3812 Amine Catalysts in Spray Polyurethane Foams: Identification, Characterization, Exposures, and Implications for Toxicology and Occupational Medicine Research

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Spray polyurethane foam (SPF) is a highly efficient building insulation material. Amine catalysts in SPF accelerate the polymerization reaction between the polymeric methylene diphenyl diisocyanate and polyols. Historically, the main concern has been the isocyanate, due to its high respiratory and skin-sensitizing potential. However, respiratory disease and non-specific complaints by workers and residents' post-SPF application continue despite measurements confirming the lack of isocyanates in the air. Amine catalysts in SPF have, in such circumstances, been considered as potential suspects. Due to the proprietary nature of SPF formulations, little is known about the exact amine catalyst/s in use, their concentrations, variability in formulation across multiple products, workplace exposures and associated health risks. The main objective of this work was to systematically document amine catalysts used in SPF applications; to develop the necessary analytical methods for their quantitation in raw materials and SPF; and to quantify inhalation and dermal exposures among SPF applicators at various worksites. Following quantitation results, a detailed literature review of the toxicological profiles of identified amine catalysts in SPF was conducted to inform unmet research needs for biomonitoring, health effects and disease prevention. We pursued 10 amine catalysts. Personal breathing zone (n=32) and glove samples (n=34) were collected among 35 sprayers and helpers at 13 SPF insulation sites. Field samples and raw materials were analyzed in our laboratory using LC-MS/MS developed for this purpose. The ten amine catalysts investigated were: diazabicyclooctane (DABCO: CAS# 280-57-9), triethylenetetramine (TETA, CAS# 112-24-3), triethanolamine (TEA# 102-71-6), bis-dimethyl aminoethyl ether (BDAE, CAS# 3033-62-3), N-[2-(dimethylamino)ethyl]-methylamino-ethanol (DMAE, CAS# 2212-32-0), pentamethyldiethylenetriamine (PMDT, CAS# 3030-47-5), 3-dimethylamino-1-amino propane (DTAP, CAS# 109-55-7), quinuclidine (QD, CAS# 100-76-5), 2,6,10-Trimethyl-2,6,10-triazaundecane (TMTU, CAS# 3855-32-1) and 3,3'-Iminobis(N,N-dimethylpropylamine) (IBDP, CAS# 6711-48-4). In air samples, the most frequently found amines were DABCO (100% of samples); TETA (94%); TEA (85%) and DBAE (85%). The remaining 6 amines were detected in 20-60% of air samples. The highest air concentrations correspond to DABCO (GM 278.2; GSD 9.4; Max 26,200 ng/m^3) followed by TETA (259.2, 6.9, 494 ng/m^3), DBEA (150.4, 31.9, 167 ×10^3 ng/m^3) and TEA (17.8, 7.0, 278 ng/m^3). In glove samples, most amines were detected in < 40% of samples, except for TEA (94% detects, median 0.16 µg/sample). The highest amounts on gloves were measured for BDAE (23.3 mg) and TMTU (28.7 mg). Toxicological profiles for most SPF amine catalysts are only partially documented. Irritation of the eyes, skin and respiratory tract, and skin burns are a common feature. Serious eye damage can result from DABCO, TETA, BDAE, DMAE and possibly others. TEA may cause kidney and liver damage, as well as dermatitis. TETA is a skin sensitizer. Airborne exposures to these catalysts were low. For TEA and BDAE, airborne concentrations were 10^4× lower than their respective TLVs. Skin exposures can be important in this cohort for contact dermatitis and internal uptake. For the majority of these amines, there are no established exposure biomarkers and no biomonitoring data for exposures and health effects. We further outline specific priority areas for future research to fill in relevant data gaps.

3813 Development of a Field Analysis Method for Metallic Aerosols in Welding Fumes

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Workers are exposed to metallic aerosols produced during manufacturing processes such as welding. Welding fumes inhaled by welders generally contain large amounts of metals like iron (Fe) and manganese (Mn) which can negatively impact worker health. Identifying the size, composition, and quantity of metallic aerosols in welding fumes is essential for assessing the risks of workplace exposures. The industry gold standard for characterizing metallic aerosols involves collecting samples using a respirable sampler and sending them to third-party labs for metal analysis using inductively coupled plasma (ICP) techniques. However, conventional respirable sampling cannot provide detailed size information and the ICP techniques are expensive and time-consuming. To overcome these limitations, a cascade impactor and X-ray fluorescence (FP-XRF) were combined. Specifically, the cascade impactor was used to collect aerosols by size and then metal contents in the collected aerosols were analyzed using the FP-XRF. To test this method, area sampling was conducted near welding stations in a local truck-trailer manufacturing facility. The metal contents in the collected aerosols were analyzed using both FP-XRF and ICP-optical emission spectroscopy (OES) and the correction factors were calculated. After applying the correction factors to the results from FP-XRF, the concentrations of metals were calculated by dividing the mass collected by the sampling volume. On average, the combined mass concentration of iron across each stage from the six sampling locations totaled 268 µg/m^3 which was 7.2 times higher than the manganese concentration of 38 µg/m^3. Two modes were found in the size distribution for Fe. One was located at a particle size smaller than 0.25 µm (235 µg/m^3) and the other was located at a particle size larger than 2.5 µm (11 µg/m^3). The singular mode of Mn size distribution was observed at a particle size smaller than 0.25 µm (34 µg/m^3). The results show the feasibility to overcome the limitation of the conventional methods. This alternative method can allow industrial hygienists to provide a more detailed understanding of metallic aerosol exposure characteristics and be also applied to further research on exposures to metallic aerosols in various occupational settings. *This work is supported by the Centers for Disease Control and Prevention/National Institute for Occupational Safety and Health (CDC/NIOSH T42 OH008455), National Institutes of Health (NIH R01 ES032478), NIOSH training grant (CDC/NIOSH T03OH008615), and the International Manganese Institute research grant.*

3814 Biomonitoring of Exposure to Metals in Apprentice Welders after Shielded Metal Arc Welding (SMAW)

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Welding fumes have been associated with multiple lung and neurological diseases and are classified as human carcinogens by the International Agency for Research on Cancer. Most welding fume exposure studies do not consider the actual doses of metals and metalloids absorbed after inhalation and only measure a few chemical elements. The objective of this research was to establish the nature and level of exposure to welding fumes and their metallic components in apprentice welders, by performing concomitant measurements in different biological matrices. A total of 86 apprentice welders enrolled in welding training programs were recruited in three different schools in the Montreal area, Canada. Urine, hair, fingernail and toenail samples were collected at the beginning of the welding program (controls) and at the end of the 135-hour practical training in shielded metal arc welding (SMAW). Twenty-one elements, including aluminum (Al), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn), were measured in these matrices by ICP-MS. Metal concentrations in control urine samples (beginning of training) were comparable to the general population values reported in the Canadian Health Measures Survey. Results showed that concentrations of Mn in urine and hair were higher in samples taken at the end of the SMAW module compared to the beginning of training, while there was no significant difference for the other elements. Significant correlations (p<0.01) were observed for most of the elements analyzed, especially between Fe and Mn in toenails, fingernails, and hair, whereas urine exhibited weak correlations between elements. Significant correlations (p<0.01) were found between fingernail and toenail levels particularly for Zn (r_P =0.86), Cu (r_P =0.78), Mn (r_P =0.52), Fe (r_P = 0.5), Ni (r_P =0.45), Pb (r_s =0.48), Cd (r_s =0.47), Al (r_P =0,45), and Cr (r_P = 0.35). The study showed the interest of hair, fingernail and toenail measurements to assess exposure to metals and metalloids. The results also point to higher Mn exposure in apprentice welders related to the SMAW process.

3815 The Plot Thickens: Determination of Heavy Metal Exposure in North Brooklyn Parks

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The history of Brooklyn has long been synonymous with industry, manufacturing, and shipping; practices known to release heavy metals and other toxicological agents into the surrounding environment. In recent decades Northern Brooklyn - particularly Williamsburg and Greenpoint - has transformed into predominantly residential areas. Due to Brooklyn's inherent lack of green space, what few open space areas remain are heavily traversed, necessitating environmental studies to identify contaminated exposure pathways and human health. To explore this question, the environmental health and community advocacy group, North Brooklyn Neighbors (NBN) partnered with the NYU Division of Environmental Medicine to examine metal contamination in public open spaces - including parks and playgrounds. The community-based science initiative collected soil from community open spaces, analyzing 27 heavy metals. Elemental analysis using ICP-MS revealed concentrations of lead (Pb) and arsenic (As) as high as 563.3 µg/g and 138.2 µg/g, respectively, greatly exceeding USEPA soil screening limits of 400 µg/g (Pb) and 0.7 µg/g (As); copper and zinc were frequently measured at concentrations >1000 µg/g. Potential human exposure risk in five age categories was assessed for each element based on receptor parameters, including ingestion and inhalation, adopted from the USEPA. Hazard indexes (HI) were within the acceptable limits of 1.00 for all sampled elements; however, the HI of As (0.16) and Lanthanum (La) (0.32) are notable as they may pose long term health risks. The carcinogenic and/or toxicologic consequences of such heavy metals in wildlife and humans are well documented. Adhering to pollutant guidelines/standards are critical for reducing adverse health effects and potential acute exposures. Despite Williamsburg and Greenpoint's gentrification, the high concentrations of heavy metal legacies in this study, familiar in other urban environments, require further investigation and potential remediation to protect public health and particularly, high-risk populations.

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