The Effects of Increased Nitrate Levels on Groundwater Quality

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GEOL 628 Geochemistry

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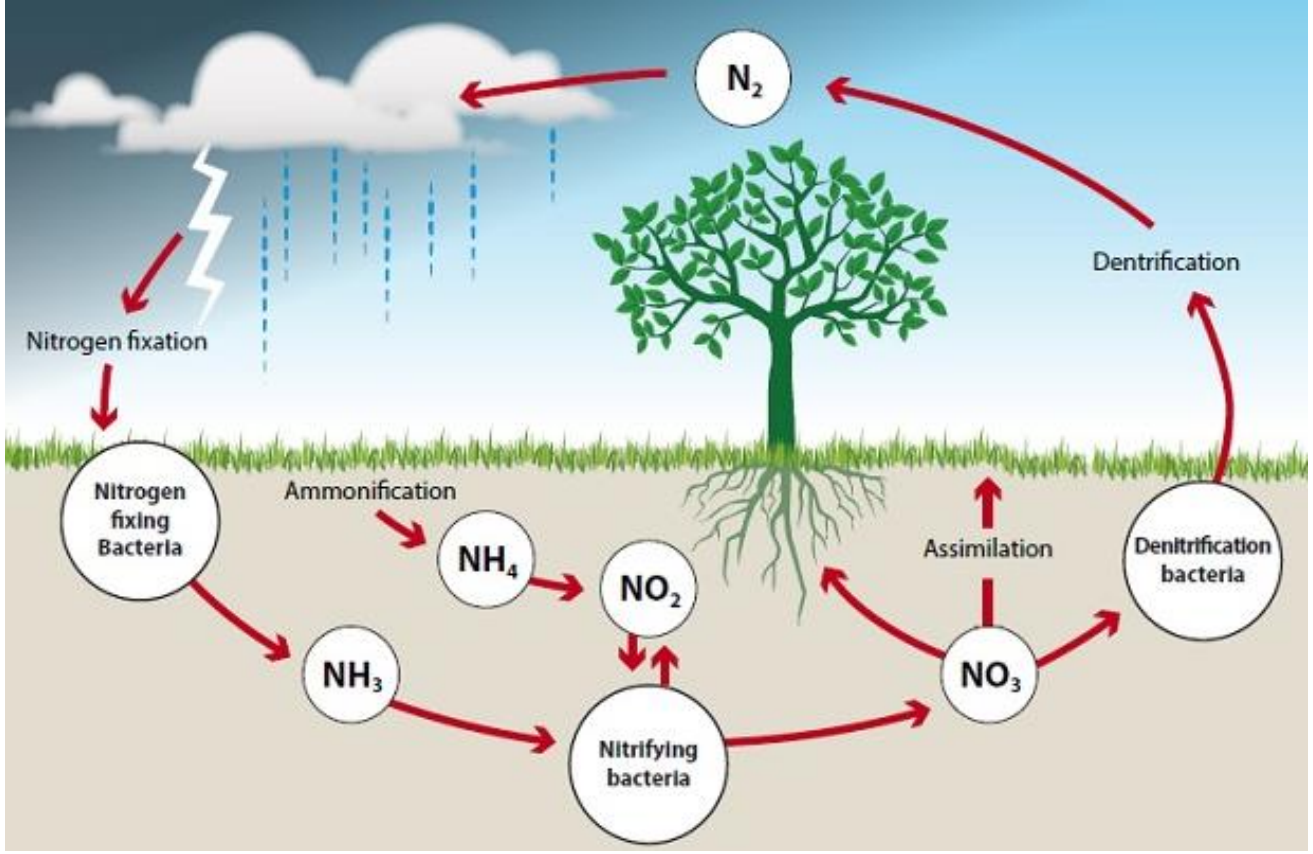


- Nitrogen Fixation: $N_2 \rightarrow NH_3$
- Hydrolysis: $NH_3 \rightarrow NH_4^+$
- Nitrification: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$
- Denitrification: $NO_3^- \rightarrow N_2$

- Nitrite and Nitrate as assimilated by plants
- Nitrogen gas can be fixated by lighting
- Decaying matter is denitrified by bacteria

- Nearly every pesticide that has been investigated has been detected in air, rain, snow, or fog across the Nation at different times of year. (Follett et al 1995)
- Figure 22.5 page 442

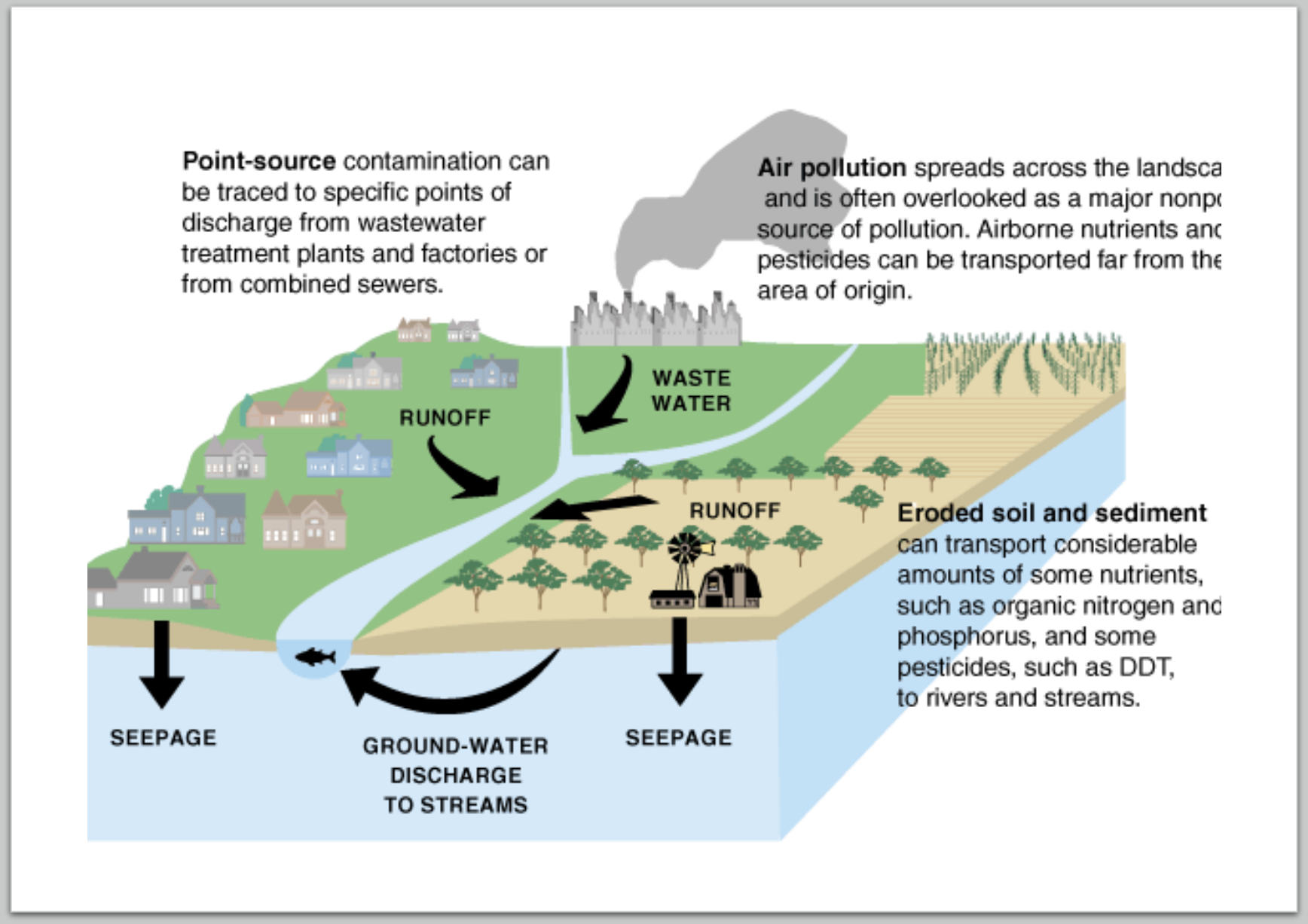
Nitrogen Cycle

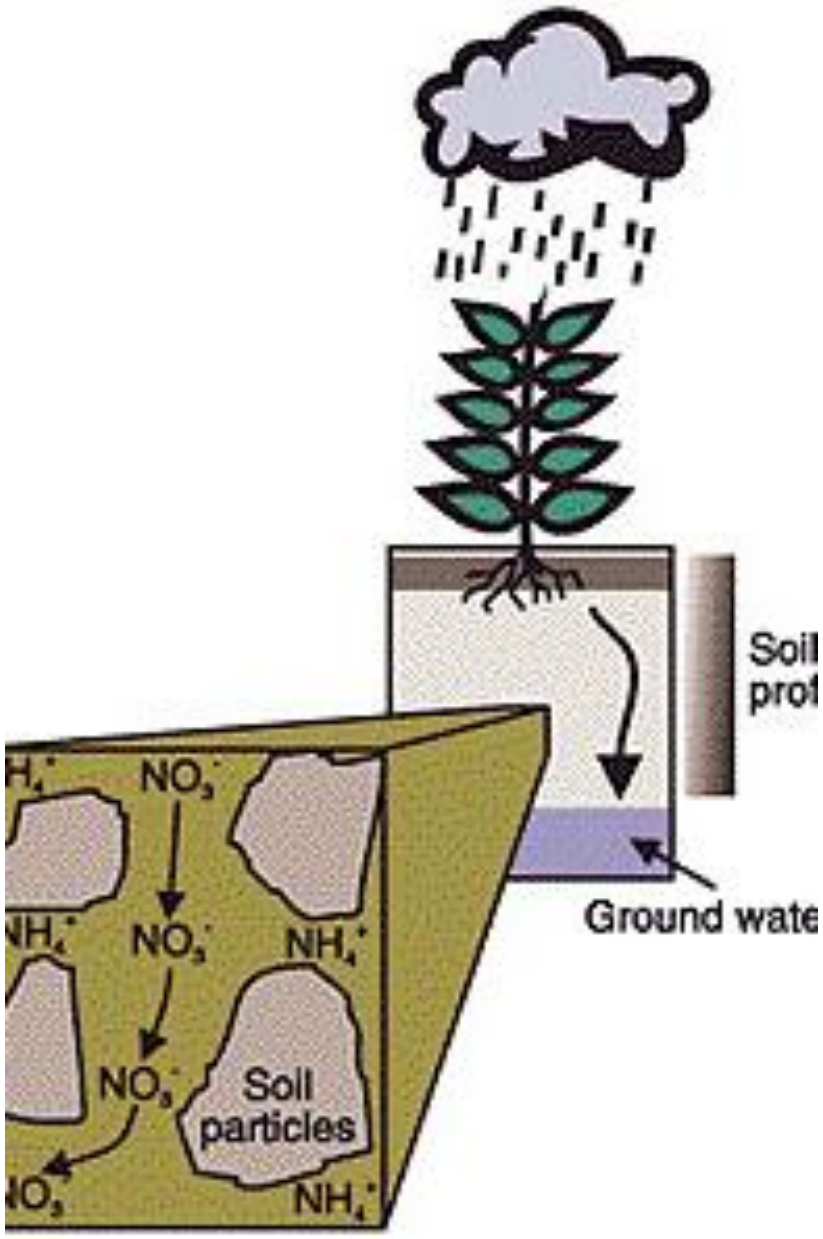
Nitrogen Cycle	$N_{2(g)}$	→	$NH_4^+{}_{(aq)}$	→	$NO_2^-{}_{(aq)}$	→	$NO_3^-{}_{(aq)}$
Oxidation Number **of N**	0	→	-3	→	+3	→	+5
Reaction Type		reduction		oxidation		oxidation	

Transport Processes

Leaching:
- Dependent on soils ability to hold water
- Drain through the soil profile
- Ex. Sandy soils leach easily

Runoff-
- Accumulation of water on the surface that runs downslope
- Results of irrigation
- Heavy rainstorms
- Little to no vegetation





- Nitrate is extremely mobile
  - Water soluble anion
  - Can not be sorbed by CEC

- The widespread appearance of NO_3^- in ground water is a consequence of its high solubility, mobility, and easy displacement by water. (Jury et all 1989)

HIGHLY VARIABLE:
- Land use
- Climate
- Chemical composition of soil
- Soil drainage
- Porosity
- Permeability
- Organic Matter Content

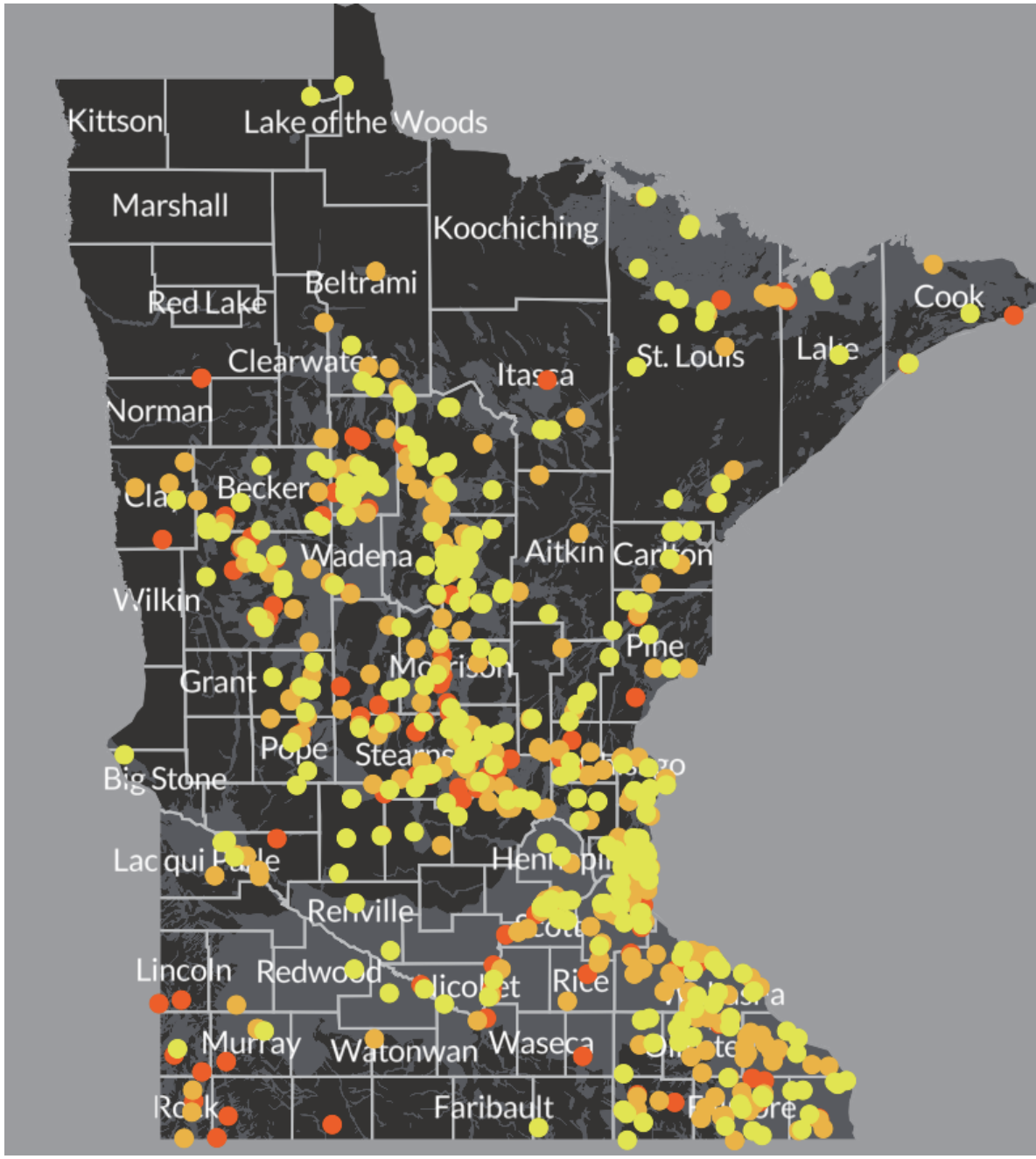
Groundwater Susceptibility to Nitrate Contamination

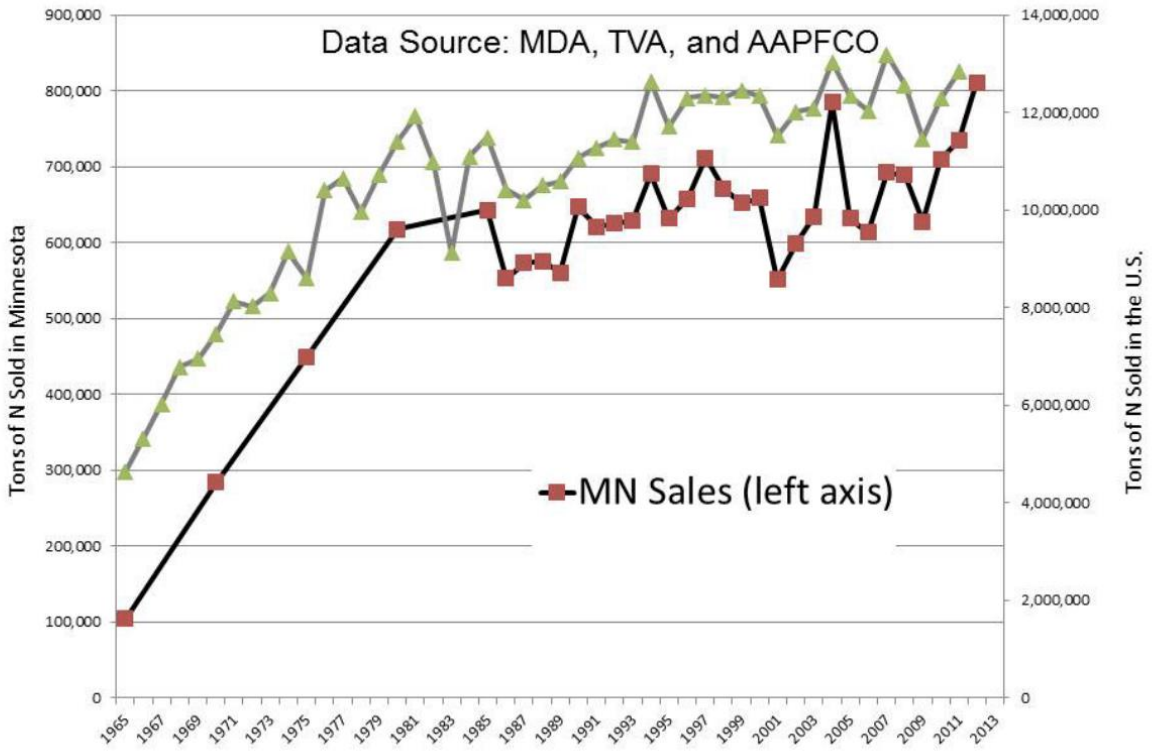
Contamination in Minnesota

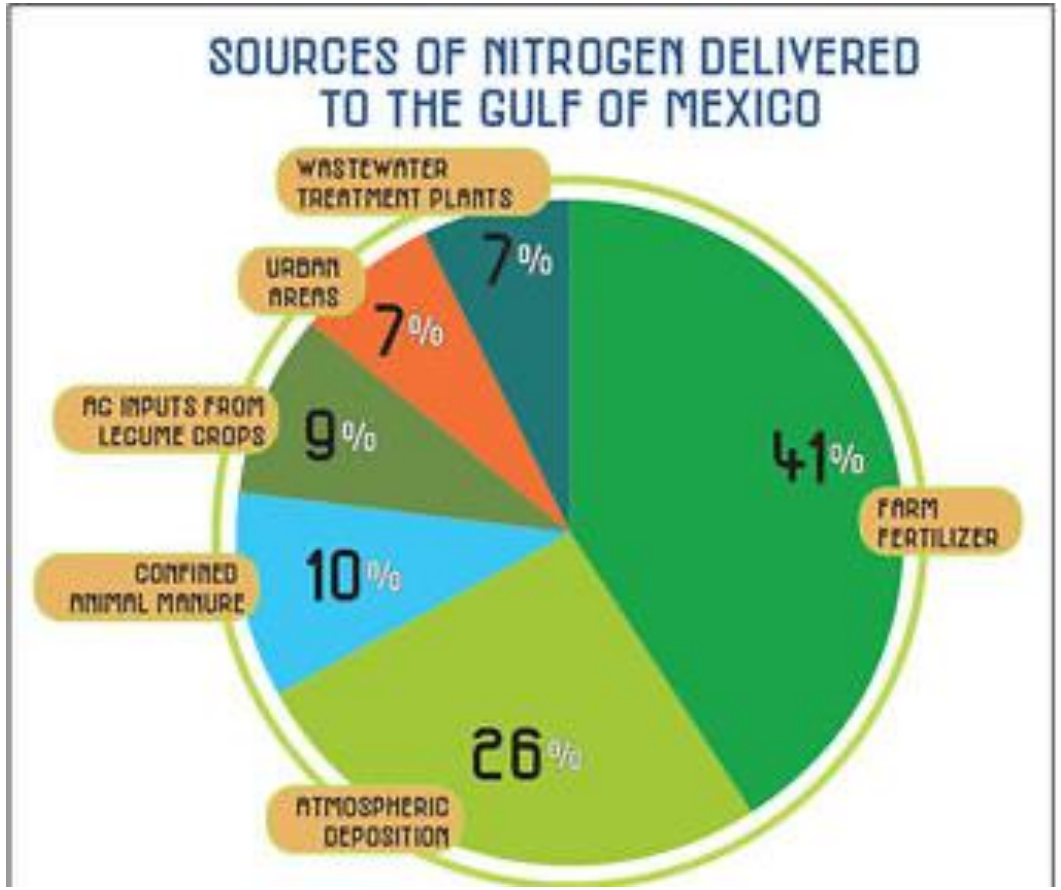
- EPA limit of nitrate in drinking water is 10 ppm
- Almost 300,000 people drink from public systems contaminated at or above 5 mg/L
- 150,000 from public systems with at least 10 mg/L.
- Blue Baby Syndrome

Table 1. Minnesota Public Water Systems With Elevated Levels of Nitrate, 2009-2018

	With at Least 1 test >= 3 mg/L		With at Least 1 test >= 5 mg/L		With at Least 1 test >= 10 mg/L	
System Type	Systems	People Served	Systems	People Served	Systems	People Served
Community	95	405,386	55	258,985	20	146,202
Non-community	632	67,597	358	38,251	104	8,448
All public ground water systems	727	472,983	413	297,236	124	154,650



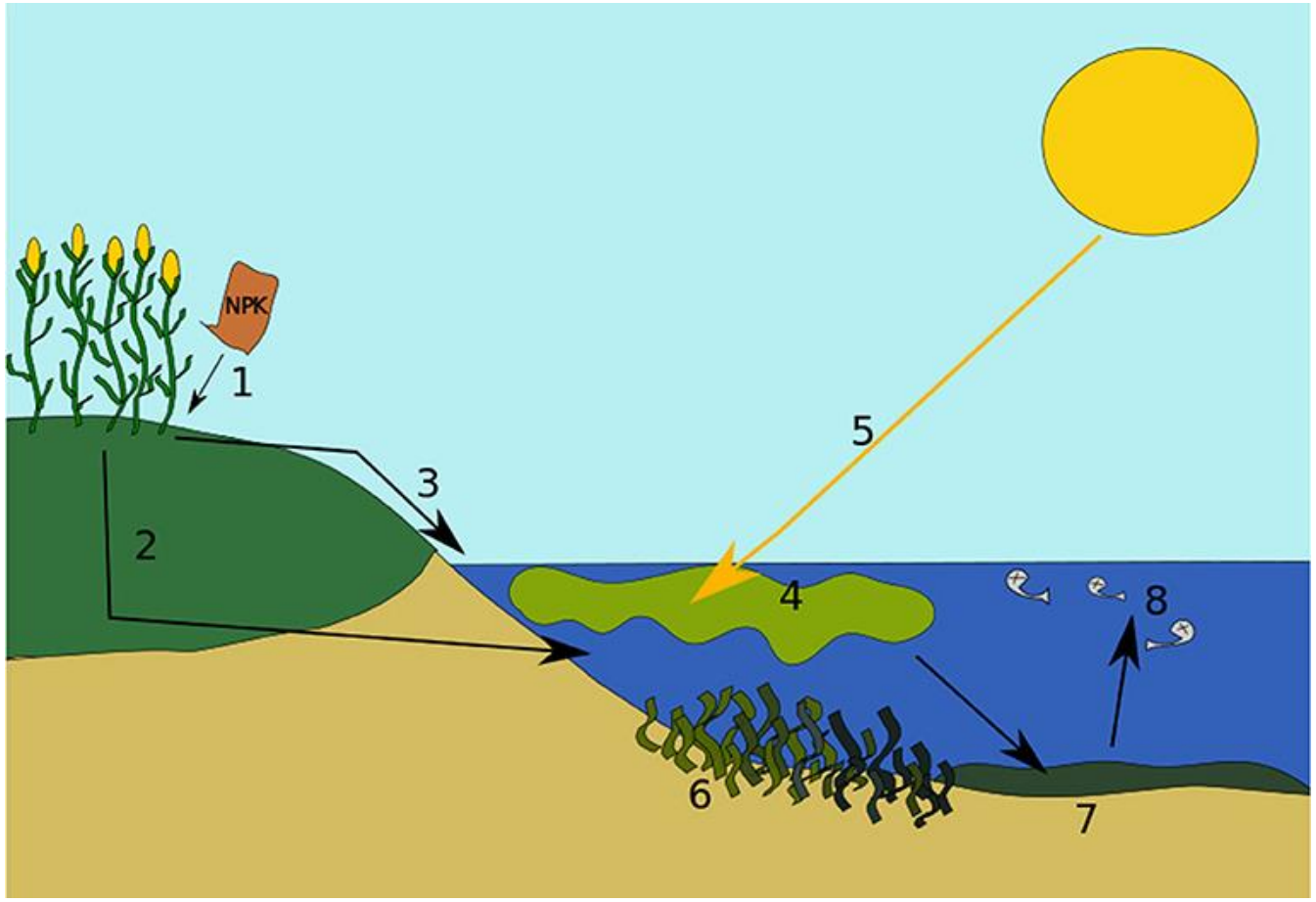




Anthropogenic Activities

- USGS estimates about 12 million tons of nitrogen and phosphorus are applied **each year** as commercial fertilizer.
- 7 million tons of nitrogen and 2 million tons of phosphorus are applied as manure.
- Nutrients primarily enter the watershed through the application of fertilizers and pesticides

Eutrophication



$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 112H_2O + 18H^+ + \text{energy} + \text{trace el}$$
$$\rightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2$$

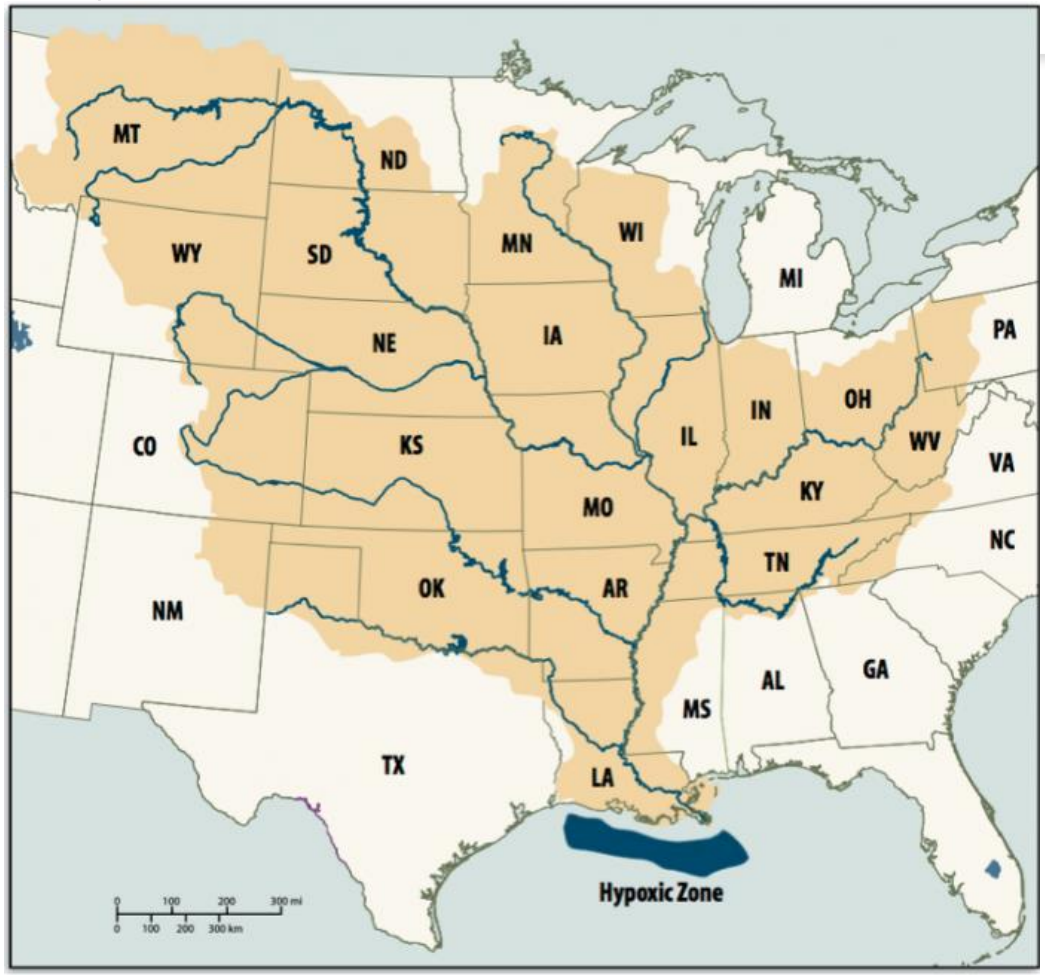
- Excess Nitrogen and Phosphorus causes an overstimulation of growth of algae
- Bacteria decompose algae after death using dissolved oxygen in the body of water
- DO in the body of water is removed
- Hypoxic or “dead zones” are formed where there is little to no DO

- Areas with algae blooms have higher pH due to increasing hydroxides levels during photosynthesis

- Plants and animals are unable to live in hypoxic zones

Dead Zones

- Mississippi River watershed drains 41 percent of the 48 contiguous states of the United States
- Covers more than 1,245,000 square miles
- Includes all or parts of 31 states and two Canadian provinces



Lake Eerie

Gulf of Mexico

Previous Work

- Inverse geochemical modeling of groundwater evolution with the emphasis on arsenic in Mississippi River Valley alluvial aquifer

- Jefferson County, AR

- Down stream of most agricultural land
- 6 samples, I used the mean for my input values

Table 5 General statistics of the chemical data of irrigation water wells used for groundwater quality monitoring in the area (Kresse and Fazio, 2002)

Parameters measured	Minimum	Maximum	Mean	Median	Std. deviation
Water level (m)	3.3	12.4	7.4	7	2.16
Temperature (°C)	17.3	19.5	17.9	18	0.47
Conductivity (μS/cm)	148	1353	528	421	309
TDS (mg/L)	168	746	327	261	157
pH	6.11	7.06	6.7	6.8	0.24
Alkalinity (mg/L as $CaCO_3$)	52	437	219	188	111
Hardness (mg/L)	43	491	203	164	127
As (μg/L)	0.73	50	14.1	7	15.3
Fe (mg/L)	1.87	41	11.9	10.5	8.1
Ca (mg/L)	10.6	143	58.7	48.6	37.6
Mg (mg/L)	4.1	33.5	13.8	10.3	8.3
Na (mg/L)	10.7	72	25.1	18.7	15.1
K (mg/L)	0.46	4.9	1.96	1.9	1.05
Mn (mg/L)	0.29	1.8	0.68	0.6	0.37
Cl (mg/L)	4.82	116	25.5	18	27.9
SO_4 (mg/L)	0.95	85.2	12.2	4	19.1
NO_3–N (mg/L)	<0.01	2.25	0.14	0.02	0.43
NH_3–N (mg/L)	0.04	1.06	0.29	0.23	0.25
PO_4–P (mg/L)	<0.005	0.1	0.03	0.02	0.03
Ni (μg/L)	<0.5	4.4	1.9	2	0.75
Cu (μg/L)	<5	46	7.2	5	7.8
SiO_2 (mg/L)	24.7	51.7	33.5	32.3	4.8
Br (mg/L)	<0.01	0.52	0.12	0.09	0.12
Ba (μg/L)	0.12	0.78	0.27	0.14	0.17
B (μg/L)	4.5	48.6	18.5	13.4	14.7
F (mg/L)	<0.01	0.4	0.24	0.23	0.08
Zn (μg/L)	<1	5	1.8	1.7	1
V (μg/L)	<0.5	1.9	1	1	0.33
Cr (μg/L)	<0.4	3	0.7	0.5	6.6
TOC (mg/L)	0.33	11	2.8	1.8	2.5

```
                                       pH  =   8.635      Charge balance
                                       pe  =  -4.076      Adjusted to redox equ:
                        Activity of water  =   1.000
                           Ionic strength  =   6.581e-03
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   2.997e-03
                       Total CO2 (mol/kg)  =   2.761e-03
                      Temperature (deg C)  =  17.900
                  Electrical balance (eq)  =   1.675e-03
rcent error, 100*(Cat-|An|)/(Cat+|An|)  =  19.02
                               Iterations  =   8
                                  Total H  = 1.110176e+02
                                  Total O  = 5.551747e+01
```

-------------------------Distribution of species---------------------------

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	2.694e-06	2.472e-06	-5.570	-5.607	-0.037
H+	2.501e-09	2.318e-09	-8.602	-8.635	-0.033
H2O	5.551e+01	9.999e-01	-0.000	-0.000	0.000

```
                                       pH  =   8.635      Charge balance
                                       pe  =  -3.865      Adjusted to redox equ:
                        Activity of water  =   1.000
                           Ionic strength  =   6.581e-03
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   2.999e-03
                       Total CO2 (mol/kg)  =   2.759e-03
                      Temperature (deg C)  =  17.900
                  Electrical balance (eq)  =   1.669e-03
     error, 100*(Cat-|An|)/(Cat+|An|)  =  18.96
                               Iterations  =   8
                                  Total H  = 1.110177e+02
                                  Total O  = 5.551748e+01
```

-------------------Distribution of species----------------------------

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	2.692e-06	2.470e-06	-5.570	-5.607	-0.037
H+	2.503e-09	2.320e-09	-8.602	-8.635	-0.033
H2O	5.551e+01	9.999e-01	-0.000	-0.000	0.000

Deeper look at Nitrate and Phosphate

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 112H_2O + 18H^+ + \text{energy} + \text{trace el} \rightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2$$

- Left has .03 ppm of Phosphate, right has .15 ppm of Phosphate
- .15 ppm of phosphate is considered algal bloom conditions
- .5 is unsafe for drinking water

Algae Bloom Equation: $106CO_2 + 16NO_3^- + HPO_4^{2-} + 112H_2O + 18H^+ + \text{energy} + \text{trace el} \rightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2$

P		9.690e-07				
	H2PO4-	3.796e-07	3.483e-07	-6.421	-6.458	-0.037
	HPO4-2	2.941e-07	2.076e-07	-6.531	-6.683	-0.151
P		4.845e-06				
	HPO4-2	2.137e-06	1.521e-06	-5.670	-5.818	-0.148

N(5)		0.000e+00				
	NO3-	0.000e+00	0.000e+00	-75.774	-75.812	-0.038

N(5)		0.000e+00				
	NO3-	0.000e+00	0.000e+00	-67.181	-67.219	-0.039

References

- Environmental Working Group., Sarah Porter., 2020, Tap Water for 500,000 Minnesotans
- Contaminated with Elevated Levels of Nitrate,https://www.ewg.org/interactivemaps/2020_nitrate_in_minnesota_drinking_water_from_groundwater_sources/, accessed 2 Nov. 2020.
- Follett, R.F., S.C. Gupta, and P.G. Hunt. 1987. Conservation practices: Relation to the
- management of plant nutrients for crop production. In R.F. Follett, J.W.B. Stewart, and C.V. Cole (eds.), Soil Fertility and Organic Matter as Critical Components of Production Systems (pp. 19-51). Spec. Pub. no. 19. SSSA. Madison, WI.
- Frontiers for Young Minds., Miriam R Aczel., What is the Nitrogen Cycle and Why is it Key to
- Life?, https://kids.frontiersin.org/article/10.3389/frym.2019.00041#KC1, 1 Dec. 2020.
- InTeGrate., Mississippi River Case Study,
- https://serc.carleton.edu/integrate/teaching_materials/food_supply/student_materials/1113, 1 Dec. 2020.
- Jury, W.A. and D.R. Nielson. 1989. Nitrate transport and leaching mechanisms. In R.F. Follett (ed.), Nitrogen Management and Ground Water Protection (pp. 139-157). Elsevier Sci. Pubs. Amsterdam.
- Study ACS., Nitrogen Cycle, https://www.studyacs.com/blog-nitrogen-cycle-37.aspx, 2 Dec. 2020.
- USGS., Nitrogen and Water, https://www.usgs.gov/special-topic/water-science-school/science/nitrogen-and-water?qt-science_center_objects=0#qt-science_center_objectsaccessed, 12 Nov. 2020.
- USDA., Fate and Transport of Nutrients: Nitrogen, https://www.nrcs.usda.gov/wps/portal/nrcs/detail/national/landuse/crops/?cid=nrcs143_014202, 2 Dec 2020.
- USDA., Mississippi River Basin Health Watershed Initiative, https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcsdev11_023950.pdf, 1 Dec. 2020.
- USGS., Nutrients and Eutrophication, https://www.usgs.gov/mission-areas/water-resources/science/nutrients-and-eutrophication?qt-science_center_objects=0#, 2 Dec. 2020.
- USGS., Phosphorus and Water, https://www.usgs.gov/special-topic/water-science-school/science/phosphorus-and-water?qt-science_center_objects=0#qt-science_center_objects, 2 Dec. 2020.
- USGS., The Quality of Our Nation's Waters, https://pubs.usgs.gov/circ/circ1225/, 20 Nov. 2020.
- Sharif, W.U., Davis R.K., Steele K.F., Kim B., Kresse T.M., and Fazio J.A., 2007, Inverse geochemical modeling of groundwater evolution with emphasis on arsenic in the Mississippi River valley alluvial aquifer, Arkansas (USA), Journal of Hydrology (2008), 350, 41-55.
- Study ACS., Nitrogen Cycle, https://www.studyacs.com/blog-nitrogen-cycle-37.aspx, 2 Dec. 2020.