MDI and the National Toxics Inventory

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Diisocyanates Panel

- The Diisocyanates Panel is a self-funded panel of the American Chemistry Council that represents the major manufacturers of diisocyanates, including MDI.
- Members of the Panel are BASF Corporation, Bayer Corporation, The Dow Chemical Company, Huntsman Polyurethanes, and Lyondell Chemical Company.

Methylene Diphenyl Diisocyanate

- MDI is widely used in the production of rigid polyurethane foams: appliance insulation, automobile parts, spray foam.
- MDI is used to a lesser extent in the production of coatings, adhesives, sealants, and elastomers, as well as in wood binding facilities to form polyurea.

General Overview

- EPA and Diisocyanates Panel worked together to update the 1996 NTI to more accurately identify the number of facilities emitting MDI and to more accurately estimate MDI emissions.
- Number of MDI-emitting facilities increased 400% while nationwide MDI emissions decreased 75%.

National Toxics Inventory

- Created in 1993 as part of National Air Toxics Assessment to measure HAP emission reductions and evaluate HAP risk reduction efforts.
- NTI designed to be model-ready inventory that would be updated every three years.

NTI Data Sources

- Five primary sources of data for 1996 NTI:
  - State and local HAP inventories
  - EPA MACT data
  - EPA TRI data
  - EPA mobile source emission estimates
  - Emission factors and activity data

MDI Emissions on 1996 NTI

- The 1996 NTI estimated MDI emissions at 129 tons, with some facilities emitting as much as 26 tons.
- 248 facilities were listed as emitting MDI.
- No emissions were listed for several industrial states.

MDI Has Many Isomers

- The HAP at issue is methylene diphenyl diisocyanate (4,4’ MDI). Many facilities use polymeric MDI, which has varying amounts of 4,4’ MDI as a component.
- The data presented reflect predominantly 4,4’-MDI emissions. Correction factors were used to account for polymeric MDI emissions.

MDI Emissions Are Extremely Low

- MDI reacts very quickly when forming polyurethane, and virtually all MDI is reacted.
- MDI has a very low vapor pressure (1×10^{-5} mm Hg @ 20°C) (5×10^{-5} mm HG @ 40°C) and is not readily emitted from handling and storage activities.

Estimating MDI Emissions: Notebook Method

- Industry developed a Notebook providing a method for calculating MDI emissions in 1991.
- The MDI Emission Notebook method was approved by EPA in 1994.
- Industry initiated outreach efforts to educate customers that MDI emissions generally do not equal MDI usage.

Monitoring MDI Emissions

- Until recently, EPA's Conditional Method 23 was only method available for sampling MDI emissions.
- Costs roughly $25,000-30,000 per stack.
- Resulted in little sampling being done.
- Sampling that was done showed emissions consistent with the MDI Emissions Notebook method.

MDI Method Development

- Richard Ode, Bayer Corp., developed Conditional Method 31, which uses 13 mm filters with 1,2 pyridyl piperazine.
- EPA reviewed and approved the test method.
- Allowed verification of Notebook method.
- Costs $5,000-7,000 per facility to use.
- Data are biased high.

Toxics Release Inventory

- From the beginning, the industry and EPA recognized that many TRI reports dramatically overestimate MDI emissions.
- The Panel reexamined all reported TRI releases for 1990 using the Notebook method to estimate likely worst case emissions.
- Reported emissions of 531,170 pounds should have been no more than 14,463 pounds.

Gross TRI Overestimates

Facility	TRI Emissions	Notebook Method Estimate
Boat Facility A	94,607 lbs	1 lb
Boat Facility B	54,180 lbs	1 lb
RV Facility	12,551 lbs	15 lbs
Foundry	261,000 lbs	13 lbs

Goal: Make NTI MDI Data More Accurate

- Just as with the TRI, the NTI greatly overstated many facilities' emissions.
- Many facilities that appeared in TRI were not listed on the NTI.

Not All MDI Facilities Were Identified on the NTI

- The NTI data for MDI came solely from state emission inventories, which were submitted by only 36 states.
- Beginning in 1994, TRI required MDI releases to be reported as part of a “diisocyanates” category without specifying CASRNs.
- When the TRI was searched for facilities emitting MDI based on the MDI CASRN, none was found.

Identification of Facilities

- The Panel examined the 1993 TRI reports of MDI releases and further analyzed the 1996 TRI releases to identify facilities likely emitting MDI that were not listed on the NTI.
- This increased the number of MDI-emitting facilities on the 1996 NTI from 248 to 1,088.

Reviewing NTI MDI Emissions

- Multi-Step Process:
  - Create source categories
  - Estimate reasonable worst-case emissions for each category
  - Conduct sampling to validate
  - Re-adjust source category estimate, if needed
  - Use most reliable/reasonable emission estimate for NTI

Creation of Source Categories

- The universe of facilities emitting MDI was divided into 30 source categories based on their SIC Code and selective contacts with facilities to confirm their method of MDI usage.
- The Panel also relied on member companies' expertise with regard to customer facilities.

Categories of MDI Emitters

Air filter
Appliance
Appliance - truck
Auto
Boat
Coating - adhesive
Coating - elastomeric
Coating - other
Coating - sealant
Coating - TPU
Custom molder
Door
Electronics
Filter devices
Foam Producer
Foundry
Laminator
Mobile home
Oil
Packaging
Producers
Rebond
Recreation
Repackagers
Shoe sole
Spandex
Specialty producer
Tire fill
Water heater
Wood binders

30 Categories, But Only 3 Types of Processes

- Enclosed
- Open
- Specialty

Enclosed Processes

- Enclosed Process: MDI or PMDI is injected, poured, or sprayed into a cavity, mold, or other enclosed space and expands to fill space.
- Examples: appliance, auto, boat, custom molder, door, foundry, laminator, mobile home, lubricant, rebond, recreation, shoe sole, water heater, wood binder.

Open Processes

- Open Processes: MDI or PMDI is injected, poured, sprayed or coated onto a surface that is exposed to the atmosphere.
- Example: adhesives, air filter, coating, electronic, foundry, packaging, spray foaming, sealants.

Specialty Applications

- Miscellaneous applications use neither open nor closed processes, such as wood binders and spandex.
- Difficult to apply Notebook estimation method to such applications.

Source Category Emission Estimates

- Using the API Notebook method and conservative assumptions, reasonable worst-case emissions estimates for each type of process were created.
- Under this method, fugitive emission estimates were based on the assumption that MDI is present throughout the area in a uniform concentration, which is far more conservative than actual observations.

Category Emissions Based on Notebook

Category	Estimated Emissions of Highest Emitting Source in Category (lbs./yr)
Air filter	15
Appliance	21
Appliance - truck	9
Auto	15
Boat	9
Coating - adhesive	15
Coating - elastomeric	15
Coating - other	15
Coating - sealant	15
Coating - TPU	15
Custom molder	9
Door	4
Electronics	15
Filter devices	9
Foam producer	21
Foundry	13
Laminator	17
Mobile home	15
Oil	9
Packaging	15
Producers	N/A
Rebond	70
Recreation	15
Repackagers	N/A
Shoe sole	15
Spandex	15
Specialty producer	10
Tire fill	4
Water heater	17
Wood binders	N/A

MDI Emissions Monitoring

- The Panel monitored MDI emissions from representative facilities to validate and better quantify emissions estimates obtained using the Notebook method.
- Roy Weston, Inc., which collaborated with the Panel in developing CM-31, conducted the monitoring.

Facilities Monitored

- The Panel monitored 66 stacks at 18 facilities nationwide representing 13 different applications.
- Types of facilities monitored account for more than 95% of MDI emissions.
- CM-31 was used as a lower cost screening method that would overestimate emissions.

Annual Stack Emissions (lbs./year/line)

Enclosed Process	Facility A	Facility B	Facility C
Appliance	9**		
Appliance -Trucks	3.3**		
Auto	3.6		
Door	0.4**		
Laminator	0.13**	2.9**	
Rebond	0.19**		
Foundry	18.5**	40.7**	
Open Process			
Adhesive	1.2**		
Air Filter	0.4		
AGRI-Fiber Particleboard	71	108	126
Spray Foaming	1.5**		
Special Process			
Belt Manufacturing	1368	6911	
Spandex	1.3**		

** Below Equipment Detection Limit

Comparison of Monitored Emissions Against Estimated

Category	Emissions Based on Stack Sampling (lbs./yr)	Emissions Based Solely on Notebook Method (lbs./yr)
Air filter	1	15
Agri-fiber	71/219/129	Specialty Application
Appliance	38.7*	21
Appliance-truck	3.3*	9
Auto	6	15
Belt mfg.	1501/6942	Specialty Application
Coating-adhesive	10	15
Door	1*	4
Foam producer	1*	21
Foundry	35*/37*	13
Laminator	4*/1*	17
Rebond	1*	70
Spandex	1*	15

*Below Detection Limit

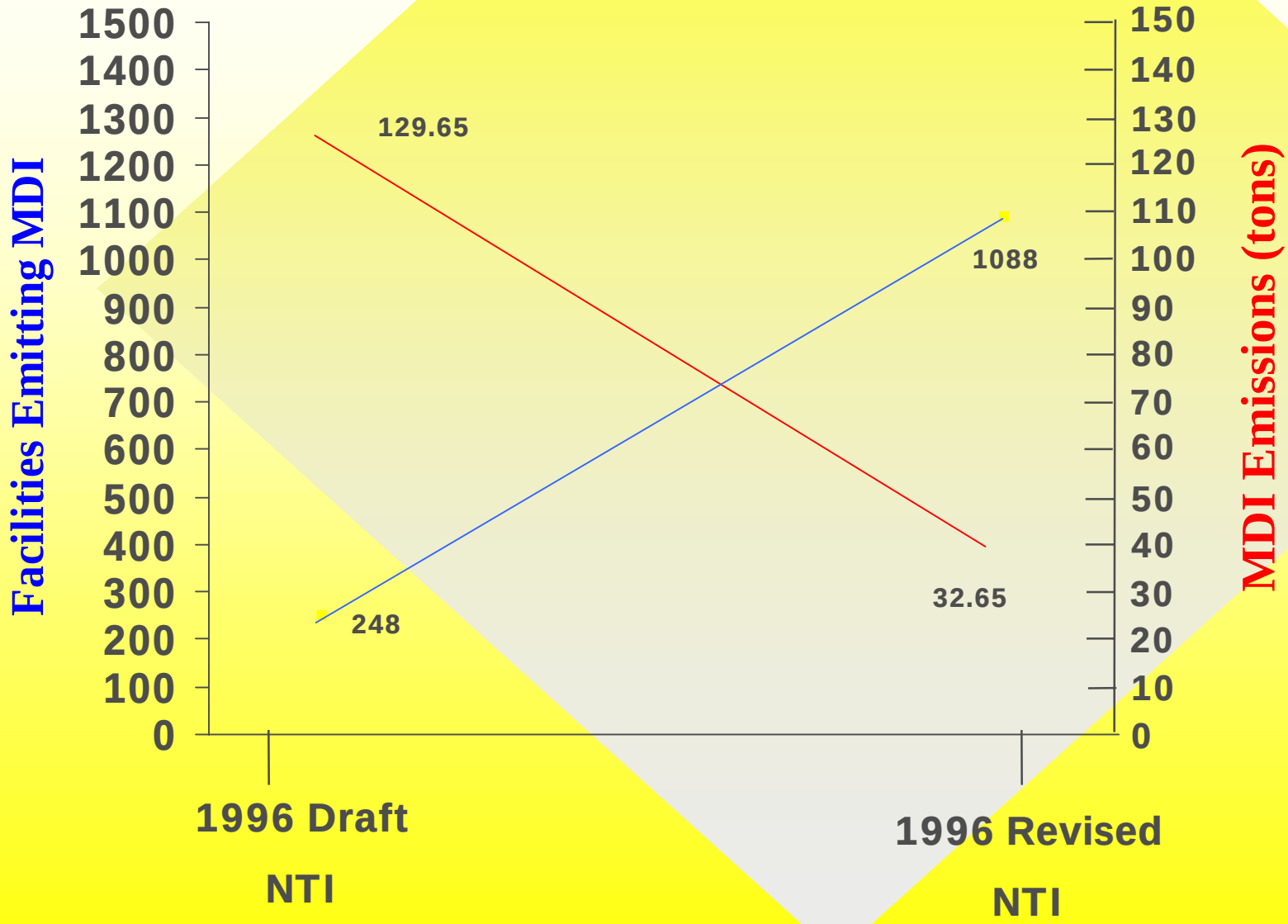
Revision of NTI

- The NTI, TRI, and source category values were compared.
- Due to the history of significant overreporting, the TRI or source category estimate was used if the NTI value appeared to be a significant overestimate.
- Thus, even with revision, the NTI still likely greatly overstates MDI emissions.

Effect on NTI

- Total MDI emissions reported on the draft 1996 NTI fell from 129.24 tons to 9.20 tons based upon modifications to 139 of 248 facilities' emissions.
- MDI emissions for 840 facilities were added to the draft 1996 NTI. Emissions for these facilities fell from 265.53 tons on the TRI to 23.45 tons on the NTI.

Summary of NTI Revisions



Conclusions

- Cooperation between industry and regulators can result in more accurate, though still highly conservative, inventories.
- Involvement by state and local agencies is imperative to obtaining accurate, complete inventories.
- Outreach efforts to facilities need to be continued.