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Evaluation of Indoor Air Pollution of Polyurethane Industries with Emphasis on Exposure with Methylene Diphenyle Diisocyanate (MDI)

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Abstract: Diisocyanates are used as a initial chemical material in different factories such as surface coatings, polyurethane foams, adhesives, resins, elastomers, binders and sealants. In the polyurethane workplace there are aerosols of diisocyanates which has important to effect on workers. They can also be exposed to partial reaction of isocyanate-containing intermediates formed during polyurethane production. The main objective of this study pointed on assessment of exposure risk factors with MDI in the workplace, determination of MDI concentration and biomonitoring of MDA in polyurethane industries. NISOH (National Institute for Occupational Safety and Health) 5522 sampling and analysis method was used by midget impinger contained dimethyl sulfoxide with tryptamine. HPLC (High Performance Liquid Chromatography) was employed for air sampling analysis and GC (Gas Chromatography) for urine analysis. Getting personality data was carried out by Health Surveillance Questionnaire and multiple linear regression models with ANOVA test was used for the statistical analysis. The result of study showed that there was a diisocyanate pollution (MDI > 96.6μg/m^3) and it have seen in the workers' urine. A new approach to assess isocyanate pollution in the workplace is risk factor assessment simultaneously with indoor air pollution and biological monitoring.

Key words: 1-Risk factor · 2-diisocyanates · 3-biological monitoring · 4-HPLC 4-Air pollution

INTRODUCTION

Isocyanates are known as highly reactive chemicals. Isocyanates/ diisocyanates are often used as raw materials in production of polyurethane [1]. The lower molecular weight isocyanates tend to vaporize at room temperature, they may create vaporized inhalation hazard. Conversely, the higher molecular weights isocyanates do not readily volatilize at ambient temperatures, but they are appeared as aerosolized inhalation hazard in the working environment [2]. The common feature of all diisocyanates (monomers) presence of two double bounds of isocyanate functional groups (-N=C=O) attached to an aromatic or aliphatic compounds generate toxic compounds as indoor pollutants [3]. Isocyanate exposure is irritative to skin, mucous membranes, eyes and respiratory tract. The most common adverse health outcome associated with isocyanate exposure is asthma due to sensitization; less prevalent are contact dermatitis (both irritant and allergic forms) and hypersensitivity pneumonitis [4]. Contact dermatitis can result in symptoms such as rash, itching, hives and swelling of the extremities [5]. As an actual evidence, the worker suspected of having isocyanate induced asthma/sensitization will exhibit the traditional symptoms of acute airway obstruction, e.g., coughing, wheezing, shortness of breath, tightness in the chest and nocturnal awakening. For the case of isocyanate-exposed worker may first develop an asthmatic condition (i.e., become sensitized) after a single (acute) exposure. But, s ensitization for exposure may usually takes in a few months to several years [5]. Methylene diphenyl diisocyanate, most often abbreviated as MDI, is an aromatic diisocyanate. The MDI is most practically useful and is also known as Pure MDI. MDI is reacted with a polyol in the manufacture of polyurethane. It is the most produced diisocyanate, accounting for 61.3% of the

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global market in the year 2000 [6]. The researchers identified isocyanates as major cause of occupational asthma in industrialised countries [7-9]. Implementation of effective control strategies is therefore very important in reducing the incidence and prevalence of isocyanate asthma. A study was conducted to evaluate the determinants of isocyanate exposure in 33 auto body repair shops. The determinants identified include shop size, outdoor and indoor temperatures, indoor and outdoor relative humidity [10]. Exposure determinants were identified using among others linear regression, tobit regression and logistic regression models. The identification of key exposure determinants was suggested to be useful in targeting exposure evaluation and control efforts to reduce isocyanate exposure [11]. Methylene dianiline is an industrial chemical metabolite that is not known to occur naturally. It is also commonly known as diamino diphenyl methane or MDA. It occurs as a colorless to pale yellow solid and has a faint odor [4]. The level of isocyanate metabolites in urine is an indicator of how much isocyanate has been absorbed and how well the pollution controllers and the prevention units in working atmosphere are working. The levels of MDA are reported as "μmol/mol creatinine". The guidance standard value for MDA, the level is 1 μmol/mol creatinine and each sample above the guidance standard value is an indication of exposure to contaminated environment [9]. The goals of this study was exposure risk assessment of diisocyanate for workers and determination of MDI concentration in polyurethane factories, also biomonitoring assessment of MDA in worker's urine.

MATERIAL AND METHODS

The sample size was determined based on pretest and the method that reported by other researchers [14-16]. using the following statistical formula:

$$n \geq N\left\{1+\frac{1}{N}\left(\frac{d}{1.96\times S}\right)^{2}\right\}^{-1}$$

Formula 2 Sample Size Determination

The air sampling procedures and analysis of isocyanates from indoor air were divided into six steps: collection, derivatization, sample preparation, separation, identification and quantification [5]. Collection is the removal of the isocyanate species from the air sample into a portion of the sampler amenable to subsequent analysis. A generalized isocyanate sampler (mini personal sampler pump, SIBATA MP302 and midget impinger) used to collect hexamethylene diisocyanates [4]. Sample handling and preparation include those steps taken to stabilize the sample or make the sample more compatible with the analytical procedure. Sample handling considerations actually began before sample collection. For air sampling in the field, sample pumps [low flow (SIBATA, MP302 Model) Japan] were attached to individual adsorbent tubes using 30 cm lengths of clear, inert polythene tubing suitable for low-level organic compounds. Each pump and tube assembly was calibrated using a bubble flow meter (SKC UK, UK) in order to measure and adjust the sampling flow-rate precisely. The pumps were adjusted to provide a flow-rate of 2 l/min ~ Samples (static and personal) were taken adjacent to an operation where MDI was being handled in the factory for the periods of 2 hours. On completion of field sampling, the tubes were sealed with vials end-caps and returned to the analytical laboratory. Samples were chilled to 2°C in a laboratory refrigerator and analysed within 24 h [4]. The midget impinger SKC personal inhalable sampler, with mini personal sampler pump SIBATA, was used. All the samplers with midget impinger were connected to mini personal sampler pump fixed to work stations near the source of pollution. The air samples were separately collected in a working shift for three periods of 2 h, each at a flow rate of 2 L/min in an impinger containing a solution of reagent in dimethyl sulfoxide in addition to tryptamine (NIOSH, 1994). After passing 120 L of air through the sampler, then the entire sample medium was transferred to the laboratory for analysis. Sample handling and preparation were done to make it compatible with the analytical procedure as per standard methods [4]. MDI polyurethane factories that use isocyanate adhesive and paints were identified and selected. They employed full time workers as they worked for private companies. At all polyurethane factories, the people who were working had direct exposure to pollutants in the working area. Due to the reportedly short half life (about 1.5-3 hours) of MDA in urine, samples were collected before, during and after the shift to detect any short term exposure as well as an estimation of the 8 hour time weighted average exposure [9]. Regression analysis procedure was used to state the statistical relationship between the variables and identify any meaningful relationship between those variables. Due to the fact that the number of independent variables is more than one, multiple linear regression analysis was used in the present analysis [11, 12] A multiple regression equation, which has four independent variables, can be expressed as follows:

$$Y = B_0 + B_1 X_1 + B_2 X_2 + B_3 X_3 + B_4 X_4 + ei$$

where:
Y is the dependent variable (MDI concentration)
X_1, X_2, X_3 and X_4 are independent variables (relative humidity, dry bulb temperature dimension and altitude,) as the predictors in this model.
B_0, B_1, B_2, B_3 and B_4 are the model coefficients.
e_i is the residual errorgfdg

RESULTS AND DISCUSSION

Table 1 shows the maximum, minimum and mean values of indoor air independent variables with respect to MDI concentration in the polyurethane factories. The lowest minimum MDI concentration in all the factories was 93 μg/m^3 and also the highest of the maximum MDI concentration was 101 μg/m^3. These values can be considered as high value, compare to NIOSH exposure limit of 50 μg/m^3. The mean MDI concentration was 96.6 μg/m^3.

Table 2 shows the descriptive statistics of urinary methylene dianiline (MDA) in different factories. The maximum concentration of MDA measured from worker's urine in the MDI polyurethane factories was 4 μmol/mol creatinine and the mean value was in the range of 3.01 to 3.58 μmol/mol creatinine for all of factories. The mean MDA concentration in the air sample for the factories was 78.8 (μg/m^3). The urine results for all of the workers indicated high exposure w i th respect to MDI, because of the lowest concentration of MDA in their urine was 2 μmol/mol creatinine. This value was higher than the guideline value reported to be 1.0 μmol/mol creatinine [9]. Figure 1 shows the statistical graph of MDA concentrations in different factories.

Table 3 described the characteristics of subjects obtained from 50 workers in MDI polyurethane factories; the summary is shown below (Table 3). The mean age of workers, who work in the MDI polyurethane factories was 34.44 years. The duration of work history was 4.7 years and the weight mean value of workers was 70 kg.

Table 4 shows that the age of exposed workers was in the range of 20-30 (38%), 31-40 (32%) and 41-50 (30%), the weight of exposed workers was ranged 41-60 kg (20%), 61-80 kg (11%) and 81-100 kg (19%) and finally, the work history of exposed workers was ranged 0-5 years (70%), 6-10 years (20%) and 11-15 years (10%).

Table 5 shows that 60% of total workers working in the MDI factories were categorized as smoking and also 52% of total MDI workers also had some symptoms [sore eyes, running nose, sore throat, coughing, wheezing (asthma) and chest tightness] relevant to diisocyanates exposure.

Table 1: Values of indoor air variables in the MDI polyurethane factories

Factories code Variables	M_1	M_2	M_3	M_4	M_5	Average
MDI concentration (μg/m^3), Max	101	98	97	96	95	101
Min	98	98	96	95	93	93
Mean	99	98	97	95.6	93.8	96.6

Table 2: Descriptive statistics of methylene dianiline (MDA) in different factories

Factory code	Mean	SD	Minimum	Maximum	Sample size
M_1	3.3	.669	2	4	10
M_2	3.27	.422	3	4	10
M_3	3.23	.537	2.5	4	10
M_4	3.2	.537	2	4	10
M_5	3.15	.715	2	4	10

Guideline value: 1 μmol/mol creatinine (Source: Williams *et al.,* 1999)

Table 3: Range of subject characteristics

	N	Mean	SD	Min	Max
Age (year)	50	34	7.83	23	48
Weight (kg)	50	70	12.14	48	89
Work history (year)	50	4.5	2.91	2	14

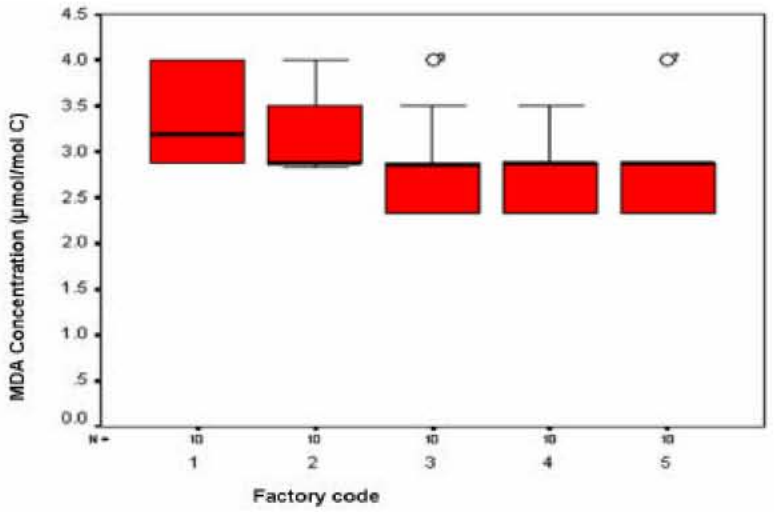

Fig. 1: MDA concentrations in different factories

Table 4: Range of subject characteristics

Variables	Range	Frequency	Percent
Age (year)	20-30	19	38
	31-40	16	32
	41-50	15	30
Weight (kg)	40-60	20	40
	61-80	11	22
	81-100	19	38
Work history (year)	0-5	35	70
	10-Jun	10	20
	15-Nov	5	10

Table 5: frequency of smoking and symptoms of disease

Variables	N	Percent
Smoking	60	30
Symptoms of disease	52	26

Table 6: Risk assessment regression model summary of MDI

Model	r	R^2	Adjusted R Square
7	0.968	0.937	0.93

Table 7: Regression summary model for MDI risk assessment

		Coefficients			
Model MDI		B	SD	t	P-value
	(Constant)	79.798	1.337	59.69	0.0001
	Age	-0.018	0.266	-0.069	0.945
	Smoking	0.850	0.763	1.115	0.271
	Weight	4.06	0.725	5.597	0.0001
	Work history	-0.113	0.313	-0.361	0.72
	Symptoms of disease	2.882	0.969	2.972	0.005

Dependent Variables: MDI concentration

A risk assessment investigation conducted to assess personal health risk factors correlation with diisocyanates pollution in the polyurethane factories. Table 6 showed that 93.7% of the MDI concentration can be attributed to any or all the independent variables (relative humidity, dry bulb temperature, dimension and altitude) ($R^2 = 0.937$).

The predictive regression model was obtained from Table 7 for relationship between health surveillance factors and MDI risk assessment. In all cases both workers' weight and disease symptoms were significant ($P<0.05$).

Risk assessment of exposure to diisocyanates among 50 workers increased with jobs task with potentially higher exposure with trends in TWA concentrations with regard to individual parameters (workers' weight and disease symptoms).

Under ascertainment is less likely among long term workers at the unit because asthmatic people who continue to work in exposed areas often develop increasingly severe symptoms, but surprisingly, there is no significant between work history and incidence of work-related disease for diisocyanates workers. The result of this study is similar to the other studies [13-16]. The present study detected effects of weight workers on work-related disease of diisocyanates and the results that is same as similar study have conducted by other researcher [17]. When comparing the present study with other studies where personally conditions have been described, this study contributed on personal and hygiene conditions [18, 19]. Isocyanates operation is usually done in a spray and molding process, with basic exhausts ventilation.

In addition, there was significant relationship in exposure levels between workers health surveillance factors (weight of workers and symptoms of disease) and concentration of MDI absorbed by workers. This indicates that health condition of workers may be an important determinant of isocyanate exposure in the polyurethane workplaces [20, 21]. It is useful to help public health professionals and also to needs of persons living or working near hazardous waste sites. It would appear that in the case of workers engaged in the polyurethane workplaces who exposed to diisocyanates pollution, the highest risks of isocyanate exposures are found on the workers that have a weight in the range of 50 to 88kg and they have some work related disease of isocyanate. In other word the weight of workers and symptoms of isocyanate related disease are risk factors to increase of pollutant exposure for diisocyanates polyurethane workers. However, while health surveys on workers in the polyurethane factories, specific inhalation challenges and animal studies suggest that diisocyanates have similar health effects on human [22, 23].

CONCLUSION

Finally this study has shown that air monitoring together with biological monitoring can be used to estimate the MDI pollution situation as well as the exposure to workers of polyurethane factories. Such a study at polyurethane factories having more than 100 workers in a factory is not known to date. Among five individual risk factors, two of them (weight of workers and symptoms of disease) had relationship with absorbed isocyanates metabolites. However, compared to other factors (age of workers, history of work and smoking situation), no significance was observed The models also showed that there is a strong relation ship between weight of workers in the polyurethane factories and appearance of symptoms of disease relevant to isocyanates on workers. Surprisingly, no significant effect was seen for the age of workers, smoking or non smoking and history of work.

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