

Evaluating Occupational Exposure of Workers for Metallurgy with Alkanol Amines

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Abstract

Liquids being used in metallurgy are a composition of dangerous chemicals including Alkanol amines. Alkanol amines include Mono-, Di- and 3- ethanol amine. Alkanol amines are used as lubricant in metallurgy. Dermal absorption of these chemical substances is so important and some studies are being done about carcinogenesis of these chemical substances. Meanwhile, ethanol amine has been recognized as a factor causing occupational asthma. The present study was done on 29 turnery and rolling workers in Cupper Industrial Complex of Sarcheshmeh in descriptive-sectional manner. Data related to concentration of Alkanol amines in the atmosphere were gathered with the method proposed by NIOSH and data for pulmonary function were extracted from spirometry experiments. Demographic data were obtained from medical files of the workers. Statistical tests were carried out using software SPSS. In this study, workers' Time Weighted Average (TWA) individual exposure to Mono-ethanol amine (MEA) with density scope 0.03- 1.16, exposure to Di-ethanol amine (DEA) with density scope 0.36-1.35 and exposure to TEA with density scope 0.49-1.28 equal 0.54, 0.87 and 0.85 mg/m³ respectively without occupational group separation for each. Also, FVC reduction in studied individuals without occupational group separation was 3.17% (SD= 6.55%). The results indicated that workers' Time Weighted Average exposure to Mono-Di-Tri- ethanol amine was lower than occupational legal limit. In rolling process, exposure to Alkanol amines is lower compared to other processes of metallurgy because of semi-enclosure of this process. Having done Pearson correlation test to determine relation between individuals' work experience and FVC reduction, it was observed that there is no meaningful relation between these two variables.

Keywords: Alkanol amines, pulmonary functions, occupational exposure

Introduction

Lubricant is a substance that is used to reduce friction and abrasion between two surfaces which move on each other (McCoy, 2006). Lubricant liquids are used for decreasing heat and friction and improving quality of products in industrial machining and grinding activities (National Institute for Occupational, 1998). During machining operations, dynamic forces applied on lubricant liquids of metalworking like strike force, centrifugal force and high pressure spray (liquid atomization) as the result of liquid flow break produce poly-dispersed aerosols. Produced aerosols in work place can float in the air for long time due to their floating feature and produce fog as the result of mist which cannot be visible with naked eyes (Tolbert, 1997). Workers may have respiratory and dermal exposure to produced aerosols and pieces contaminated by these oils (National Institute for Occupational, 1998). Dermal problems caused by aerosols of lubricant oils include folliculitis, acne, keratosis, irritative and allergic contact dermatitis. Respiratory exposure

causes pneumonia, hyper allergy, asthma, Chronic Bronchitis, pulmonary failure function (Suuronen et al, 2007). Metalwork liquids are complicated mixture of chemical substances. Kind and ratio of chemical species in this mixture depend on various factors as manufacturer and need of machining process to cooling and lubricating. In addition, other additives are added into metalwork liquids for improvement of their life like biocides and substances preventing from foam production. Also unknown number and amount of pollutants are placed in composition of these liquids during their application.

Lubricant liquids of metalwork have been used for life improvement of metalwork tools since early 1900's. Workers may have dermal exposure due to 1) liquids released while using these liquids for tools and grinding piece and 2) carrying components, tools and equipment contained by these liquids. Because of characteristics of metalwork industries i.e. being competitive and exclusive, there is limited information about nature of existing chemical substances in metalwork lubricant liquids. There are a number of chemical substances in each group of metalwork lubricant liquids and so different production processes, different degrees of infiltration, recycling or reusing, different degrees of purity for chemical substances and potential chemical reactions between components impose various levels of risk on workers. Since recognizing and determining all chemical substances existing in metalwork lubricant liquids are beyond the scope of this study, information related to Alkanol amines or ethanol amines (Mono, Di, Tri ethanol amine) which are the aim of this study has been brought into discussion.

Alkanol amines and ethanol amines (Mono, Di, Tri ethanol amine) are used to fix PH or to prevent from corrosion in lubricant liquids of metalwork. Lubricant liquids usually contain 2-3% Mono or Di- ethanol amine and up to 25% Tri ethanol amine. Diluting these liquids with ratio 1 to 10 in water provides a composition of Mono or Di ethanol amine with 0.5% concentration and Tri ethanol amine with concentration 2.5%. Ethanol amine cannot concentrate because of continuous addition of water. There are considerable worries about carcinogenesis potential of Tri and Di ethanol amine. Tri ethanol amine can also cause asthma. Tri- ethanol amine has been used for carcinogenesis studies by National Institute of Cancer because of its vast usage in consuming goods, frequent occupational exposure in the industries and potential for changing into N-nitroso Di ethanol amine (Nomination of Metal Working Fluids for Testing by the National Toxicology Program, 2001).

Many studies have been done due to importance of these compositions as MAJ-LEN et al (2006) has measured occupational exposure to Alkanol amines existing in lubricant liquids of metalwork in 9 work room. In the study, they investigated dermal exposure after 2 hours from beginning of the work and respiratory exposure by sampling of respiratory air. Dominant hand of each worker was washed with 200 milliliter isopropanol 20% in a plastic bag after 2 hours from beginning of the work and for 1 minute to determine dermal exposure. Individual samples of the workers' respiratory air have been gathered on fiber glass filter smeared by acid for 2 hours. They reported samples obtained from respiratory air and samples of washing workers' hands using chromatography of analysis mass spectrum liquid and mean value of concentration of Mono-, Di- and Tri- ethanol amine were respectively 57, 64 and 6 microgram/ m³. Mean concentration values of these pollutants in samples obtained from these people's hand skin were 9-43 times than respiratory concentration for Mono- ethanol amine, 100 times than respiratory concentration for Di- ethanol amine and 173 times than respiratory concentration for Tri- ethanol amine. Main channel of metalwork workers' exposure to Alkanol amines is dermal contact based on results of the study. Ethanol amine is the only Alkanol amine that its respiratory exposure value is analogue to dermal

contact. They proposed dermal contact reduction as one of ways for reducing exposure and hand washing for evaluating protective gloves (Henriks-Eckerman et al, 2006).

Johannes Geier et al (2004) investigated contact allergy in metalworkers affected by occupational dermatitis who have used lubricant liquids being soluble in water. They characterized allergens causing allergy in lubricant liquids using Patch test:

Allergy to Mono-ethanol amine, rosin, abietic acid and aromatic compounds, cobalt formaldehyde, formaldehyde releasing and other biocides are most important allergens (Geier et al, 2004).

Holger Lessmann et al (2009) obtained data related to Patch Test done on metalworkers from German Dermatology Institute and they analyzed and interpreted the data to determine allergenicity of ethanol amines. 85098 patients underwent Patch test by 2.5% TEA for recognizing allergenicity effect of TEA. Among these patients, 323 people (0.4%) showed positive test. The result showed that TEA has poor stimulating potential; so it is not a strong allergen. Therefore, allergenicity of Tri- ethanol amine seems very low. Patch test was done on 9602 patients with Mono ethanol amine and on 8791 patients with Di ethanol amine and the results showed that contact allergy prevalence was 3.8% for Mono ethanol amine and 1.8% for Di ethanol amine. Then Mono ethanol amine is predominant allergen in lubricant liquids of metalwork (Lessmann et al, 2009).

Ducos and Gaudin (2003) evaluated amount of N- nitroso and Di ethanol amine (NDELA) in the urine of workers being exposure to solvable metal liquids in water. NDELA is produced in these liquids as the result of reaction between nitrite and ethanol amines as Di and Tri ethanol amine. In the study, they took urine of 100 exposed workers before and after work shift and also urine of 48 not exposed workers and analyzed them by GC-TEA. Amount of NDELA was not in recognizable limit in urine of control group individuals while mean of this substance in the urine was 44.6 g/l μ in exposed people after work shift and 0.4 g/l μ before work shift. There is strong relation between amount of NDELA in lubricant liquids and in the urine of exposed people in the study .

Material and Methods

Workers' exposure of turnery and rolling units in Copper Complex of Sarcheshmeh to chemical pollutants was measured in a descriptive- sectional study that was due to using solvable lubricant liquids in water in these processes.

Based on early information about number of workers exposed by required pollutants, number of these workers was 29 people in Sarcheshmeh Complex and measuring of sample size was done based on this number. In similar papers, amount of these pollutants in the environment was determined. According to comparing formula, mean value was calculated with a constant value for sample size. $\alpha=0.05$ and power= 0.8 have been considered. Max required sample was calculated 20. We investigated 29 people but during the study, this number reached 32 people by recognizing all exposed people and all these people were studied for increasing study reliability. Calculation formula of sample size is:

$$n = \frac{(Z_{(1-\frac{\alpha}{2})} + Z_{(1-\beta)})^2 \sigma^2}{d^2}$$

Mean and standard deviation is respectively 0.14 and 0.1 in K. Suruunen's study (Ref. 6)

Required data includes: a) concentration of ethanol amines in workers' respiratory air and sampling and analysis of ethanol amine was done based on proposed method NIOSH. Sampling steps are as following: 1) calibration of individual sampling pump was done for 1 lit/ min output volume while there is a sampling device jointed to it. 2) We filled impinger with 15 ml liquid of 2mM hexane sulfonic acid. 3) Sampling was done in 1lit/ min output volume for gathering 100- 120 lit air. 4) After end of sampling, content of each impinger were transformed into poly ethylene bottle

and brought to the laboratory. Stages of drawing calibration curve include: 1- certain values of original solution from each analysis were poured into flasks with 50 ml volume and it was brought to volume with solvent (ELUENT). Important point is that standard work solutions must be kept in poly ethylene bottles because sodium ion may be released by the glass which is a chromatographic interferer. 2- Calibration curves were drawn after injecting standard solutions into chromatograph ion device and obtaining chromatography peaks as peak height against μg analyte for each analyte. Measuring and calculating concentration of each ethanol amine include: 1. Chromatograph ion device was set according to manufacturer recommendations and previously mentioned conditions. It is worth mentioning that when applying micro membrane suppressor, several injections must be made with sample loop to reduce field level if field level is high. All samples, solvents and water that were passed through chromatograph device were filtered for preventing from blockage of columns and system taps. 3. A little of each sample was poured into autonomous sampling vials. 4. Injection volume was set on 50 μlit . 5. Height of the peaks was measured. In cases that peak height was higher than curve value of calibration the sample was diluted and dilution factor was applied after reinjection and in final calculation. 6. Required analyte value was determined in imprinter (W) and witness samples using calibration curve and concentration of each analyte in sampled air (lit) was calculated:

$$C = \frac{W - B}{V}, \text{mg/m}^3$$

Date related to pulmonary functions including parameters FVC, FEV₁, FEV₁/FVC was obtained from spirometer papers existing in studied individuals' medical files with their percent (ratio of test and predicted values) and they were recorded in SPSS Software paper and statistical analyses were done on data. Individual information including age, work experience and smoking were obtained and recorded from medical files.

Statistical tests were carried out using SPSS Software version 16. These tests include one sample t-test to compare exposure values to studied pollutants with legal limit of occupational contact, one-way ANOVA and Scheffe to compare exposure values and pulmonary parameters in different processes and Correlation and Regression Tests to investigate relation between various variables. In all tests, confidence level was considered 95%. Normality of the data was supported by doing Normality test. So the results were expressed as arithmetic mean and standard deviation.

Results and Findings

Ethanol amine: standard calibration curve for standard work solutions of Mono ethanol amine in concentration range 0.01, 0.03, 0.05, 0.07, 0.1 and 0.2 mg/ml versus drawing concentration and its linear equation was obtained as following equation based on conductivity (micro siemens).

Table1: Conductivity value recognized by conductivity detector of ion chromatograph system in given concentration scope of liquid Mono-ethanol amine

Concentration (mg/ml)	Conductivity (μS)
0.01	3.5
0.03	6.42
0.05	8
0.07	12
0.1	15
0.2	30

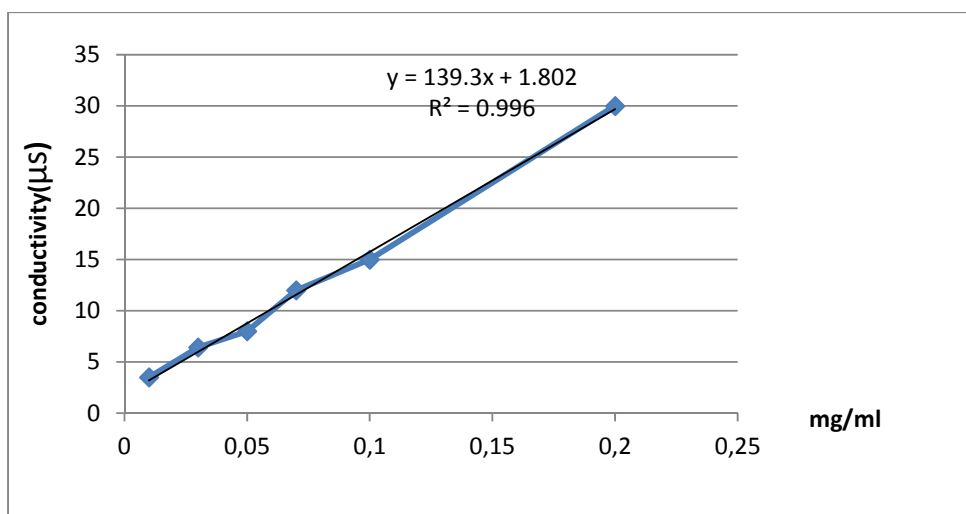


Figure 1. Conductivity calibration curve recognized by conductivity detector of ion chromatograph system in given concentration scope of liquid Mono-ethanol amine

Calibration equation is: $Y = 139.3X + 1.802$

Mono ethanol amine concentration for exposed individuals was calculated by substituting absorption values of main samples and witness in $Y = 139.3X + 1.802$ and using calculation equation of pollutant concentration in sampled air which was offered in methodology section and shown in table 2.

Table 2. Workers' Time Weighted Average individual exposure to Mono- ethanol amine in different occupational groups

Occupational group	Number	Density of Mono-ethanol amine (mg/m^3)		
		Mean	Standard deviation	Density scope
Grinding	7	0.54	0.87	0.84-0.34
Milling	7	0.69	0.24	0.96-0.34
Drilling	4	0.15	0.11	0.3-0.03
Rolling	6	0.33	0.12	0.49-0.11
Turnery	8	0.75	0.22	1.16-0.42

Table 3. Comparison of workers' Time Weighted Average (TWA) individual exposure to Mono- ethanol amine with occupational legal limit (TLV=8 mg/m^3)

Occupational group	Mean (mg/m^3)	Comparison index=8		Confidence limit 95%	
		P-value	Mean difference (mg/m^3)	Lower limit	Higher limit
1	0.54	<0.001	-7.46	0.35	0.74
2	0.69	<0.001	-7.13	0.47	1
3	0.15	<0.001	-7.85	0	0.33
4	0.33	<0.001	-7.66	0.2	0.47
5	0.75	<0.001	-7.25	0.6	0.94

Occupational group: 1grinding, 2milling, 3drilling, 4rolling, 5turnery

Workers' individual exposure weighted time average (TWA) to Mono- ethanol amine is considerably lower than TLV in all occupational groups (P-value <0.001).

Table 4: Comparison of workers' Time Weighted Average (TWA) individual exposure to Mono- ethanol amine in all occupational groups

Occupational group	Time Weighted Average(TWA)	Occupational group	Time Weighted Average (TWA)	P-value	Confidence limit 95%	
					Lower limit	Higher limit
1	0.54	2	0.69	0.7	-0.5	0.19
1	0.54	3	0.15	0.06	-0.01	0.8
1	0.54	4	0.33	0.5	-0.15	0.57
1	0.54	5	0.75	0.3	-0.55	0.12
2	0.69	3	0.15	0.005	0.13	0.95
2	0.69	4	0.33	0.05	-0.004	0.72
2	0.69	5	0.75	0.9	-0.4	0.27
3	0.15	4	0.33	0.7	-0.6	0.23
3	0.15	5	0.75	0.001	-1	-0.2
4	0.33	5	0.75	0.01	-0.77	-0.06

Occupational groups: 1grinding, 2milling, 3drilling, 4rolling, 5turnery

Post Hoc-Scheffe Test showed that exposure mean to ethanol amine for milling workers is statistically higher than drilling and rolling workers (p-value<0.05). Also exposure mean for grinding workers is statistically higher than drilling and rolling workers (p-value<0.05).

Di- ethanol amine: standard calibration curve for standard work solutions of Di- ethanol amine in concentration range 0.01, 0.03, 0.05, 0.07, 0.1 and 0.2 mg/ml versus drawing concentration and its linear equation was obtained as following equation based on conductivity (micro siemens).

Table 5: Conductivity values recognized by conductivity detector of ion chromatograph system in given concentration scope of liquid Di-ethanol amine

Concentration (mg/ml)	Conductivity (µS)
0.01	1.5
0.03	3.5
0.05	6.8
0.07	10.2
0.1	16
0.2	28.8

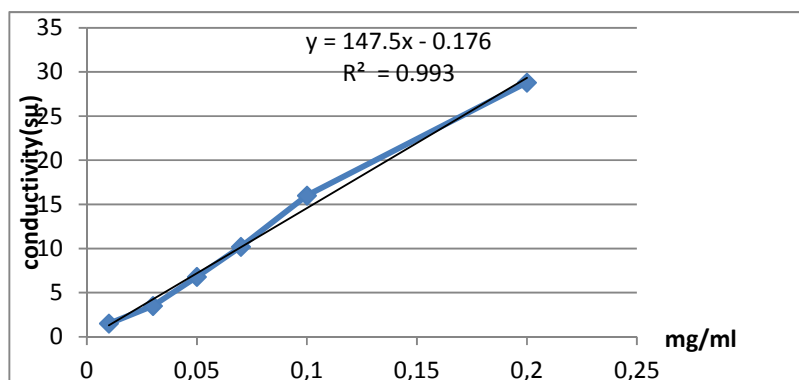


Figure 2: Conductivity calibration curve recognized by conductivity detector of ion chromatograph system in given concentration scope of liquid Di-ethanol amine

Calibration equation is: $Y = 147.5 X - 0.176$

Di- ethanol amine concentration for exposed individuals was calculated by substituting absorption values of main samples and witness in $Y = 147.5 X - 0.176$ and using calculation equation of pollutant concentration in sampled air which was offered in methodology section and shown in table 6.

Table 6. Workers' Time Weighted Average (TWA) individual exposure to Di- ethanol amine in different occupational groups

Occupational group	Number	Density of Di-ethanol amine (mg/m ³)		
		Mean	Standard deviation	Density scope
Grinding	7	0.89	0.22	1.09-0.51
Milling	7	1.14	0.12	1.35-1.02
Drilling	4	0.68	0.17	0.91-0.51
Rolling	6	0.53	0.14	0.69-0.36
Turnery	8	0.96	0.16	1.09-0.62

Table 7: Comparison of workers' Time Weighted Average (TWA) individual exposure to Di- ethanol amine with occupational legal limit (TLV=1 mg/m³)

Occupational group	Mean (mg/m ³)	Comparison index=1		Confidence limit 95%	
		P-value	Mean difference (mg/m ³)	Lower limit	Higher limit
1	0.89	0.24	-0.11	0.68	1.1
2	1.14	0.02	0.14	1.03	1.26
3	0.68	0.03	-0.32	0.42	0.95
4	0.53	0.001	-0.47	0.4	0.69
5	0.96	0.5	-0.04	0.83	1.1

Occupational group: 1grinding, 2milling, 3drilling, 4rolling, 5 turnery

Workers' exposure to Di-ethanol amine in different occupational groups was compared for TLV and T-Test in table7. Workers' Time Weighted Average (TWA) individual exposure to Di- ethanol amine in milling workers is meaningfully higher than TLV (p-value=0.02) and exposure average in rolling and drilling ones is meaningfully lower than TLV.

Table 8. Comparison of workers' Time Weighted Average (TWA) individual exposure to Di- ethanol amine among occupational groups

Occupational group	Time Weighted Average(TWA)	Occupational group	Time Weighted Average(TWA)	P-value	Confidence limit 95%	
					Lower limit	Higher limit
1	0.89	2	1.14	0.13	-0.55	0.04
1	0.89	3	0.68	0.4	-0.14	0.56
1	0.89	4	0.53	0.02	0.05	0.67
1	0.89	5	0.96	0.9	-0.36	0.22
2	1.14	3	0.68	0.005	0.11	0.8
2	1.14	4	0.53	<0.001	0.3	0.92
2	1.14	5	0.96	0.38	-0.1	0.47
3	0.68	4	0.53	0.7	-0.2	0.5
3	0.68	5	0.96	0.1	-0.6	-0.06
4	0.53	5	0.96	0.002	-0.07	-1.26

Occupational groups: 1grinding, 2milling, 3drilling, 4rolling, 5 turnery

Test Post Hoc-Scheffé showed that exposure average to Di-ethanol amine in grinding workers is higher than rolling ones (p-value= 0.02). It is higher in milling workers than drillers (p-value=0.005) and rollers (p-value=0.001) and is higher in rolling and turnery workers compared to rollers.

Tri- ethanol amine: standard calibration curve for standard work solutions of Tri- ethanol amine in concentration range 0.01, 0.03, 0.05, 0.07, 0.1 and 0.2 mg/ml versus drawing concentration and its linear equation was obtained as following equation based on conductivity (micro siemens).

Table 9: Conductivity values recognized by conductivity detector of ion chromatograph system in given concentration scope of liquid 3-ethanol amine

Concentration (mg/ml)	Conductivity (µS)
0.01	1.1
0.03	1.8
0.05	2.8
0.1	7.1
0.2	14

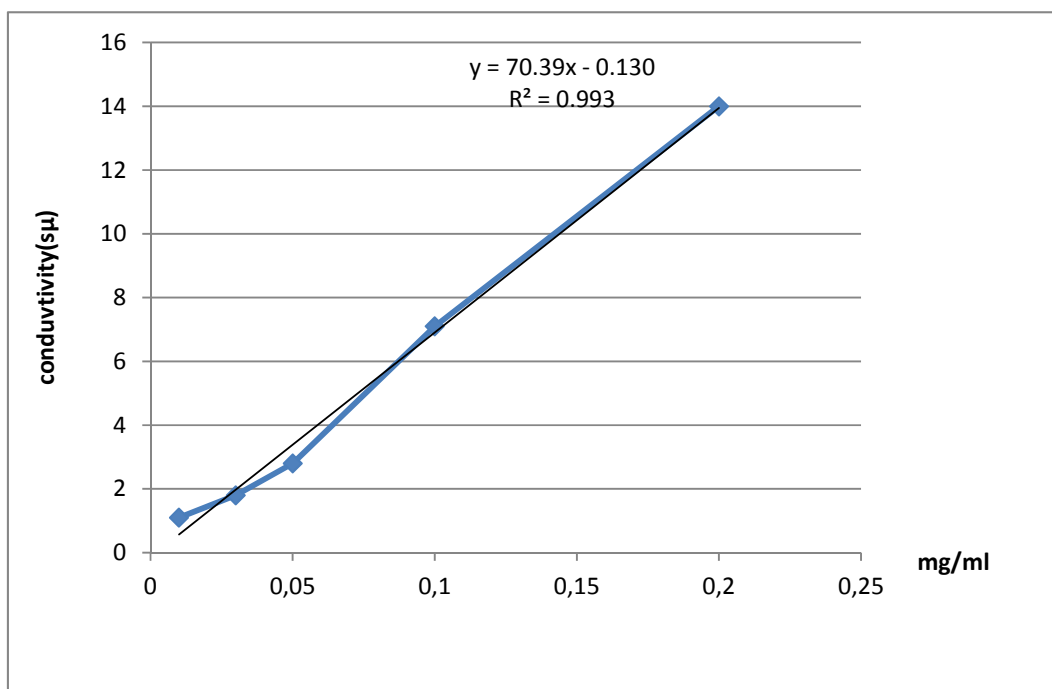


Figure 3. Conductivity calibration curve recognized by conductivity detector of ion chromatograph system in given concentration scope of liquid 3-ethanol amine

Calibration equation is: $Y=70.39 X - 0.13$

Tri - ethanol amine concentration for exposed individuals was calculated by substituting absorption values of main samples and witness in $Y=70.39 X - 0.13$ and using calculation equation of pollutant concentration in sampled air which was offered in methodology section and shown in table 10.

Table 10. Workers' Time Weighted Average (TWA) individual exposure to Tri- ethanol amine in different occupational groups

Occupational group	Number	Density of 3-ethanol amine (mg/m ³)		
Average		Standard deviation	Density scope	
Grinding	7	0.88	0.2	1.07-0.49
Milling	7	0.94	0.22	1.18-0.54
Drilling	4	0.55	0.07	0.65-0.49
Rolling	6	0.59	0.08	0.7-0.49
Turnery	8	1.08	0.1	1.28-0.97

Table 11: Comparison of Workers' Time Weighted Average (TWA) individual exposure to Tri- ethanol amine with occupational legal limit (TLV=5 mg/m³)

Occupational group	Average (mg/m ³)	Comparison index=7		Confidence limit 95%	
		P-value	Mean difference (mg/m ³)	Lower limit	Higher limit
1	0.88	<0.001	-4.11	0.7	2.1
2	0.94	<0.001	-4.06	0.8	1.15
3	0.55	<0.001	-4.44	0.45	0.67
4	0.59	<0.001	-4.4	0.5	0.7
5	1.08	<0.001	-3.91	1	1.2

Occupational group: 1grinding, 2milling, 3drilling, 4rolling, 5turnery

Workers' exposure to Tri-ethanol amine in different occupational groups was compared for TLV and T-Test in table 11. Workers' Time Weighted Average (TWA) individual exposure to Tri-ethanol amine in all occupational groups is significantly lower than TLV (p-value=0.001)

Table 12: Comparison of workers' Time Weighted Average (TWA) individual exposure to Tri-ethanol amine among occupational groups

Occupational group	Time Weighted Average(TWA)	Occupational group	Time Weighted Average(TWA)	P-value	Confidence limit 95%	
					Lower limit	Higher limit
1	0.88	2	0.94	0.13	-0.33	0.22
1	0.88	3	0.55	0.4	0.01	0.66
1	0.88	4	0.59	0.02	0.004	0.58
1	0.88	5	1.08	0.9	-0.46	0.07
2	0.94	3	0.55	0.005	0.06	0.71
2	0.94	4	0.59	<0.001	0.06	0.64
2	0.94	5	0.96	0.38	-0.46	0.13
3	0.55	4	0.59	0.7	-0.37	0.29
3	0.55	5	1.08	0.1	-0.85	-0.21
4	0.59	5	1.08	0.002	-0.77	-0.2

Occupational groups: 1grinding, 2milling, 3drilling, 4rolling, 5 turnery

The results obtained from Post Hoc-Scheffe were shown in table 12 in which exposure average among occupational groups were compared. Grinding workers' exposure average is meaningfully higher than drillers and rollers (p-value=0.04). Also milling workers' exposure is higher compared to drilling and rolling ones (p-value=0.01).

Table 13: Descriptive data about chemical pollutants to which studied workers exposure

Pollutant	Sample size	Time Weighted Average(mg/m ³)	Standard deviation	Density scope
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Mono-ethanol amine	32	0.54	0.28	1.16-0.03
Di-ethanol amine	32	0.87	0.26	1.35-0.36
Tri-ethanol amine	32	0.85	0.25	1.28-0.49

Pulmonary Functions Changes

Table14: Values of pulmonary functions changes

Occupational group	Reduction value average of pulmonary functions based on % (SD)		
	FVC	FEV ₁	FEV ₁ / FVC
	2.54 (2.7)	4.42 (3.7)	2.1 (5.5)
	6.8 (13.8)	4.7 (12.4)	-3 (6.3)
	2.2 (1.7)	3.7 (4.6)	1.36 (5.7)
	2.23 (1)	2.31 (9.3)	-0.5 (9)
	1.74 (1.26)	3.44 (8.6)	1 (9.8)
Mean	3.17(6.55)	3.75(8.1)	0.12 (7.4)

(-):values have increased.

Among studied individuals, only a person in grinding occupational group experienced blockage pattern and a person in rolling occupational group faced with restrictive pattern.

Table 15: Relation between individuals' reduction value of pulmonary functions and work experience based on year (without occupational group separation)

Independent variable Dependent variable	Work experience (year)	Correlation coefficient
FVC	p-value=0.26	-0.2
FEV ₁	p-value=0.57	-0.1
FEV ₁ / FVC	p-value=0.6	0.09

(-): has decreased, (+): has increased.

In table 15, results of Pearson Correlation Test showed that relation between work experience and variation in pulmonary functions is not statistically meaningful (p-value>0.05).

Table 16: Relation between reduction values of each pulmonary variables and exposed pollutants

Independent variable Dependent variable	FEV ₁ / FVC			FEV ₁			FVC		
	MEA	7.34	0.4	-5	7.8	0.5	-5.23	5.49	0.9
DEA	7.4	0.5	-7.9	7.9	0.9	0.8	5.53	0.1	8.05
TEA	8.98	0.2	1.85	9.6	0.6	14.17	6.7	0.1	9.93
Work experience	0.22	0.68	0.09	0.23	0.6	-0.11	0.16	0.3	-0.17

Table 16 shows results of multi variable linear regression test. As it is observed there is no meaningful and strong relation between variable values of FVC and Alkanol amines.

Discussion and Conclusion

In our study, workers' Time Weighted Average (TWA) individual exposure to Mono ethanol amine (MEA) without occupational groups separation was 0.54 mg/m³ with density scope 0.03- 1.16

mg/m³. Exposure average of all occupational groups is significantly lower than legal occupational limit (TLV=8mg/m³) (P-value<0.001). So there is appropriate safety limit for pollutants. To determine kind influence of metalwork process on mist or MEA steam rate spread in workers' respiratory air, Post Hoc Scheffe showed that milling and turnery processes have been spread more MEA compared to drilling and rolling processes (p-value<0.05).

Also, in this study, workers' Time Weighted Average (TWA) exposure to Di- ethanol amine (DEA) without occupational group separation was 0.87 mg/m³ with density scope 0.36- 1.35 mg/m³ and its comparison with legal occupational limit (1mg/m³) specified that workers' exposure average is lower than TLV (P-value = 0.01). But in the case of occupational group separation, exposure average for rolling and drilling processes was meaningfully lower than legal limit (p-value<0.05). Also comparing exposure average among occupational groups determined exposure rate in grinding process was higher than rolling (p-value=0.02), in milling is higher than drilling and rolling units (p-value<0.05) and in grinding process is higher than rolling (p-value=0.002).

In the present study, there is Tri ethanol amine (TEA) in all samples. workers' Time Weighted Average (TWA) exposure to TEA without considering occupational group separation was 0.85 mg/m³ with density scope 0.49- 1.28 mg/m³ which is significantly lower than TLV (5mg/m³). This value is considerably lower than TLV in case of occupational group separation. Also exposure rate in rolling unit is meaningfully lower than grinding, milling and turnery processes (p-value<0.05).

In rolling process, exposure to Alkanol amines is approximately lower than other metalwork processes because of its being enclosure in the process.

The current study has also investigated variation amount of personnel's pulmonary functions after some years working in these places in each occupational group of metalwork. As shown in table14, amount of FVC has decreased from 1.74% in turners to 6.8% in metalworkers. Reduction average of FVC in studied individuals without occupational group separation was 3.17% (standard deviation= 6.55%). Having done Pearson Correlation Test to determine relation between work experience of the individuals and FVC reduction, it was observed that there is not meaningful relation between these two variables (p-value=0.2). Cause of this issue can be attributed to few number of the sample or we can deduce that work experience does not significant influence on FVC reduction and in this case, FVC reduction depends on dose of pollutants. So it was observed that FVC reduction has meaningful relation with workers' exposure rate to mineral oil mist (p-value= 0.009) when multi variable regression test was done to determine relation between each pollutant and reduction rate of FVC. For Alkanol amines, it can be explained that most important problem is respiratory allergy and in the case FEV₁ but not FVC reduces.

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