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Case study of occupational mercury exposure during decontamination of turnaround in refinery plant

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ABSTRACT

Decontamination during turnaround (TA) can lead to high exposure to toxic chemicals among workers. The decontamination process in refinery plants usually comprises two types, i.e. steam and chemical decontamination. No matter the method used, concentrations of toxic chemicals must be measured using the direct reading instrument at the end of each decontamination cycle, which maybe repeated several times until the readings are in acceptable level. To evaluate mercury exposure of decontamination workers during decontamination procedure in comprehensive turnaround of a refinery plant. Thirty personal and 16 area air samples were collected using passive dosimeters and absorbent tubes, respectively, during 8 days of the decontamination in comprehensive turnaround. All samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). Good practices and standard procedures for air sampling and analysis were performed. The TWA concentrations were calculated and compared between steam and chemical decontamination workers. All area samples were well below TLV (ND – 0.0016 mg/m³) while 5 of 14 samples collected at the steam team and 1 of 16 samples taken from the chemical team exceeded the TLV. The geometric mean (GSD) of TWA concentration of the steam team was 0.0057(10.4906) mg/m³, which is about twice as high as that of the chemical team, 0.0031(6.9422) mg/m³. The highest mercury concentration, 0.1037 mg/m³, was collected from a steam decontamination worker. According to the activities and observation, the steam team may have high exposure while reading the chemical concentrations at the end of the decontamination cycle.

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Introduction

Mercury is a chemical of global concern due to its toxicity and prevalence in atmosphere and environment. This rare element occurs naturally in the earth's crust combined with rock, fossil fuels, etc. The concentration of mercury in crude oil, condensate and natural gas varies globally e.g. in the Gulf of Thailand and the Middle East presented 593 µg/kg [1] and 0.8 µg/kg [2] respectively. These products are used as feedstock in petrochemical industries in Rayong Province, Thailand. In 2010, approximately 13,000 kg of mercury was released from anthropogenic sources in Thailand and about 5% was from oil and gas production, e.g. petroleum refineries [3]. The release of chemicals in the environment could occur due to leaks, spills, and fugitive sources during normal operations and maintenance. Certainly chemical exposure during maintenance could be several

times higher than normal work routines and during the comprehensive turnaround (TA) workers could have significant exposure. TA shutdown of refineries to allow for decontamination, repairs, replacements, inspections, and overhauls to increase equipment reliability to maintain production integrity and reduce the risk of catastrophic failures [4–7].

After shutdown, the remaining feeds in the production system will be drained in underground storage tanks to start the decontamination. Two decontamination methods are employed, i.e. chemical and steam. For a unit with high concentration of mercury, chemical decontamination would be employed (Figure 1). The hydrocarbon decontamination chemical is pumped in the cleaning loop to remove residual oil, hydrogen sulfide (H₂S), benzene, combustible gasses, and pyrophoric iron sulfides including mercury accumulated on the

Figure 1. Chemical decontamination process of the studied site.

surface of equipment, parts. Then the system is flushed with water and the wastewater is sent to waste storage tanks or cooled with nitrogen gas. For a unit with high hydrocarbon compounds but low mercury, the steam decontamination method would be used. The process is similar, but hot water and steam are used to flush and purge the system instead of using chemicals, and the wastewater is drained to a storage tank or wastewater treatment system depending on the concentration of the toxic chemicals. No matter of what method is used, the decontamination process will be repeated until the toxic chemicals are at acceptable levels.

Reports have been published of mercury exposure during TA for welding, confined space entry, and manual removal of scale from vessels [8], but not for decontamination. This study focused on mercury exposure during decontamination of decontamination workers in a refinery plant.

Material and methods

Study site and decontamination process

This study was conducted in a refinery plant located in Map Ta Phut District, Rayong Province, Thailand, where a comprehensive turnaround was conducted between May and June 2016. The decontamination work was performed in the first 8 days. The production process and

utilities were divided in five sections. Each section was controlled by each control panel, and only panels 1, 2, 3, and 5 were covered by this study. They comprised 34 chemical decontamination loop systems (15 columns and 32 vessels) located in the same area and each panel comprised several units as shown in Figure 2. Panel 4 was excluded because as utility unit, it does not involve mercury.

When setting up a TA plan, high, and low mercury contaminated equipment or units are identified. The low mercury contaminated units would be cleaned up using the steam method and the chemical decontamination would be employed for those units with high mercury contamination. Decontamination workers were divided in two groups; steam decontamination and chemical decontamination. Decontamination workers of the steam decontamination team measured the concentrations of the toxic chemicals at a manhole using direct reading instruments at the end of each decontamination cycle. The decontamination process ended only when toxic chemical, e.g. mercury and benzene concentrations are lower than their TLV (0.025 mg/m^3 , 0.5 ppm), otherwise the decontamination cycle must be repeated.

Participants

The decontamination workers participating in the study were from two sources; the steam decontamination workers comprised of the refinery plant staff and the chemical team comprised of subcontracted workers. However, both teams were familiar with the work procedures well although some of them had worked in this position less than 1 year. Moreover, the contracted workers must pass the safety training course before recruitment to the TA project. While working in the TA area, they wore working coveralls suits and half face respirators with 3 M mercury cartridges, 6009 for the steam team and 6096 [mercury and organic vapor] for the chemical team.

Due to short duration of TA execution and high intense work, the work ran around the clock. For the two shifts, workers were split in two teams, day and night shifts. Both worked for 12 h daily everyday throughout 58 days of the TA project.

Sampling strategy

Approximately 110 decontamination workers were employed each shift, 70 in the chemical team and 40 in the steam team. Thirty passive sampling badges (SKC Inc., model # 520-02A, Lot No. 9962) were attached at the coverall collar of 16 steam decontamination workers and 14 chemical decontamination workers when they signed in to work and collected before they left the TA site. Sixteen Hydrar packed sorbent tubes (Carulite, Lot 10187 Cat. No. 226-17-1A) were used to collect area air samples according to the NIOSH method #6009. The air

Note: Panel 1: Crude Distillation Unit (CDU), High Vacuum Unit (HVV), Visbreaker Unit (VBU), Hydrodesulphurization Unit (HDS) and HDS fractionation Section (HDF); Panel 2: Crude Re-contacting Unit (CDR), Naphtha Hydrotreater (NHT), Platformer Unit (PLF), LPG Treating Unit (LPG); Panel 3 consists of Hydrocracking Unit (HCU), HCU Fractionation section (HCF), Adip Regeneration Unit (ADIP), Sulfur Recovery Unit (SRU), Shell Claus Off-gas Treating (SCOT) and Sour Water Stripping (SWS); Panel 4: Hydrogen Manufacturing Unit (HMU), Hydrogen Purification Unit (PSA), Raw/Potable/Service Water System, Steam Generation & Distribution Unit, Boiler Feed System and Nitrogen System and Panel 5: Condensate Residue Splitter (CRS), Kerosene Mercox Unit (KMU) and Deep Hydrodesulphurization Unit (DHDS).

All workers who carried the badge were informed about the study and asked for their voluntary enrollment before signing a consent form approved by the Ethics Committee on Human Rights Related to Human Experimentation, Mahidol University. This research proposal was reviewed and approved under No. MUPH 2016-029.

The analyzer was an ICP-MS (Agilent 7500 series, JP82802997); thus, the sample preparation procedure in ID 140 [9] and NIOSH method #6009 [10] were modified so that the samples were suitable for the analyzer. A series of known concentrations of 2.5, 5, 10, 15, 20, and 25 ppb [mercury standard solution, $\text{Hg}(\text{NO}_3)_2$], were used to prepare standard curves. The r^2 of the linear regression of the standard curve was 1. The LOD was less than $0.3 \mu\text{g}/\text{m}^3$, and the desorption efficiency ranged in

The data were analyzed and described using descriptive statistics, e.g. mean and standard deviation. Correlations between variables were assessed using Pearson's correlations coefficient. Differences of mercury exposure between groups was assessed using the paired simple *T*-test, Mann–Whitney test, and the Kruskal–Wallis test, respectively. Furthermore, to analyze all data, the “not detected (ND)” samples were replaced with half of the LOD [11]. Statistical analyses were performed using the software package SPSS, version 22.0v.

Due to the nature of the refinery plant, the production process was established outdoors; therefore, air movement in the site could affect chemicals concentration. The results of the air samples collected and analyzed for mercury are presented in Table 1. Among 16 area

Table 1. Mercury concentrations in air samples collected during system decontamination.

Panel	Area sample			Steam decontamination workers			Chemical decontamination workers		
	Sampling area	Date ^a	Hg conc. (mg/m ³)	Responsibility area	Date ^a	Hg conc. (mg/m ³)	Responsibility area	Date ^a	Hg conc. (mg/m ³)
1	CDU, De-salter # 1	3rd	ND	CDU, HVU, VBU, HDS, HDF	2nd	0.0646	CDU, De-salter	3rd	0.0116 ^{b e}
	CDU, De-salter # 2	3rd	ND		3rd	0.0046	CDU, De-salter	3rd	ND ^b
	CDU, V1093, C1091	6th	ND		4th	ND	CDU, V1093, C1091	6th	0.0211 ^b
	CDU, V1691, V1693	6th	ND		6th	0.0027	CDU, V1093, C1091	6th	0.0128 ^b
	CDU, FFU4, T5542	8th	ND						
2	CDR, V1053	1st	0.0005	CDR, NHT, PLF	1st	0.0020	CDR, S1402	2nd	0.0017 ^b
	CDR # 1	2nd	ND		5th	ND	CDR, S1402	2nd	0.0027 ^c
	CDR # 2	2nd	ND		5th	0.0034			
	NHT, S1402	2nd	0.0016		7th	ND			
3	ADIP, C2001	5th	ND	HCU, ADIP, SRU	1st	0.1037	AD-IP, C2001, C2051	5th	0.0093 ^b
	SCOT, C2301	5th	ND		3rd	0.0457	SCOT, C2301, V2301	5th	0.0116 ^d
							SCOT, C2301, V2301	5th	0.0060 ^c
5	CRS # 1	1rd	0.0006	CRS, KMU, DHDS	4th	0.0609	CRS, C2501	1st	0.0102 ^b
	CRS # 2	1rd	0.0008		5th	0.0237	CRS, C2501	1st	ND ^b
	DHDS, C2804 # 1	4th	ND		6th	0.0381	CRS, V2501	7th	0.0065 ^b
	DHDS, C2804 # 2	4th	ND		7th	0.0094	CRS, V2501	7th	ND ^b
	DHDS, V2808	4th	ND				CRS, V2501	8th	ND ^b
							DHDS, C2804	4th	0.0329 ^b
							DHDS, C2804	4th	0.0078 ^b

Note: ND: not detected, (LOD $\leq$ 0.0003 mg/m³).

^aSampling date.

^bChemical cleaning.

^cSet up pipe system of chemical cleaning.

^dSafety supervision.

^eMaintenance.

samples, only 4 were detectable and the highest concentration was 0.0016 mg/m³, which was lower than the TLV. Thus, workers in the TA site not involved with the system decontamination were less likely to be exposed to mercury above TLV.

Six members of the decontamination team were exposed to mercury above the TLV, and one of these was in the chemical team. The highest exposure (0.1037 mg/m³) was among the steam decontamination worker who operated near the HCU, ADIP, and SRU Units, whereas the highest among the chemical team was 0.0329 mg/m³ obtained from a worker who cleaned at the DHDS Unit, C2804 of panel 5. The statistical characteristic of the mercury concentrations are presented in Table 2. The data of all mercury concentrations, comprising log normal distribution. Mann–Whitney test was used to

analyze the difference between the median of TWA concentrations of the steam and the chemical teams, showed no significant differences (p -value = 0.357), while those of the area and the personal samples analyzed by paired simple T -test differed significantly (p -value = 0.001). In addition, the Kruskal–Wallis test was used to analyze the difference between mercury exposures of workers in each panels presented in Table 3. The median values of mercury exposure of workers working in each panel did not significantly differ (p -value = 0.060).

Discussion

Chemical concentrations in the decontamination area were anticipated to be high due to the activities of decontamination; thus, area samples were collected

Table 2. Summary of statistical characteristics and test of the data.

Sample	<i>n</i>	Mercury concentration (mg/m ³)						<i>p</i> -value
		Median	AM	SD	GM	GSD	Range	
Personal sample								0.357 ^a
Steam team	14	0.0070	0.0256	0.0324	0.0057	10.4906	ND-0.1037	
Chemical team	16	0.0071	0.0084	0.0088	0.0031	6.9422	ND-0.0329	
Area sample								0.001 ^b
Area	16	0.0002	0.0003	0.0004	0.0002	2.1723	ND-0.0016	

Note: ND: not detected (significance at p -value < 0.05).

^aBy Mann–Whitney Test.

^bDifferent test of area and personal sample (paired sample- t test).

Table 3. Mercury exposure of workers in each panel.

Panel	N	Mercury exposure (mg/m ³)						p-value
		Median	AM	SD	GM	GSD	Range	
1	8	0.0081	0.0147	0.0214	0.0039	2.6379	ND-0.0646	0.060
2	6	0.0018	0.0014	0.0015	0.0006	1.9667	ND-0.0034	
3	5	0.0116	0.0353	0.0415	0.0198	1.6811	ND-0.1037	
5	11	0.0094	0.0173	0.0195	0.0048	2.7532	ND-0.0609	

Notes: AM; arithmetic mean, SD; standard deviation, GM; geometric standard deviation; ND: not detected; The mean difference was significant at *p* level 0.05.

to estimate exposure. Moreover, higher mercury concentrations than those of the personal samples were expected because they were at the site at all times. However, the result showed an incompatibility between area and personal sampling, i.e. mercury concentrations obtained from the area samples were significantly different and lower. This could be because the work was conducted in a well ventilated area [12] and another possibility is the contamination of the workers clothing with mercury-contaminated wastewater or chemicals which lead to continued exposure associated with evaporation of mercury from the contaminated clothing [13].

Based on the statistical analysis, both teams had similar exposure; however, most exceeding TLV samples, five of six, were collected from the steam decontamination team. Interestingly, the chemical decontamination team worked with higher mercury contamination units but did not exhibit elevated exposure. Thus, it seems unlikely that the high mercury exposure among the steam decontamination team would result from decontamination activities. The activity apart from the decontamination of the steam decontamination team included measuring toxic chemicals in the manhole at the end of the decontamination cycle, both for steam and chemical decontamination. The highest mercury exposure involved the steam decontamination workers responsible for toxic chemical measurement and steam decontamination at the HVU, ADIP Unit, and SRU of panel 3.

Another possibility of exposure source of the steam decontamination workers could have been the drainage of wastewater after purging the system; wastewater with low concentrations of toxic chemicals would be drained for wastewater treatment. Because the wastewater was hot and agitated due to the movement, mercury vapor could have been released from the wastewater [14–15].

Conclusion

Mercury exposure was several times higher than the TLV and the highest levels were found among steam decontamination workers. Potential exposure sources could be the decontaminated units when measuring toxic chemical concentrations and in the wastewater drained in the water treatment system.

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