Relationships among Fluid Ethanolamine Formulation, Airborne Ethanolamines, and Aerosol Levels in Machining Operations

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ABSTRACT

Alkanolamines or ethanolamines - triEA (TEA), di-EA (DEA), and mono-EA (MEA) - may be used in water-soluble metalworking fluids to stabilize pH or inhibit corrosion. The objectives of this study were to compare EAs levels from air and used fluid bulk among the various metalworking operations, and to examine the relationship not only between aerosol concentration and total airborne EA levels, but also between aerosol levels and the proportion of each type of EA in the total EA in air and fluid bulk. The EA from air and fluid bulk collected from machining operations were quantified by ion chromatography. Airborne EA were taken into de-ionized water (DI) using an impinger. Average aerosol levels were 1.15 mg/m^3 for machining and 0.84 mg/m^3 for grinding operations. The highest aerosol and total EA levels were for (i) washing operations (4.06 mg/m^3 and 1.33 mg/m^3, respectively), where compressed air was frequently used to clean metal machine parts, and (ii) individual tanks (1.83 mg/m^3 and 2.31 mg/m^3, respectively). Airborne MEA was detected in all samples (n = 53), while TEA was not detected in any air samples (n = 13) taken from areas without machining operations. Machining operations showed a significant relationship between aerosol and total EA levels (n = 21, R^2 = 0.74). The EA content ratio (EA$_R$: level of each EA in air as a% of total EA in air)/(level of each EA in bulk fluid as a% of total EA in bulk fluid) showed a significant association with the aerosol level, but showed a different pattern according to the EA type. A negative exponential relationship was observed for MEA$_R$ (n = 9, R^2 = 0.64), with MEA$_R$ being greater than "1" at low aerosol concentrations (< 1 mg/m^3). In contrast, TEA$_R$ increased linearly with increasing aerosol levels, reaching almost "1" when the aerosol concentration was higher than 2.0 mg/m^3. The relationship between fluid EA formulation, airborne EA levels, and aerosol levels in machining operations was found to be quite different according to the type of EA.

Keywords: Machining fluids; Ethanolamine; Alkanolamines; Water-soluble metalworking fluids; Metalworking fluids (MWF).

INTRODUCTION

Metalworking fluids (MWFs) are used extensively to lubricate and cool the tool-workpiece interface, as well as the work surfaces of metal parts that are being drilled, ground, milled, or turned in various metalworking operations, such as cutting, grinding, and metal-forming. In broad terms, there are essentially two types of MWF: oil-based (straight) and water-based (soluble, synthetic and semi-synthetic).

In water-based metalworking fluids (wbMWFs), mono-ethanolamine (MEA), di-EA (DEA) and tri-EA (TEA) are used as rust-preventing agents with emulsifying properties. Howere, they may induce asthma even at air concentrations below occupational exposure limits (OELs) (Savonius *et al*., 1994; Piipari *et al*., 1998). Savonius *et al*. (1994) reported two metalworkers who, after several years of exposure, developed asthma attributed to TEA in the MWF they used, although the exposure concentrations were not reported. To the best of our knowledge, few articles have reported the EA levels from either bulk metalworking fluid or air in metalworking operations (Kenyon *et al*., 1993; Henriks-Eckerman *et al*., 2007; Suuronen *et al*., 2007), although there have been several studies examining respiratory health effects of EA exposure (Savonius *et al*., 1994; Piipari *et al*., 1998; Lessmann *et al*., 2009). Kenyon *et al*. (1993) assessed airborne TEA, DEA and MEA levels in machining operations of automotive plants. The results showed that TEA did not account for more than 1% of the particulate mass, except when the MWF contained more than 10% TEA bulk formulation. All three ethanolamines were in bulk samples of synthetic and semi-synthetic MWF. The authors concluded that although airborne TEA levels generally increase with

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an increasing percentage of TEA in the bulk fluids, the concentration is also operation-specific.

In this work, we measured the aerosol and EA levels from the air and fluid bulk in the machining operations of automotive manufacturing plants. The results thus obtained were extensively analyzed to achieve the following objectives: (i) compare EA levels in air and bulk MWF across different metal working operations; (ii) examine whether the total EA concentration in air is a function of the total EA concentration in the bulk MWF (for example, whether they have a simple proportionate relationship); and (iii) examine if the same relationship between the concentrations in air and in bulk MWF holds for each of the three EA species.

METHODS

Aerosol Levels

Analytical method #0500 of the National Institute for Occupational Safety and Health (NIOSH) was used to measure levels of airborne aerosols generated in machining operations (NIOSH, 1994a). PVC filters (37 mm diameter, 5 μm pore size, cat no.: P/N 225-8-01, SKC Inc.) were desiccated for one day and pre-weighed using a semi-micro electro-balance (Model ANALYTICAL, accuracy: 10^{-5} g) in a room with a controlled environment (temperature: 23.5 ± 3°C, relative humidity: 50 ± 15%).

EA Levels from Bulk Fluid and Airborne Samples

Automotive plants were studied in which cylinder blocks, con-rods, cylinder heads, crank shafts and cam shafts were machined using wbMWFs. The machining or metalworking operations measured include milling (no of personal air sample (N = 6), boring (N = 7), drilling (N = 4) and grinding (7)). EA levels were measured not only from airborne samples, but also from fluids that had been used for various periods in machining operations. EA can appear simultaneously as both aerosol and vapor in the workplace air. Although acid-treated glass fiber filters can be used to collect both phases (Henriks-Eckerman *et al*., 2007), it is not easy to obtain new filter sampling media. De-ionized water (DI) was thus used as sampling media instead of the 15 mL of 2 mM hexanesulfonic acid (HSA) recommended in the NIOSH method #3509 (NIOSH, 1994b), because we were unable this to obtain due to lack of distributor information in the catalog. The use of DI as the sampling media was based on the method recommended in Krol *et al*. (1992). They

proved that the use of a poly (butadiene-maleic acid)-coated silica column and a mobile phase of EDTA-nitric acid containing acetonitrile or methanol was the most versatile of the separation methods studied for amine analysis. The use of this highly efficient and flexible separation approach enabled the determination of a wide variety of amines at low μg/L levels. Airborne EAs were taken into DI using an impinger near the machining operations for a long enough duration to be able to show the representative EA levels and to measured them separately. After the air was collected, the impinger glass was completely rinsed with DI. In addition, the EA levels from used fluid were also analyzed. In the machining operations, a bulk sample of sump MWF was taken from a flowing stream at the cutting points of each machine when the circulation system was in operation. If the system was not in operation, the MWF circulation system was run for at least 10 minutes prior to sampling. The sample was collected in a 50-mL sterile, tissue-culture grade centrifuge tube (Fisher Scientific cat. #05-538-55). Portions of the liquid sample from both impinger and centrifuge tube were filtered using a micro-syringe with a 0.4 μm pore-size filter, and EA levels were quantified by ion chromatography (Water 717 plus auto sampler, Waters Corporation) using an IC PAK™ C M/D guard column (Alltech, Lexington, KY), an IC PAK™ Cation M/D column (3.9 × 150 mm WAT 036570, Alltech) and a 432 conductivity detector (Waters Corporation). The eluent (0.1 mM EDTA and 2 mM nitric acid) was filtered through a 47 mm diameter, 0.45 μm pore-size Super 450 membrane filter (Waters Corporation), and then sonicated (Model 3210, Branson, Danbury, Conn.) for 40 minutes to remove dissolved air. Samples for quantification were diluted to achieve optimum levels for analysis (Table 1). Our previous study reported that the recovery rate for injected MEA ranged from 94.8% to 103.9%, indicating that most of the injected MEA was fully recovered and that the reliability of our sampling and analytical method was validated. These results are also in agreement with the recovery levels obtained by the NIOSH method #3509 using a midget impinger containing 15 mL of 2 mM has, which ranged from 94% to 106% (NIOSH, 1994b).

Relationship between Aerosol and Total EA Levels

A simple linear regression was used to examine the relationship between the aerosol and total EA levels that were recorded in a paired sampling from the same area. The aerosol sampler and EA impinger sampler were

Table 1. Analytical method for ethanolamines.

Analytical method	NIOSH Method # 3509	This study
Technique	Water Ion Chromatography	
Detector	Waters 432 conductivity	
Separator	Waters cation M/D column	
Guard column	Cation M/D guard column	
Mobile phase	2 mM nitric acid - 0.1 mM EDTA	
Flow rate	1.0 mL/min	
Absorbent (sampling media)	Hexanesulfonic acid(free acid)	De-ionized water (18 mΩ)
Retention time	10–20 min	5–10 min
Reference	Bouyoucos *et al*., 1986	Krol *et al*., 1992

positioned parallel. to each other in order to collect air with a similar composition Fixed locations near machining operations that were thought to generate high EA and aerosol levels were selected as sampling sites, in order to determine the existence of any meaningful relationship between these levels.

Relationship between Aerosol Levels and the EA Content Ratio in Air and Bulk Fluid

Based on the assumption that airborne EA levels may be affected by the EA levels in bulk fluid formulation, the relationship between the level of each EA as a proportion of total EA in air and used fluid was examined. The mean ratio of the content of each EA relative to that of total EA in the fluid bulk and air was calculated as follows.

- $MEA_{R(air/bulk)}$ = (level of MEA in air as a% of total EA in air)/(level of MEA in bulk formulation as a% of total EA in bulk formulation)
- $DEA_{R(air/bulk)}$ = (level of DEA in air as a% of total EA in air)/(level of DEA in bulk formulation as a% of total EA in bulk formulation)
- $TEA_{R(air/bulk)}$ = (level of TEA in air as a% of total EA in air)/(level of TEA in bulk formulation as a% of total EA in bulk formulation)

The relationship between each EA_R ratio and the aerosol concentration was analyzed to examine how the content of each of the former was associated with the latter. The curve fit and linear regression methods were tested to find the most reliable equation to explain this relationship.

RESULTS

Aerosol and EA Levels

The aerosol and EA levels measured from various machining operations (boring, drilling, milling), grinding, washing, central control system (CCS) operations and near the conveyer belt, where water-soluble fluids were found, are shown in Table 2. Washing operations showed the highest aerosol levels (4.06 mg/m^3) and second-highest total EA levels (1.33. mg/m^3). The main reasons for this could be the high fluid temperatures (around 52°C) and the automatic use of compressed air to clean the machined metal parts. A high concentration of aerosols (1.83 mg/m^3) and total EA (2.31 mg/m^3) was also found for individual tanks attached to the metalworking machines. The average aerosol levels measured from machining (1.15 mg/m^3) and grinding operations (0.84 mg/m^3) were both higher than the recommended exposure limit (REL) (0.5 mg/m^3) given by National Institute for Occupational Safety and Health (NIOSH). Aerosol levels higher than 0.2 mg/m^3 were found even at the CCS and near the conveyor belt area, where no machining works were performed. Airborne TEA was not detected in the 13 samples taken from the CCS and near the conveyor belt. Only two samples showed DEA, at 0.45 mg/m^3. In contrast, MEA was detected in all samples (n = 53) taken where wbMWFs were handled. As detailed in Table 2, there were operations or areas showing no TEA or DEA, even though machining work was actually performed at these sites. For total EA, areas near individual tanks

showed the highest level (2.31 mg/m^3), followed by areas associated with washing (1.33 mg/m^3), grinding (0.60 mg/m^3), and machining (0.36 mg/m^3) operations.

Relationship between Aerosol Levels and Total EA Concentration

A comparison between aerosol and total EA concentration was made according to operation type. In the individual tank areas, the total EA concentration (2. 31 mg/m^3) was higher than the aerosol concentration (1.83 mg/m^3), while the reverse was found in other operations (Fig. 1). Work practices, operating conditions, EA fluid formulation, and the tools used in each operation may substantially affect the airborne aerosol and EA levels.

When data were examined only for machining operations (boring, drilling, and milling) using similar work characteristics and fluid temperature (30–31°C), independently from the data for other operations, a significant relationship was identified between fluid EA content (fluids G, B, D and F) and aerosol levels (n = 21, R^2 = 0.74) (Fig. 2(a)). After data from operations with bulk "F" fluid were excluded, a more highly-significant relationship was detected (n = 11, R^2 = 0.83) (Fig. 2(b)). Our results showed that airborne EA levels increased with increasing aerosol concentrations in machining operations where similar bulk fluid formulations were used, such as in boring, drilling, and milling. The results taken from the individual tank areas and washing operations were excluded, because work practices or job characteristics dissimilar to those used in machining operations were employed, such as the use of compressed air, and this may affect the relationship between airborne EA and aerosol concentrations. In addition, EA levels from the CCS and the conveyor belt were not included in this analysis, because they are not associated with any metalworking work.

Relationship between Aerosol Levels and the EA Content Ratio Relative to Total EA, in Air and Bulk Fluid

The ratio given by the level of each EA over the total EA level in air and used fluid was calculated in relation to the aerosol levels, measured from machining and grinding operations (fluids B, D, E and G) (Table 3). A significant negative exponential relationship between MEA_R (MEA/total EA in air)/(MEA/total EA in bulk fluid) and aerosol concentration was found through curve fit analysis (Fig. 3(a)). The MEA_R exponentially declines as the MWF mist concentration increases. MEA_R was over "1" (average = 2.08) in aerosol concentrations lower than approximately 1 mg/m^3, indicating that under these conditions MEA accounted for a greater percentage of total airborne EA levels ($MEA_{R(AIR)}$) than of total bulk fluid EA levels ($MEA_{R(BULK)}$). Airborne MEA concentrations may have been substantially affected by the vaporization of MEA from used fluid when the fluid mist concentration was lower than 1 mg/m^3. In contrast, as the aerosol levels increased, the airborne MEA concentration was mostly influenced by its bulk formulation.

The TEA_R and MWF mist concentrations detected from operations with similar TEA bulk formulations (55%–77%) were also examined. The TEA_R was found to be significantly regressed against the MWF mist concentration (n = 9, R^2 =

Table 2. Aerosol and ethanolamine levels by metalworking operation or area.

Metalworking operation or area	Fluid type (brand symbol)	Number of sample	Temp. (°C)	Aerosol level (mg/m^3)	Ethanolamine Conc. (mg/m^3)			
					MEA	DEA	TEA	total
Machining								
Boring	Synthetic (G)	2	31	2.42	0.17	0.23	0.58	0.98
Drilling	Synthetic (G)	2	31	2.23	0.15	0.23	0.48	0.86
Drilling	Soluble (B)	2	31	0.66	0.11	0.17	ND	0.28
Milling	Soluble (B)	2	31	1.81	0.10	0.19	0.38	0.67
Boring	Synthetic (D)	3	32	0.27	0.06	0.03	ND	0.09
Boring	Synthetic (F)	4	30	0.99	0.13	ND	0.06	0.19
Milling	Synthetic (F)	6	30	0.86	0.10	ND	0.06	0.15
	Total	21	31	1.15	0.11	0.08	0.16	0.36
	RSD		0.02	0.68	0.59	1.35	1.39	0.95
Grinding								
Grinding	Soluble (C)	3	30	0.98	0.19	ND	ND	0.19
Grinding	Synthetic (E)	3	31	0.61	0.17	0.58	0.31	1.06
Grinding	Synthetic (F)	1	30	1.08	0.20	0.00	0.26	0.45
	Total	7	30	0.84	0.18	0.25	0.17	0.60
	RSD		0.02	0.87	0.90	1.32	1.04	0.88
Washing								
Washing	Washing fluid (I) $	3	52	6.62	0.15	0.27	1.65	2.07
Washing	Washing fluid (I)	2	31	0.22	0.02	0.18	0.02	0.22
	Total	5	44	4.06	0.10	0.23	1.00	1.33
	RSD	10	0.26	1.00	0.87	0.37	0.99	0.86
Individual tanks attached to metalworking machines								
Tank	Synthetic (G)	4	31	1.37	0.18	0.44	0.79	1.41
Tank	Synthetic (H)	2	39	3.55	0.00	1.58	3.55	5.13
Tank	Synthetic (F)	1	30	0.24	0.11	ND	0.18	0.28
	Total	7	33	1.83	0.12	0.70	1.49	2.31
	RSD		0.13	1.25	0.82	1.29	1.43	1.29
Central tank reserve fluid								
Central tank	Soluble (B)	2	31	0.59	0.12	ND	ND	0.12
Central tank	Synthetic (D)	2	33	0.20	0.28	0.45	ND	0.73
Central tank	Synthetic (F)	2	30	0.52	0.12	ND	ND	0.12
	Total	6	31	0.44	0.17	0.15	ND	0.32
	RSD		0.04	0.55	0.67	1.57		1.02
On Transfer Belt	Total	7	27 (air)	0.50	0.02	ND	ND	0.02
	RSD		27 (air)	0.63	1.71			1.71

Notes: $ Fluid containing ethanolamines used to clean machined metal parts.
Abbreviations: MEA = mono-ethanolamine (EA), DEA = di-EA, TEA = tri-EA.
Total EA = monoethanolamine (MEA) + di-EA(DEA) + tri-EA(TEA), RSD = relative standard deviation.

0.64), and the TEA$_R$ sharply increased with increasing aerosol concentration (Fig. 3(b)). The value of TEA$_R$ approached "1" (average 0.82) when aerosol concentrations were > 2.0 mg/m^3. This result indicates that at high aerosol concentrations (1.5 mg/m^3), airborne TEA concentrations may be related to TEA levels in the bulk fluid. TEA in drilling operations with low aerosol concentrations (0.57 mg/m^3 and 0.76 mg/m^3) was not detected, although the bulk content of TEA in MWF "B" accounted for 76.5% of the total EA associated with this fluid. The relationship between the DEA levels and the aerosol levels could not be analyzed, due to the lack of samples in which DEA was detected, and the low DEA levels in the fluid formulations. The DEA content in most samples was not sufficient (6–9% of total EA) to yield meaningful results. However, based on the similar physical and chemical properties of DEA and TEA, we assume that

DEA may show a similar trend to that of TEA, rather than MEA.

DISCUSSION

EA generally have low vapor pressure (at 25°C MEA: 0.404 torr, DEA: < 0.01 torr, TEA: < 0.01 torr), and the airborne concentrations of TEA and DEA are usually expressed as aerosol units (mg/m^3). Based only on those physical and chemical properties, it would appear unlikely that DEA and TEA, in particular, would vaporize and cause inhalation hazards in workplaces running at room temperature. However, various work or job characteristics and operation-specific conditions can affect the way that EA disperse and escape into the air, such as those that occur when wbMWFs containing EA are used in various

metalworking operations. Marked exposure through the airway is in fact possible when chemicals containing EAs are heated or vaporized, thereby liberating the amino alcohols (Piipari *et al.*, 1998). With the introduction of high speed machinery, in particular, substantial exposure to various components, including EA present in the fluid, can also occur via inhalation of the aerosols (Eisen *et al.*, 1994; Jarvholm and Lavenius, 1987). Most of the aerosols containing EAs that arise from machining operations could be formed by the mechanical forces produced by the moving tools and/or
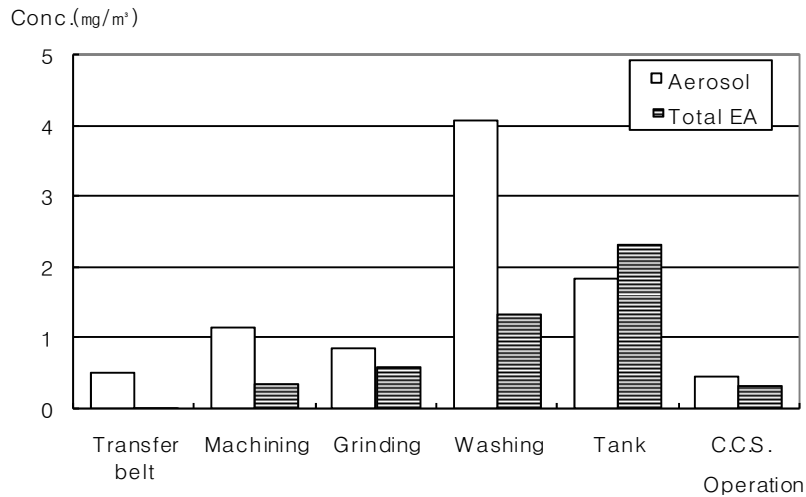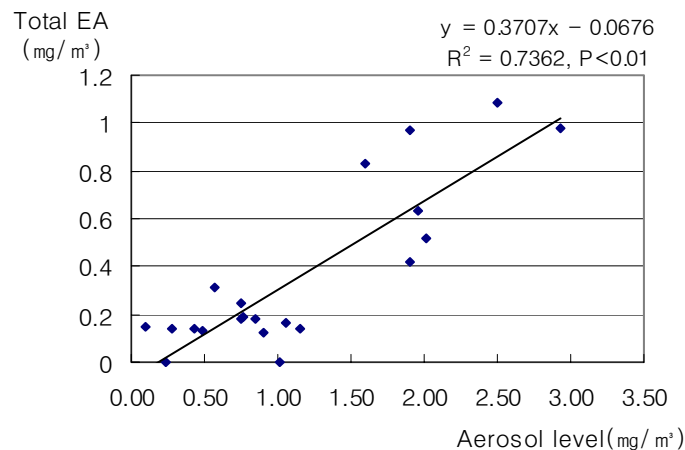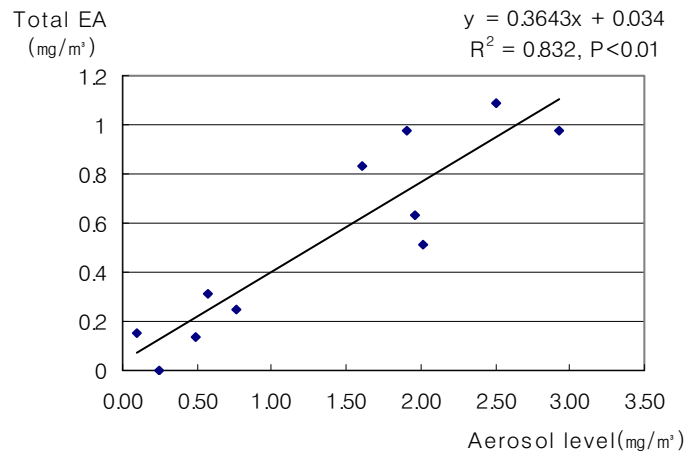
Fig. 1. Comparison of total EA and aerosol levels by operation and area (CCS = central control system).

(a) All samples from machining operations (n = 21)

(b) Samples from machining operations using fluids "G", "B" and "D"

Fig. 2. Relationship between aerosol and total EA levels for machining operations.

Table 3. Comparison by operation type of EA content as a% of total EA content, for airborne and fluid bulk samples.

Machining Operation	Fluid brand (fluid type)	Aerosol conc. (mg/m^3)	Airborne EA Content (% of total airborne EA) (A)			Bulk fluid EA Content (% of total bulk fluid EA) (B)			EA Content Ratio (A/B)		
			MEA	DEA	TEA	MEA	DEA	TEA	MEA_R	DEA_R	TEA_R
Boring	Synthetic (G5)	2.93	17.7	22.9	59.4	25.3	8.4	66.4	0.70	2.73	0.90
Boring	Synthetic (G5)	1.91	17.5	23.5	59.0	25.3	8.4	66.4	0.69	2.80	0.89
Drilling	Synthetic (G4)	1.96	22.6	34.5	43.0	23.0	9.0	68.0	0.98	3.81	0.63
Drilling	Synthetic (G4)	2.50	14.9	22.0	63.0	23.0	9.0	68.0	0.65	2.44	0.93
Drilling	Soluble (B)	0.57	39.4	60.6	<LOD	17.3	6.2	76.5	2.28	9.71	0.00
Drilling	Soluble (B)	0.76	40.7	59.3	<LOD	17.3	6.2	76.5	2.35	9.51	0.00
Milling	Soluble (B)	1.60	13.3	39.7	47.0	17.3	6.2	76.5	0.77	6.36	0.61
Milling	Soluble (B)	2.02	18.0	8.8	73.2	17.3	6.2	76.5	1.04	1.41	0.96
Boring	Synthetic (D)	0.10	100.0	<LOD	<LOD	23.0	73.0	4.0	4.34	0.00	0.00
Boring	Synthetic (D)	0.48	27.7	72.3	0.0	23.0	73.0	4.0	1.20	0.99	0.00
Grinding	Synthetic (E)	1.04	12.7	60.1	27.2	9.9	33.9	56.3	1.28	1.77	0.48
Grinding	Synthetic (E)	0.06	20.4	49.6	29.9	9.9	33.9	56.3	2.07	1.47	0.53
Grinding	Synthetic (E)	0.74	10.3	58.0	31.7	9.9	33.9	56.3	1.04	1.71	0.56

Notes: Limits of detection (LOD) for DEA and TEA were 0.1 % and 0.005 %, respectively.

(a) MEA

$y = 2.4194e^{-0.512x}$
$R^2 = 0.6715$

(b) TEA

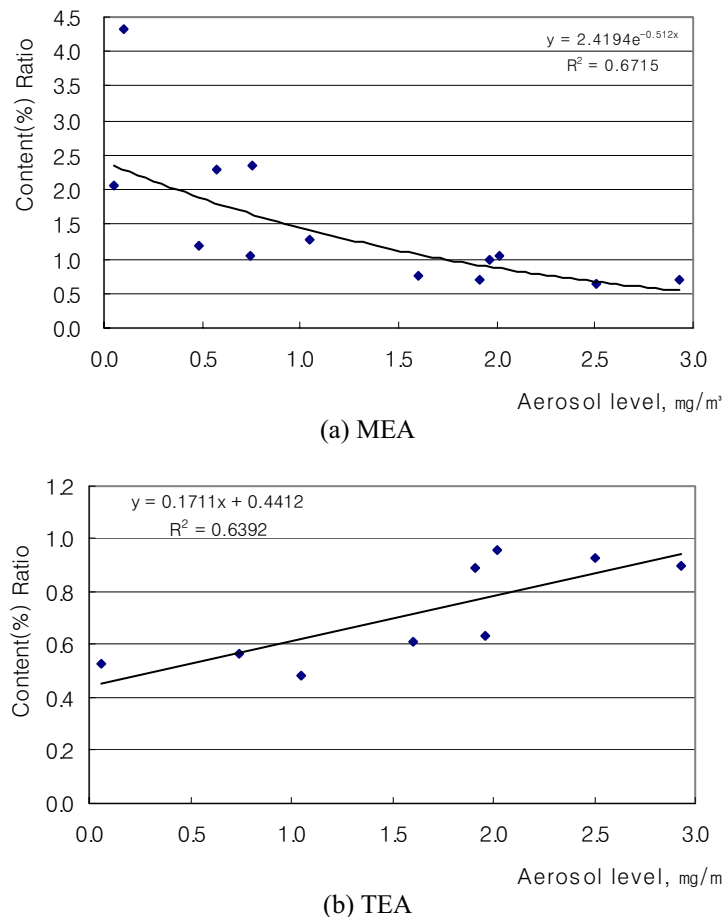$y = 0.1711x + 0.4412$
$R^2 = 0.6392$

Fig. 3. Relationship between aerosol levels and the level of each EA as a percentage of total EA in fluid bulk formulations and air (EA/total EA in air)/(EA/total EA in bulk fluid).

work pieces, as well as high-pressure spray or jet methods. Furthermore, fluids can be delivered as a mist in a high-velocity air stream (NIOSH, 1998). In addition, fluid aerosol can be generated by condensation occurring as soon as the fluids vaporize, due to the extreme heat generated in metalworking operations.

The airborne generation of EAs during machining operations is less well understood, despite the results of several studies showing that exposure to EAs in metalworking fluids can induce acute allergic responses, including asthma

(Savonius *et al*., 1994; Bruze *et al*., 1995; Piipari *et al*., 1998; Sandin *et al*., 1990; Suuronen *et al*., 2007; Anderson *et al*., 2009; Lessmann *et al*., 2009). To the best of our knowledge, only airborne TEA exposure levels, and not those of MEA and DEA, have been reported in automotive parts manufacturing plants that use wbMWFs (Kenyon *et al*., 1993). To date, there have been no studies examining how EA are generated and vaporize into the air during metalworking operations, including machining and grinding operations at the workplace field. We previously reported that in laboratory experiments MEA may vaporize even at 23.5°C, and that no other EA (i.e., DEA or TEA) vaporize at less than 60°C (Kim *et al*., 2010).

Our results are far lower than EA exposure levels reported in another study (Suuronen *et al*., 2007). Kenyon *et al*. (1993) reported that the TEA exposure levels measured in the automotive parts manufacturing industry were in the range of < 0.01 μg/m³–244 μg/m³ (n = 70), far lower than in our results (ND–0.98 mg/m³). Suuronen *et al*. (2007) reported that the alkanolamine exposure levels assessed in 10 metal workshops was 0.057 mg/m³ for MEA (range = 0.004–0.345 mg/m³), 0.064 mg/m³ for DEA (range = < 0.004–0.180 mg/m³) and 0.006 mg/m³ for TEA (range = 0.001–0.166 mg/m³).

While the airborne MEA, DEA and TEA levels measured in various machining operations cannot be regarded as the actual inhalation exposure levels, our findings could be used to characterize not only airborne EA levels, but also the relationships among aerosol concentrations and EA levels in air and fluid.

First, based on the significant relationship observed in this study between airborne total EA and aerosol levels, total EA levels could be either qualitatively or semi-quantitatively classified for exposure assessment, if aerosol levels are provided for machining operations that use fluid containing EA. This is in agreement with the results by reported by Suuronnen *et al*. (2007), that a statistically significant association between oil mist and alkanolamines was found in nine of the 10 metal workshops they examined. Total EA classification estimated from the aerosol level could be used in association with information on adverse health effects to undertake epidemiological studies of conditions that may be caused by EA exposure. Although there have been several reports concerning respiratory acute allergic responses, including dyspenea and asthma (Savonius *et al*., 1994; Piipari *et al*., 1998), EA exposure from machining operations has not thus far been assessed in association with respiratory health effects or other adverse health complaints. To the best of our knowledge, there is as yet no medium available for simultaneous collection of the three types of EA via the inhalation exposure route, because the EA appear in the air either as vapor or as aerosols. Further work is thus required to examine the relationship between respiratory health effects and exposure to both total EA and each type of EA.

Secondly, MEA was detected in all samples taken not only from machining operations, but also from several areas not associated with machining work, despite the low vapor pressure. MEA can vaporize into the air regardless of the machining operation type, whereas no vaporization of either DEA or TEA was detected in operations without metalworking. We have previously reported that, of all the EA, only MEA was found to evaporate even at 23.5°C, and that MEA evaporation increases along with increasing temperature, without condensation (Kim *et al*., 2010). These results demonstrate that airborne MEA can arise through the process of vaporization from sumps or tanks, where fluids are simply stored and circulated. Therefore, engineers who handle fluids containing MEA in areas without metalworking operations can still be exposed to substantial levels of airborne MEA (Kim *et al*., 2010).

Thirdly, the level of each EA as a percentage of the total EA levels in air and fluid was found to be associated with the aerosol level. However, this relationship was found to be quite different for MEA and TEA. MEA_R showed a negative exponential relationship with the aerosol levels, while a positive linear regression relationship was recorded for TEA_R. This result indicated that, when aerosol levels are low (< 1 mg/m³), airborne MEA may account for a substantial proportion of total airborne EA levels through vaporization of MEA from bulk fluid. On the other hand, MEA accounts for a lower percentage of the total airborne EA level when the aerosol concentration becomes higher. At these higher aerosol EA levels, EAs with low vapor pressure, such as TEA and DEA, may account for most of the total airborne EA. A significant effect of fluid EA contents on the airborne EA contents was found when the aerosols levels were high, which may vary depending, for example, on the EA type, fluid EA formulation, and operation or job title. Our result is partially in agreement with the results reported by Kenyon *et al*. (1993), who found that TEA air levels (n = 5, < 0.244 mg/m³) were related in an operation-specific manner with TEA levels in the bulk fluid formulations. Most of the airborne DEA and TEA may originate from the fluid aerosol mist, as a result of fluid splashing from the machine, fluid applied to cool the cutting zone, and the use of air or aerosol-powered aspirating equipment to disperse the fluid and clean the work pieces. Based on these results, machinists who are involved in machining operations that generate aerosols may be exposed to DEA and TEA via fluid aerosols, rather than evaporation.

A major limitation of this study is that it is not possible to know how representative our findings are with regard to the various metalworking operations where fluid types, work and operation characteristics, and EA formulations are quite different. Most of the key findings of this study are based on a small number of samples taken only from machining operations, which involve similar formulations and operating characteristics. Another limitation is that the relationships we found were based on results that were not adjusted to take into account the effects of engineering controls, such as the level of enclosure and local exhaust ventilation. Our results were obtained from operations with basic control facilities, such as enclosures and local exhaust ventilation, and the effectiveness of these was not evaluated. There may obviously many things affecting the formation of aerosol and its composition, in addition to the EA. The level of each EA in the air is basically dependent on some of the following factors: the level of EA in the fluid, the

volatility of the EA and the process temperature, and in case of non-volatile EAs, the aerosolization connected to the process techniques. Further work is needed to examine the effects of other factors, such as variations in work practices and level of engineering controls, which can also affect the generation of airborne EA.

In conclusion, for machining operations that use wbMWFs containing EA, overall inhalation exposure to EA could be estimated using aerosol levels, and this could in turn be used to assess their respiratory effects. The relationships found in this work among fluid EA formulation, airborne EA levels, and aerosol levels in machining operations were quite different according to EA type. When aerosol levels are low (< 1 mg/m^3), the level of airborne MEA may make a significant contribution to the total level of EA, through vaporization of MEA from the bulk fluid. In contrast, if aerosol levels are high, much of the total airborne EA may be accounted for by DEA and TEA, through aerosolization of the bulk fluid. Further study is thus needed to examine the validity and practical usefulness of calculating the EA ratios and relating them to the aerosols.

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