellow Water environment without further knowledge of the identity of the C15-C28 hydrocarbons detected in the present study, some general conclusions can be made. Based on the levels of petroleum hydrocarbons detected in the present study and the acute toxicity data summarised above, it appears unlikely that acute toxicity would be observed for local animal and plant species at Yellow Water. However, the potential for sub-lethal toxicity due to continual low-level hydrocarbon contamination of Yellow Water may represent a concern, although this may be somewhat mitigated by annual flushing of the system during the wet season.

The intention of the present study was to assess hydrocarbon levels during the late-dry season (ie early December), when it was thought hydrocarbon build-up would be at its greatest. However, tour boat activities at Yellow Water during November–December (average of 243 cruises per month) average only 50% of the July–August peak period (average of 512 cruises per month) (Braithwaite et al 1996). It is likely that private boat usage also reflects that of the tour boat operations, resulting in the vast majority of boating activity at Yellow Water occurring during the months of July–September. Although the volume of water within the system is far greater at this point than during the late-dry season, it is still highly possible that levels of petroleum hydrocarbons will exceed those detected in the present study. Supporting

this, periods of peak boating activity have previously been shown to be associated with elevated PAH concentrations (Mastran et al 1994, Trapido & Veldre 1996). In addition, the samples in the present study were taken approximately two weeks later than was considered ideal, with Yellow Water having already received significant volumes of inflowing water from Jim Jim Creek and the South Alligator River (P. Shaughnessy, Senior Ranger Jim Jim District, pers. comm.). While this was not likely to have affected sediment composition, petroleum hydrocarbons in the water column may have been substantially diluted.

The fact that petroleum hydrocarbons were detected at only one site indicated that contamination of Yellow Water was not widespread, instead, occurring in localised areas as a result of fuel leakage and exhaust emissions from outboard motors. In addition, exposure to high UV radiation levels and a diverse microbial population, factors that assist in the degradation of petroleum hydrocarbons in the aquatic environment (Robotham & Gill 1989), would decrease the risk of widespread contamination. However, it is still possible that contamination during the peak boating periods may be greater and more widespread, as has previously been demonstrated for other, larger freshwater bodies (Mastran et al 1994; Trapido & Veldre 1996).

5 Conclusions and Recommendations

Petroleum hydrocarbon contamination, albeit at low levels, was found to occur at Yellow Water, during a period which, in hindsight, did not necessarily represent the 'worst-case-scenario' initially anticipated. At the time of sampling, boating activity was relatively low, while Yellow Water had already received significant freshwater input, yet petroleum hydrocarbons were detected at levels that have previously been shown to result in sub-lethal toxicity to aquatic organisms. As a result, the development and implementation of a more comprehensive and statistically sound monitoring program, focussed on periods of peak boating activity is recommended. Periodic collection and analysis of water (surface water and water column) and sediment samples should be carried out prior to, during, and after the period of peak boating activity (July - September), in order to detect whether a significant boating-related increase in contamination exists, and if so, to monitor the persistence of contamination as boating activity decreases.

In addition, further chemical characterisation/identification of the petroleum hydrocarbons present in water or sediment at Yellow Water should be carried out, to assist in the prediction of the potential adverse effects on the aquatic environment. Finally, given significant and consistent levels of contamination, an assessment of the toxicity of relevant petroleum hydrocarbons, or contaminated Yellow Water water on local aquatic organisms, using standard laboratory toxicity testing procedures would also assist in predicting the risk of adverse environmental effects associated with boating activities at Yellow Water.

References

- Ahokas JH 1991. Detoxication of xenobiotics in aquatic animals. *Proceedings of the 29th Congress of the Australasian Society of Limnology*. Supervising Scientist for the Alligator Rivers Region, Canberra, ACT, 86–96.
- Braithwaite RW, Reynolds PC & Pongracz GB 1996. Wildlife Tourism at Yellow Waters: an analysis of the environmental, social, and economic compromise options for sustainable operation of a tour boat venture in Kakadu National Park. Federal Department of

Tourism, Australian Nature Conservation Agency, Gagudju Association Inc. Final Report, 267 pp.

- Brunström B 1991. Toxicity and EROD-inducing potency of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in avian embryos. *Comparative Biochemistry and Physiology* 100C, 241-243.
- Budavari S (ed.) 1996. The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals, 12th Edition. Merck & Co. Inc., Whitehouse Station, NJ, USA, p. 741.
- Finlayson CM, Bailey BJ & Cowie ID 1989. Macrophyte vegetation of the Magela floodplain, Alligator Rivers Region, Northern Territory. Supervising Scientist for the Alligator Rivers Region, Research Report 5, Jabiru, Australia.
- Gill RA & Robotham PWJ 1989. Composition, sources and source identification of petroleum hydrocarbons and their residues. In: *The Fate and Effects of Oil in Freshwater*, eds J Green & MW Trett. Elsevier Science Publishers, Essex, England, 11–40.
- Jackivicz TP & Kuzminski LN 1973. The effects of the interaction of outboard motors with the aquatic environment. *Environmental Research* 6, 436–454.
- King JM & Coley KS 1985. Toxicity of aqueous extracts of natural and synthetic oils to three species of Lemna. In Aquatic Toxicology and Hazard Assessment: Eighth Symposium, ASTM STP 891 eds RC Bahner & DJ Hansen. American Society for Testing and Materials, Philadelphia, 302-309.
- Mastran TA, Dietrich AM, Gallagher DL & Grizzard TJ 1994. Distribution of polyaromatic hydrocarbons in the water column and sediments of a drinking water reservoir with respect to boating activity. *Water Research* 11, 2353-2366.
- McConkey BJ, Duxbury CL, Dixon DG & Greenberg BM 1997. Toxicity of a PAH photooxidation product to the bacteria *Photobacterium phosphoreum* and the duckweed *Lemna gibba*: effects of phenanthrene and its primary photoproduct, phenanthrenequinone. *Environmental Toxicology and Chemistry* 16(5), 892–899.
- Montz WE, Puyear RL & Brammer JD 1982. Identification and quantification of watersoluble hydrocarbons generated by two-cycle outboard motors. Archives of Environmental Contamination and Toxicology 11, 561-565.
- Morton SR & Brennan KG 1991. Birds. In: Monsoonal Australia: Landscape, Ecology and Man in Northern Lowlands, eds CD Haynes, MG Ridpath & MAJ Williams. AA Balkema, Rotterdam, Netherlands, 133-149.
- Müller H 1987. Hydrocarbons in the freshwater environment: a literature review. Arch. Hydrobiol., Advances in Limnology 24, 1-69.
- Mullins T 1977. The chemistry of water pollution. In: *Environmental Chemistry*, ed. J O'M Bockris. Plenum Press, NY, 331-400.
- Muratori A 1968. How outboards contribute to water pollution. Conservationist 22, 6-8.
- Ramusino MC & Zanzottera D 1986. Crude Dubai oil toxicity on some fresh-water invertebrates. Bulletin of Environmental Contamination and Toxicology 36, 150–158.
- Robotham PWJ & Gill RA 1989. Input, behaviour and fates of petroleum hydrocarbons. In: *The Fate and Effects of Oil in Freshwater*, eds J Green & MW Trett. Elsevier Science Publishers, Essex, England, 41-79.

- Roper JM, Cherry DS, Simmers JW & Tatem HE 1996. bioaccumulation of toxicants in the zebra mussel, *Dreissena polymorpha*, at the Time Beach Confined Disposal Facility, Buffalo, New York. *Environmental Pollution* 94(2), 117–129.
- Shales S, Thake BA, Frankland B, Khan DH, Hutchinson JD & Mason CF 1989. Biological and ecological effects of oils. In: *The Fate and Effects of Oil in Freshwater*, eds J Green & MW Trett. Elsevier Science Publishers, Essex, England, 81–171.
- Taylor JA & Tulloch D 1985. Rainfall in the wet-dry tropics: Extreme events at Darwin and similarities between years during the period 1870–1983 inclusive. Aust. J. Ecol. 10, 281– 295.
- Trapido M & Veldre I 1996. On polynuclear aromatic hydrocarbon contamination levels in the ecosystem of Lake Peipsi in the 1970s-1980s. *Hydrobiologia* 338, 185-190.
- Tsvetnenko JB in press. Derivation of Australian tropical marine water quality criteria for protection of aquatic life from adverse effects of petroleum hydrocarbons. *Environmental Toxicology and Water Quality*.
- Whitehead P & Chatto R 1996. Northern Territory. In: A Directory of Important Wetlands in Australia 2nd Edition, ANCA, Canberra, ACT, 119–175.
- Woodward DF, Little EE & Smith LM 1987. Toxicity of five shale oils to fish and aquatic invertebrates. Archives of Environmental Contamination and Toxicology 16(2), 239-246.
- Zeng EY & Vista CL 1997. Organic pollutants in the coastal environment off San Diego, California. 1. Source identification and assessment by compositional indices of polycyclic aromatic hydrocarbons. *Environmental Toxicology and Chemistry* 16(2), 179– 188.

Appendix A Copy of permit to carry out research at Yellow Water

1

á.

RECEIVED

1 6 DEC 1997

AUSTRALIA NORTH Kakadu National Park Parks Australia North PO Box 71 Jabiru NT 0886 Tel 08 8938 1100 08 8938 1115 Fax: Permit Number: RK 471 Date of Issue : 12 December 1997

Mr Rick van Dam **Environmental Research Institute** of the Supervising Scientist Locked Bag 2 Jabiru NT 0886

PERMISSION TO CONDUCT SCIENTIFIC RESEARCH IN KAKADU NATIONAL PARK

Permittee: Rick van Dam of the Environmental Research Institute of the Supervising Scientist is given permission under Regulation 27 of the National Parks and Wildlife Regulations to conduct scientific research in Kakadu National Park.

Research permitted: Sampling of water and sediment for hydrocarbons in Yellow Water

Period of permit:

15 to 19 December 1997

Access to specific locations requires the approval of relevant District Supervisor/s. Permit holders must obtain such approval before commencing work.

Subject to the conditions overleaf.

Manja titico 14.

DELEGATE **DIRECTOR OF NATIONAL PARKS & WILDLIFE**



58

PARKS

Appendix B Quality assurance/quality control report for chemical analyses



OA/OC APPENDIX NO. 7E02139

Method Description

Chromatography QA/QC

Retention Time Window

Check Standard Within

E052	Benzene, Toluene, Ethylbenzene & Xylene	•
E054	Benzene, Toluene, Ethylbenzene & Xylene	
E083	Total Petroleum Hydrocarbons	
E084	Total Petroleum Hydrocarbons	

Acceptance Criteria($\pm 10\%$) **Recalibration Within** Acceptance Criteria($\pm 15\%$) Other OA/OC

Within Acceptance Criteria($\pm 2\%$)

Holding time conforming With Method Specification	\checkmark
Chain of Custody Attached	\checkmark

N/A=Not Applicable

N/A

No

Comments

1. Laboratory QA/QC including Duplicates, Matrix Spike Duplicates, and check/reference samples are included in this QA/QC appendix. (Where applicable)

Yes

 $\sqrt{}$

 $\sqrt{}$

 $\sqrt{}$

- 2. Inter-Laboratory proficiency trial results available on request. (Where applicable)
- 3. Surrogate description and recoveries are recorded in the Report. (Where applicable)
- 4. Acceptance criteria for specific analytes are listed on each QA/QC page.
- 5. Practical Quantitation Limit (PQL is typically 2-10 x method detection limit (MDL)).
- 6. PQL's are matrix dependent and are increased accordingly where sample extracts are diluted.

7. Results are uncorrected for matrix spike or surrogate recoveries.

2 -24

ber G.W. ANDERSON Manager Environmental Sydney



Job Number : 7E02139

Page 1 of 4

¿AQC : Matrix Spike / Check Solution

		Level	Detected	Recovery Details			
Analyte	Level (ppm)	Result1 (ppm)	Result2 (ppm)	Rec 1 (%)	Rec 2 (%)	Average (%)	RPI (%)
E052 BTEX (P&T) in Water							
Benzene	0.010	0.010	0.010	100%	100 %	100 %	0%
Toluene	0.010	0.013	0.010	130%	100 %	115%	26%
Ethylbenzene	0.010	0.010	0.010	100 %	100%	100 %	0%
Total Xylene	0.030	0.032	0.031	107 %	103 %	105%	3%
E083 TPH in Water							
TPH C6-C36 as C8	9.5	11	11	116%	116%	116%	0%
C6-C9 Fraction	4.0	4.1	4.1	103 %	103%	103%	0%
C15-C28 Fraction	5.5	6.8	7.0	124%	127%	125%	3%
•							

PQL = Practical Quantitation Limit

(S) Soils : mg/kg (ppm) dry weight (W) Waters : mg/l (ppm) nd = Not Detected -- = Not Applicable

्हें

All results are within the acceptance criteria:

Refer to Amdel-Sydney Quality Control Manual SPM-01 4th Edition 1/7/97



AQC : Duplicates

Analyte	PQL	Dupl 1	Dupl 2	Average	RPD (%)
E052 BTEX (P&T) in Water					
Benzene	0.001	nd	nd		
Toluene	0.001	nd	nd		
Ethylbenzene	0.001	nd	nd		
Total Xylene	0.003	nd	nd		
E083 TPH in Water					
TPH C6-C36 as C8	-	nd	nd		
C6-C9 Fraction	0.02	nd	nd		
C10-C14 Fraction	0.04	nd	nd		
C15-C28 Fraction	0.2	nd	nd		
C29-C36 Fraction	0.2	nd	nd		
· · · · · · · · · · · · · · · · · · ·					
			• •		
				1	

PQL = Practical Quantitation Limit

(S) Soils : mg/kg (ppm) dry weight (W) Waters : mg/L (ppm) nd = Not Detected -- = Not Applicable

Ś

All results are within the acceptance criteria:

Refer to Amdel-Sydney Quality Control Manual SPM-01 4th Edition 1/7/97

Page 2 of 4



Job Number : 7E02139

QAQC : Matrix Spike / Check Solution

Level (ppm) 10 10 10 30	Result1 (ppm) 11 13 11 33	Result2 (ppm) 9.5 11 9 26	Rec 1 (%) 110% 130% 110% 110%	Rec 2 (%) 95% 110% 90% 87%	Average (%) 103% 120% 100% 98%	RPI (%) 15% 17% 20% 24%
10 10 30	13 11	11 9	130% 110%	110% 90%	120 <i>%</i> 100 <i>%</i>	17 <i>%</i> 20 <i>%</i>
10 10 30	13 11	11 9	130% 110%	110% 90%	120 <i>%</i> 100 <i>%</i>	17 <i>%</i> 20 <i>%</i>
10 30	11	9	110%	90%	100%	20%
30						
	33	26	110%	87%	98%	24%
					1	
0.50						
950	1150	1050	121%	111%	116%	9%
400	460	420	115%	105%	110%	9%
550	690	625	125%	114%	120%	10%
					<u></u>	
	···	400 460	400 460 420	400 460 420 115%	400 460 420 115% 105%	400 460 420 115% 105% 110%

PQL = Practical Quantitation Limit

(S) Soils : mg/kg (ppm) dry weight (W) Waters : mg/l (ppm) nd = Not Detected -- = Not Applicable

All results are within the acceptance criteria:

Refer to Amdel-Sydney Quality Control Manual SPM-01 4th Edition 1/7/97

Page 3 of 4

a.



QAQC : Duplicates

Analyte	PQL	Dypl i	Dupl 2	Average	RPD (%)
E054 BTEX (P&T) in Soil					
Benzene	0.5	nd	nd		
Toluene	1	nd	nd		
Ethylbenzene	1	nd	nd		
Total Xylene	3	nd	nd		
E084 TPH in Soil					
TPH C6-C36 as C8	-	nd	nd		
C6-C9 Fraction	10	nd	nd		
C10-C14 Fraction	20	nd	nd		
C15-C28 Fraction	100	nd	nd		
C29-C36 Fraction	100	nd	nd		
۰. - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹۹۰ - ۱۹					
· · · · · · · · · · · · · · · · · · ·					

PQL = Practical Quantitation Limit

(S) Soils : mg/kg (ppm) dry weight (W) Waters : mg/L (ppm)

= Not Detected = Not Applicable nd

s.

.....

--

All results are within the acceptance criteria:

Refer to Amdel-Sydney Quality Control Manual SPM-01 4th Edition 1/7/97

Page 4 of 4 Appendix C Analysis report for all samples

é

¢



Job Number: 7E02139 ient : Environmental Research Institute Reference : --

Page 1 of 4 plus Cover Page

	Lab No	E41041	E41042	E41043	E41044	E4104
		WATER	SITE A	SITE B	SITE B	SITE
	Sample Id	BLANK	REP 1	REP 1	REP 2	REP
Analyte	PQL					
E052 BTEX (P&T) in Water						
Benzene	0.001	nd	nd	nd	nd	1
Toluene	0.001	nd	nd	nd	nd	1
Ethylbenzene	0.001	nd	nd	nd	nđ	1
Total Xylene	0.003	nd	nd	nd	nd	1
E083 TPH in Water						
TPH C6-C36 as C8	-	nd	nd	nd	nd	
C6-C9 Fraction	0.02	nd	nd	nd	nd	
C10-C14 Fraction	0.04	nd	nd	nd	nd	
C15-C28 Fraction	0.2	nd	nd	nd	nd	
C29-C36 Fraction	0.2	nd	nd	nd	nd	

PQL = Practical Quantitation Limit

Soils

LNR = Samples Listed not Received

Waters

nd = Not Detected (<PQL)

Leachates

: mg/L (ppm) unless otherwise specified

: mg/kg (ppm) dry weight unless otherwise specified

-- = Not Applicable



Job Number: 7E02139 Lient : Environmental Research Institute Reference : --

Page 2 of 4 plus Cover Page

Lab No	E41046	E41047	CB		
	SITE C	SITE C	CONTROL		
Sample Id	REP 1	REP 2	BLANK		
PQL					
0.001	nd	nd	nd		
0.001	nd	nd	nd		
0.001	nd	nd	nd		
0.003	nd	nd	nd		
			and the first of t		
-	0.20	0.20	nd		
0.02	nd	nd	nd		
0.04	nd	nd	nd		
0.2	0.2	0.2	nd		
0.2	nd	nd	nd	· · · · · · · · · · · · · · · · · · ·	
	2 				
		······	· · · · · · · · · · · · · · · · · · ·		
	Sample Id PQL 0.001 0.001 0.001 0.003 - 0.003 - 0.02 0.04 0.2	Sample Id SITE C Sample Id REP 1 PQL 0.001 nd 0.001 nd 0.001 nd 0.003 nd 0.004 nd 0.02 nd 0.02 0.2	SITE C SITE C Sample Id REP 1 REP 2 PQL 0.001 nd nd 0.003 nd nd 0.02 nd nd 0.02 nd nd 0.20 0.20 0.2	SITE CSITE CCONTROLSample IdREP 1REP 2BLANKPQLImage: Control of the second sec	SITE CSITE CSITE CCONTROLSample IdREP 1REP 2BLANKPQLImage: strain of the strain of

PQL = Practical Quantitation Limit

LNR = Samples Listed not Received

Soils

Waters

Leachates

: mg/kg (ppm) dry weight unless otherwise specified

: mg/L (ppm) unless otherwise specified

: mg/L (ppm) in leachate

nd = Not Detected (<PQL)

-- = Not Applicable



Job Number: 7E02139 _ient : Environmental Research Institute Reference : --

Page 3 of 4 plus Cover Page

	Lab No	E41048	E41049	E41050	E41051	E4105
		SEDIMENT	SITE A	SITE A	SITE B	SITE
	Sample Id	BLANK	REP 1	REP 2	REP 1	REP
Analyte	PQL					
E054 BTEX (P&T) in Soil						
Benzene	0.5	nd*	nd	nd	nd]
Гоluene	1	nd*	nd	nd	nd	1
Ethylbenzene	1	nd*	nd	nd	nd	
Fotal Xylene	3	nd*	nd	nd	nd	
E084 TPH in Soil						
ГРН C6-C36 as C8	-	nd	nd	nd	nd	
C6-C9 Fraction	10	nd	nd	nd	nd	
C10-C14 Fraction	20	nd	nd	nd	nd	
C15-C28 Fraction	100	nd	nd	nd	nd	
C29-C36 Fraction	100	nd	nd	nd	nd	
E1042 Moisture Content %(w/w)	1		75	27	65	
						·····
						,
					-	
			_			

PQL = Practical Quantitation Limit

Soils

LNR = Samples Listed not Received

: mg/kg (ppm) dry weight unless otherwise specified

Waters

: mg/L (ppm) unless otherwise specified Leachates : mg/L (ppm) in leachate

nd = Not Detected (<PQL) -- = Not Applicable

* BTEX result taken from TPH, GC-FID run.



Job Number : 7E02139 Lient : Environmental Research Institute Reference : --

Page 4 of 4 plus Cover Page

	Lab No	E41053	 E41054	СВ		
		SITE C	SITE C	CONTROL		
	Sample Id	REP 1	REP 2	BLANK		
Analyte	PQL				· · · · · · · · · · · · · · · · · · ·	
E054 BTEX (P&T) in Soil			<u> </u>			
Benzene	0.5	nd	nd	nd		
Toluene	1	nd	′ nd	nd		
Ethylbenzene	1	nd	nd	nd		
Total Xylene	3	nd	nd	nd		
E084 TPH in Soil						
ГРН C6-C36 as C8	-	nd	nd	nd		
C6-C9 Fraction	10	nd	nd	nd		
C10-C14 Fraction	20	nd	nd	nd		
C15-C28 Fraction	100	nd	nd	nd		
C29-C36 Fraction	100	nd	nd	nd		
E1042 Moisture Content %(w/w)	1	73	54			

PQL = Practical Quantitation Limit

Soils

LNR = Samples Listed not Received

-- = Not Applicable

Waters

Leachates

: mg/kg (ppm) dry weight unless otherwise specified

: mg/L (ppm) unless otherwise specified

nd = Not Detected (<PQL)

: mg/L (ppm) in leachate

47