Biomonitoring of CdTe PV Manufacturing and Recycling Workers

Parikhit Sinha¹, Michael Fischman², Jim Campbell¹, Gaik Cheng Lee³, Lein Sim Lim³

¹First Solar, Tempe, AZ, 85281, USA, ²University of California San Francisco, San Francisco, CA, USA 94143, ³First Solar, Kulim, Kedah Darul Aman, Malaysia, 09000

Abstract — Biomonitoring data from nearly 3,000 workers over a five year period (2009-2014) from First Solar's CdTe photovoltaics manufacturing and recycling facility in Malaysia were evaluated to determine longitudinal trends in the body burden of Cd in workers. Biomonitoring data consisted of baseline and periodic sampling of blood and urine Cd, with workers grouped according to gender, smoking status, and potential occupational exposure risk to Cd compounds. Average worker blood and urine Cd concentrations were below occupational biological limits and background values, and show a statistically significant decreasing trend as a function of years worked for non-smokers. For smokers, smoking is the predominant factor affecting blood Cd results among First Solar Malaysia workers.

Index Terms — manufacturing, thin films, photovoltaic cells, occupational health, cadmium compounds.

I. INTRODUCTION

First Solar manufactures thin film cadmium telluride photovoltaic (PV) modules in facilities in the United States and Malaysia. The manufacturing process involves the three main steps of semiconductor deposition, cell definition, and final assembly. Since pilot scale operations began over a decade ago, First Solar has maintained comprehensive safety, industrial hygiene, and occupational health programs to manage worker health and safety, and control exposure to Cd compounds [1]. Due to the use of engineering controls such as enclosed tools equipped with high efficiency particulate air (HEPA) filtration systems, indoor air concentrations of cadmium compounds are maintained at levels over an order of magnitude below permissible exposure limits (PELs) [2]. During tool maintenance operations, personal protective equipment (PPE) including respiratory protection is used to control exposure. Based on the use of these engineering controls and measured indoor air quality, the body burden of Cd in workers is not expected to increase as a function of years worked at First Solar manufacturing facilities. The objective of this study is to test this hypothesis using worker biomonitoring data from First Solar's largest manufacturing and recycling facility (Kulim, Malaysia).

II. METHODS

Biomonitoring data from nearly 3,000 workers over a five year period (2009-2014) were evaluated for longitudinal trends (Table 1). Biomonitoring data consisted of approximately 11,000 individual samples of both blood Cd (detection limit 0.1 μ g/L) and urine Cd (detection limit 0.1 μ g/g creatinine; Cr), where blood Cd is an indicator of recent exposure (over several months) to Cd compounds, and urine Cd reflects cumulative chronic exposure (over several years).

TABLE I DEMOGRAPHICS OF FIRST SOLAR MALAYSIA MANUFACTURING AND RECYCLING FACILITY

Demographic Characteristics	Number partici		
Overall Total	2,936		
Gender			
Female	439	(15%)	
Male	2497	(85%)	
Average Age During Years Worked			
20-29	1897	(65%)	
30-39	853	(29%)	
40-49	129	(4%)	
50+	12	(<1%)	
Not Available	45	(2%)	
Current Smoking Status			
No	1549	(53%)	
Yes	1252	(43%)	
Not Available	135	(5%)	
Potential Exposure Risk Group			
Low	375	(13%)	
Medium	1667	(57%)	
High	894	(30%)	
Samples	%	> detection limit	
Blood Cd	10908	(62%)	
Urine Cd	10761	(54%)	

The worker population consists mainly of young male associates, approximately half of whom are smokers. The smoking rate among workers (43%) is similar to that in the general male population in Malaysia (44%) [3]. In addition to gender and smoking status, workers were also grouped according to potential exposure risk to Cd compounds. The group considered to have high exposure potential were those involved in the production and maintenance of the semiconductor deposition process, equipment engineering, and

recycling. The medium exposure potential group included all other workers directly involved in PV module production as well as other workers spending more than 25% of their time on the manufacturing floor (facilities, wastewater, manufacturing engineering, environmental health and safety workers). The low exposure potential group had little or no potential exposure as they worked in offices or non-manufacturing areas in which Cd compounds were not utilized. As such, the low exposure potential group functioned as a control group in this study.

Replacement values for non-detect samples were imputed using lognormal regression-on-order (ROS) statistics in USEPA ProUCL (V. 4) software [4], in which the distribution of detected samples was used to estimate values for non-detect samples. The ROS method is an improvement over simple substitution of non-detect values with values that are half the detection limit, where the latter skews the variability of the data by resulting in numerous repeated values. Simple substitution is not recommended when non-detect samples represent more than 15% of the data [5]. Each employee's sampling history was treated as a unique data set when imputing replacement values for non-detect samples, an approach that maintained the suitability of the data for longitudinal statistics. The chronological sample order was randomized in order to prevent the creation of artificial chronological trends when imputing replacement values for non-detect samples. In cases where an employee's sampling history contained too few samples or too few detected samples for ROS statistics, simple substitution with half the reporting limit was used.

III. RESULTS AND DISCUSSION

A. Baseline

Average baseline blood and urine Cd, representing preemployment body burden of Cd, are summarized in Figures 1 and 2. Figure 1 indicates that smokers have a significantly higher blood Cd baseline than non-smokers, consistent with inhalation exposure to the Cd content in tobacco leaves [6]. Average baseline urine Cd does not differ significantly by smoking status (Figure 1), perhaps due to the predominance of young workers that have not yet had long-term chronic exposure to Cd content from smoking. Figure 2 indicates that females have a significantly higher blood and urine Cd baseline than males, consistent with background population statistics [7]. The U.S. OSHA occupational biological limits for blood and urine Cd are 5 μ g/L and 3 μ g/g Cr, respectively.

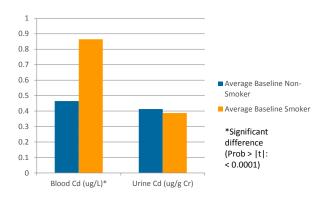


Fig. 1. Baseline blood and urine Cd by smoking status

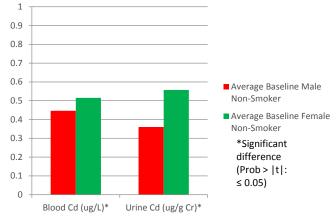


Fig. 2. Baseline blood and urine Cd by gender

B. Effect of Smoking

As indicated in the baseline data, smoking is expected to elevate blood Cd concentrations. In Figure 3 workers are grouped by exposure risk group. This figure shows that during their employment history, smokers on average have three to four times the blood Cd concentration of non-smokers. For non-smoking workers, average blood Cd concentrations for medium and high exposure risk workers during their employment history are not significantly higher than those for low exposure risk workers. As with the baseline data, the urine Cd concentrations during employment do not differ significantly by smoking status for each exposure risk group (Figure 4).

		Blo	ood Cd Delta	(ug/L) per	Years Wor	ked	Urine Cd Delta (ug/g Cr) per Years Worked					
Smoker	Risk Group	Slope	Standard Error	DF	t Value	Pr > t	Slope	Standard Error	DF	t Value	Pr > t	
n	1Low	-0.096	0.020	620	-4.9	<.0001*	-0.066	0.019	607	-3.4	0.0007*	
У	lLow	0.113	0.056	306	2.02	0.0442*	-0.039	0.027	305	-1.44	0.1505	
n	2Med	-0.054	0.007	2808	-7.34	<.0001*	-0.038	0.007	2784	-5.56	<.0001*	
У	2Med	0.111	0.016	2100	6.91	<.0001*	-0.031	0.007	2082	-4.48	<.0001*	
n	3High	-0.068	0.011	2069	-6.29	<.0001*	-0.047	0.007	2043	-6.71	<.0001*	
У	3High	0.105	0.017	2626	6.36	<.0001*	-0.031	0.010	2594	-3.04	0.0024*	

TABLE II BLOOD AND URINE Cd DELTA BY YEARS WORKED

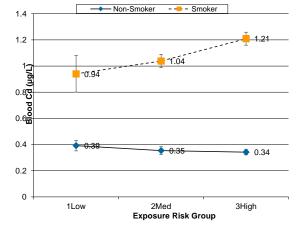


Fig. 3. Average blood Cd by exposure risk group and smoking status (occupational limit of 5 μ g/L)

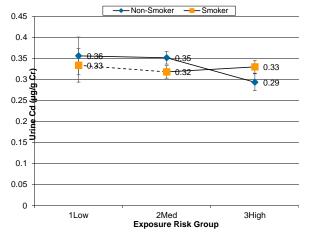


Fig. 4. Average urine Cd by exposure risk group and smoking status (occupational limit of 3 $\mu g/g Cr$)

C. Effect of Years Worked

The effect of years worked was evaluated by considering the change (delta) in blood and urine Cd compared to a

When blood Cd delta was regressed worker's baseline. against years worked, the slope of the best-fit line was negative for non-smokers and positive for smokers for all exposure risk groups (Table II). As indicated by the probability (Pr) values in Table II, the slope of the best-fit line for non-smokers is both negative and significantly different than a zero-slope, indicating a statistically significant decrease in blood and urine Cd delta for non-smokers for all exposure risk groups (Figures 5 and 6). In contrast, smokers show a statistically significant increase in blood Cd delta, while the trend for urine delta is similar for non-smokers and smokers (Table II). Since the low exposure risk group is effectively a control group and since it also shows a declining trend for blood and urine Cd delta, the cause for the decline may be due to improving background public health conditions in Malaysia. Consistent with this notion, general population data in the U.S. have revealed decreasing blood and urine cadmium results over time [7].

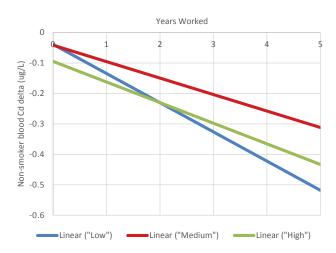


Fig. 5. Non-smoker blood Cd delta as a function of years worked for low, medium, and high exposure risk groups.

COMPARISON OF WORKER BIOMONITORING RESULTS WITH BACKGROUND DATA IN MALAYSIA AND THE UNITED STATES									
	Sample Years	Smoking status	Arithemetic mean (95% confidence interval)	Geometric mean (95% confidence interval)	50th percentile	75th percentile	90th percentile	95th percentile	Sample size
This study: most recent	2009-2014	Smokers and non-smokers	0.651 (0.616-0.687)	0.213 (0.200-0.227)	0.190	0.900	1.800	2.519	2904
blood Cd (µg/L)		Non-smoker	0.252 (0.230-0.273)	0.098 (0.091-0.106)	0.050	0.250	0.760	1.130	1535
Malaysia adult women blood Cd (µg/L) [8]	1991-1998	Non-smoker	-	0.74	-	-	-	-	47
U.S. 20 years and older blood Cd (µg/L) [7]	2011-2012	Smokers and non-smokers	-	0.337 (.323353)	0.300	0.550	1.140	1.700	5030
This study: most recent	2009-2014	Smokers and non-smokers	0.271 (0.259-0.283)	0.139 (0.133-0.146)	0.100	0.390	0.633	0.860	2882
urine Cd (µg/g Cr)		Non-smoker	0.275 (0.257-0.292)	0.138 (0.129-0.146)	0.100	0.390	0.669	0.981	1527
Malaysia adult women urine Cd (µg/g Cr) [8]	1991-1998	Non-smoker	_	1.51	-	-	-	-	47
U.S. 20 years and older urine Cd (µg/g Cr) [7]	2009-2010	Smokers and non-smokers	-	0.229 (0.213-0.245)	0.230	0.430	0.790	1.13	2019

TABLE III Comparison of Worker Biomonitoring Results with Background Data in Malaysia and the United States

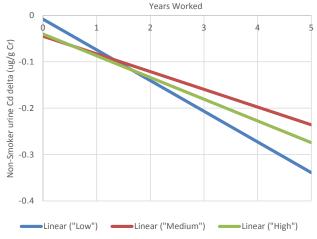


Fig. 6. Non-smoker urine Cd delta as a function of years worked for low, medium, and high exposure risk groups.

D. Background Comparisons

Worker biomonitoring data were compared with background data from the general population in the United States [7] and Malaysia [8] (Table III). The worker geometric mean blood and urine Cd values were below background values for both countries. The worker 50th to 95th percentile blood and urine Cd values were generally lower than background values in the U.S. In the case of blood Cd, non-smoking worker 75th to 95th percentile values were below background values (for smokers and non-smokers combined) in the U.S., whereas the same percentiles for all workers (smoking and non-smoking) were above background values in the U.S. These varying results may be partly due to a difference in the smoking rate in workers in this study (43%) and that in the U.S. general population (~20% over the sample years 2011-2012) [9]).

E. Analysis of variance

Based on analysis of variance (ANOVA) results, there are some statistically significant variations in delta blood and urine Cd by gender, smoking status, exposure risk group, and years worked (Table IV). However, there are no cases of positive mean delta blood or urine Cd for non-smokers, and non-smokers in the medium and high exposure risk groups have similar or greater decreases in blood and urine Cd (negative mean delta values) as compared to the low exposure risk group.

ANOVA of statistical outliers (blood and urine Cd samples exceeding the 95th percentile) was conducted to determine if there were statistically significant variations in outlier values among non-smokers by exposure risk group. No significant variations were found for urine Cd (Prob>F: 0.325), but a significant variation was found for blood Cd (Prob>F: 0.016), with a significantly higher mean outlier blood Cd concentration in the medium exposure risk group than the low and high exposure risk groups. Because the number of blood Cd outlier samples among non-smokers was small (less than 25 in each exposure risk group), it was possible to investigate the medical history of each of the workers with outlier samples. Upon closer investigation, it was found that most of these workers had been designated non-smokers despite being current smokers, providing further evidence of the importance of this variable.

Delta blood and urine Cd for workers with a true baseline (onset of employment after the biomonitoring baseline date of April, 2009) were compared by ANOVA to data for workers that started employment prior to the biomonitoring baseline date (Table V). There are some statistically significant differences in delta blood and urine Cd by true baseline. However, there are no cases of positive mean delta blood and urine Cd for non-smokers. An exception is for urine Cd for the low exposure risk group with true baseline, where the latter value is not significantly different from zero given the magnitude of the standard error relative to the mean.

		Blood Cd Delta (ug/L)							Urine Cd Delta (ug/g Cr)					
Gender	Smoker	Risk Group	Years Worked	Mean	Standard Error	DF	F Ratio	Prob > F	Mean	Standard Error	DF	F Ratio	Prob > F	
		1Low		0.029555	0.03731				-0.07798	0.0214		22 2.4619	0.0853	
		2Med		0.092064	0.01633	10904	1.2813	0.2777	-0.09532	0.00935	10722			
		3High		0.092203	0.01663				-0.11929	0.0095				
	n			-0.16945	0.01348	10504	500 4070		-0.11439	0.00841	10400	c	0.00014	
	У			0.27888	0.01409	10534	528.4973	<.0001*	-0.08267	0.00878	10420	6.8032	0.0091*	
f				-0.15505	0.03086	10004	50 4005		-0.17698	0.01756	10700	10 5000		
m				0.12239	0.01188	10904	70.4005	<.0001*	-0.0936	0.00682	10722	19.5832	<.0001*	
			(-0.01089	0.02106				-0.01059	0.01197				
			1	0.12632	0.02337				-0.1154	0.01336		2 20.1863		
			2	0.17292	0.02489				-0.11837	0.01427			3 <.0001*	
			3	0.026	0.03375	10904	8.9887	<.0001*	-0.17987	0.01931	10722			
			4	0.09096	0.03263				-0.17852	0.01857				
			5	0.18151	0.04097				-0.16451	0.02331				
	n	lLow		-0.13157	0.02763				-0.07217	0.02236		36 4.9322	2 0.0072*	
	n	2Med		-0.12428	0.01299	5499	18.5209	<.0001*	-0.10326	0.01045				
	n	3High		-0.24212	0.01513				-0.14211	0.0122				
	У	lLow		0.241961	0.07154				-0.08774	0.03928	-	83 0.0701	L 0.9323	
	У	2Med		0.274625	0.02735	-	0.195	0.8228	-0.07842	0.01506				
	У	3High		0.286594	0.02446				-0.08549	0.01349				
f	n			-0.15759	0.01861	5 4 6 6	0 5403	0.4616	-0.16466	0.01503	5400	14 0701		
m	n			-0.17341	0.01076	5499	0.5421	0.4616	-0.09787	0.00861	5436	14.8701	0.0001	
f	У			0.048905	0.32362				0.00345	0.17739				
m	У			0.279565	0.01769	5034	0.5065	0.4767	-0.08293	0.00975	4983	0.2364	0.626	
	n		0	-0.00343	0.01673				-0.00545	0.0135				
	n		1	-0.14725	0.01899				-0.11792	0.01538				
	n		2	-0.24102	0.0208	5 4 6 6	40 2220		-0.14828	0.01699	5 4 9 6		<.0001	
	n		10	-0.42836	0.03087	5499	40.7778	<.0001*	-0.22722	0.02499	5436	22.8568	<.0001	
	n		4	-0.28255	0.02754				-0.18223	0.02232				
	n			-0.2432	0.03287				-0.21857	0.02647				
	У		C	-5.55E-05	3.47E-02				0.00173	0.0192				
	У		1	2.73E-01	3.75E-02				-0.09128	0.02077				
	У		2	4.23E-01	3.90E-02	E 0 0 4	04 6400	< 0001 t	-0.07886	0.02164	4000			
	У		3	2.61E-01	4.86E-02	4.86E-02 5034 24.6493 <.0001*	4983	7.074	4 <.0001*					
	У		4	4.09E-01	4.92E-02		-0.16976	0.02744						
	У		5	6.75E-01	6.45E-02				-0.10198	0.0361				

TABLE IV Anova of Blood and Urine Cd Delta by Gender, Smoking status, Exposure Risk Group, and Years Worked

 TABLE V

 ANOVA OF BLOOD AND URINE CD DELTA BY TRUE BASELINE

			Blood Cd Delta (ug/L)					Urine Cd Delta (ug/g Cr)					
Smoker	Risk Group	True Baseline	Mean	Standard Error	DF	F Ratio	Prob > F	Mean	Standard Error	DF	F Ratio	Prob > F	
n	1Low	No	-0.13943	0.02523	619	0.3296	0.5661	-0.10612	0.02484	606	6.3782	0.0118*	
n		Yes	-0.11275	0.03904	019			0.00983	0.03861				
n	2Med	No	-0.15937	0.01533	2807	10 0000	12.9282 0.0003* -	-0.15021	0.01423	2783	26.8221	<.0001*	
n		Yes	-0.07275	0.01858		12.9202		-0.0346	0.0172				
n	3High	No	-0.19613	0.02259	2068	10.4515 0.0	0.0012*	-0.18154	0.01471	2042	18.0552	<.0001*	
n		Yes	-0.31209	0.02786			0.0012^	-0.0824	0.01811				
У	1Low	No	0.272234	0.06863	205		0.3529	-0.09421	0.03326	304	0.1677	0.6825	
У		Yes	0.137539	0.12746	305	0.8658		-0.06553	0.06164				
У	2Med	No	0.373551	0.03519		1.6 . 600.6	4 00014	-0.10229	0.01511	2081	5.2658	0.00104	
У		Yes	0.164662	0.0371	2099	16.6886	<.0001*	-0.05195	0.01591			0.0218*	
У	3High	No	0.59143	0.03383	2625	181.721	< 0001+	-0.12072	0.02166		5.9173	0.0151*	
У		Yes	-0.09069	0.03763		181./21	<.0001*	-0.0419	0.0241	2593		0.0151*	

IV. CONCLUSION

Based on biomonitoring data from nearly 3,000 workers over a five year period (2009-2014) at First Solar's manufacturing and recycling facility in Malaysia, worker blood and urine Cd concentrations were below occupational biological limits and background values, and show a statistically significant decreasing trend as a function of years worked for non-smokers. For smokers, smoking is the predominant factor affecting blood Cd results among First Solar Malaysia workers. In conclusion, the environmental controls combined with the health and safety practices at First Solar are effective at controlling occupational exposure to cadmium compounds. Analysis of biomonitoring data provided useful information regarding the adequacy of controls, complementary to industrial hygiene data.

REFERENCES

 J. Bohland, and K. Smigielski, "First Solar's CdTe module manufacturing experience; environmental, health and safety results," in 28th IEEE Photovoltaic Specialists Conference, Anchorage, AK, 2000.

- [2] L.S. Lim, "Photovoltaic Cadmium Telluride Technology Exposure Assessment," in 9th IOHA International Scientific Conference, Kuala Lumpur, Malaysia, 2012.
- [3] Institute for Public Health, "Report of the Global Adult Tobacco Survey (GATS) Malaysia, 2011," Ministry of Health Malaysia, Kuala Lumpur, 2012.
- [4] U.S. Environmental Protection Agency, "ProUCL Version 4.00.05 User Guide," Office of Research and Development, Washington, D.C., 2010.
- [5] P. Sinha, M.B. Lambert, and V.L. Trumbull, "Evaluation of Statistical Methods for Left-Censored Data with Non-Uniform Detection Limits," *Environmental Toxicology and Chemistry*, vol. 25, no. 9, pp. 2533-2540, 2006.
- [6] D. Bernhard, A. Rossmann, and G. Wick, "Metals in Cigarette Smoke," *IUBMB Life*, vol. 57, no. 12, pp. 805-809, 2005.
- [7] Centers for Disease Control and Prevention, "Fourth National Report on Human Exposure to Environmental Chemicals, Updated Tables, February 2015," U.S. Department of Health and Human Services, Atlanta, GA, 2015.
- [8] M. Ikeda, Z.W. Zhang, S. Shimbo T. Watanabe, H. Nakatsuka, C.S. Moon, N. Matsuda-Inoguchi, and K. Higashikawa, "Urban population exposure to lead and cadmium in east and south-east Asia," *The Science of the Total Environment*, vol. 249, pp. 373-384, 2000.
- [9] A. Jamal, D.M. Homa, E. O'Connor, S.D. Babb, R.S. Caraballo, T. Singh, S.S. Hu, and B.A. King, "Current Cigarette Smoking Among Adults — United States, 2005–2014" *MMWR Morbidity* and Mortality Weekly Report, vol. 64, no. 44, pp. 1233-1240, 2015.

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TITLE OF PAPER/ARTICLE/REPORT: Biomonitoring of CdTe PV Manufacturing and Recycling Workers COMPLETE LIST OF AUTHORS: Sinha, Parikhit; Fischman, Michael; Campbell, Jim; Lee, Gaik Cheng; Lim, Lein Sim IEEE PUBLICATION TITLE (Journal, Magazine, Conference, Book): 43^d IEEE Photovoltaic Specialists Conference LINK TO FINAL PUBLICATION: <u>http://ieeexplore.ieee.org/Xplore/home.jsp</u>