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The Evaluation of Atmospheric Soluble Mist Concentrations on Longwall Faces at Illawarra Coal

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1. INTRODUCTION

Soluble hydraulic oils are a fire-resistant hydraulic fluid and have been used within chocks on longwalls for many years, however little information exists to demonstrate that longwall operators are not being exposed to unacceptable levels of organic contaminants arising from these oils. This project aimed to address this information deficiency by quantifying operator inhalable exposures on longwall faces to the atomised components of soluble oil mist and to determine if the levels experienced are a health risk.

Riley *et al* (ACARP C7034) suggests that somewhere between 50 and 1200 litres per day can escape from the closed hydraulic system commonly used on longwall chocks. While much of the soluble oil finds its way to mine water and biodegrades, an unknown proportion is invariably atomised and dispersed into the general airbody. This unintentional action has raised questions in the minds of longwall operators as to the potential health effects arising from breathing this atmosphere.

Soluble oils are manufactured using a number of different ingredients and as a neat product are classified as hazardous by the National Occupational Health and Safety Commission (NOHSC). Typically soluble oils are diluted to 2 - 4% for use on the longwall and under normal conditions of use should be non harmful and are classified non hazardous by NOHSC.

Airborne exposure can occur if the emulsion leaks from the longwall, and mists under pressure. However, leaks are generally eliminated as soon as possible due to the safety risk of injection of the emulsion under high pressure.

Twenty-two (22) personal samples were taken on both the West Cliff and Dendrobium longwalls, resulting in forty-four (44) personal samples in total. Following the initial monitoring and interpretation of the data, an additional 10 personal samples were collected on the Dendrobium longwall for formaldehyde as it was determined this could be a by-product of other contaminants breaking down.

The levels of all agents monitored showed very low levels of exposure to the workers, indicating the inhalation of this emulsion should not cause or contribute to adverse health effects, and thus additional controls for airborne mists are not required.

2. LITERATURE SEARCH

A search of available literature as well as discussions with other relevant parties, including local Australian mining companies and Mine Safety and Health Administration (MSHA) indicated that exposure to soluble oil mist during longwall mining to longwall operators and associated workers had not been investigated previously.

The literature search therefore focused on similar products in different working environments to determine the likely risk to longwall operators from soluble oil mist. In addition, all prior investigations completed, focussed on the oil only – sampling for oil mist. This is not the case for this monitoring program, as it was determined the levels of oil in the emulsion that Illawarra Coal use were too low to accurately use and determine oil mist as a whole. It was more accurate to investigate the individual components of the soluble oil. Individual components had not been sampled in any of the studies located during the literature search.

Overall investigations of workers exposed to oil mist have shown that such exposure may have deleterious effects on lungs, even at relatively low levels. A factor that does confuse the study data is that there are three basic types of oils – these are straight mineral oil (insoluble), mineral oil-in-water emulsions (soluble) and synthetic oils (Mackerer, 1989). This study is focussed on soluble oil only, however some of the studies are not clear in their description of what the exposure was that caused the symptoms. Skyberg *et al* (1986) reported increased prevalence of slight basal lung fibrosis to low levels of oil mist and vapour (0.15-0.3mg/m^3). An increase in pulmonary fibrosis has been reported by Cullen *et al*, (1981) and an increase in respiratory symptoms has been reported by Jarvholm *et al* (1982). Older studies by Goldstein and Benoit (1970) demonstrated no increase in respiratory mortality or morbidity.

Svendensen and Bjorn (1997) reviewed exposure to mineral oil mist and respiratory symptoms to Marine Engineers. In this situation mineral oil mist is generated by moving machinery parts and the aerosolization of vapourised oil. An increased prevalence of mucous membrane irritation, 1.38 (95% CI 1.0-1.9), dyspnea, 1.53 (95% CI 1.2-1.9) and severe dyspnea, 1.63 (95% CI 1.0-2.6) was noted for those who were still working as marine engineers as compared to those that had not worked as a marine engineer (Svedensen and Bjorn, 1997). Dyspnea itself is unspecific and may reflect other conditions such as being overweight, lack of exercise or cardiovascular disorders. Further investigation attributed the increased prevalence of respiratory symptoms found was more likely due to a combination of past asbestos exposure as well as past and current oil mist exposure. However it is important to note that even after controlling for asbestos exposure, symptoms are still attributable to mineral oil. It was estimated that the marine engineer's exposure was 0.45mg/m^3 on average, although quantifying this was difficult due to the exposures occurring in the past and monitoring not being conducted at the time. Monitoring was conducted in the engine rooms and resulted in 0.2mg/m^3 oil mist. The number of samples taken was limited and therefore the estimated results are questionable.

Massin *et al* (1996) researched exposure to soluble oil mists in a plant manufacturing ball bearings and resultant respiratory symptoms and airway responsiveness. Monitoring was completed using area samplers rather than personal sampling and ranged in time from 1979 to 1993. The geometric mean concentrations ranged from 0.65mg/m^3 to 2.2 mg/m^3 (depending on when the samples were collected; the lower figure relates to post improvement of ventilation). If these were personal samples, these results would be comparable to the 5mg/m^3 Oil Mist from American Conference of Governmental Industrial Hygienists (ACGIH) 2010. The prevalence of chronic cough or phlegm, bouts of bronchitis and dyspnea was greater amongst exposed workers than among controls (odds ratio (OR)) 4.64, P=002 for chronic cough and phlegm. The conclusion from the study was that exposure to soluble oil mist in the metal industry may result in the development of respiratory symptoms and airway hyper-responsiveness. The paper did discuss that these fluids used are a complex mixture of oil (mineral or synthetic) and other substances such as water, emulsifiers, corrosion inhibitors, bactericides. However the study did not consider these mixtures in the monitoring.

Ameille *et al* (1995) examined workers exposed to mists of straight cutting oil, soluble mineral oil or a mixture of straight cutting oil and soluble mineral oil and compared the results to a control group. Overall it was concluded that only slight adverse effects on respiratory symptoms and lung function were found which were restricted to workers exposed to straight cutting oil. They found there was no effect on airway responsiveness for any of the groups.

Robertson *et al* (1988) tested 25 patients who were exposed to oil mists at their workplace, to determine if they had work related asthma. During this process they determined that some people had a response to the unused/clean oil, while another reacted to used oil but not to clean oil. Robertson *et al* (1988) concluded that occupational asthma due to oil mists is common and the provoking agent within the oil may vary from worker to worker.

Hendy *et al* (1985) also conducted studies of a worker that experienced occupational asthma. The worker was found to react to the whole emulsified oil, as well components within the oil, and components within those components.

The literature indicated that it is inconclusive as to whether emulsified soluble oil has a health risk or not. The literature search indicates that there may be a health risk associated with soluble oil exposure, however there is no quantification of exposure apart from some general oil mist results. There has been no in-depth sampling conducted on the constituents of the soluble oils, and the results of soluble oil are questionable, particularly on sampling conducted on emulsions.

Based on the above review of literature there is not enough evidence to determine if exposure to soluble oil mist causes health issues. The scenarios are different between the above job locations and the longwall area. One of the main differences between the exposure to the workers in the longwall study as compared to other studies is the presence of ventilation or airflow as a control. The engine rooms of ships are enclosed and relatively confined spaces with minimal ventilation and workshops generally only have a flow of air through them if the roller doors are left open, and they may also have some local ventilation for specific tasks. Longwalls at Illawarra Coal generally have a ventilation rate of 4-6ms^{-1} which allows soluble oil mist, gases, dust and other contaminants to be moved quickly past the workers. However, bearing this in mind, as well as the uncertainly of the exposure outcome to soluble oil mist it is pertinent that the exposure to operators on the longwall is assessed to understand the magnitude of their exposure to the soluble oil used on the longwalls.

3. BACKGROUND

At the time of monitoring, 30 March to 29 June 2009, Illawarra Coal were using two types of soluble oil on their longwalls. Quaker Fluid, Quintolubric 814-03 (Quintolubric) was used on one longwall system and Fuchs Solcenic 2020 Oil (Solcenic) used on the remaining two longwall systems.

The project was designed to investigate soluble oil exposure on longwalls as an Australia wide process, although there was a focus on NSW to allow for ease of sampling and transport of samples. It was determined important to keep the monitoring with one group of people rather than have a number of groups performing monitoring to reduce any variation in the sampling.

MSHA and the wider BHP Billiton (BHPB) group were consulted as to previous similar monitoring and investigation having been completed. At the time, there was no evidence of similar work having been completed or being conducted through mines, through the BHPB network or through MSHA.

One Illawarra Coal site had recently conducted a review of their use of soluble oil usage and found a number of areas where the oil was lost due to spillage during transport. Since May 2009 all three Illawarra Coal mine sites are using Solcenic oil, however this was a business decision rather than a health related decision. The change over occurred when the monitoring was completed, which allowed the assessment of Quintolubric product even through it is no longer a product used on Illawarra Coal sites.

3.1 CLASSIFICATION OF SOLUBLE OIL VARIETIES

The hazardous nature of both Quintolubric and Solcenic in concentrate form and emulsion has been evaluated according to the criteria of National Occupational Health and Safety Commission - Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(2004)], 3rd edition. During this process the hazardous nature of all ingredients in the formulation are individually assessed at their respective concentrations. The outcome of this assessment is recorded in the Material Safety Data Sheet (MSDS) for each product and this is reviewed every 5 years as a minimum.
The results of the evaluations are as follows:

- -Solcenic 2020 concentrate has been evaluated as hazardous. It has been assigned the risk phrase R43 – may cause sensitisation by skin contact.
- -Solcenic 2020 2-4% v/v emulsion has been evaluated as non-hazardous, as a result no short term or long term adverse health effects are expected to be associated with this product.
- -Quintolubric 814-03 concentrate has been classified as hazardous. It has been assigned the risk phrase R43 – may cause sensitisation by skin contact.
- -Quintolubric 814-03 (3% w/w in water) has been evaluated as non-hazardous, as a result no short term or long term adverse health effects are expected to be associated with this product.

3.2 HEALTH EFFECTS – INGREDIENTS LISTED ON MSDS

The following table is a list of the ingredients from the Quintolubric and Solcenic MSDSs and their associated health effects.

Table 1: Health effects by ingredient listed in Quintolubric and Solcenic MSDS		
Ingredient	**Other name**	**Health effects**
2,2'Oxybisethanol	Diethylene Glycol	Irritates the eyes, the skin and the respiratory tract and may cause effects on the central nervous system, liver, and kidneys.
Diethanolamine	2,2'-Iminadiethanol	Acute (short-term) inhalation exposure to diethanolamine in humans may result in irritation of the nose and throat, and dermal exposure may irritate the skin. No information is available on the chronic (long-term) health effects
Mineral Oil mist		Exposure to mineral oil mists can cause eye, skin, and upper respiratory tract irritation as well as central nervous system effects in humans
N-Butanol	n-Butyl alcohol	Moderate skin irritation and severe eye irritation
Ethylene glycol (vapour)	Ethane-1,2-diol	Low levels of ethylene glycol by inhalation may give rise to throat and upper respiratory tract irritation.
Solvent refined light naphtha (as mineral oil mist)		Can cause eye, skin, and upper respiratory tract irritation as well as central nervous system effects in humans
2-Butoxyethanol	Butyl cellosolve Butyl glycol Ethylene glycol, monobutyl ether Glycol, monobutyl ether	Exposure can cause eye, nose, and throat irritation

The overwhelming effects indicate eye, nose and throat irritation, and thus additive effects must be considered.

3.3 SITE INVOLVEMENT

Two sites were chosen from Illawarra coal to follow up the soluble oil usage and conduct monitoring, these were West Cliff and Dendrobium. It was determined that Appin was similar enough to Dendrobium in usage to not conduct monitoring there, and in addition to this, a longwall move was scheduled during the monitoring program, which eliminated the availability of the longwall area and thus the site for this monitoring.

Meetings were held with longwall engineers, and others responsible for soluble oil usage on each site. Initial meetings were centred around determining the type and amount of soluble oil used, the history of its use, the risk of exposure and the tasks involved during exposure risk, including transport, storage, operation of the longwall, maintenance, cleaning and, spill and leak procedures.

Following this initial contact, site visits were conducted to gain a more comprehensive understanding and to finalise the monitoring program, in addition to understanding limitations on site due to non operation of the longwall, maintenance days and other planned events.

3.4 DETERMINING METHODS FOR MONITORING SOLUBLE OIL MIST

The literature search showed that previous studies monitored for Soluble Oil Mist used a general Oil Mist method. Although it was not clarified within the research exactly which method had been used, information within the method section of the papers, indicated it was likely to be similar to National Institute for Occupational Safety and Health (NIOSH) method 5026 Oil Mist, Mineral (http://www.cdc.gov/niosh/docs/2003%2D154/method-o.html, accessed April 2010).

To ensure a comprehensive and scientifically proven method was developed and used for the project, TestSafe Australia, and Mr Greg O'Donnell in particular, was engaged to assist in determining an appropriate method for collection of personal air samples. Following discussion with Mr O'Donnell, it was determined that the NIOSH method was not appropriate for monitoring emulsified oil with additional constituents, and analysis would be problematic and inaccurate if this method was used. Instead of a sample being collected and a total result analysed, it was recommended that individual constituents be monitored and analysed.

The WorkSafe documentation for Oil Mist refined Mineral (WorkSafe Australia 1996) also indicates that the standard for Oil Mist (5 mg/m^3) may not be appropriate for unrefined oils and those containing contaminants or additives. Where oils contain such contaminants or additives, the mixture formula should be used to derive an exposure standard more suited to the application (WorkSafe Australia 1995).

Therefore, analysis of bulk samples was used to determine a suitable method(s). The methods needed to be sustainable and reproducible for future use. The process involved to determine the methods was as follows:

1. Review of the MSDS's to determine the major components.
2. Liaison and discussion with the manufacturers to determine if there were other components that should be considered that are not listed on

the MSDS, i.e those considered non hazardous to health and therefore not necessary to list.

3. Collection of bulk samples of the materials from the sites for analysis by TestSafe.
4. Analysis of bulk samples by TestSafe to provide a fingerprint and quantify the components in soluble oil using gas chromatography mass spectroscopy (GCMS) to identify key marker compounds (or components of compounds).
5. Review of the components with known current methods of collection.
6. Review of components of the oil that did not have standard analytical methods to determine a method and appropriate absorbent that could subsequently be analysed using GCMS and provide an accurate result.

3.5 REVIEW OF THE MSDS'S

The major components and ingredients of each of the neat products as per the MSDS's are listed below.

Table 2:

Quaker Quintolubric 814-03 Listed Ingredients

*	Ingredient	Formula	CAS No.	Content
1	Diethanolamine	C4-H11-N-O2	111-42-2	<10%
2	Ethylene glycol monobutyl ether	C6-H14-O2	111-76-2	1-10%
-	Hexahydro-1,3,5, tris-(2-hydroxyethyl)-triazine	C9-H21-N3-O3	4719-04-04	<10%
5	Paraffin oil – highly solvent refined	Not available	64742-65-0	10%
5	Solvent refined light Naphtha	Not available	64742-53-6	<2.7%
3	Diethylene Glycol	C4-H10-O3	111-46-6	<0.6%
4	Ethylene Glycol	C2-H6-O2	107-21-1	<0.1%
6	N-Butanol	C4-H10-0	71-36-3	<0.1%
-	1-methyl benzotriazole	C7-H7-N3	29385-43-1	0.1-1%
-	Additive	Not available	Not Available	Not available

*The allocated sequential numbers in Table 2 corresponds to ingredient in Table **3.**

Table 3: Ingredients of Quintolubric with exposure standards (from MSDS)					
*	Ingredient	TWA		STEL	
		ppm	mg/m3	ppm	mg/m3
1	Diethanolamine (h)	3	13	-	-
3	2.2'-Oxybis(ethanol)	23	100	-	-
2	2-Butoxyethanol (EGBE)	20	97	50	242
4	Ethylene glycol (vapour)	20	52	40	104
5	Mineral Oil mist	-	5	-	-
6	N-Butanol	50	152	-	-
5	Solvent refined light naphtha (as mineral oil mist)	-	5	-	-
	All exposure standards are from SafeWork (NOHSC) *The sequential numbering in Table 3 corresponds to the same ingredient in Table 2.				

Table 4: Solcenic 2020 Listed Ingredients			
Ingredient	Formula	CAS No.	Content
Hexahydro-1,3,5, Tris-(2-hydroxyethyl)-triazine	C9-H21-N3-O3	4719-04-4	<10%
Inorganic salts	Not available	Not available	30-60%
Mineral oil (solvent refined)	Not available	Not available	30-60%
Organic materials	Not available	Not available	30-60%
Non hazardous ingredients	Not available	Not available	remainder

Table 5: Ingredients of Solcenic 2020 with exposure standard (from MSDS)					
Ingredient	Reference	TWA		STEL	
		Ppm	mg/m3	ppm	mg/m3
Mineral oil Mist	NOHSC (AUS)	-	5	-	-

3.6 MANUFACTURERS' INPUT

Discussions were held with the manufacturers to alert them to the project Illawarra Coal was undertaking, as well as to determine if there were additional ingredients that could be included in the monitoring. Further information was not provided by the manufacturers; however a sample of triazine was supplied by Fuchs to TestSafe, as TestSafe were unable to source a sample to allow for analysis and determination of a suitable method of collection.

3.8 COLLECTION OF BULK SAMPLES OF PRODUCT

Test Safe supplied appropriate sample containers to collect a bulk sample of each of the oils from site. The sample was collected from the tanks on the surface, as a concentrated (undiluted/neat) sample.

3.9 ANALYSIS OF CONCENTRATE SAMPLES

Initial identification of the components of the soluble oils were conducted using GCMS analysis by completing a scan of the headspace of the products to see what components were actually present. TestSafe then determined standards to use to allow a comparison of results.

The above approach has a number of advantages in that it is very specific to the soluble oil in use on the longwall being evaluated and it would provide an estimate of exposure to any potentially harmful components identified (if any are present) in the soluble oil.

The results of the analysis indicated a number of volatile organic compounds (VOC) present in both samples as presented in Table 6.

Table 6: Analysis for VOCs in undiluted Solcenic and Quintolubric Results (% of VOC)		
Compound	**Solcenic**	**Quintolubric**
Iso-propanol	35.7	2.1
2-Methyl-1-Propanol	ND	16.7
Toluene	8.8	ND
3-Methyl-oxazolidine	2.1	ND
2-Butoxyethanol	ND	81.2
Dipropylene glycol	48.6	ND
Di-sec-butyl ether	4.8	ND

3.10 REVIEW OF THE COMPONENTS WITH KNOWN CURRENT METHODS OF COLLECTION

Using the information supplied in the MSDS's, a deskstop study of currently available methods of sampling was conducted.

One contaminant, Diethanolamine was collected using a standard method (NIOSH 3509) that required the use of an impinger. Using an impinger to collect a sample is difficult due to spillage and potential breakage of the impinger. It was determined this method would not be practical underground.

Tables 7 and 8 outline eight different methods that could have been used to collect the data to allow comprehensive analysis.

The list of methods for Quintolubric was very long and extensive and would have been difficult to conduct in an underground environment, on limited people with a limited time frame. The list for Solcenic however was limited, and relied mostly on the Mineral Oil Mist method of sampling, which as described earlier is insensitive.

As a result of this, TestSafe assisted in determining alternate, yet scientifically proven methods of analysis to allow accurate data collection in a more timely and manageable fashion.

Table 7: Initial desk top Sampling information - Quintolubric					
Ingredient	**Other name**	**Sampling Ref**	**Filter/Tube/ Impinger**	**Flowrate**	**Sample Time**
2,2'Oxybisethanol	Diethylene Glycol	NIOSH 5523	XAD-7 OVS tube	0.5-2L/min	5-60L
2-Butoxyethanol (EGBE)	Ethylene glycol monobutyl ether	NIOSH 1403 (alcohols IV)	Solid Sorbent tube	0.01-0.05L.min	2-10L
Diethanolamine		NIOSH 3509 (Aminoethanol Compounds II)	Impinger	0.5-1L/min	5-300L
Ethylene glycol (vapour)		NIOSH 5500 ethylene glycol	Filter and sorbent (glass fibre filter + silica gel 520/260mg)	0.2L/min	0.3-60L
Mineral Oil Mist	Oil mist, refined mineral Parafin oil – highly solvent refined	NIOSH 5026 (oil Mist, mineral)	37mm Membrane filter	1 to 3L/min	20-500L
Solvent Refined Light Naphta		NIOSH 5026 (oil Mist, mineral)	37mm Membrane filter	1 to 3L/min	20-500L
N-Butanol	n-butyl alcohol	NIOSH 1405	Solid sorbent tube	0.01-0.2L/min	2-10L
Hexahydro-1,3,4,TRIS-(2-Hydroxyethyl)-Triazine	Triazinetriethanol	ASTM4861	PUF 226-92	2L/min	960L
1-Methyl Benzotriazole	Tolyltriazole	None located			

Table 8: Initial desk top Sampling information - Solcenic					
Ingredient	**Other name**	**Sampling Ref**	**Filter/Tube/Impinger**	**Flowrate**	**Sample Time**
Mineral Oil Mist	Oil mist, refined mineral	NIOSH 5026 (oil Mist, mineral)	37mm Membrane filter	1 to 3L/min	20-500L
Hexahydro-1,3,4,TRIS-(2-Hydroxyethyl)-Triazine	Triazinetriethanol	ASTM4861	PUF 226-92	2L/min	960L

4. METHODS OF COLLECTION

Table 9 and 10 outline the sampling requirements, sampling media and analysis methods that were determined in conjunction with TestSafe that would provide accurate results of the components of both oils. The same sampling and analysis was recommended for both oils. It was determined not to sample for Oil Mist as a general overarching result. This decision was based on the evidence that analysis of low levels of soluble oil in emulsion is problematic and inaccurate in the Oil Mist method as this method is more appropriate for undiluted oils.

Dupont 2500 intrinsically safe approved air sampling pumps were used together with appropriate sampling media and heads to sample the VOCs, glycols and Triazine. The pumps were calibrated pre and post sampling to ensure the correct flowrate was achieved and maintained. 3M 3500 passive badges were also used to sample for VOCs. Sampling was undertaken in accordance with the WorkCover method or their reference method.

Monitoring was scheduled to be conducted on workers along the longwall face. The workers included a fitter, chock operators, Shearer drivers and Main Gate operators.

Information regarding the tasks, and maintenance that was conducted by the workers was collected and is reported in the Appendix results. If a fitter changed a soluble oil hose, then this was recorded, if nothing related to soluble oil occurred during their shift, then the Occupation and Duties were added to the Activities undertaken.

Table 9: Methods of Analysis				
Analysis Required	**Applicable Ingredients**	**Sampling Media**	**Flow Rate**	**Sampling Requirements**
Analysis of VOCs in Air by WCA.207	N-Butanol	Charcoal tube (SKC 226-01) or passive monitor 3M or SKC	0.02 - 0.2L/min	1 to 100L of air to be sampled depending on atmosphere conc
Analysis of Glycols in Air by WCA.209	2,2'Oxybis(ethanol) (Diethylene Glycol) , Ethylene glycol (vapour),	XAD-7 OVS tube 200/100mg (SKC 226-57)	0.5 - 2L/min	5 - 60L Ship to lab in esky with ice brick
Analysis of Glycol ethers by WCA.224	2-Butoxyethanol (Ethylene glycol monobutyl ether),	Charcoal tube (SKC 226-01) or passive monitor 3M or SKC	0.02 - 0.2L/min	2 to 10L of air to be sampled depending on atmosphere conc
Analysis of Diethanolamine	Diethanolamine	Silica gel tube (SKC - 226-10)	0.1 to 1.0 L/min	Max vol: 96L
Analysis of Hexahydro-1,3,5,Tris-(2-Hydroxyethyl)-Triazine by GC/MS on a filter	Hexahydro-1,3,4,TRIS-(2-Hydroxyethyl)-Triazine	GLA - 5000 PVC filter 5μm	2L/min	

Table 10: Methods of Analysis used by TestSafe	
WCA.207	Analysis of Volatile Organic Compounds in Workplace Air by Gas Chromatography/Mass Spectrometry
WCA.224	Analysis of Glycol Ethers and Cellosolves in Air by Gas Chromatography/Mass Spectrometry
	Analysis of Hexahydro-1,3,5-tris-(2-hydroxyethyl)-s-triazine in Industrial Workplace Air by Ion Chromatography by determination of Ethanolamine*
WCA.209	Gylcols Screen in Air, GC-FID
	Analysis of Diethanolamine in air

*In this method, Hexahydro-1,3,5-tris-(2-hydroxyethyl)-s-triazine (TA) is measured indirectly by hydrolysis to ethanolamine, which is analysed by ion chromatography using conductivity detection. This is achieved using a 1.7nM HNO_3 solution to desorb TA from a collection filter and then quantitating the amount of ethanolamine by ion chromatography. The amount of TA is in a ration of 1:3 (molar) TA to ethanolamine i.e. TA (µg) = 1.19 Ethanolamine (µg).

4.1 METHOD OF WORKPLACE SAMPLING

All samples were collected using personal sampling such that a true picture of any exposure of operators could be established. As can be seen from Tables 9 and 10, the problem with this is the number of components to monitor within the oils, and the lack of a specific sampler make it difficult to collect all ingredients on one or even a number of samplers. Two operators were required to carry/wear all of the monitoring equipment required for sampling one complete sample. Passive samplers were used where appropriate to reduce weight and equipment that had to be worn by operators.

A random sampling program was implemented as best as possible, however this had limitation due to available time for monitoring (particularly for quintolubric), reduced cutting on the longwalls during particular shifts and maintenance days.

All monitoring was conducted using the expertise of Coal Services Health Sampling Officers who have a good working knowledge of both underground mining and the sampling techniques required to conduct the monitoring.

At the time of monitoring the soluble oil concentration was recorded to provide an understanding of the dilution level.

A minimum of twenty-two (22) samples in each Similar Exposure Group (SEG) were collected over the duration of the sampling period. The SEGs monitored were the longwall SEGs at West Cliff (W1) and Dendrobium (DB8).

1-Methyl Benzotriazole was not monitored due to there being no identifiable exposure standard or method of analysis. As previously outlined, Mineral Oil mist was not monitored, due to reported low sensitivity of this method with diluted product, and it was therefore determined that the components of the product would provide a more accurate result.

The sampling was conducted over an 11 week period commencing Monday 31 March 2009. The aim of the sampling was to follow a statistical sampling plan as close as possible taking account of the following:

- All samples had to be monitored for a minimum seven hours for 12 hour shifts or five hours for eight hour shifts or as near as possible, depending on operational conditions and number of SEGs being sampled. The aim was to obtain a comprehensive picture of each SEG's exposure during the longest available sampling period. Some samples had a much shorter monitoring duration than the shift, and were sampled according to specified methods as listed (see: Table 9 Methods of Analysis).
- Crib to crib room sampling is required for this monitoring due to the short nature of some of the samples.
- Due to reduced hours of work on sites, some days were unavailable for monitoring.
- If a SEG could not be sampled due to operational factors then it was sampled on the next available equivalent shift.
- Sampling was only to be conducted within the longwall area. If the workers left the area due to a meeting or breakdown then monitoring was to cease and be rescheduled.

- Data that was collected at the time of monitoring included

  - *RPE (Respiratory Protective Equipment) used including type.*
  - *Description of major tasks completed during monitoring*
  - *Full first names of those sampled (e.g. John Smith rather than J Smith)*
  - *Employment status; if the person monitored was a contractor (name of contractor company required) or an employee*
  - *Shift length*
  - *Air Velocity during monitoring*
  - *Any events that occurred during monitoring that may indicate potential exposure? Burst pipes etc.*

- The person from the SEG was accompanied by a Coal Services employee each monitoring shift.

4.2 OUTCOME OF MONITORING - FORMALDEHYDE

As analysis began, TestSafe noted that when hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine (TA) was analysed, it was shown to be a relatively unstable species. Under mildly acidic or warm/hot conditions it breaks down to an oxazolidine intermediate and then to mono-ethanolamine and formaldehyde. It is thought that the formaldehyde is likely to be coming from the antimicrobial agent. This restricted the use of Gas Chromatograph (GC) analysis. TestSafe therefore modified the analysis and instead analysed the mono-ethanolamine to estimate the amount of the parent TA compound. This test was performed using ion chromatography. It was determined additional monitoring needed to be conducted for formaldehyde to determine levels of exposure.

4.3 METHOD OF MONITORING FOR FORMALDEHYDE

Dupont 2500 intrinsically safe air sampling pumps were used to collect air samples through a glass fibre filter which had been impregnated with 2,4-dinitrophenylhydrasine (DNPH) derivatising agent. The sample was analysed using HPLC with 365nm UV detection.

Ten (10) samples were collected on the Dendrobium Longwall during day, afternoon and night shift.

5.0 RESULTS

The results of the monitoring are listed in Tables 11, 12 and 13. Results for all agents are well below exposure standards and when calculating the effects of the mixtures, the results remain very low. There were no exposures detected for glycol, ether or triazine. Exposure to Diethnolamine was detected in both oil mists. Toluene was also detected in both samples, although the initial head space analysis indicated it was only likely to be found in the solcenic oil. A number of additional VOCs were detected during the solcencic monitoring, with the origin of the agents not understood (Table 13).

Table 11: Longwall Soluble Oil Mist Monitoring Program Results West Cliff 30 March – 30 April 2009											
Sample	Date	Shift	Main Occupation	Toluene* (mg/m^3)	Diethanolamine (mg/m^3)	Glycol (mg/m^3)	Ether (mg/m^3	Triazine (mg/m^3)	Air Velocity on face. (Chock 8, 80, 160)	Sol Oil Conc refractometer (%)	Comments
W1	30.3.09	A/S	Fitter [1]	0.3[1]	ND	ND	ND	ND	4.1, 3.9. 3.8	1.3	[1] Repairs to low pressure control line – 167CH
W2	31.3.09	A/S	Fitter[1]	0.9[1]	ND	ND	ND	ND	4.0, 4.0, 3.9	1.4	
W3	8.4.09	N/S	Chockman	0.1	ND	ND	ND	ND	4.3, 4.1,4.0	1.0	
W4	8.4.09	N/S	Shearer Operator	0.4	ND	ND	ND	ND	4.3, 4.1, 4.0	1.0	
W5	18.5.09	A/S	Fitter	ND	ND	ND	ND	ND	4.0, 4.1, 3.9	1.0	
W6	18.5.09	A/S	Shearer Operator	ND	ND	ND	NA	ND	4.0. 4.1, 3.9	1.0	
W7	7.4.09	A/S	Fitter[1]	ND	ND	ND	ND	ND	6.0, 5.5, 5.2	1.4	[1]Repairs at emulsion station Hanging Brattice on chocks (Chockman)
W8	16.4.09	N/S	Fitter	ND	ND	ND	ND	ND	4.3, 4.2, 4.0	1.4	Hoses replaced during sampling
W9	16.4.09	N/S	Shearer Operator	ND	ND	ND	ND	ND	4.3, 4.2, 4.0	1.4	

Table 11:
Longwall Soluble Oil Mist Monitoring Program Results
West Cliff
30 March – 30 April 2009

Sample	Date	Shift	Main Occupation	Toluene* (mg/m^3)	Diethanolamine (mg/m^3)	Glycol (mg/m^3)	Ether (mg/m^3	Triazine (mg/m^3)	Air Velocity on face. (Chock 8, 80, 160)	Sol Oil Conc refractometer (%)	Comments
W10	15.4.09	D/S	Fitter	ND	ND	ND	ND	ND	4.1, 4.0, 3.9	1.2	
W11	15.4.09	D/S	Chockman	ND	ND	ND	ND	ND	4.1, 4.0. 3.9	1.2	
W12	20.4.09	D/S	Fitter[1]	0.13	ND	ND	ND	ND	4.1, 4.0, 4.0	1.1	[1]Undertakng maintenance on emulsion station pumps Fault finding along face (Fitter)
W13	21.4.09	A/S	Fitter	ND	ND	ND	ND	ND	4.1, 4.1, 4.0	0.7	Maintenance on yield valves. DN12 2.5m hose replaced on CH16.
W14	21.4.09	A/S	Chockman	ND	ND	ND	ND	ND	4.1, 4.1, 4.0	0.7	
W15	22.4.09	N/S	Fitter	0.13	0.04	ND	ND	ND	4.1, 4.1, 4.0	1.0	DN10, 1.2m Hose replaced on CH95
W16	22.4.09	N/S	Chockman	ND	0.04	ND	NA	ND	4.1, 4.1, 4.0	1.0	
W17	27.4.09	D/S	Chockman	ND	0.04	ND	ND	ND	4.3, 4.1, 4.0	1.0	Shovelling in TG
W18	15.5.09	D/S	Fitter	ND	0.03	ND	ND	ND	4.2, 4.0, 3.9	1.0	Face Maintenance

Table 11: Longwall Soluble Oil Mist Monitoring Program Results West Cliff 30 March – 30 April 2009											
Sample	**Date**	**Shift**	**Main Occupation**	**Toluene*** (mg/m³)	**Diethanolamine** (mg/m³)	**Glycol** (mg/m³)	**Ether** (mg/m³	**Triazine** (mg/m³)	**Air Velocity on face. (Chock 8, 80, 160)**	**Sol Oil Conc refractometer (%)**	**Comments**
W19	27.4.09	A/S	Shearer Operator	ND	0.04	ND	ND	ND	4.1, 4.0, 4.0	0.9	
W20	27.4.09	A/S	Fitter	ND	0.04	ND	ND	ND	4.1, 4.0, 4.0	0.9	
W21	27.5.09	A/S	Chokeman	ND	ND	ND	ND	ND	4.1, 3.8, 3.7	1.0	
W22	30.4.09	N/S	Fitter	0.66	0.04	ND	ND	ND	4.5, 4.4, 4.2	0.9	
Exposure Standard (mg/m³)				191	13						

NA – Not Available
ND – Not detected
*No other VOC's were detected.
[1]. refers the occupation that received the result and any tasks they were doing.

Occupations monitored: Fitter, Chockman, Shearer Operator, Main Gate Operator

Table 12: Longwall Soluble Oil Mist Monitoring Program Results Dendrobium 4 May – 29 June 2009											
Sample	**Date**	**Shift**	**Main Occupation**	**VOC***(mg/m³) T=toluene A=Acetone M-MEK P=n-Pentane 2-M=2-Methylbutane	**Diethanolamine** (mg/m³)	**Glycol** (mg/m³)	**Ether** (mg/m³	**Triazine** (mg/m³)	**Air Velocity on face (Chock 8, mid face, Tailgate)**	**Sol Oil Conc refractometer (%)**	**Comments**
DB1	4.5.09	A/S	Fitter	ND	ND	ND	ND	ND	5.8, 4.4, 4.2	2.6	High pressure hose replaced CH137
DB2	12.5.09	N/S	Fitter	ND	ND	ND	ND	ND	4.2, 4.1, 4.1	2.7	Hydrofuse replaced CH89
DB3	12.5.09	N/S	Chock Operator	ND	ND	ND	ND	ND	4.2, 4.1, 4.1	2.7	
DB4	11.5.09	N/S	Fitter	ND	0.04	ND	ND	ND	5.2, 4.2, 4.1	2.7	
DB5	19.5.09	A/S	Shearer Driver	ND	ND	ND	ND	ND	NA	2.6	Large slabbing on face
DB6	19.5.09	A/S	Fitter	ND	ND	ND	ND	NA	NA	2.6	Large slabbing on face
DB7	20.5.09	N/S	Chock Operator	ND	ND	ND	ND	ND	4.7, 4.3, 4.2	2.5	No shears, Chock malfunction
DB8	26.5.09	A/S	Shearer Operator	0.13	ND	ND	ND	ND	4.2, 4.0, 4.0	2.3	
DB9	9.6.09	A/S	Fitter	0.66	ND	ND	ND	ND	5.0, 4.5, 4.4	2.5	
DB10	9.6.09	A/S	Chock Operator	0.93	ND	ND	ND	ND	5.0, 4.5. 4.4	2.5	
DB11	2.6.09	A/S	Fitter	ND	ND	ND	ND	ND	5.1, 4.6, 4.4	2.3	

Table 12: Longwall Soluble Oil Mist Monitoring Program Results Dendrobium 4 May – 29 June 2009											
Sample	**Date**	**Shift**	**Main Occupation**	**VOC***(mg/m^3) T=toluene A=Acetone M-MEK P=n-Pentane 2-M=2-Methylbutane	**Diethanolamine** (mg/m^3)	**Glycol** (mg/m^3)	**Ether** (mg/m^3	**Triazine** (mg/m^3)	**Air Velocity on face (Chock 8, mid face, Tailgate)**	**Sol Oil Conc refractometer (%)**	**Comments**
DB12	2.6.09	A/S	Fitter	ND	ND	ND	ND	ND	5.1, 4.6, 4.4	2.3	Maintenance on emulsion tanks
DB13	1.6.09	N/S	Shearer Operator	8.1T 1.2A 15.5M	ND	ND	ND	ND	5.0, 4.5, 4.4	2.6	
DB14	1.6.09	A/S	Chock Operator	ND	ND	ND	ND	ND	5.1, 4.6, 4.4	2.3	
DB15	15.6.09	A/S	Chock Operator	ND	ND	ND	ND	ND	5.0, 4.5, 4.4	2.3	
DB16	15.6.09	A/S	Chock Operator	ND	ND	ND	ND	ND	5.0, 4.5, 4.4	2.3	
DB17	10.6.09	N/S	Fitter	0.1T	ND	ND	ND	ND	5.1, 4.7, 4.5	2.7	High flow hoses replaced on Chocks 20,23, 24, 25, 27
DB18	10.6.09	N/S	Fitter	ND	ND	ND	ND	ND	5.1, 4.7, 4.5	2.7	High flow hoses replaced on Chocks 20,23, 24, 25, 27
DB19	22.6.09	A/S	Fitter	0.1T 0.1 2-M 1.6 P	ND	ND	ND	ND	5.0, 4.6, 4.4	2.3	
DB20	22.6.09	A/S	Shearer	0.1T	ND	ND	ND	ND	5.0, 4.6, 4.4	2.3	

Table 12: Longwall Soluble Oil Mist Monitoring Program Results Dendrobium 4 May – 29 June 2009											
Sample	**Date**	**Shift**	**Main Occupation**	**VOC***(mg/m³) T=toluene A=Acetone M-MEK P=n-Pentane 2-M=2-Methylbutane	**Diethanolamine** (mg/m³)	**Glycol** (mg/m³)	**Ether** (mg/m³	**Triazine** (mg/m³)	**Air Velocity on face (Chock 8, mid face, Tailgate)**	**Sol Oil Conc refractometer (%)**	**Comments**
			operator	1.1 P							
DB21	29.6.10	A/S	Fitter	1.3 P	ND	ND	ND	ND	5.1, 4.6, 4.5	2.3	Hose replaced at emulsion tank station
DB22	29.6.10	A/S	Chock operator	ND	ND	ND	ND	ND	5.1, 4.6, 4.5	2.3	
Exposure Standard (mg/m³)				T-191 A-1185 M-445 P-1770	13						

NA – Not Available
ND – Not detected

Table 13: Longwall Formaldehyde Monitoring Results, Dendrobium						
Sample	Date	Shift	Main Occupation	Formaldehyde (µg/m3)	Air Velocity on face	Comments
F1	4.5.10	A/S	Fitter	ND	-	-
F2	4.5.10	A/S	Chockman	0.01	-	-
F3	4.5.10	A/S	Chockman	0.014	-	-
F4	5.5.10	N/S	Shearer operator	Void*	4.1, 3.8	-
F5	5.5.10	N/S	Chockman	0.008	4.1	-
F6	5.5.10	N/S	Chockman	0.015	4.1	-
F7	5.5.10	N/S	Maingate Operator	0.016	4.1	-
F8	6.5.10	D/S	Fitter	ND	3.8, 3.6	Repairs to low pressure control line – 167CH
F9	6.5.10	D/S	Chockman	0.005	3.8, 3.6	-
F10	6.5.10	D/S	Chockman	ND	3.8, 3.6	-
Exposure Standard				0.0012		
*breakthrough occurred due to the front filter not being seated correctly in the cassette and was touching the back filter. Sample void, as unable to determine how much sample lost.						

5.1 STATISTICAL ANALYSIS

Limited statistical analysis was conducted due to the low levels of exposure monitored. Where there were 6 results available for a particular agent, statistical analysis was conducted using Lognorm2, using a result of half the detection limit for those samples with a non detect.

Table 14: Statistical Analysis Results				
Site	**Agent**	**95% UCL MVUE (mg/m3)**	**GSD**	**Exposure Standard (mg/m3)**
West Cliff	Toluene	0.2	2.4	191
	Diethanolamine	0.03	1.5	13
Dendrobium	Toluene	0.5	3.4	191
	Formaldehyde	<0.001	1.6	1.2

There was more instances of Toluene and Diethanolamine detected at West Cliff who were using Quintolubric. There were a number of agents that were detected at Dendrobium using Solcenic, that were not detected at West Cliff. It was unable to be determined where the low levels of Acetone, MEK, 2-Methylbutane and n-Pentane were originating at Dendrobium, however it is likely another task in-bye (towards the surface, with the ventilation bringing contaminants to the longwall face) was causing the exposure. The levels were very low and very unlikely to cause a health effect at the exposure recorded.

Table 15: Number of Sample Agents Detected from 22 Samples		
Agents Detected	**Quintolubric West Cliff**	**Solcenic 2020 Dendrobium**
Toluene	14	7
Diethanolamine	14	2
Acetone	-	1
MEK	-	1
2-Methylbutane	-	3
n-Pentane	-	3

6.0 DISCUSSION

6.1 EXPECTED OUTCOME

The project was envisaged to provide:

a) A viable and sensitive method to evaluate the levels of atmospheric soluble oils on longwall faces.

b) Data regarding the levels of exposure of longwall face operators arising from soluble oil entering the general airbody on longwall faces.

c) Health effects (potential) from exposure to breathing the atmosphere.

6.2 RESULTANT OUTCOME

The original question posed was whether exposure to soluble oil mist on the longwall face was detrimental to the workers health. No previous research was found to have been completed on longwall mining, and in the projects and research that were located during the literature search, components within the soluble oil were not monitored for, but rather soluble oil as a whole. It was determined early on in this project that monitoring for Oil Mist, as a whole, would not be beneficial for this project, as the soluble oil is used as an emulsion, and is only 2-4% oil. The methods for Oil Mist are not sensitive enough for emulsion oils, and therefore new methods, and methods for the contaminants within the oils were investigated and agreed with the analysing laboratory TestSafe. Testing was conducted at two sites for two different oils with twenty-two (22) samples taken at each site. An additional 10 samples were later taken for formaldehyde, as it was determined during the analysis process that when hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine (TA) was analysed, it was shown to be a relatively unstable species and ultimately turned into mono-ethanolamine and formaldehyde. It is thought that the formaldehyde was likely to be coming from the antimicrobial agent.

All results were low and were well below the current exposure standards. One sample was voided due to incorrect seating of the filters causing break-through or leakage. A number of additional agents were also detected during the monitoring that may have been from external tasks impacting on the longwall during monitoring. However, again, all of these results were very low and even considering an additive effect, would not pose an adverse effect to health.

The methods of analysis used are viable for Quintolubric and Solcenic Soluble Oil Mists. These methods are more sensitive than monitoring for Oil Mist when the oil has been emulsified and additional ingredients added to the product. If in future additional airborne monitoring needs to be completed for Solcenic soluble oil then the same methods including formaldehyde should be used. If different products are used, then it is advisable to contact TestSafe to have a bulk sample analysed to ensure all additives are accounted for. Additional agents were found in both

Quintolubric and Solcenic that were not expected from the analysis of bulk samples.

Although small amounts of contaminants were sampled in the breathing zone of the operators from the soluble oils used at the time, all contaminants were well below the exposure standards and would not pose a health risk from inhalation when compared to the current exposure standards. Mine Managers can now have confidence that with the current products, usage and controls they are not exposing their operators to levels of soluble oil mist that will adversely affect their health.

Due to the fact that the pressure the emulsion is ejected from a hose is very high, most of the sites considered High Pressure Injection Injuries a bigger risk than inhalation or skin contamination, and these leaks are stopped as a matter of priority.

The issue of sensitization and skin exposure was not investigated, and this area would be worth investigating in future, with a focus on transporting the neat product from the surface to the underground where it is then diluted. It is unlikely the diluted product would cause sensitisation, however discussions with fitters that contact this product extensively during maintenance should be included in further investigation.

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