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Occupational Exposure to Chromium and Nickel in Metalworking Fluid Operations Environment

Hui-Ming Liu[1,2], Yuh-Shen Wu[1] and Chia-Chan Wu[2]

[1] Department of Safety, Health and Environmental Engineering, Hungkuang University, Taichung Hsien, 433, Taiwan, R.O.C.

[2] Institute of Occupational Safety and Hazard Prevention, Hungkuang University, Shalu, Taichung, 433, Taiwan, R.O.C.

Abstract. This study summarizes biological monitoring and occupational hygiene findings from a survey of metalworkers exposed to chromium and nickel in a socket manufacturing plant. Airborne samples were taken from thread-cutting workers and punch press operators by using IOM personal inhalable aerosol sampler and respirable cyclone sampler during an 8-h work shift. All the levels of airborne Cr and Ni were lower than OSHA's permissible exposure limit. There were positive correlations between the airborne concentrations of Cr and Ni and the corresponding levels of urine for all the exposed. The results indicate punch press workers were at a higher risk of exposure to Cr and Ni, and thread-cutting workers were at higher risk of exposure to Cr. However, exposure to sump fluids did not contribute to the levels of airborne Cr and Ni.

Keywords: Occupational exposure, Metalworking fluid, Chromium, Nickel, Biological monitoring, Urine

1. Introduction

Metalworking fluids (MWFs) are pure mineral oils or water-based fluids poured or sprayed onto metals to lubricate and cool the metals, and to prevent corrosion as well as to remove metal scraps during machining operations. The use of MWFs during mechanical operations results in the formation of aerosols that are associated with adverse health effects, including asthma, hypersensitivity pneumonitis, rectal cancer, rhinitis-related symptoms, and dermatitis (Hodgson et al., 2001; Roff et al., 2004). Until now, most studies have focused on the effects of occupational exposure to MWF bioaerosols, endotoxin -containing particles (Liu et al., 2010) and alkanolamines (Henriks- Eckerman et al., 2007). Only little studies assessed the exposure to metals in industrial settings (Stridsklev et al., 2007).

Workers in metalworking processes such as cutting and grinding environments are exposed to fumes of Cr and Ni. The bodily excretion of absorbed Cr primarily occurs via urine. Therefore, urine was used as a biomarker of the workweek chromium exposure in this study. Health hazards associated with exposure to nickel in the environment are primarily from inhalation. The cutaneous absorption of nickel is quantitatively minor. The biological half-life of soluble nickel in urine following inhalation is reported 17 to 39 hours in humans (Tossavainen et al., 1980). Urinary nickel (Ni-U) levels provide an estimate of recent exposure to soluble nickel compounds and nickel metal powders. Therefore, Ni-U provides an integrative measure of the amount of nickel that has been absorbed in the body from all routes of exposure.

Occupational exposure to Cr and Ni during MWFs operation has not been well characterized through both biological and environmental monitoring. The aim of this study was to investigate the relations between the concentrations of Ni and Cr in the work atmosphere generated by thread-cutting, CNC punch press operation and to compare the airborne levels of Cr and Ni to the corresponding levels in urine.

2. Materials and Methods

2.1. Sampling Plant and Sampling Strategies

This study was investigated at a socket manufacturing plant located in Taichung, Taiwan. The manufacturing of sockets involves several processes, including surface treatment, cutting, grinding, electroplating, cleaning, packaging and shipping. The sites that use MWFs in their operations were chosen as exposed sites. Air samples were taken at the following sites: (1) thread cutting machines, (2) the grinding machine (3) administrative office. All employees had worked in the plant for at least one year and none had any previous work-related exposure to the metals being assessed. The workers involved in the use of MWFs were selected as the exposed group, including 22 thread-cutting workers and 12 punch press operators. Airborne samples were obtained using both IOM personal inhalable aerosol sampler (SKC Inc., Eighty-four, PA, USA) and respirable cyclone sampler. The sampling flow rate was set at 2 L/min, and the sampling time was 8 h for each collected sample. Urine samples were collected from the exposed after each work shift over a five-day workweek. Concentrated NHO_3 was added to the aliquots, which were then stored at -20°C for analysis within two weeks.

2.2. Reagents

All glassware and polyethylene bottles were cleaned by soaking them in 10% HNO_3 and rinsing them three times with deionized water. The deionized water was produced using a Millipore Milli-Q system (Milford, MA, USA), and it was used to prepare all solutions. Both the hydrochloric acid (37%) and the nitric acid (65%) were of suprapure grade (Merck, Darmstadt, Germany). The standard stock solution was an inductively coupled plasma multi-element standard solution IV, containing Cr (III) and Ni (II) (Merck).

2.3. Sample Analysis

All samples were spiked with mixed acids (NHO_3 and HCl) before digestion, and the fluids were spiked only with concentrated nitric acid. All samples were digested using the MARS Xpress microwave digestion system (CEM Corporation, Matthews, USA) at 800 W for 15 min, except for the urine samples, which were digested for 30 min. Metal concentrations were measured with a 2100 DV inductively coupled plasma atomic emission spectrometer (PerkinElmer, Norwalk, USA). The limits of detection were 0.34 μg/L for Cr and 0.43 μg/L for Ni.

2.4. Calibration and Quality Control

The viability and validity of the urine analyses were confirmed using the Standard Reference Material (SRM) 2670a-Toxic Elements in Urine (Nycomed, Oslo, Norway), with recoveries of 90.0–106.0%. We demonstrated the feasibility of the metal analysis using the National Institute of Standards and Technology (NIST) SRM 1084a Wear-Metals in Lubricating Oil. The MWF samples were spiked with metal solutions of known concentrations, and the resulting metal recoveries were 90.7–105.6%. The recovery test for target metals in the filters was the same as for the MWF samples, and the recovery ranged from 91.6% to 105.4%.

2.5. Questionnaires and Statistical Analysis

To assess occupational exposure to the metals measured in MWFs environment, all workers involved in the thread-cutting and punch press operations were invited to participate in a questionnaire. Each worker was asked to describe clinical symptoms, such as coughing, sore throat, nasal irritation, phlegm discharge, sneezing, musculoskeletal coordination and certain nervous system symptoms, associated with exposure to the studied metals (Vitayavirasuk et al., 2005).

Statistical analyses were carried out using the SPSS statistical software package (Version 12.0 for Windows). The log-normality of each concentration for each exposure group was examined using the W-test. Non-parametric Mann-Whitney tests were applied to compare data sets. Spearman's rank correlation tests were used to determine correlations between sequences of pairs of values. A p-value of 0.05 was regarded as the level of statistical significance (two-tailed).

3. Results

3.1. Questionnaire Results

Many clinical symptoms, such as coughing, sore throat, nasal irritation, phlegm discharge, sneezing and some affecting the nervous system, are associated with exposure to certain metals (Vitayavirasuk et al., 2005). The findings revealed a significantly higher prevalence of respiratory symptoms among the exposed workers than the controls, including coughing (29% vs. 0%), nasal irritation (35% vs. 17%), nasal congestion (41% vs. 0%), phlegm discharge (29% vs. 0%) and sneezing (47% vs. 33%). A high occurrence of poor musculoskeletal coordination (6% vs. 0%), irritation and allergic reactions of the skin (6% vs. 0%) and tremors (6% vs. 0%) were also found among the exposed workers.

3.2. Concentrations of Airborne MWF Aerosols

Respirable aerosols were present at a concentrations ranging from 0.04 to 0.12 mg/m^3. The measured inhalable aerosol levels were as follows: thread-cutting sites (0.24 mg/m^3) > punch press sites (0.20 mg/m^3). The measured respirable exposure concentrations for the thread-cutting and punch press sites were 0.12 mg/m^3 and 0.08 mg/m^3, respectively. All the observed concentrations were lower than the permissible exposure level (PEL) adopted by OSHA, NIOSH, ACGIH, HSE, and the government of Taiwan (5 mg/m^3).

The concentrations of airborne Cr (Cr-A), ranging from 6.94 to 56.7 μg/m^3 (Table 1), were lower than OSHA's PEL for total chromium (100 μg/m^3). Levels of of airborne Ni (Ni-A) were also lower than the OSHA PEL for soluble nickel compounds (1000 μg/m^3). Cr-A and Ni-A were all below the current proposed limits of the government of Taiwan, at 100 μg/m^3 and 500 μg/m^3, respectively. The inhalable aerosol concentrations for the workers at the thread-cutting sites were higher than those in the office personnel. As a chemical plant is near this plant which contributed fairly high levels Ni-A outdoors. The high Ni-A and Cr-A in the office could be related to a confined space and insufficient local exhaust ventilation.

3.3. Concentrations of Cr and Ni in Post-shift Urines

There is no BEI for Ni, anf the BEI for Cr is 25 μg/L (ACGIH 2005). In Table 2, the concentrations of Cr-U were variable, and the workers can sometimes be exposed to concentrations above the ACGIH BEI. Cr-U was higher than those of Cr-exposed workers in Taiwan, 3.67 μg Cr/g creatinine (Wu et al., 2006). The post-shift Cr-U and Ni-U for the thread-cutting workers were significantly higher than the controls, with p values of 0.004 and 0.003, respectively. The Cr-U and Ni-U for the punch press operators and the controls also showed a significant difference, p = 0.023 and 0.003, respectively. Our data indicate no significant differences found between the two exposed in Cr-U and Ni-U.

The differences between the urinary levels of metals in a work shift were compared using a Wilcoxon test. Both Cr and Ni in the end-of-shift urine samples showed a tendency to increase over a work shift. This trend was more significant for the thread-cutting workers. However, there was no significant difference in Cr-U and Ni-U among the thread-cutting workers in a work shift. The Spearman's rank correlation analysis indicated that there were positive correlations between Cr-A and Ni-A and the corresponding levels of urine. No correlations were found between the levels of Cr-A and Ni-A in sump fluids at the punch press sites.

3.4. Concentrations of Cr and Ni in Chippings and Sump Fluids

Fe and Zn were the main contents in the chippings and in sump fluids used in this study (Table 3). The Levels of Cr and Ni in sump fluids were higher than those measured in the unused fluids for the exposed sites. This study showed an almost twofold increase in levels of Cr in sump fluids. However, there was no correlation between the levels of Cr-A in the air and in sump fluids at the exposed sites. Levels of Ni in sump fluids at the thread-cutting sites had a negative correlation, but no correlation found at the punch press sites.

4. Discussions

It was reported the occurrence of upper respiratory tract symptoms in workers exposed to MWF mist concentrations within a range of 0.25–0.84 mg/m^3 (Oudyk et al., 2003). The mean concentrations of the respirable mists, ranging from 0.04 to 0.12 mg/m^3, were lower other report (Oudyk et al., 2003). Based on our study, the health hazards imposed on workers in the socket industry should be assessed. The thread-cutting workers were exposed to higher concentrations of MWF mists than the workers at punch press sites; this pattern is similar to other reports (Chen et al., 2007). Elevated aerosols generated at the thread-cutting site could be attributed to the evaporation and condensation that occurs during the thread-cutting process and to the emission aerosols by the impact force. The difference between stamp press and thread cutting was simply the larger volume of MWFs required and the greater degree of aerosolization that occurs during thread cutting. These results were consistent with Simpson et al.'s survey, which concluded that grinding and drilling operations produce greater exposure than turning and milling for water-mix fluids (Simpson et al., 2003). Punch press seemed not to contribute significantly to the uptake of Cr, which may be because most of the Cr in the air at the punch press site was present in the metallic form, with hardly any as Cr(VI), and therefore, had less tendency to be taken up in the airways. The punch press operators' uptake of Ni seemed to be the same as in the thread cutters.

There was a significantly higher prevalence of nasal congestion among the exposed workers than in the controls (41% vs. 0%). This result was consistent with Vitayavirasuk et al.'s report (2005), which occupational exposure to Cr (VI) was associated with symptoms of respiratory irritation and nasal congestion. The Cr-A at the thread-cutting sites were significantly higher than those at the office (p = 0.003) and the punch press sites (p = 0.001). The results indicated a higher occupational risk of exposure to Cr among thread-cutting workers, which may be due to the greater level of water yields from the thread-cutting process. Based on the results, significantly different Cr-U and Ni-U concentrations were found for thread-cutting workers when compared with the controls (p=0.004, 0.003). The mean Cr-U and Ni-U among the punch press workers was higher than in the controls, and the differences reached the level of statistical significance (Table 2). Cr-U and Ni-U have scientific support as an indicator of the occupational exposure level of these metals (Chen et al., 2007). This study indicated the punch press workers were at a higher risk of occupational exposure to Cr and Ni. All the Ni-A exceeded 10 $\mu g/m^3$, indicates the exposed workers may be at risk of low-level occupational nickel exposure. Ni-U among the thread-cutting workers were higher than those reported for residents of areas in Taiwan with a high density of electroplating factories with mean values of 7.86 µg/L (Wilhelm et al., 2004). The high Ni-U in the exposed workers indicates the major source was inhalation, and the workers may be at a risk of occupational nickel exposure. The Spearman's rank correlation analysis indicated the positive correlations between the Ni-A and the levels of urine for all the exposed workers. A positive correlation occurred between the airborne and urine concentrations of Cr for all the exposed workers. The elevation in Cr-U was inferred from the increase in airborne inhalable Cr aerosols for the thread-cutting workers. The inhalable aerosol sampling results could explain the variation in the exposed workers' Cr-U, which approached 87% (Chen et al., 2007). The absorption of Cr(VI) through the skin can cause irritation and allergic reaction, which was found among the exposed workers and the controls. This study confirmed that both the environmental and biological monitoring of urine could be used to assess external and internal exposure to Cr (Kazi et al., 2008).

In this study, levels of Cr and Ni in sumps fluids were higher than in the unused fluids. No correlations between the airborne concentrations of the two metals and the levels of sump MWFs were observed, except for a minor negative correlation between the levels of Cr in sump MWFs at punch press sites. These data indicated that occupational exposure to sump fluids did not contribute to levels of Cr-A and Ni-A, which maybe attributed the to good MWF management.

5. Conclusion

This study is limited to thread cutting and punch press and may not be representative of all metalworking operations. The results indicate the thread-cutting workers had a significantly higher body burden of total chromium than did the controls. This study also shows that the change in urinary excretion of total chromium in a work-shift can be used to evaluate recent exposure to total Cr compounds among all the exposed workers. A positive correlation between Cr-U and Cr-A among the thread-cutting workers indicates that they were at a risk of occupational chromium exposure. The integration of biological and environmental monitoring is an efficient way to measure metal exposure and related impacts on workers' health.

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7. References

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Table 1: Airborne exposure levels of the studied elements (μg/m^3) at the two exposed sites, office.

	Cr		Ni	
	Mean ± S.D	Range	Mean ± S.D	Range
Thread cutting group	48.4*±18.5	6.94~56.7	26.1±11.2	10.2 ~34.1
Punch press group	34.5±19.5	6.94~48.3	24.2±14.0	10.2~38.2
Control group	36.8±12.5	21.3~52.2	35.0±12.0	10.2 ~59.7

[a] Each value is arithmetic mean, and concentrations below the LOQ were calculated as LOQ/2.

Table 2: Biological levels [a] (μg/L) of the studied elements in urine within a work-shift.

	Thread cutting group (n=22)				Punch press group (n=12)				Control group (n=6)			
	Monday		Friday		Monday		Friday		Monday		Friday	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Cr	0.17 ~ 20.2	6.43	2.13 ~ 22.1	9.68*	6.94 ~ 47.6	14.9	6.94 ~ 36.3	16.6*	2.13 ~ 54.8	21.6	2.13 ~ 8.64	5.75
Ni	0.25 ~ 32.3	4.01	10.2 ~ 71.0	17.7*	10.2 ~ 35.6	12.0	10.2 ~ 12.5	10.4*	0.25 ~ 0.25	0.25	0.25 ~ 0.25	0.25

[a] Each value is arithmetic mean, and concentrations below the LOQ were calculated as LOQ/2.

Table 3: Metal concentrations of chips and MWFs from the two exposed sites.

	Thread cutting site			Punch press site		
Metal	metal chippings (μg/mg)	unused MWF (mg/L)	sump fluids (mg/L)	metal chippings (μg/mg)	unused MWF (mg/L)	used MWF (mg/L)
Cr	0.18±0.00	26.4±1.02	46.9±1.94	0.09±0.00	24.1±0.70	29.7±0.41
Cu	0.16±0.00	26.8±1.68	66.6±2.06	0.12±0.00	28.3±1.79	139±2.86
Fe	796±18.3	57.6±5.89	392±50.0	1001±56.7	46.6±1.64	325±18.5
Mn	2.73±0.06	23.9±1.13	38.0±0.43	3.42±0.16	22.6±1.11	32.6±0.25
Ni	0.09±0.00	23.2±1.55	29.6±0.45	0.40±0.01	22.6±1.64	30.0±0.85
Zn	2.73±0.06	77.7±5.26	8650±1061	3.42±0.16	160±8.59	21860±677

[a] Each value is the arithmetic mean of triplicate analyses of three samples.