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Letters to the Editor

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Letters to the Editor

MEASUREMENTS OF AIRBORNE METHYLENE DIPHENYL DIISOCYANATE CONCENTRATION IN THE U.S. WORKPLACE — COMMENT

We read with interest the recently published article "Measurements of Airborne Methylene Diphenyl Diisocyanate (MDI) Concentration in the U.S. Workplace"[1] that addresses an important and widespread workplace exposure. MDI, essential to the production of numerous polyurethane foams and other products, is a potent sensitizer that can cause isocyanate asthma. This article presents a unique exposure data set, including extensive personal and area samples (over 8,000) collected from over 300 different MDI production facilities. However, we have concerns related to three issues: (1) the sampling and analytical methods used to measure MDI airborne exposures, (2) the presentation and interpretation of the airborne MDI data, and (3) the underlying premise that maintaining airborne isocyanate levels below monomer occupational exposure limits ensures a safe workplace, with little mention of skin as a potential route of exposure and sensitization.

(1) *Sampling and Analytical Methods:* As the authors note, several technical factors could have contributed to the underestimation of MDI airborne exposures in these manufacturing facilities. Importantly, the majority of samples (>90%) were collected using filters, which are more likely to underestimate MDI exposure than impingers, especially for spray applications.[2–4] For example, Lesage et al.,[4] reported that the filter-based Iso-Check method measured on average 25% (median 20%) of the impinger values. Additionally, measurement of only monomeric MDI and not also oligomers of MDI would have resulted in an underestimation of total biologically active NCO exposures in some environments.[5]

In contrast to the statements in the article about the unavailability of methods and standards to measure oligomers of MDI, methods existed as far back as 1987 that do not require analytical standards for measuring isocyanate oligomers.[6] Although there continue to be limitations to the measurement of oligomeric species in MDI-based products, the contribution of such species to the exposure hazard should not be overlooked, particularly when their contribution to the total isocyanate is substantial relative to that of the MDI monomer.

We also question the authors' statement that "there is no objective definition of what is meant by 'total isocyanate' by those methods claiming to analyze for total NCO functional groups." Total free isocyanate group is routinely measured in bulk products by the titration with di-n-butylamine.[7] When using this procedure, species that react with the amine are effectively defined as free isocyanates. Air sampling methods for total isocyanate rely on the same operational definition, although all species thus derivatized may not prove to be measurable using chromatographic methods.

Finally, other factors could have contributed to an underestimation of MDI exposures, including the type of derivatizing agent and the use of older, less sensitive quantitative laboratory methods.[2] While the authors point out issues with the different sampling and analytical methods used, they do not discuss or estimate the impact of the analytical methods on their own data.

(2) *Presentation and Interpretation of the Airborne MDI Data*: Despite the rich data set of over 8,000 samples collected from 1984 to 1999, the authors provide relatively limited information regarding sampling strategies, task-specific exposure levels, or potential changes in the manufacturing operations or products over time. Further analysis of the data, including potential exposure determinants, may have yielded additional valuable information. The authors conclude, "workplace airborne MDI concentrations are extremely low in a majority of the manufacturing operations." However, without additional information, it is difficult to know how relevant these exposure data are to the many different current MDI end-user settings or what work conditions or factors produce higher exposure levels. The authors highlight spray and heating operations as having higher exposure potential. It would have been helpful if the authors compared their exposure data to other published data, such as spray-on applications of truck bed liners and rigid foams for insulation,[4,8,9] which have documented notably high MDI airborne exposures. The authors also do not discuss their unexpected finding that over 30% of area and personal samples taken in an area where cured rigid foam was "cut to length, stacked, and made ready for shipment" were above the TLV for MDI.

(3) *Occupational Exposure Limits:* The MDI exposure data are presented in comparison to the OSHA PEL and ACGIH® TLV® for MDI monomer, rather than using a total NCO metric, and without including a reference to the lower occupational exposure limits (OELs) used by a number of countries, including the U.K., Australia, and Sweden.[5] Comparison of airborne MDI data to MDI OELs perpetuates

an outdated premise that maintaining airborne levels below these monomer mass standards will prevent isocyanate asthma. Isocyanate sensitization and/or asthma has occurred where measured airborne MDI monomer levels are below OELs or below the limits of detection with the methods used, or where similar MDI levels would be expected, but MDI air monitoring data are not available.(10–13) Potential MDI skin exposure is frequently noted in such cases but has been difficult to quantify due to limited isocyanate skin sampling and analytical methodologies.(11–14) Although the authors recommend gloves "where dermal contact to MDI or PMDI is likely to occur," they largely ignore the important role that MDI skin exposure likely plays in inducing systemic sensitization that can develop into asthma following subsequent respiratory tract exposure.(14–16)

Thus, for the reasons noted, we are concerned that the data from this publication may underestimate the risk to workers and industries that use MDI, and that the authors do not adequately highlight the importance of targeting prevention efforts at both skin and airborne exposures. Hopefully, future collaborative efforts among industry, academia, and government will lead to a greater understanding of MDI exposure determinants and risks and more effective strategies to minimize such exposures.

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AUTHORS' REPLY

We appreciate the interest Redlich et al. expressed in their Letter to the Editor regarding our recently published article "Measurements of Airborne Methylene Diphenyl Diisocyanate (MDI) Concentration in the U.S. Workplace."(1) In particular, their recognition that the article "presents a unique exposure data set including extensive personal and area samples (over 8,000) collected from over 300 different MDI production facilities" is gratifying since the primary purposes of the article were: (1) to make available to the practicing industrial hygienist the wealth of data on airborne exposures to MDI collected by isocyanate producers, and (2) use the data to focus the practicing industrial hygienists' efforts on the most important processing operations from an MDI airborne exposure perspective among the various common processing techniques used to make polyurethane products from MDI.

Given the fact that the article was *retrospectively* reporting on data that had been gathered during the period 1984–1999, the majority of the comments made by Redlich et al. have little relevance to the present article. In many cases, the detailed information on individual samples mentioned by Redlich et al. ("sampling strategies, task-specific exposure levels, or potential changes in the manufacturing operations or products over time") simply were not available to the authors. If we were to design a study today to gather similar data *prospectively*, many of their comments would likely be reflected in the design. These facts notwithstanding, we have briefly addressed some of the issues raised in the letter below.

(1) *Sampling and Analytical Methods*: The selection of sampling and analytical methods always involves tradeoffs between many factors, some technical and some practical. Among the MDI methods, all of the common derivatizing agents are primary amines that react rapidly with the isocyanate group; the primary technical consideration is ensuring efficient sampling of the physical form(s) (i.e., vapor, aerosol) expected to be present and whether or not the airborne MDI is expected to be present as the isocyanate alone or as a reacting system. As noted in the article, impingers are preferred over treated filter samplers when air sampling for two-component, spray-applied polyurethane systems that are fast reacting. For most other processing situations, either sampling technique will give results that are valid and meaningful.(2)

Redlich et al. express concern that monitoring MDI monomer alone would lead to an underestimation of the airborne concentration of isocyanate-containing species, since MDI oligomers are not quantified. While this is certainly a consideration in processes where polymeric MDI is mechanically sprayed or may be present on the surface of airborne particulate matter, for the vast majority of other applications (which rely on evaporation to produce airborne MDI) this is of little consequence from the perspective of practical exposure control evaluation: the vapor pressure of polymeric MDI (a mixture of MDI monomer and oligomers; typically about 50% monomer) is almost exclusively the result of its monomeric MDI content.(3) The experience of those of us who have conducted exposure monitoring for the oligomeric components of polymeric MDI confirms the conclusion reached by the physico-chemical argument: when oligomers are detected at all, the ratio of monomeric MDI to MDI oligomer found are usually considerably below what would be expected from the bulk composition of the polymeric MDI being used.

The authors stand by their statement that "there is no objective definition of what is meant by 'total isocyanate' by those methods claiming to analyze for total NCO functional groups." Redlich et al. correctly point out that dibutyl amine titration is used by isocyanate producers to assay bulk liquid isocyanates "active isocyanate group"; however, none of the "total isocyanate" air monitoring methods uses a direct assay technique like titration. All of the "total isocyanate" air monitoring methods that the authors are aware of rely on relative detector response of chromatographically eluted species as an indirect means of identifying eluting peaks as "containing isocyanate group," a scheme that has been shown to lead to false negatives and false positives under some conditions.(4)

(2) *Presentation and Interpretation of the Airborne MDI Data*: The statement by Redlich et al., "The authors also do not discuss their unexpected finding, **that over 30% of** area and personal **samples taken in an area where cured rigid foam was 'cut to length, stacked and made ready for shipment'** were above the TLV for MDI," appears to be based on a misunderstanding of the following sentences on page 233 of the document: "The cured, sandwich foam bonds to the facings and exits the press where it is cut to length, stacked and made ready for shipment. The area and personal sample results that were above 0.051 mg/m^3, (42/113) 37.2%, and (17/53) 32.1%, respectively, were non-spray applications." The authors of the letter apparently interpreted those sentences to imply that all the samples above the TLV for MDI were taken in the area at the exit end of the curing oven only where the boards are cut and stacked, which is not true. While the paragraph probably could have been worded better to avoid such confusion, the samples in fact were taken during board stock production along various areas of the process line (pour, curing oven and cutting/stacking areas), and in instances when process upsets and calibrations occurred. These latter conditions and tasks can result in airborne sampling data above the TLV for MDI — more details on these conditions and tasks are given in the document on pages 233 and 234.

(3) *Occupational Exposure Limits (OELs)*: Redlich et al. suggest that a review of exposure limits for MDI should have been included in the article. Once again, this suggestion is not pertinent to the scope of the article. The data were collected at facilities in the United States; the relevant OELs were (and still are) the OSHA PEL and ACGIH TLV, which were used as the OELs for comparison in the article. Similarly, a discussion of the mechanisms of isocyanate sensitization seems entirely out of the practical scope of the article as noted above.

We appreciate the opportunity for dialog on the important topic of controlling worker exposure to MDI and share the desire of Redlich et al. for better understanding and control of such exposures.

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