Novel Risk-Based Approach to Address Amines Released into the Environment

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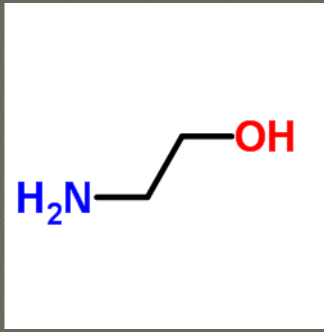
AMINES BACKGROUND AND USE

- Widespread use since the 1920s for a number of industrial purposes as well as consumer products.
- The amino and alcohol function group allows the amine to undergo a variety of chemical reactions.



- Frequently used in natural gas processing to "sweeten" natural gas by removing hydrogen sulfide from it.
- Commonly used for carbon capture technologies.

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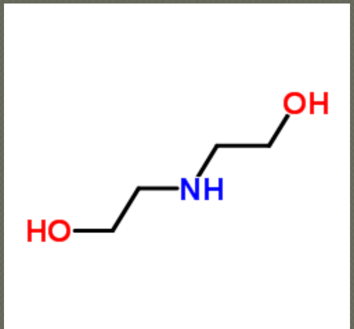
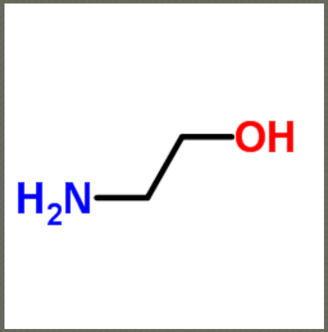
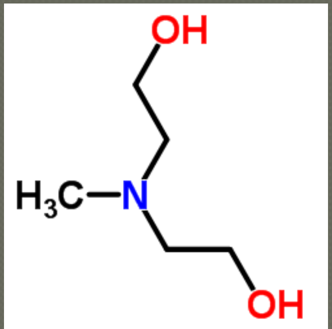
Amines Used as "Sweeteners"



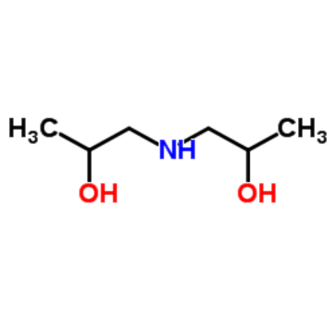
Diethanolamine*



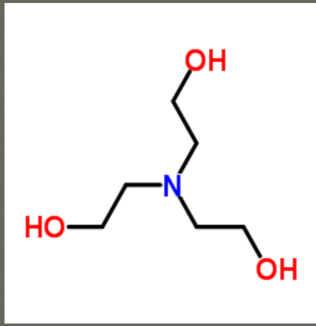
Monoethanoloamine*



Methyl Diethanolamine*



Diisopropanolamine*



Triethanolamine

+Other proprietary amines

*Commonly used in natural gas industry (RRC, 2011)

Chemical structures from Chemspider, 2017

THE AMINES "PROBLEM"

- TX Railroad Commission guidance (RRC, 2011) addresses spills and on-site waste management but no reporting requirements are specified.
- Can default to TCEQ's TRRP but only DEA, MEA, and TEA listed and the ${}^{GW}Soil_{Ing}$ PCLs are very low (TCEQ, 2017).
- No specific guidance in New Mexico for addressing amine spills.
- Unclear how to address proprietary amines.
- Analytical costs to measure amines can be expensive and there are difficulties when analyzing amines in soil.

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THE AMINES "PROBLEM" (CONT'D)

- Producer X reports a spill of exceeding RD (DEA or DEA comparison).
- Regulatory Agency Y says clean up and assess residual impacts.
- Question becomes where do we stop or do we investigate first.
  - Typical questions that leads to possible risk-based evaluation instead of jumping in on spill response with no data (digging with no plan).

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FATE, TRANSPORT, AND TOXICITY

- Unlikely to partition from soil or groundwater into soil gas or ambient air based on Henry's Law Constants and low to moderate vapor pressures.
- Miscible in water but tend to bind to charged surfaces of clay minerals.
- Empirical data shows less mobility than predicted by models that use water solubility and octanol-water partition coefficients.
- Not likely to bioaccumulate or bioconcentrate.
- Relatively low oral toxicity; less toxicity via inhalation route.
- Toxicity values available for DEA, MEA, and TEA. No evidence that these compounds are carcinogenic.

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RISK-BASED PROCESS

- Evaluated mobility of amines using empirical data for Kd and default TCEQ Tier 2 PCL calculation and assumptions for other parameters.

- Determined at what depth that the target Soil concentration that is protective of underlying groundwater (via the ingestion of groundwater pathway) becomes less than the target Soil concentration for direct contact.

- **The "theoretical" answer is 75 meters.**

EQUATIONS

$$Ksw = \frac{Pb}{(Kd * Pb + nw + na * H')}$$

$$LDF = \frac{\text{Leachate Dilution Factor} * L2}{L1}$$

$$^{GW}Soil = \frac{^{GW}GW * LDF * L2}{Ksw * L1}$$

$$\text{Organics } Kd = 10^{\text{Log Koc}} * foc$$

PARAMETER DESCRIPTIONS	TRRP DEFAULT	VALUES USED
^{GW}GW = Residential Tier 1 PCL in groundwater (mg/L)		
$^{GW}Soil$ = groundwater protective soil concentration (mg/kg)		
Kd = soil water partition coefficient		Alberta, 2010
Koc = organic carbon partition coefficent		
foc = soil organic carbon fraction	0.002	
Pb = dry soil bulk density	1.67	
n = total soil porosity	0.37	
na = air filled soil porosity	0.21	
L1 = thickness of impacted soil zone (cm)	site-specific	1 meter
L2 = distance from top of impacted soil zone to groundwater (cm)	site-specific	
nw = volumetric water content of vadose zone soils (cm3-water/cm3-soil)	0.16	
H' = dimensionless Henry's Law Constant		
LDF = Lateral dilution factor	10	

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RISK-BASED PROCESS (CONT'D)

- Derived non-carcinogenic toxicity values for amines based on available RfDs used in different regulatory programs (Alberta, 2010).

- Calculated Risk-Based Limits for soil and groundwater using standard residential and industrial exposure assumptions and the derived toxicity values.

SOIL RISK-BASED LIMITS (mg/kg)

COMPOUND	CAS No.	RESIDENTIAL LAND USE		INDUSTRIAL LAND USE	
		DC RBL	SPGW RBL	DC RBL	SPGW RBL
Diethanolamine (DEA)	111422	165	0.115	1,700	0.35
Monoethanolamine (MEA)	141435	1,672	1.216	18,240	3.648
Methyl diethanolamine (MDEA)*	105599	165	0.115	1,700	0.35
Diisopropanolamine (DIPA)*	110974	165	0.115	1,700	0.35
Triethanolamine (TEA)	102716	13,000	9.4	140,000	28

GROUNDWATER RISK-BASED LIMITS (mg/L)**

COMPOUND	CAS No.	RESIDENTIAL LAND USE	INDUSTRIAL LAND USE
		GW RBL	GW RBL
Diethanolamine (DEA)	111422	0.06	0.185
Monoethanolamine (MEA)	141435	0.638	1.824
Methyl diethanolamine (MDEA)*	105599	0.06	0.185
Diisopropanolamine (DIPA)*	110974	0.06	0.185
Triethanolamine (TEA)	102716	4.9	15

Notes:

*DEA was used as a conservative surrogate for compounds with no toxicity information.

** Groundwater classification and management varies between states and, as such, some regulatory programs do not recognize industrial land use for groundwater and assume all groundwater can be and is used for drinking water.

DC RBL - direct contact risk-based limit

SPGW RBL - soil concentration protective of groundwater risk-based limit

GW RBL - groundwater risk-based limit

Source: Calculations based on Texas Commission on Environmental Quality Texas Risk Reduction Program Tier 1 Protective Concentration Limits but using an average of several toxicity factors from TCEQ (2017), EPA (2016) and Alberta Environment (2010) if available (ie., adjusting by a factor of 5 for DEA and 15.2 for MEA).

INVESTIGATE…

- IF depth to GW > 75 m?

- Compare to DC RBL for applicable land use.
  - If soil concentration < DC RBL, no further action is necessary*.
  - If soil concentration > DC RBL, a response action may be necessary*.

- IF depth to GW < 75 m?

- Compare to SPGW RBL for applicable land use.
  - If soil concentration < SPGW RBL, no further action is necessary*.
  - If soil concentration > SPGW RBL, conduct a SPLP test and compare to GW RBL.

*Reporting requirements and eco screen may be necessary.

INVESTIGATE…

- IF SPLP > GW RBL
  - A response action may be necessary*.
    - Groundwater data can be used to eliminate this pathway if available but may not be helpful to show that future migration is not of concern.

- IF SPLP < GW RBL
  - No further action is necessary*.
    - Groundwater data can be used to eliminate this pathway if available but may not be helpful to show that future migration is not of concern.

*Reporting requirements and eco screen may be necessary.

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THINGS TO CONSIDER

- The soil comparison can be completed using either an individual sample comparison or the 95 percent upper confidence limit if adequate data are available.

- Ecological impacts should be evaluated if the impacted soil area is greater than 1 acre, the release impacts surface water, or if the release impacts habitat potentially used by Threatened or Endangered species.



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THINGS TO CONSIDER (CONT'D)

- Other site considerations may come into play when managing a release and good housekeeping practices are always recommended.

- If amines used are proprietary, chose RBLs for the most prevalent amine present in MSDS or DEA since it is most conservative.

- Restrictive covenants or deed restrictions can be part of the response action for sites when ecological impacts are not likely.

Examples

DESIGNING AN INVESTIGATION

- Know your amine (DEA, MEA, TEA, MDEA…)
  - On-going source considerations (closed loop process)
- Know your site
  - Review any available site characterization
  - Understand physical setting, soil type, eco receptors and depth to GW
  - Regulatory and third party drivers
- Design sampling plan
  - Statistically significant data set for soil (analytical challenges)
  - Vertical delineation near source (especially in clayey soils)
  - Mindful of process areas that limit response actions (IC's?)
  - Always collect additional volume for SPLP
- Consider submitting a work plan

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LOGISTICAL CHALLENGES

- Atypical "spill" sampling/analytical program
- Availability of analytical labs for soil characterization
- Interaction with lab is critical for additional analysis
- Field QA/QC for soil may be difficult
- Accessibility to affected area (incorporate IC's) and biased data

REGULATORY CHALLENGES

- It should be noted that no regulatory review and approval of the described approach has been given.
- Always helpful to walk regulators through a process.

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REFERENCES

- Alberta Environment, 2010. Soil and Groundwater Remediation Guidelines for Monoethanolamine and Diethanolamie. Government of Alberta. Edmonton, Alberta. ISBN No. 978-7785-9005-7 (Printed Edition). http://environment.gov.ab.ca/info/.

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Questions?