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Abstract: The Department of Defense's (DOD's) Chemical and Materials Risk Management (CMRM) Directorate is using a scan-watch-action process to identify, rank and manage risks associated with emerging contaminants. Naphthalene is characterized as a likely human carcinogen by the National Toxicology Program (NTP) and in the Environmental Protection Agency's (EPA's) most recent draft health risk assessment. Thus, naphthalene-related environmental health regulations are evolving. The potential impacts have been assessed, using multi-criteria decision analysis, for five of the DOD's functional areas. One of the areas of concern is exposure to naphthalene among fuel handlers. To determine whether these exposures present unacceptable risk, the Army Research Office awarded a Small Business Innovative Research (SBIR) Project for the development of a miniature real-time naphthalene sensor. The National Institute of Occupational Safety and Health's (NIOSH's) Biomonitoring Research Team and investigators from the Army Research Institute for Environmental Medicine, University California-Davis, Temple University, and the Army Corps of Engineers are collaborating on related projects. The research will validate the prototype sensor as a dosimeter by defining correlations between measured exposures and biomarkers of exposures to-be-collected from military fuel handlers. To date, naphthalene specificity with sensitivity of 0.5 mg/m³ has been demonstrated and definition of the firmware chemometrics is underway. Implementation of the human subjects research protocol is pending institutional review boards' (IRBs') approval.

Introduction: The NTP conducted a series of rodent exposure studies between 1985 and 2002. In 2005, the EPA published a draft risk assessment that characterized naphthalene as a likely human carcinogen based on results from these and other rodent studies. The DOD CMRM Directorate subsequently assessed the potential impacts to five DOD functional areas and implemented risk management options that included funding projects that will develop and validate a naphthalene dosimeter. In addition to the DOD, the Army, National Institute of Environmental Health Sciences (NIEHS), National Science Foundation (NSF) and NIOSH are each funding components of the research. Collaborating scientists are from the Army Corps of Engineers, Army Research Office, Army Research Institute of Environmental Medicine, CDC Foundation, NIOSH, University of California-Davis and Temple University. Several other Defense organizations are represented on an interagency advisory committee.



 2006_{Na}

natene State of the Science Meeting, 10/06



Potential impact to DOD's occupational health programs: Naphthalenes are 1-3 % of iet fuels and DOD's annual consumption is approximately 5 billion gallons. In 2002, the National Research Council reported that P8 fuel is likely the largest chemical exposure war fighters experience.



Potential impacts to DOD's environmental restoration programs: If the EPA's draft risk assessment is finalized as written, a cancer potency value will be developed for the first time. New screening values for the evaluation of the vapor intrusion pathway will also be developed. The additional risk assessments may increase the cost to complete remediation and old sites may need to be reassessed. The EPA's health risk assessment is to be finalized in 2012.

An advisory group was chartered in 2008 in the Office of the Deputy Under Secretary of Defense for Installations and Environment. The Group will guide the development of the dosimeter and ensure best return on the agencies' investments.

9/06-09/07: Noblis, the Corps of Engineers and others take part in the Directorates's first Phase I Impact Assessment. It's on naphthalene.

Action taken by the

DOD Chemical & Materials Risk Management Directorate:

2005



The Naphthalene Dosimeter Advisory Group

Janis Hulla, PhD, DABT (Chair) Senior Toxicologist, Sacramento District

U.S. Army Corps of Engineers



Photon Systems' innovations include applying newly developed light emitting diodes (LEDs) to generate deep UV excitation of naphthalene's native fluorescence. This analytical approach offers the advantage of a favorable signal to noise ratio since there is little natural background fluorescence in this region of the spectrum as shown in the illustration below. Diodes being developed offer improved illumination of the target molecules.

Photon Systems' naphthalene dosimeter concept



The performance of bench scale prototypes will be evaluated against GS/SM analyses of test atmospheres generated in an exposure chamber.

Figure 4. Chemometric Differentiation of volatiles found in JP-8 using only 6 discrete fluorescence

Up to six different diodes may be incorporate to

principal component analysis.

ensure the naphthalene-specificity illustrated by this

6/07: The SBIR project is solicited

12/07: Two SBIR Phase I Awards, \$100K/6mo, each 9-11/08: SBIR projects are evaluated for Phase II award

2008

12/08: Photon Systems Awarded Phase II project

12/07: The CMRM Directorate forms the Naphthalene Dosimeter Advisory Group.

4/08-11/09: CTC conducts the Directorates's Phase II Impact Assessment

Conc. by prototype dosimeter

Biomarker								Under NEHSJRB	
study		Number of		Nunberaf	Number of	Number of exhaled	Number of	approval- Number of	
Phase I	Number of Bases	Samplers per Area	Number of Dase	Subjects at each base	Areasper	samples per day	urine voids	Nasal	Total # Samles
		parior	1.11,5	catalouse	- uy	uiy	patuy	sarpas	Sarpes
Stationary Area Dosimeter									
Readings									
1/day X5 locations X2 days	2	1	2	X	5	X	X	X	20
Conventional Sationary Area Air									
1/day X5 locations X2 days	2	1	2	X	5	х	X	X	20
Dosimeter, Task specific									
15 subjects X~12 hours/day X2									
days	2	X	2	15	X	X	X	X	60
Conventional personal breathing									
zone									
15 dosimeter subjects X 12									
hours/day X 2 days									~
Task specific	2	X	2	15	X	X	X	X	60

Phase II	Number of Bases	Number of Samplers per Areas	Number of Days	number of Subjects at each base	Number of	Number of Exhaled Samples per Day	Number of urine voids per day	Number of Nasal	Total # Samples
Stationary Area air (conventional) 1/day X /5	Dases	per Aleas	Days	Dase	Aleas	ра Бау	uay	samples	Samples
ocations X 4 days	2	1	4	X	5	X	X	X	40
Sationary Dosimeter in Area 1/day X 5 locations X 4 days	2	1	4	x	5	x	x	x	40
Dosimeter Wearing 15 dosimeter subjects									
15 X 12 hours/day X 4 days	2	x	4	15	x	x	x	x	120
Conventional personal preathing zone workshift 15 dosimeter subjects X 12 hours/day X 4 days	2	x	4	15	x	x	x	x	120
exhaled breath up to 4 Samples/day X 15 Dosimeter Subjects	2	x	4	15	x	4	x	x	480
dermal 15 subjects x 2 (pre&post) samples/body location/2 ocations X 4 days hand & back of neck (washing or 2x takes of tape strips)	2	2	4	15	2	X	X	x	480
urine- Morning Pre-shift, Post- shift, Bedtime, First Void in the morning 4 voids X 15 subjects X 4 days	2	х	4	15	x	х	4	х	480
Under NIEHS-IRB approval: nasal epithelial cells 15 dosimeter subjects X (pre & cost)/day X 4 days P4502F13 mRNA expression and Protein, naphth adducts	3	X	4	15	X	X	X	2	360
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are; a) field validate the prototype dosimeter and b) define the relationships between concentration of exposure biomarkers and concurrently collected dosimeter-measured exposures. Exposures measured by the prototype dosimeter will be compared to concurrent exposures measured by conventional pump-trap-purge technology. exposure `uptake Making it a Stratum corneum Dosimeter $K_{\rm pv} \times A_{\rm exp} / P_{\rm sc:ve}$ Viable QE/P_{ve:b} Naph. mg/m³ ermal. Exhaled A: Prototype **Urine** Metabolite/Adduct⁴ analytical data will inform the PBPK & **BBDR Models. Prototype Dosimeter Data** $00 \rightarrow$ Exhaled Breath Concentrations of Naphthalene, Kim, et al. **Conclusions**: This poster outlines naphthalene risk management actions that integrate five multi-disciplinary research projects with funding from five federal agencies. The research will generate a real-time, data-logging \mathbf{a} naphthalene sensor and independently validate its performance. The dosimeter will provide new protection for Mercapturic Acids eliminated in the urine) Toxicity industrial site workers, military fuel handlers and civilian Trihydroxymercapturate, Dihydroxydimethylthio, and Trihydroxymethylthio Metabolites ?/ (eliminated in urine) transportation workers. The data generated will extend what is known about naphthalene's mode of action and fill the single most important data gap in the naphthalene Naph. mg/m³ health risk assessment. The governance efficiency to be captured is improved health protection at lower cost. (Prototype) Capabilities measured by Temple University 2/10-09/12: The Naphthalene Dosimeter Advisory Group anticipates providing the CMRM Directorate with progress reports, future work statements, 2/10-10/10: Advisory Group reviews the protocol for NIOSH's budgets and justifications. Continued funding of the dosimeter biomarker and Army's institutional review board submission and approval. _validation study is to be determined through a competitive process. **University of California-Davis investigator's NIEHS-funded research renewal application is submit-Ited 9/09.** Goals include collection of nasal epithelium from military fuel handlers for analyses of biomarkers of exposure and disease progression. Work to be conducted under NIEHS IRB approval.

9/09: The Naphthalene Dosimeter Advisory Group proposes independent validation of the dosimeter's performance. The National Science Foundation will provide about \$70K to Temple University investigators to do the evaluations. 8/09: Ancillary NIOSH/NORA proposal submitted. Goals are: a) extend the dosimeter's detection capability to include other polycyclic aromatic hydrocarbons, b) biomonitor transportation industry workers and c) develop clinical sampling capability. NIOSH funding awarded 11/09 for a 3-year project. Total values about \$850K.

2009

11881-436

10/10-10/12: The goals of the biomarker validation study

The CMRM Directorate will continue to monitor to ensure that the naphthalene risk management actions are sufficient. The Directorate will continue to act as the contract officer's representative for the dosimeter validation study.

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2012