

Toxicity and exposures associated with air emissions from concentrated animal feedlot operations

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Topics

- For NH_4 and H_2S :
 - Sources
 - Mechanism of effect
 - Range of toxic concentrations
 - Health standards and guidelines



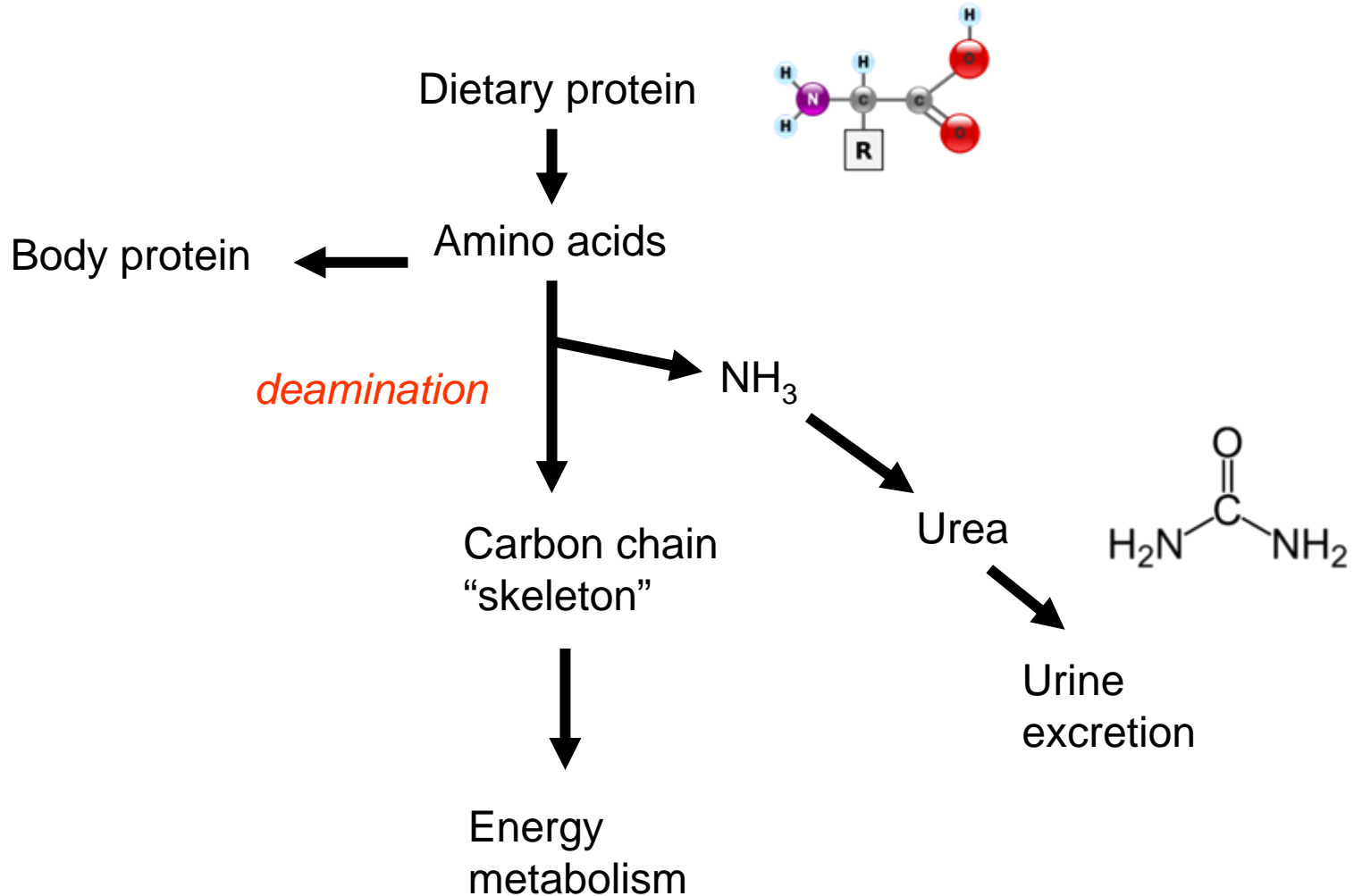
Chemicals Found in Manure

- **Hydrogen Sulfide**
- Methane
- Nitrogen Heterocycles
- Mercaptans
 - Methyl, Ethyl, Propyl
- Volatile Fatty Acids, Alcohols, & Aldehydes
 - Propionic, Butyric, Isovaleric, Isobutyric
- **Ammonia**
- Amines
 - Methyl, Ethyl, Dimethyl
- Carbon Dioxide
- Phenolics
- Sulfides
 - Dimethyl, Diethyl

Ammonia

- Ammonia= moderate base in water solution
 - Infinite water solubility
 - Biological solvent
 - OSHA: TWA 50 ppm, IDLH 300 ppm

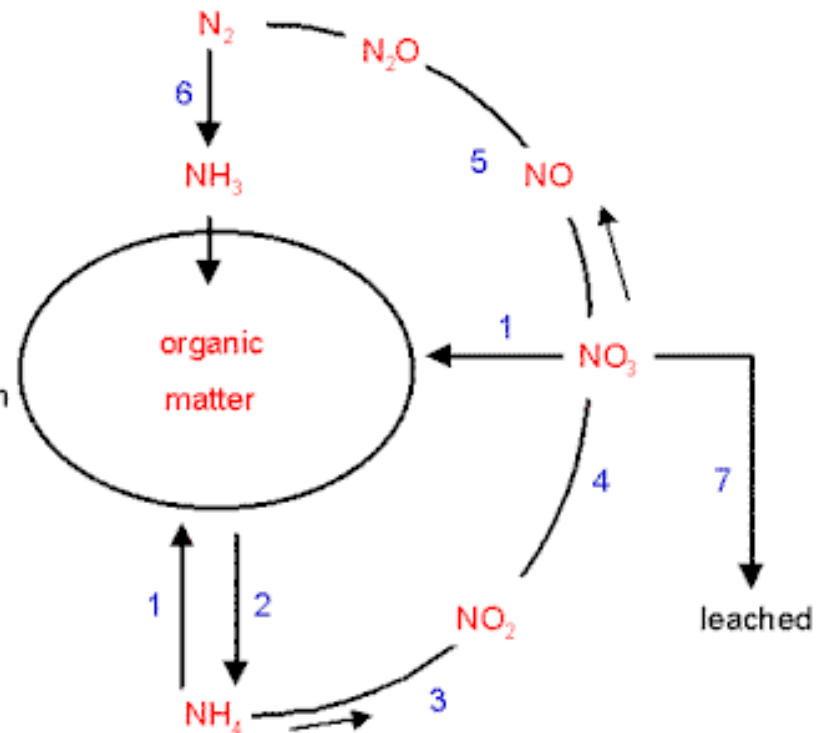
Deamination and ammonia waste



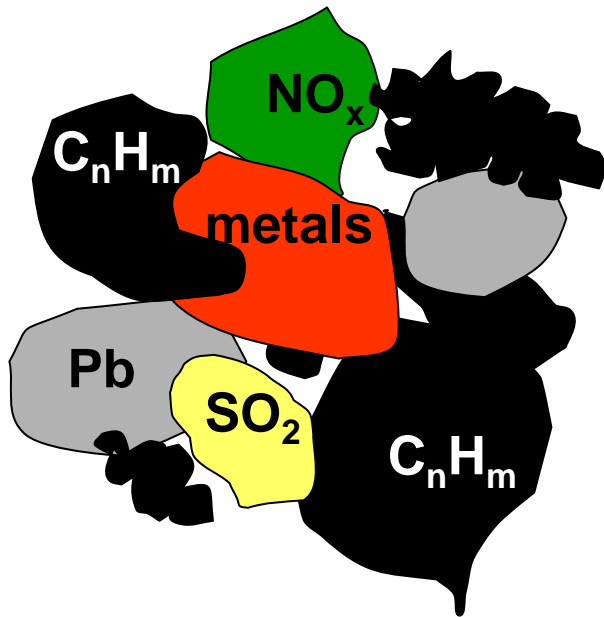
–Implications of non- linear increase in manure NH₃ w/ incr. feed protein content (swine).

Environmental fate of ammonia

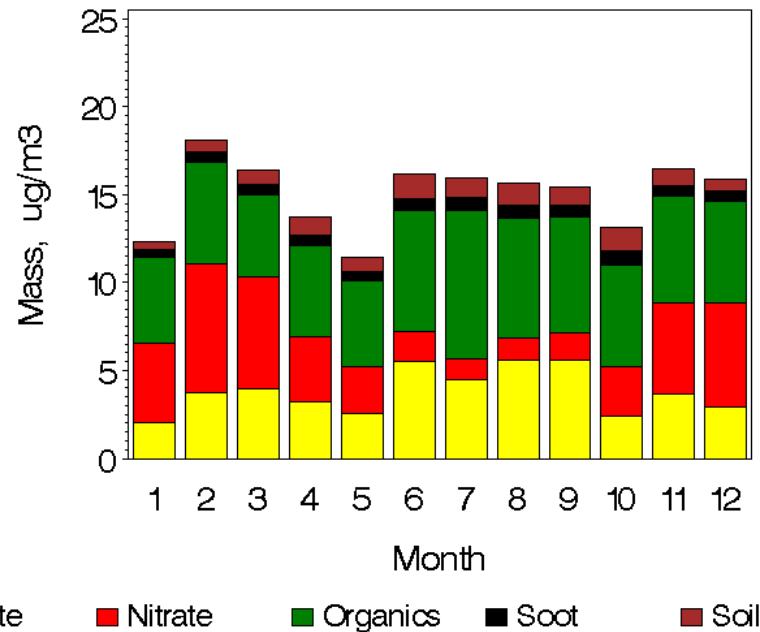
1. Uptake of NH_4 or NO_3 by organisms
2. Release of NH_4 by decomposition
- 3,4. Microbial oxidation of NH_4 (yields energy in aerobic conditions)
5. Denitrification (NO_3 respiration) by microbes in anaerobic conditions (NO_3 is used instead of O_2 as the terminal electron acceptor during decomposition of organic matter)
6. Nitrogen fixation
7. Nitrate leaching from soil



Ag Ammonia contributes to regional air quality?



Reconstructed Fine Mass
WI—Waukesha



See also: Harper and Flesch. **Wintertime Ammonia Emissions from Dairy Production Systems. Technical quarterly report to the USDA-ARS, Specific Cooperative Agreement Project Numbers 13655-12630-001-02S and 258-3655-6-F157, March 31, 2007.**

NH₃ toxicity progression

compiled by Michigan Dept Env. Quality. 2006. CAFO chemicals associated with air emissions

property	Concentration in air ppm
Detectable odor	0.04-53
Eye, nose irritation	50-100
Strong cough	50-100
Airway dysfunction	150
Lethal in 30 minutes	2500-4500
Immediately lethal	5000-10,000

Minot ND Ammonia accident January 2002





Particulate bioaerosols

- Unspecified animal proteins/allergens
- Endotoxin
 - LPS component of cell wall of gram(-) bact.
 - e.g. *E.coli*
 - Worker exposure
 - Gradual decline in lung function
 - ODTS organic dust toxic syndrome-
 - immune dysfunction following excessive dust exposure.
 - Possible synergy with ammonia exposure

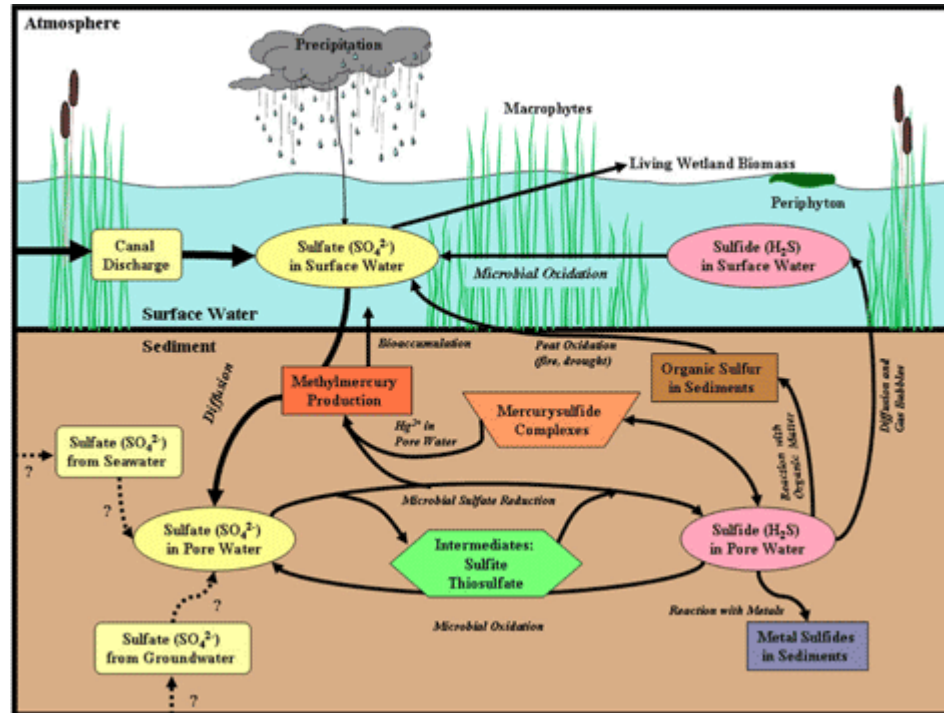
H₂S Properties and Sources

- Colorless; “rotten egg” odor
- Natural sources
 - Geo venting: volcanoes, springs, crude petroleum
 - Microbial: stagnant (anaerobic) aquatic systems
- Industrial
 - High BOD waste: Pulp mills, sugar processing.
 - Petrol refining
 - Landfill demolition waste
 - Microbial sulfate reduction
 - gypsum breakdown ($\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$) : H₂S = 4:1 wt:wt)

H₂S: Synonyms

- Acide sulfhydrique [French]
- Acide sulphhydrique
- Dihydrogen monosulfide
- Dihydrogen sulfide
- EINECS 231-977-3
- FEMA No. 3779
- HSDB 576
- Hydrogen sulfide
- Hydrogen sulfide (ACGIH:OSHA)
- Hydrogen sulfide (H₂S)
- Hydrogen sulfure [French]
- Hydrogen sulfuric acid
- Hydrogen sulphide
- Hydrogene sulfure [French]
Hydrogene sulphure
- Hydrosulfuric acid
- Idrogeno solforato [Italian]
- RCRA waste number U135
- Schwefelwasserstoff [German]
- Sewer gas
- Siarkowodor [Polish]
- Stink DAMP
- Sulfur hydride
- Sulfureted hydrogen
- Zwavelwaterstof [Dutch]

H₂S: Enteric/Environmental sources



Ref: USGS

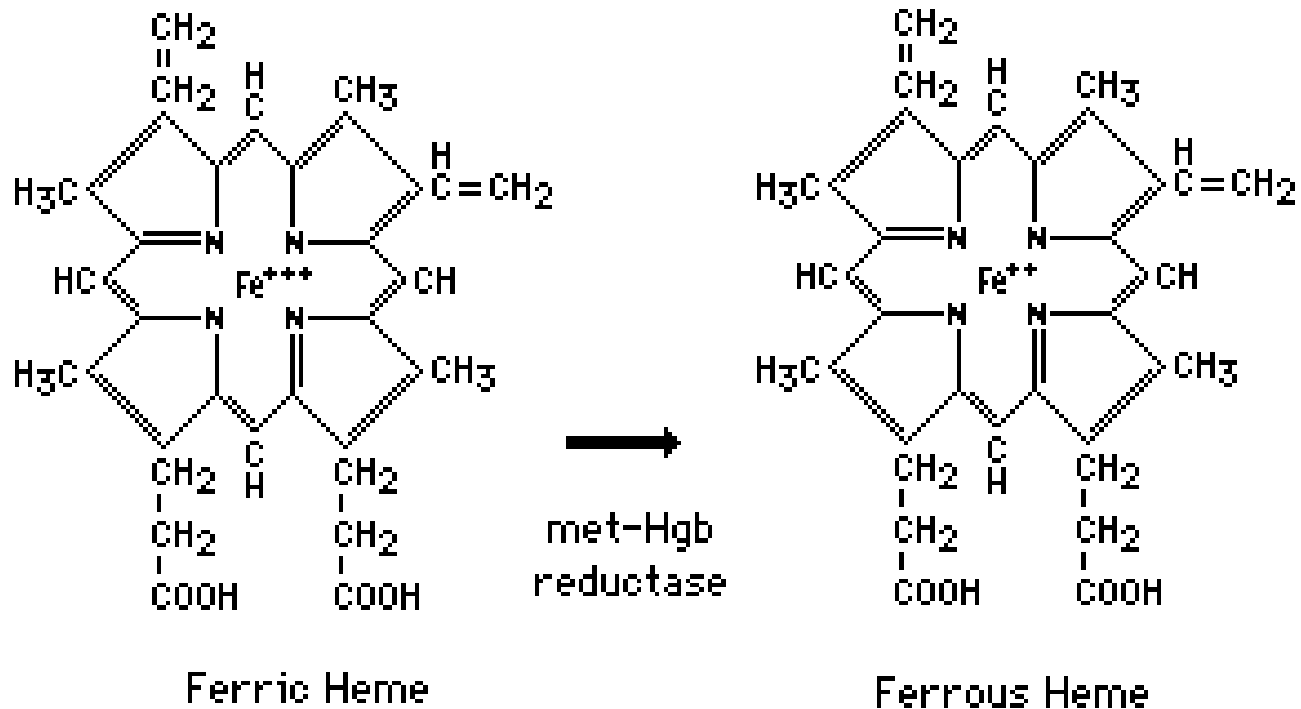
H₂S Lethal Accidents

- Stagnant, anaerobic sewage may contain 6000 ppm H₂S.
 - Max solubility in water 4000 ppm
- H₂S gas is heavier than air. When agitated, increase production and erupt from solution with pressure to fill confined space.

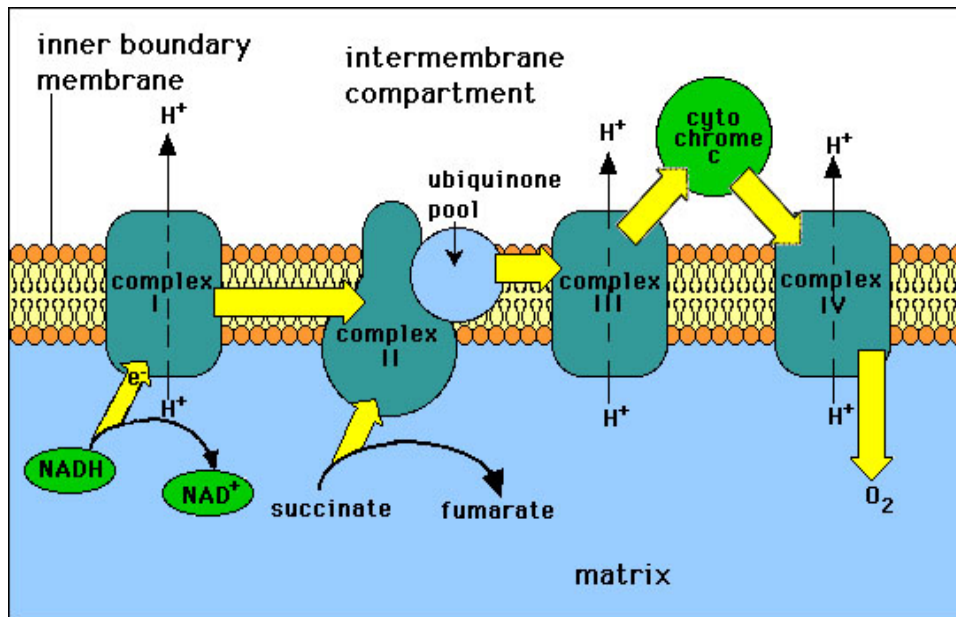
H₂S Toxicity Progression

- Acute, very high conc.
 - Actual conc. in accidents usually unknown
 - >600-1000 ppm ? : Lung paralysis, collapse, death
- Acute, high conc. >500 ppm, <1 hr
 - CNS depression, loss of consciousness
 - Recovery; neurological problems may persist
- Acute, lower concentrations
 - 2 ppm: asthmatics affected
 - 150 ppm: olfactory paralysis
- Chronic exposure
 - 0.0002 ppm typical background level
 - 0.3 ppm offensive odor, headache
 - 3-5 ppm very offensive
 - 0.001-0.008 ppb odor threshold (AI HA 1989)
 - Human flatus: 3-18ppm normal

Mechanics of H₂S toxicity

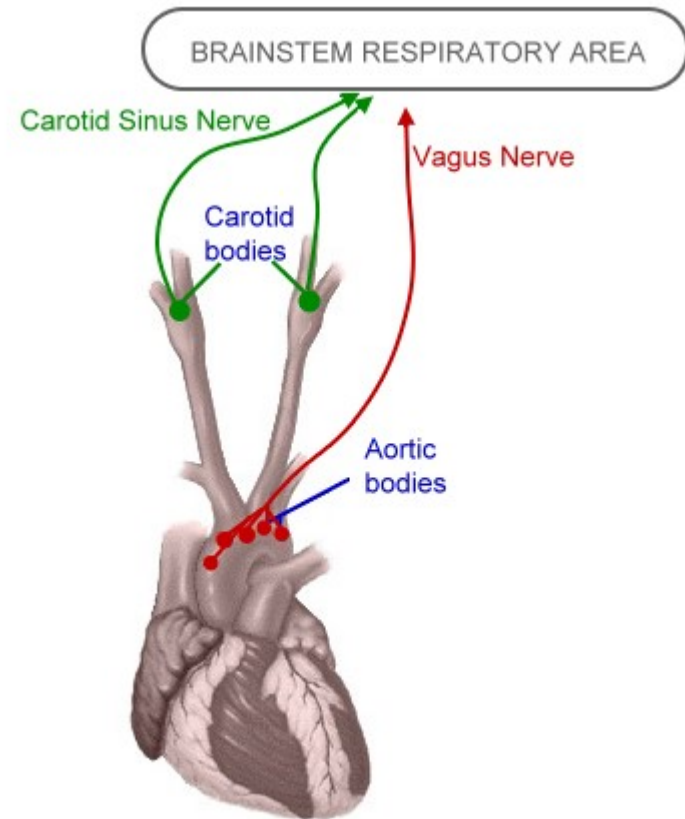
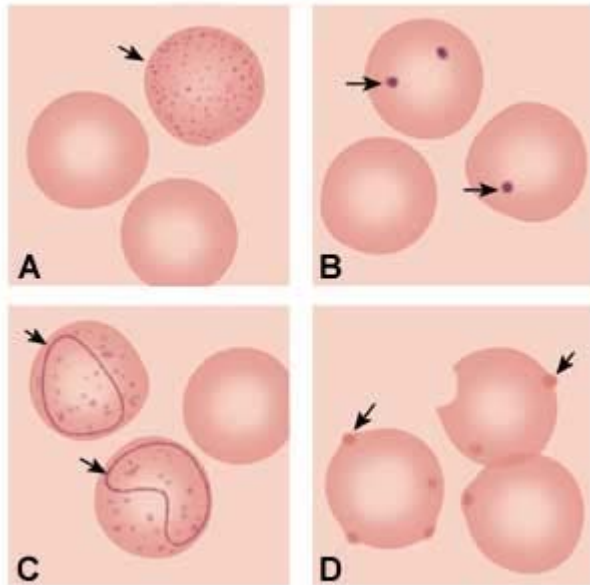


Mechanics of H₂S toxicity (2)



- **Soft nucleophile**
- **Targets cytochrome oxidase (binds to iron of heme-containing protein in complex IV)**
- **Inhibitor of electron transport**
- **Impairs mitochondrial ATP synthesis**

Mechanics of H₂S toxicity (3)



-Casarett & Doull's Toxicology

-Irwin and Kirchner Am Fam Physician. 2001 Oct 15;64(8):1379-1387.

-elrinajoubert-huebner.online

Occupational standards for H₂S

- OSHA *permissible exposure limit*:
 - 20 ppm (10 minute ceiling limit)
- NIOSH *recommended exposure limit*:
 - 10 ppm (10 minute ceiling limit)
- 8-hour limit not available

EPA IRIS Summary of H₂S

Critical Effect	Experimental Doses (Inhalation)	UF	RfC
Nasal lesions of the olfactory mucosa	NOAEL: 13.9 mg/m ³ (10 ppm) NOAEL (ADJ): 3.48 mg/m ³		
Rat Subchronic Inhalation Study	NOAEL (HEC): 0.64 mg/m ³ (0.46 ppm)	300	2 ⁻³ mg/m ³ (0.0014 ppm)
Brenneman <i>et al.</i> , 2000. Toxicol. Pathol. 28: 326-333.	LOAEL: 41.7 mg/m ³ (30 ppm) LOAEL (ADJ): 10.4 mg/m ³		

NR 445 annual std 100ug/m³ (71 ppb)

Endogenous role for H₂S?

- Numerous cellular roles for sulfhydryl molecules.
 - Cysteine (protein crosslinking; enzyme active sites)
 - Glutathione (conjugation and antioxidant detox)
- Evidence of interaction with brain NMDA receptor- may account for neurotoxicity.
- H₂S possible neuromodulator.
 - Whiteman et al. 2005. *BBRC*, 326:794-798
 - H₂S in brain normally 50-160 μM.
 - H₂S lower in Alzheimer brain; corresponding increase in hypochlorous acid.
 - H₂S inhibits hypochlorous production in brain.
- In rats, H₂S modulates physiological inflammation and contributes to the resolution of colitis. –Wallace et al. 2009. *Gastroenterol.* 137: 2181-2.

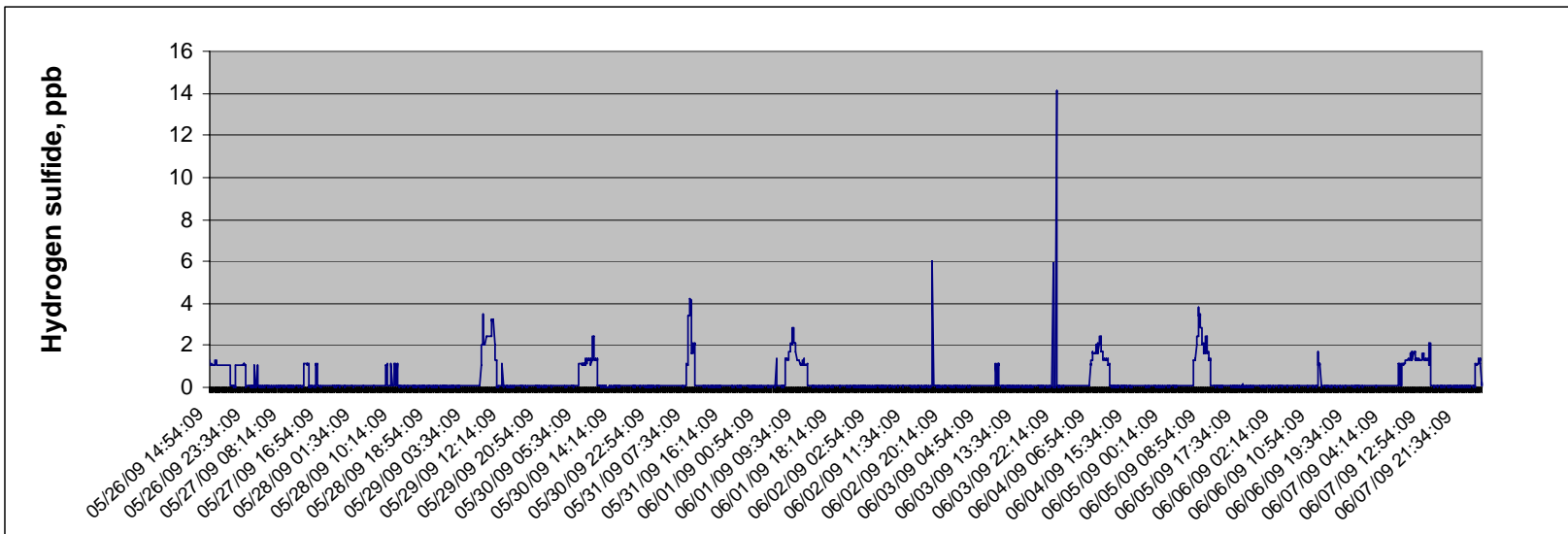
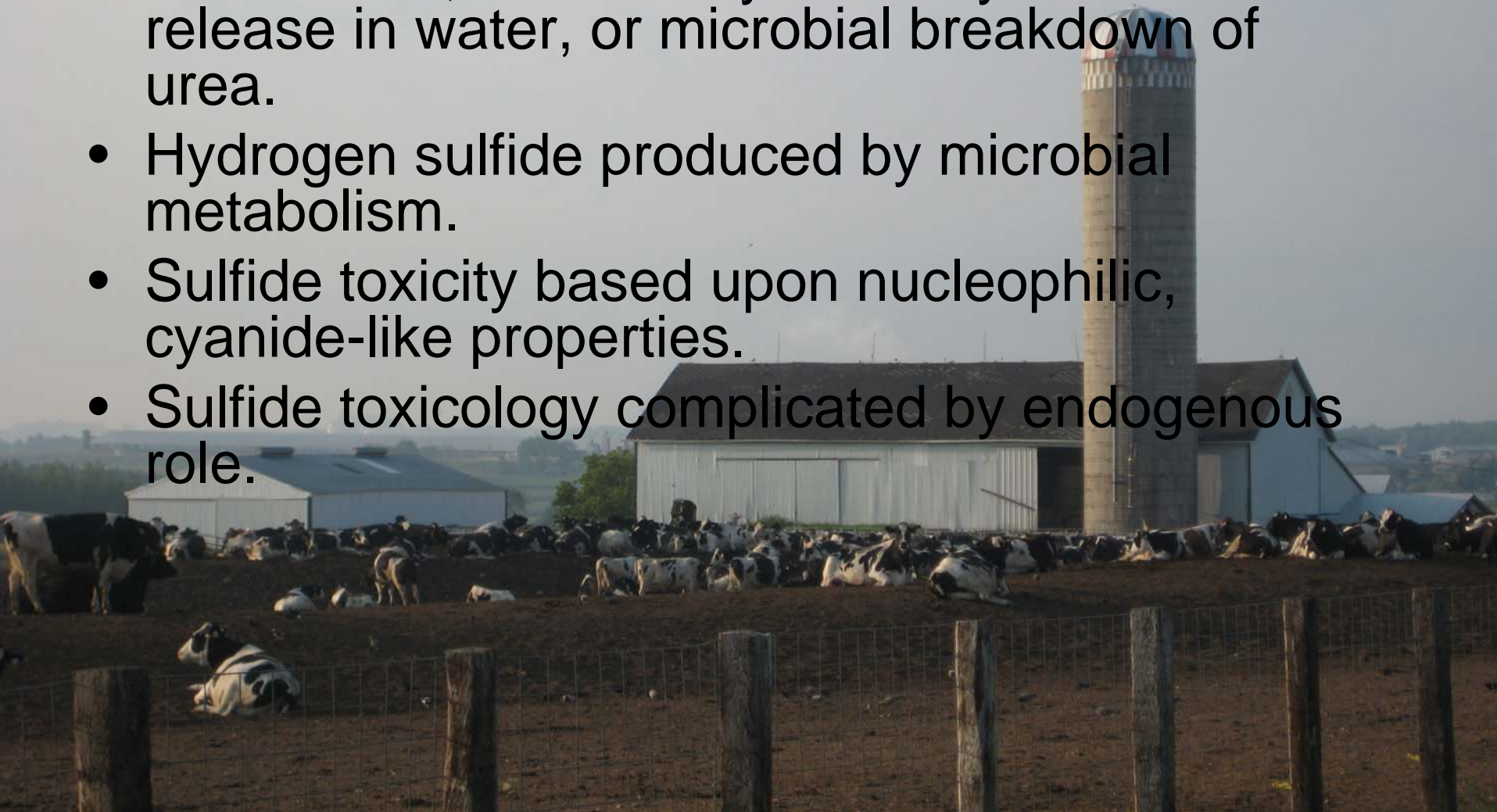


Figure 2. Hydrogen sulfide concentration in air 1950 feet downwind of the AV Roth Feeder Pig farm versus date and time, measured over two monitoring intervals. A: First monitoring period = May 26-June 9 2009; B: Second monitoring period = June 18-July 1, 2009. ppb: parts per billion.

Summary

- Ammonia toxicity based upon caustic properties.
- Ammonia in manure product of livestock metabolism, followed by nonenzymatic NH_4 release in water, or microbial breakdown of urea.
- Hydrogen sulfide produced by microbial metabolism.
- Sulfide toxicity based upon nucleophilic, cyanide-like properties.
- Sulfide toxicology complicated by endogenous role.



WDNR Statewide Air Monitoring

<http://maps.dnr.state.wi.us/imf/dnrimf.jsp?site=wisards>

Jan 5, 2006 9:00:00 AM OZONE and PM25

