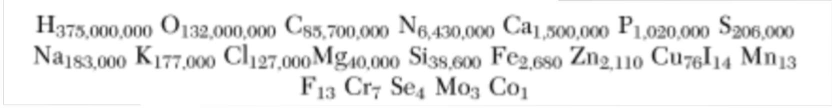
The Global P Cycle

The recipe for life contains more than carbon!

It is mostly... CHNOPS

The stoichiometric formula for a living human being is:



$$H_{375,000,000}\ O_{132,000,000}\ C_{85,700,000}\ N_{6,430,000}\ Ca_{1,500,000}\ P_{1,020,000}\ S_{206,000}\ Na_{183,000}\ K_{177,000}\ Cl_{127,000}Mg_{40,000}\ Si_{38,600}\ Fe_{2,680}\ Zn_{2,110}\ Cu_{76}I_{14}\ Mn_{13}\ F_{13}\ Cr_{7}\ Se_{4}\ Mo_{3}\ Co_{1}$$

The Global P Cycle is importance because:

Hydroxyapatite (Bones & Teeth)
$Ca_{10}(PO_4)_6(OH)_2$

Fluoroapatite (Teeth)
$Ca_5(PO_4)_3F$

Sedimentary – having no significant gaseous phase
Gaseous

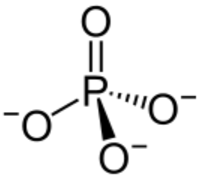
Processes

Geologic Uplift

Rock Weathering

Congruent Dissolution Weathering

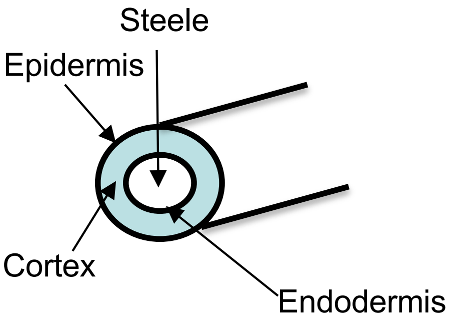
$$Ca_5(PO_4)_3OH + 4H_2CO_3 \rightarrow 5Ca^{++} + 3HPO^{=}_4 + 4HCO_3^- + H_2O$$



Orthophosphate

Uptake/Assimilation

Mycorrhizae



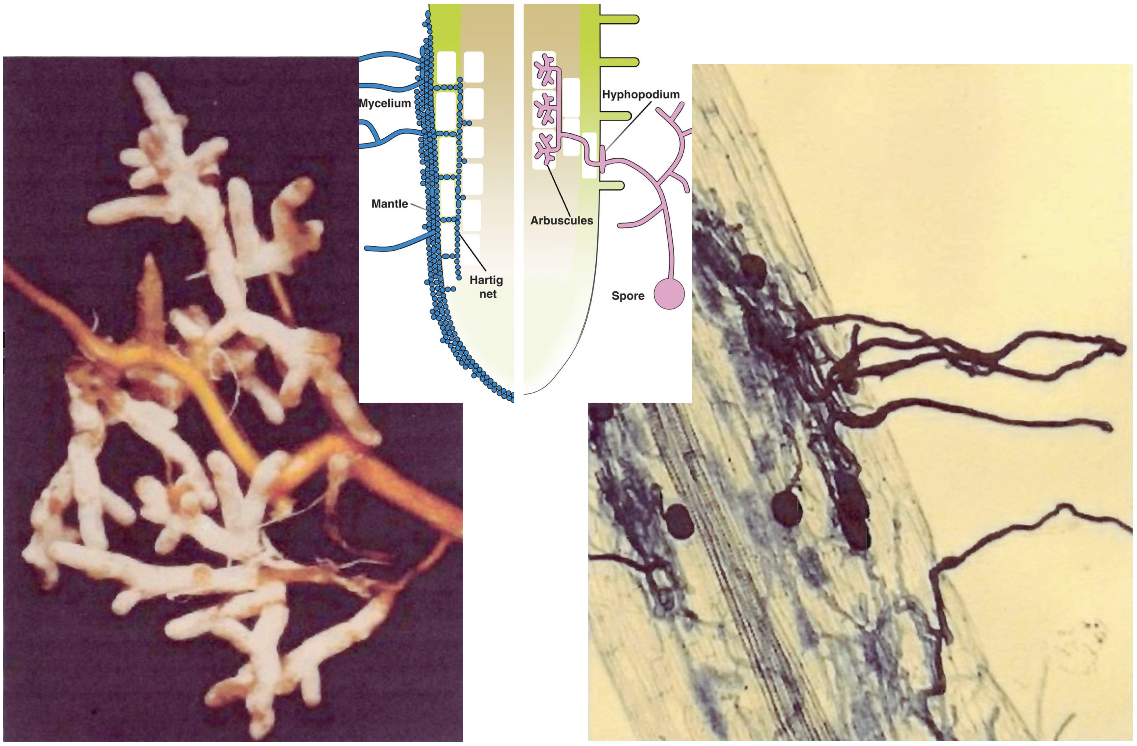
Ectotrophic

Pinaceae, Fagaceae, Betulaceae

Salicaceae

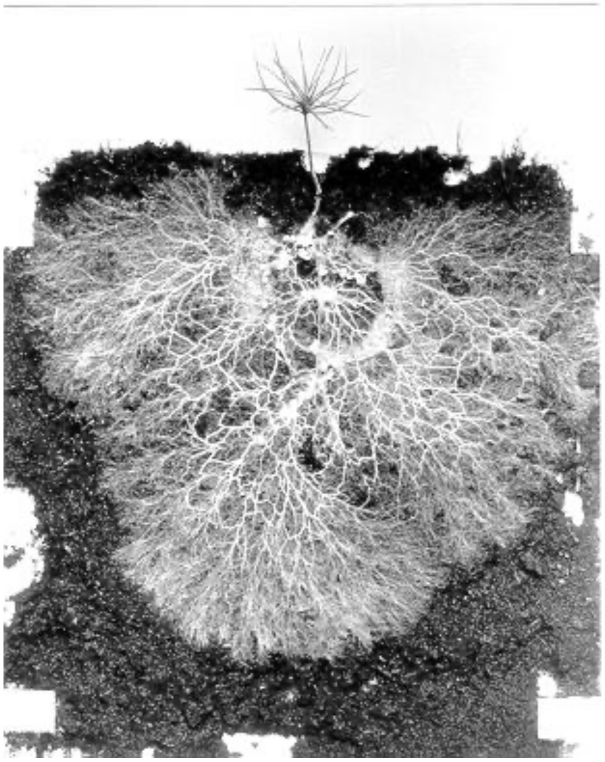
Endotrophic

Almost all cultivated plants



Ectotrophic mycorrhizae

Endotrophic mycorrhizae



Extensive network of mycorrhizal hyphae radiating from roots of a larch (*Larix*) seedling grown in peat

http://www.biology.ed.ac.uk/research/groups/jdeacon/mrhizas/ecbmycor.htm

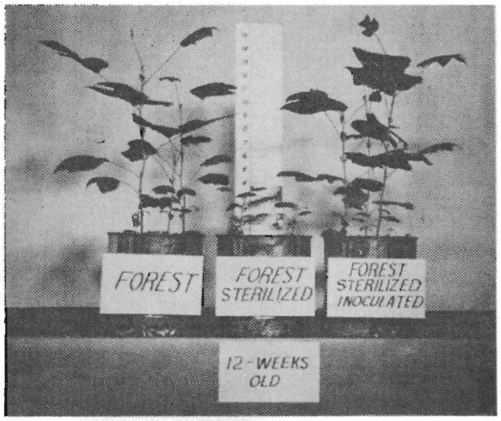


Fig. 1. Seedlings of yellow poplar, tulip tree (*Liriodendron tulipifera* L.) grown for 12 weeks in undisturbed soil cores from a forest site demonstrated that endotrophic mycorrhizal fungi influence growth. (Left) Seedlings grown in unsterilized soil were infected. (Center) Seedlings grown in sterilized soil were nonmycorrhizal and nonvigorous. (Right) Seedlings in sterilized soil inoculated with yellow poplar roots were mycorrhizal.

TABLE 7.2 Some Characteristics of White Pine (*Pinus strobus*) Seedlings Grown for 1 yr with and without Mycorrhizal Infection[a]

	Seedling		Leaf (% oven dry weight)		
Treatment	Dry weight (g)	Root/shoot	N	P	K
Mycorrhizal	405	0.78	1.24	0.20	0.74
Nonmycorrhizal	321	1.14	0.85	0.07	0.43

[a] Data from Hatch (1937). Waring + Schlesinger 1985

Table 6.3 Effects of Mycorrhizae and N-Fixing Nodules on Growth and Nitrogen Fixation in *Ceanothus velutinus* Seedlings.[a]

	Control	+Mycorrhizae	+Nodules	+Mycorrhizae and Nodules
Mean shoot dry weight (mg)	72.8	84.4	392.9	1028.8
Mean root dry weight (mg)	166.4	183.4	285.0	904.4
Root/shoot	2.29	2.17	0.73	0.88
Nodules per plant	0	0	3	5
Mean nodule weight (mg)	0	0	10.5	44.6
Acetylene reduction (mg/nodule/h)	0	0	27.85	40.46
Percent mycorrhizal colonization	0	45	0	80
Nutrient contents (% ODW in shoot)				
N	0.32	0.30	1.24	1.31
P	0.08	0.07	0.25	0.25
Ca			1.07	1.15

[a] From Rose and Youngberg (1981). Schlesinger 1991

Processes (Cont’d.)

Mineralization

C/P Ratio of OM	Result
<200	Net Mineralization
200-300	No net change
>300	Net Immobilization

Acid Phosphatases	pH optimum 4-6
Alkaline Phosphatases	pH optimum 9-11

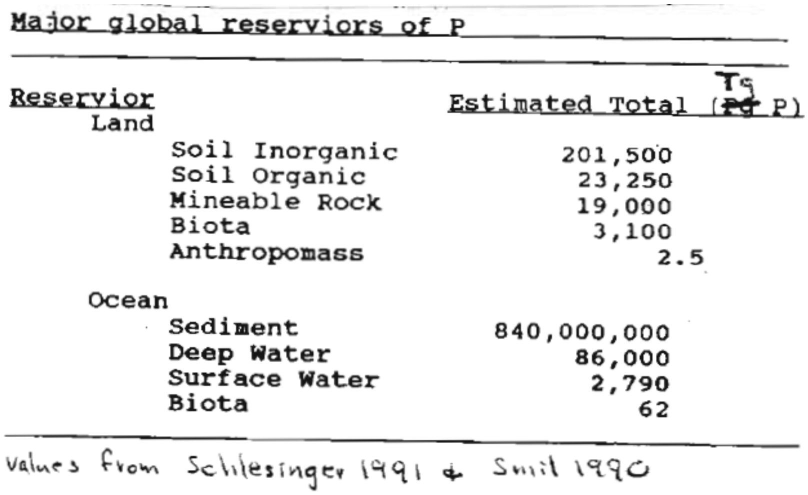
Excretion & Death

Leaching & Erosion

THE WASHINGTON POST

The depletion of Peru's guano islands lay at the heart of the War of the Pacific.

Sedimentation



Major global reserviors of P

Reservior	Estimated Total (~~Pg~~ Tg P)
Land	
Soil Inorganic	201,500
Soil Organic	23,250
Mineable Rock	19,000
Biota	3,100
Anthropomass	2.5
Ocean	
Sediment	840,000,000
Deep Water	86,000
Surface Water	2,790
Biota	62

Values from Schlesinger 1991 & Smil 1990

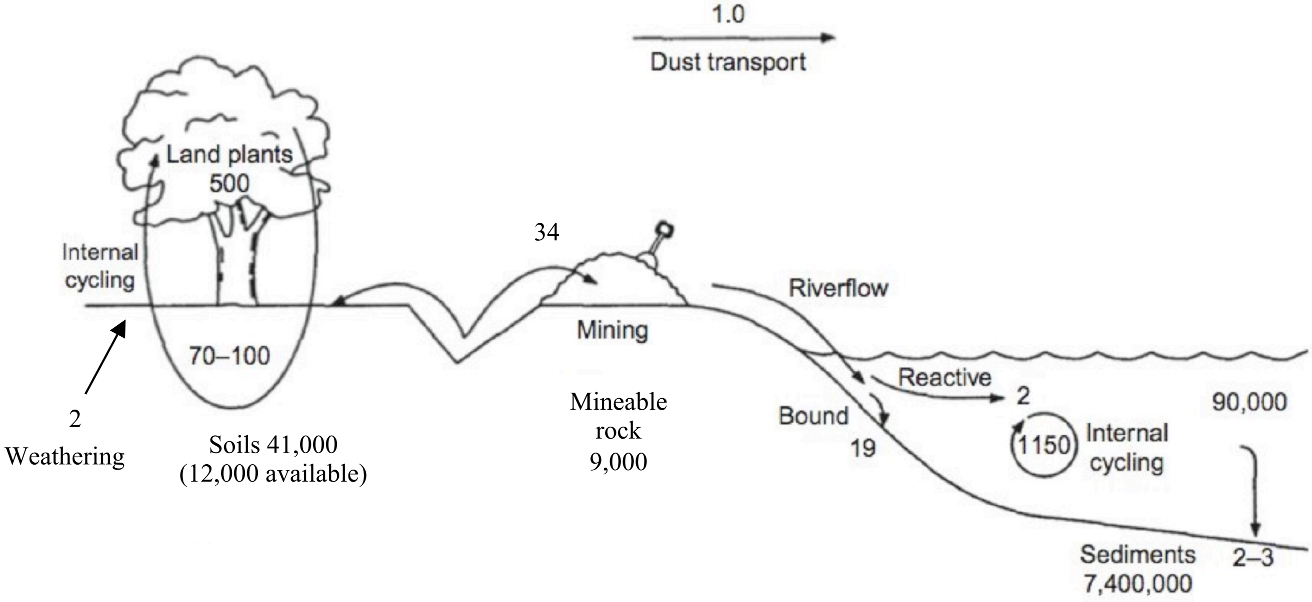


FIGURE 12.7 The global phosphorus cycle. Each flux is shown in units of 10^{12} g P/yr. Values for P production and reserves are taken from the U.S. Geological Survey. Estimate for sediments is from Van Cappellen et al. (1996), and estimates for other pools and flux are derived from the text.

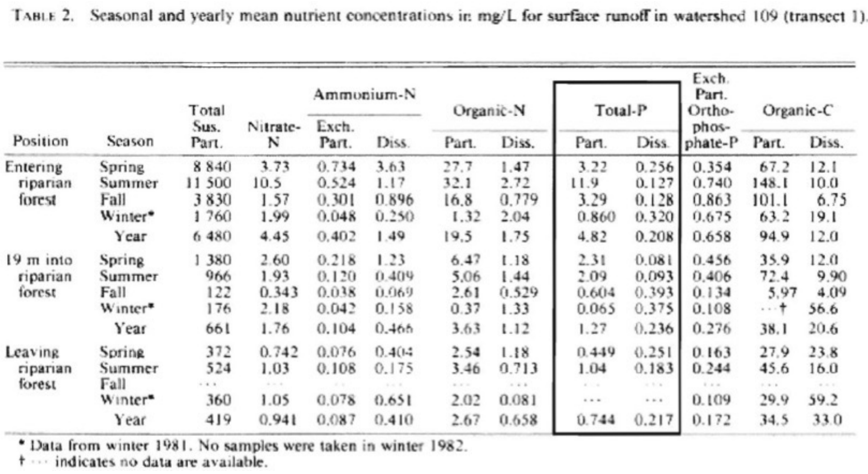
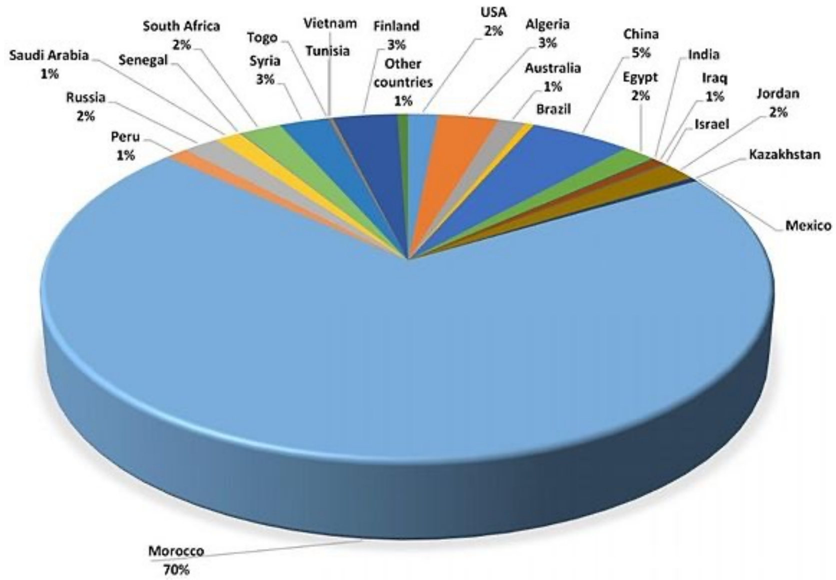


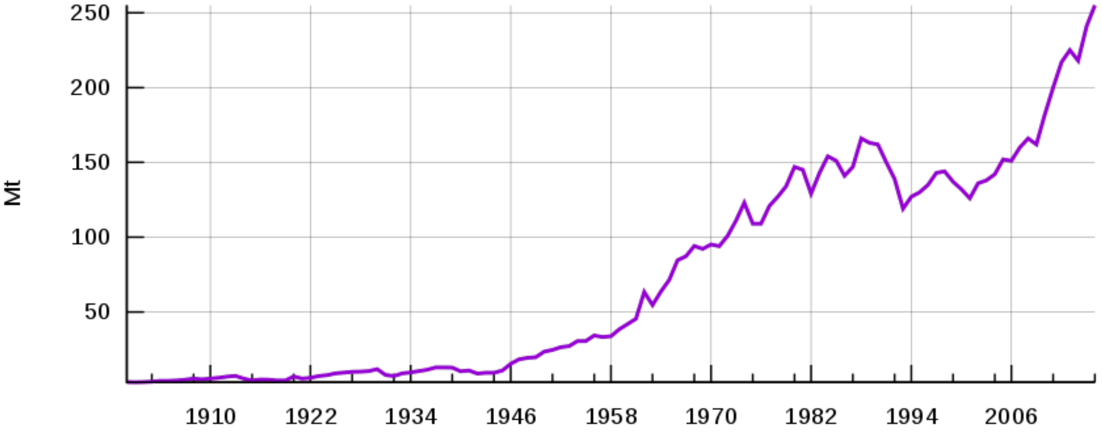
TABLE 2. Seasonal and yearly mean nutrient concentrations in mg/L for surface runoff in watershed 109 (transect 1).

Position	Season	Total Sus. Part.	Nitrate-N	Ammonium-N		Organic-N		Total-P		Exch. Part. Ortho-phos-phate-P	Organic-C	
				Exch. Part.	Diss.	Part.	Diss.	Part.	Diss.		Part.	Diss.
Entering riparian forest	Spring	8 840	3.73	0.734	3.63	27.7	1.47	3.22	0.256	0.354	67.2	12.1
	Summer	11 500	10.5	0.524	1.17	32.1	2.72	11.9	0.127	0.740	148.1	10.0
	Fall	3 830	1.57	0.301	0.896	16.8	0.779	3.29	0.128	0.863	101.1	6.75
	Winter*	1 760	1.99	0.048	0.250	1.32	2.04	0.860	0.320	0.675	63.2	19.1
	Year	6 480	4.45	0.402	1.49	19.5	1.75	4.82	0.208	0.658	94.9	12.0
19 m into riparian forest	Spring	1 380	2.60	0.218	1.23	6.47	1.18	2.31	0.081	0.456	35.9	12.0
	Summer	966	1.93	0.120	0.409	5.06	1.44	2.09	0.093	0.406	72.4	9.90
	Fall	122	0.343	0.038	0.069	2.61	0.529	0.604	0.393	0.134	5.97	4.09
	Winter*	176	2.18	0.042	0.158	0.37	1.33	0.065	0.375	0.108	···†	56.6
	Year	661	1.76	0.104	0.466	3.63	1.12	1.27	0.236	0.276	38.1	20.6
Leaving riparian forest	Spring	372	0.742	0.076	0.404	2.54	1.18	0.449	0.251	0.163	27.9	23.8
	Summer	524	1.03	0.108	0.175	3.46	0.713	1.04	0.183	0.244	45.6	16.0
	Fall	···	···	···	···	···	···	···	···	···	···	···
	Winter*	360	1.05	0.078	0.651	2.02	0.081	···	···	0.109	29.9	59.2
	Year	419	0.941	0.087	0.410	2.67	0.658	0.744	0.217	0.172	34.5	33.0

* Data from winter 1981. No samples were taken in winter 1982.
† ··· indicates no data are available.

Where is phosphate rock found and how has its extraction changed?





Graph showing world phosphate rock production, 1900–2016, reported by US Geological Survey[1]

You can too much of a good thing!

Cultural eutrophication is a nutrient-induced increase in aquatic productivity due to anthropogenic nutrient additions

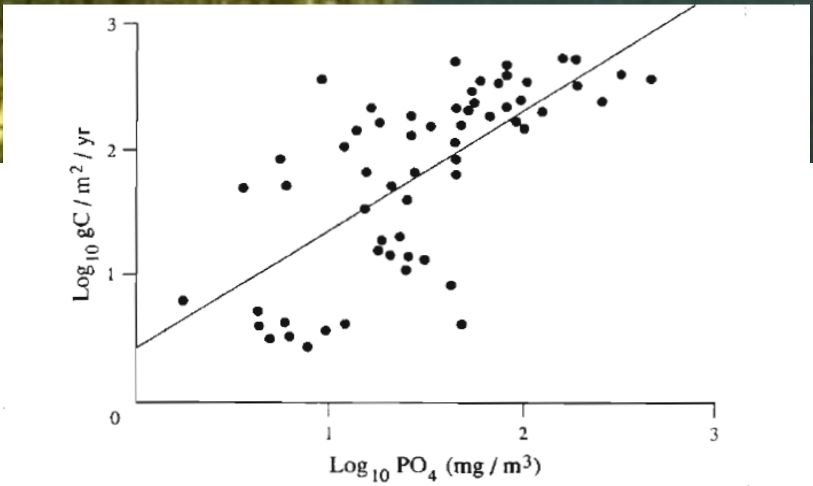
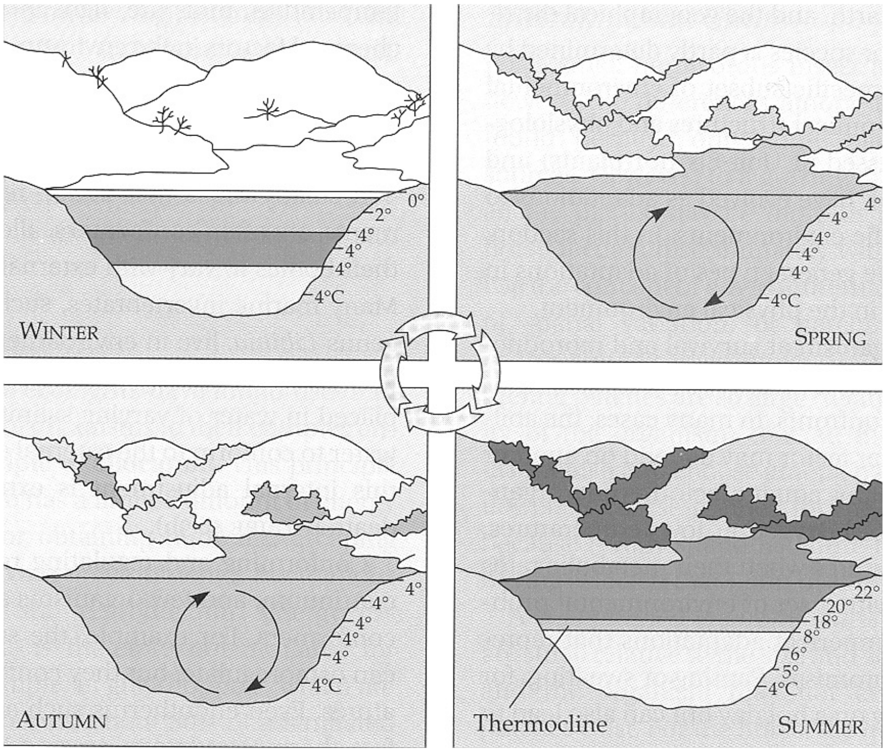
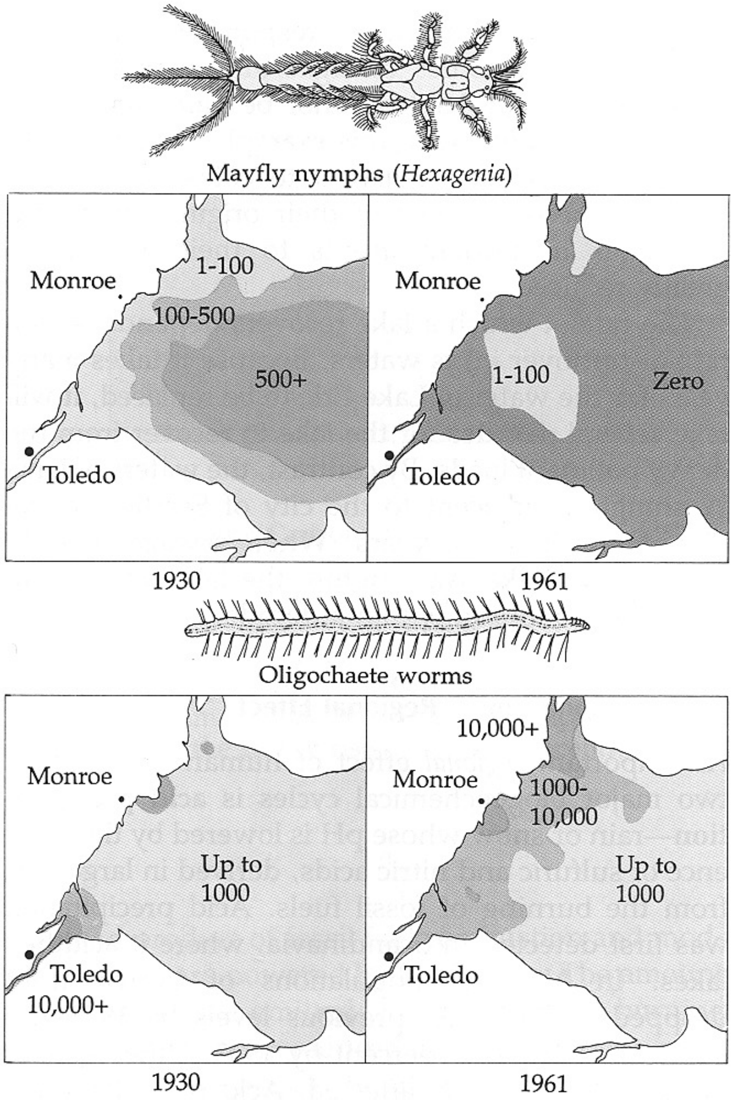


Figure 7.8 Relationship between net primary production and the phosphorus concentration in lakes of the world. From Schindler (1978). Schlesinger 1991


0°
2°
4°
4°
4°
4°C
Winter
4°
4°
4°
4°
4°
4°C
Spring
4°
4°
4°
4°
4°
4°C
Autumn
22°
20°
18°
8°
6°
5°
4°C
Thermocline
Summer


Mayfly nymphs (*Hexagenia*)
Monroe
1-100
100-500
500+
Toledo
1930
Monroe
1-100
Zero
Toledo
1961
Oligochaete worms
Monroe
Up to 1000
Toledo
10,000+
1930
10,000+
Monroe
1000-10,000
Up to 1000
Toledo
1961


AFP

Shores of Lake Erie
Summer 2013

Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions

6448–6452 | PNAS | April 16, 2013 | vol. 110 | no. 16

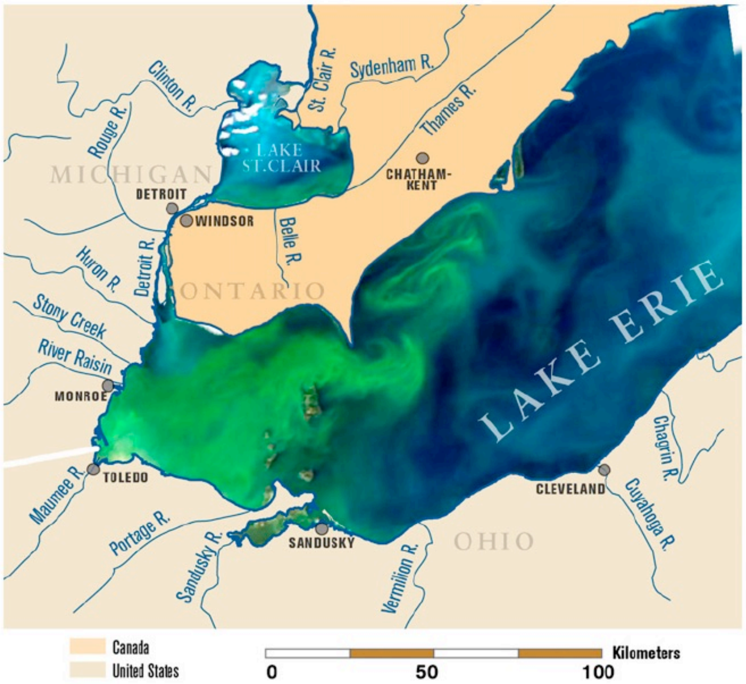
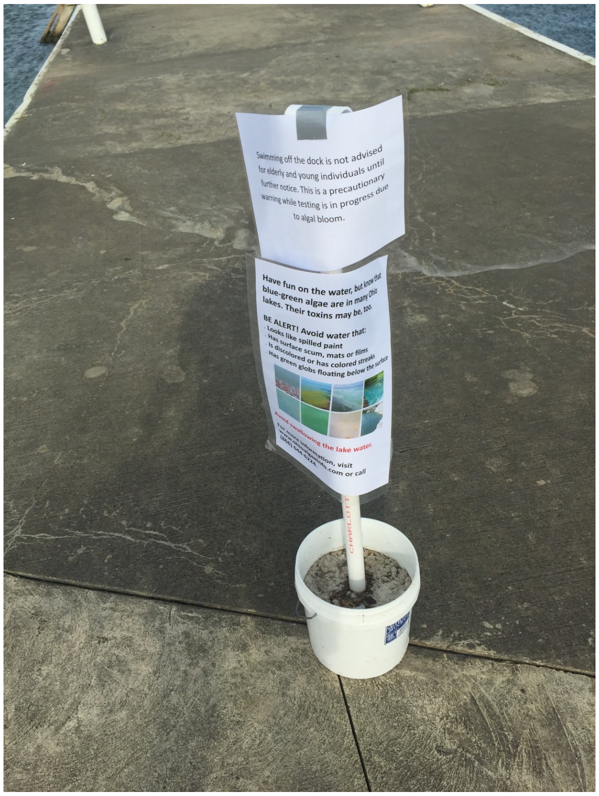


Fig. 1. MODIS satellite Image of Lake Erie on September 3, 2011, overlaid over map of Lake Erie tributaries. This image shows the bloom about 6 wk after its initiation in the western basin. On this date, it covers the entire western basin and is beginning to expand into the central basin, where it will continue to grow until October (Fig. S1).



Swimming off the dock is not advised for elderly and young individuals until further notice. This is a precautionary warning while testing is in progress due to algal bloom.

Have fun on the water, but know that blue-green algae are in many Ohio lakes. Their toxins may be, too.

BE ALERT! Avoid water that:
- Looks like spilled paint
- Has surface scum, mats or films
- Is discolored or has colored streaks
- Has green globs floating below the surface

Avoid swallowing the lake water.

For more information, visit www.ohioalgaeinfo.com or call (866) 644-6224.

Lake Erie just won the same legal rights as people

Ohio voters passed groundbreaking legislation that allows citizens to sue on behalf of the lake when it's being polluted.

By Sigal Samuel | Updated Feb 26, 2019, 11:00pm EST

"Lake Erie Bill of Rights"

Feb. 2019

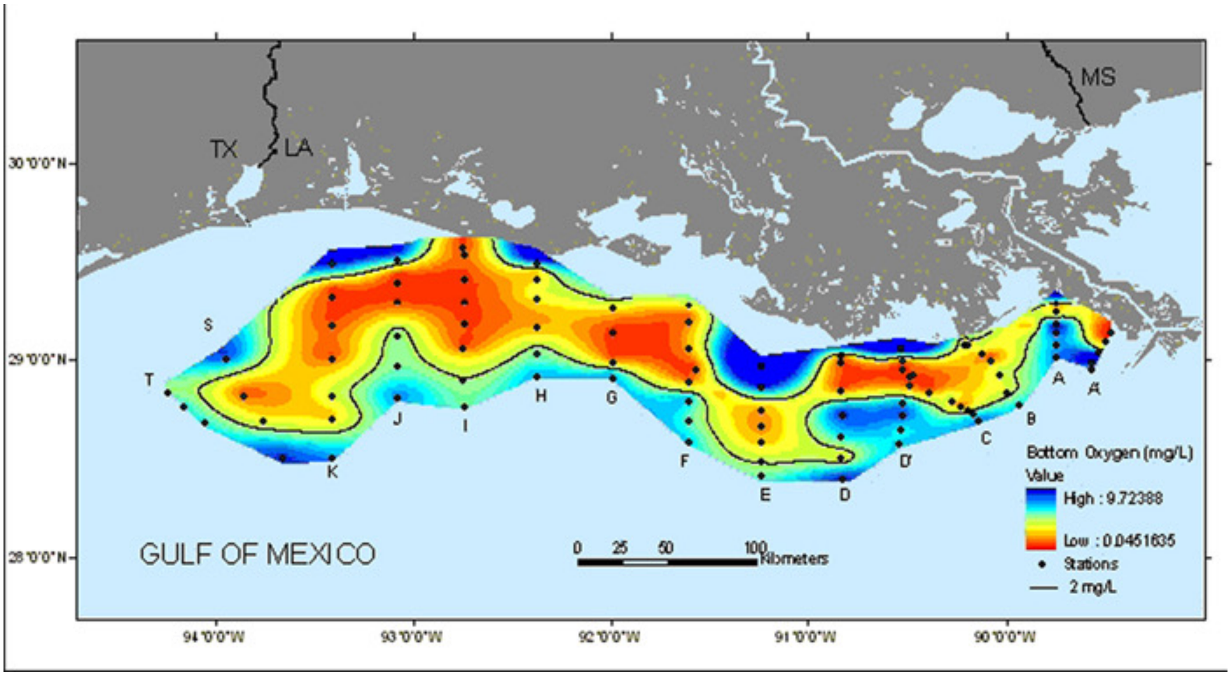
An Ohio resident collects water from Lake Erie in 2014 after a ban due to algae-related toxins. | Getty Images

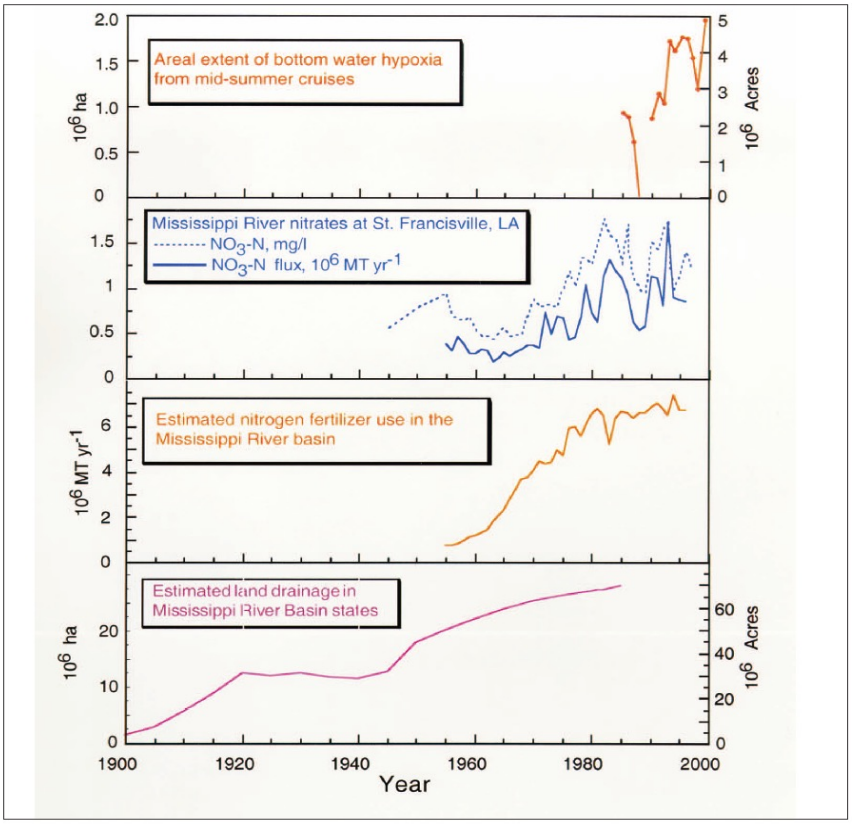
> **FUTURE PERFECT**
>
> *Finding the best ways to do good. Made possible by The Rockefeller Foundation.*

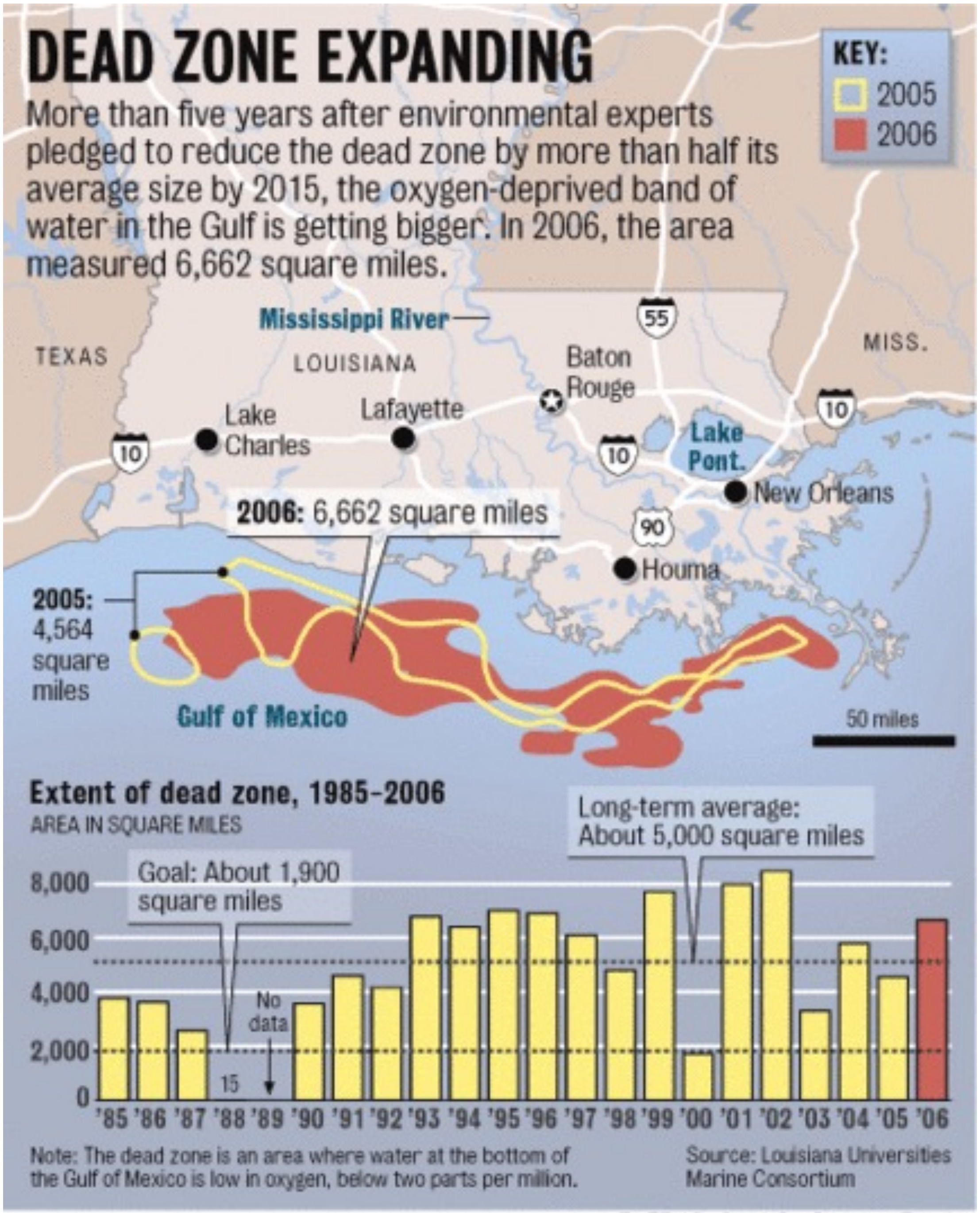
It started in a pub. A handful of people, hunched over beers in Toledo, Ohio, were talking about a water crisis that had plagued the city in 2014. The pollution of Lake Erie had gotten so bad that it had taken a **serious toll** on their lives. The government, they felt, wasn't doing enough to protect the lake. And so they wondered: What if the lake could protect itself?

THIRD-LARGEST "DEAD ZONE" SINCE 1985
AREA SIZE OF NEW JERSEY

Mid-Summer 2007







DEAD ZONE EXPANDING

More than five years after environmental experts pledged to reduce the dead zone by more than half its average size by 2015, the oxygen-deprived band of water in the Gulf is getting bigger. In 2006, the area measured 6,662 square miles.

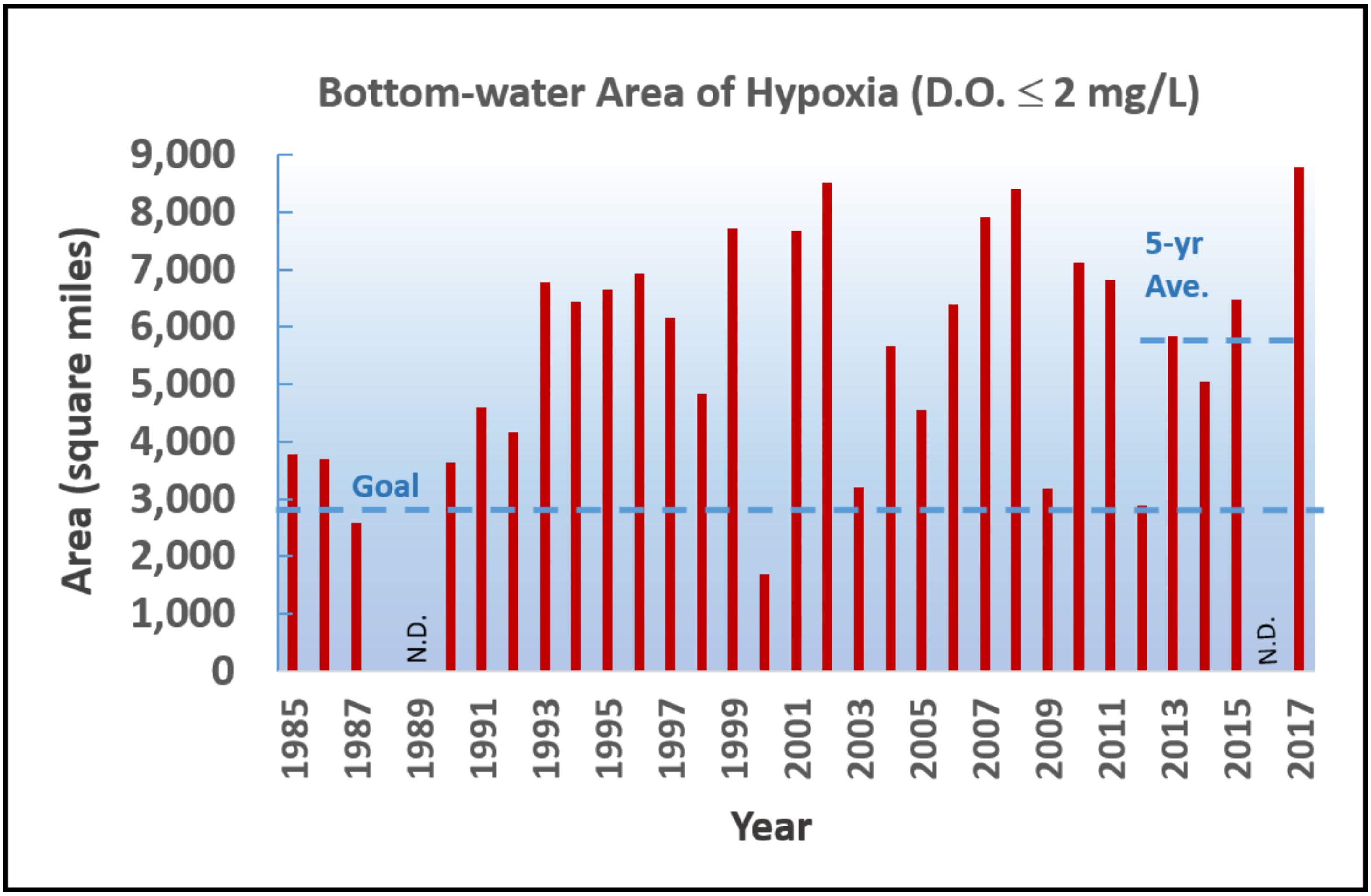
Extent of dead zone, 1985-2006

AREA IN SQUARE MILES

Note: The dead zone is an area where water at the bottom of the Gulf of Mexico is low in oxygen, below two parts per million.

Source: Louisiana Universities Marine Consortium

STAFF GRAPHIC BY DAN SWENSON


Bottom-water Area of Hypoxia (D.O. ≤ 2 mg/L)

Graph showing measured size of hypoxia zone on Louisiana Gulf of Mexico shelf, 1985–2017. Credit: LSU/LUMCON and NOAA.


Gulf 'Dead Zone' Chokes Marine Life

The Gulf of Mexico at the Mississippi River Delta experiences a seasonal *hypoxia*, or "dead zone," where there is not enough oxygen in the water to sustain marine life.

SOURCE: NOAA

InsideClimate News

Spreading Dead Zones and Consequences for Marine Ecosystems

Robert J. Diaz[1]* and Rutger Rosenberg[2]

Dead zones in the coastal oceans have spread exponentially since the 1960s and have serious consequences for ecosystem functioning. The formation of dead zones has been exacerbated by the increase in primary production and consequent worldwide coastal eutrophication fueled by riverine runoff of fertilizers and the burning of fossil fuels. Enhanced primary production results in an accumulation of particulate organic matter, which encourages microbial activity and the consumption of dissolved oxygen in bottom waters. Dead zones have now been reported from more than 400 systems, affecting a total area of more than 245,000 square kilometers, and are probably a key stressor on marine ecosystems.

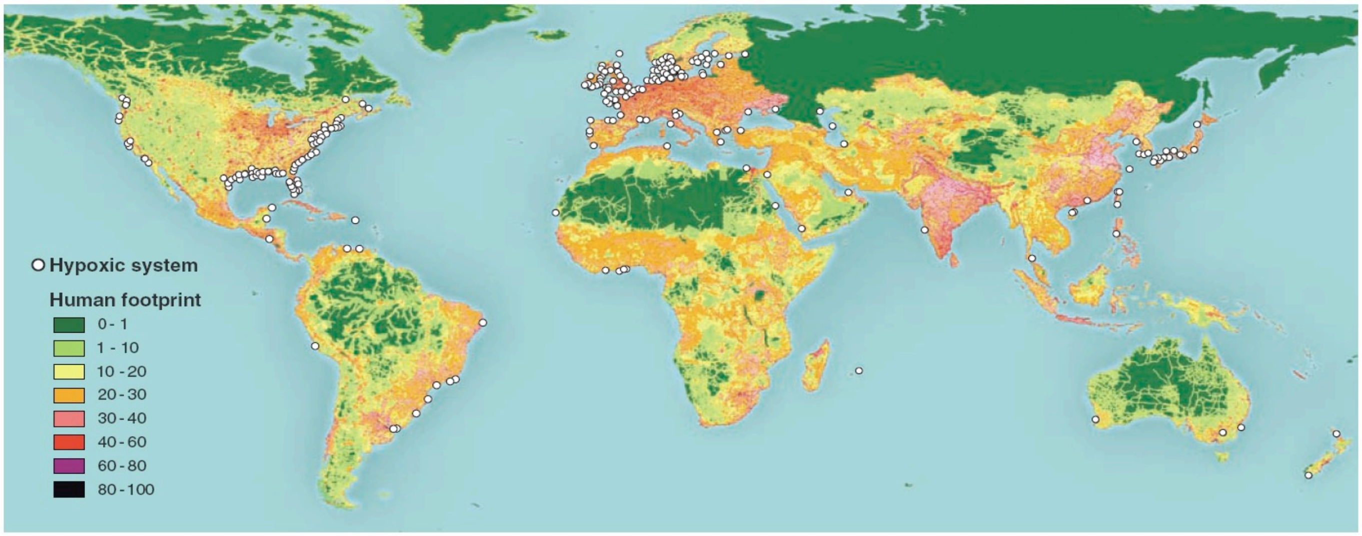


Fig. 1. Global distribution of 400-plus systems that have scientifically reported accounts of being eutrophication-associated dead zones. Their distribution matches the global human footprint [the normalized human influence is expressed as a percent (*41*)] in the Northern Hemisphere. For the Southern Hemisphere, the occurrence of dead zones is only recently being reported. Details on each system are in tables S1 and S2.

The Global S Cycle

Important because:

Clinical Toxicology ›
Volume 48, 2010 - Issue 7

Brief Communications

Hydrogen sulfide toxicity in a thermal spring: a fatal outcome

Hale Daldal, Bayram Beder, Simay Serin & Hulya Sungurtekin

Pages 755-756 | Received 19 May 2010, Accepted 09 Jul 2010, Published online: 12 Aug 2010
Download citation https://doi.org/10.3109/15563650.2010.508044

Abstract

Introduction. Hydrogen sulfide (H_2S) is a toxic gas with the smells of "rotten egg"; its toxic effects are due to the blocking of cellular respiratory enzymes leading to cell anoxia and cell damage. *Case presentation.* We report two cases with acute H_2S intoxication caused by inhalation of H_2S evaporated from the water of a thermal spring. Two victims were found in a hotel room were they could take a thermal bath. A 26-year-old male was found unconscious; he was resuscitated, received supportive treatment and survived. A 25-year-old female was found dead. Autopsy showed diffuse edema and pulmonary congestion. Toxicological blood analysis of the female revealed the following concentrations: 0.68 mg/L sulfide and 0.21 mmol/L thiosulfate. The urine thiosulfate concentration was normal. Forensic investigation established that the thermal water was coming from the hotel's own illegal well. The hotel was closed. *Conclusion.* This report highlights the danger of H_2S toxicity not only for reservoir and sewer cleaners, but also for individuals bathing in thermal springs.

Keywords: Inhalation exposure, Acute toxicity, Hydrogen sulfide

TABLE 3-11

Chemical Forms of Sulfur

Formula	*Name*	*Oxidation number*	*Comments*
H_2S	Hydrogen sulfide	−2	"Rotten egg" gas, extremely toxic
HS^-	Hydrosulfide ion	−2	Constituent of amino acids
$S^=$	Sulfide ion	−2	Forms insoluble compounds with metals
$S_2^=$	Disulfide ion	−1	Plays crucial role in stiffening protein
S_2, S_n, S_n	Elemental sulfur	0	Crystalline solid
SO_2	Sulfur dioxide	+4	Colorless, toxic gas
H_2SO_3	Sulfurous acid	+4	Weak acid from SO_2 plus water
SO_3	Sulfur trioxide	+6	Gas from oxidizing SO_2 in air
H_2SO_4	Sulfuric acid	+6	Strong acid from SO_3 plus water
$SO_4^=$	Sulfate ion	+6	Forms many compounds in atmosphere and soil

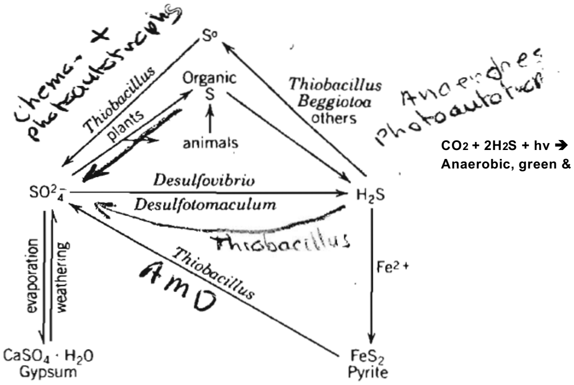
Ehrlich et al. 1977

TABLE 3-12

Sulfur Chemistry of Biologic Assimilation and Decomposition

Transformation	*Mechanism*
$SO_2, SO_4^= \longrightarrow$ organic S	Assimilation and synthesis by plants
Organic S $\longrightarrow H_2S$	Many anaerobic and aerobic bacteria
Organic S $\longrightarrow SO_4^=$	Most plants and animals, many bacteria
$SO_4^= \longrightarrow H_2S$	Anaerobic bacteria (*Desulforvibrio, Desulfotomaculum*)
$H_2S \longrightarrow S \longrightarrow SO_4^=$	Aerobic bacteria (*Thiobacillus*), photosynthetic bacteria (*Chromatium, Chlorobium*)

The Sulfur Cycle



$CO_2 + 2H_2S + hv \rightarrow CH_2O + 2S + H_2O$

Anaerobic, green & purple sulfur bacteria

Fig. 8.9

Pathways of S transformations. The list of organisms involved in oxidation-reduction is incomplte (see text). (Adapted from Kaplan.[99]) Stevenson 1986

	C/S Ratio	
< 200	200 to 400	> 400
Net gain of SO_4^{2-}	Neither a gain or loss of SO_4^{2-}	Net loss of SO_4^{2-}

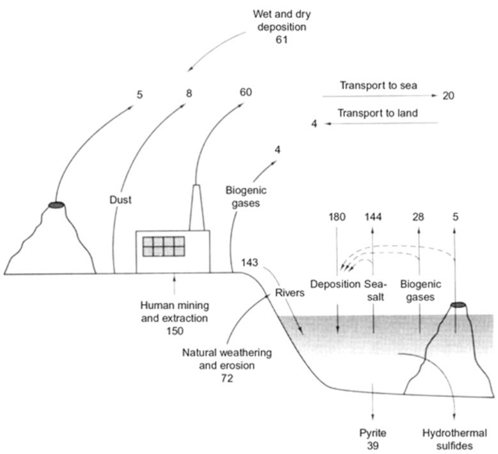
Stevenson 1986

Table 13.1 Reservoirs of Sulfur near the Surface of the Earth[a]

Reservoir	10^{18} g S			
Deep oceanic rocks				
Sediments	75	±	20	
Mafic rocks	2300	±	800	
Sedimentary rocks				
Sandstone	250	±	60	
Shale	2000	±	580	10,175
Limestone	380	±	110	
Evaporites	5100	±	1600	
Volcanics	50	±	18	
Connate water	27	±	5	
Total sediments	7800	±	1700	
Freshwater	0.003	±	0.002	0.009
Ice	0.006	±	0.002	
Atmosphere	3.6	×	10^{-6}	
Sea	1280	±	55	
Organic reservoir				
Land plants	0.6	×	10^{-3}	
Marine plants	0.024	×	10^{-3}	
Dead organic matter	5.0	×	10^{-3}	
Total organic	5.62	×	10^{-3}	

[a] From Trudinger (1979). Schlesinger 1991

Global S Cycle
(10^{12} g S/yr)



Schlesinger & Bernhardt 2013

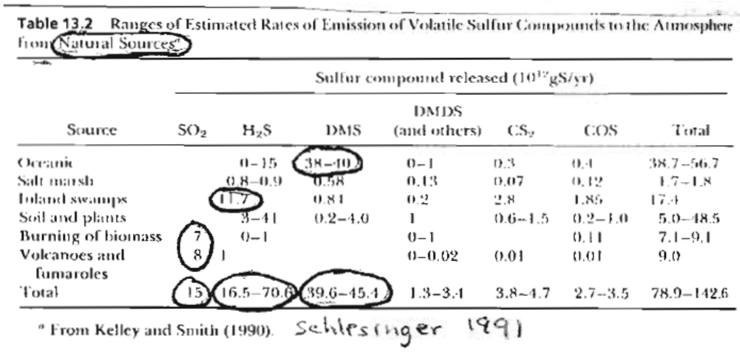


Table 13.2 Ranges of Estimated Rates of Emission of Volatile Sulfur Compounds to the Atmosphere from Natural Sources[a]

	Sulfur compound released (10^{12}gS/yr)						
Source	SO_2	H_2S	DMS	DMDS (and others)	CS_2	COS	Total
Oceanic		0–15	38–40	0–1	0.3	0.4	38.7–56.7
Salt marsh		0.8–0.9	0.58	0.13	0.07	0.12	1.7–1.8
Inland swamps		11.7	0.84	0.2	2.8	1.85	17.4
Soil and plants		3–41	0.2–4.0	1	0.6–1.5	0.2–1.0	5.0–48.5
Burning of biomass	7	0–1		0–1		0.11	7.1–9.1
Volcanoes and fumaroles	8	1		0–0.02	0.01	0.01	9.0
Total	15	16.5–70.6	39.6–45.4	1.3–3.4	3.8–4.7	2.7–3.5	78.9–142.6

[a] From Kelley and Smith (1990). Schlesinger 1991

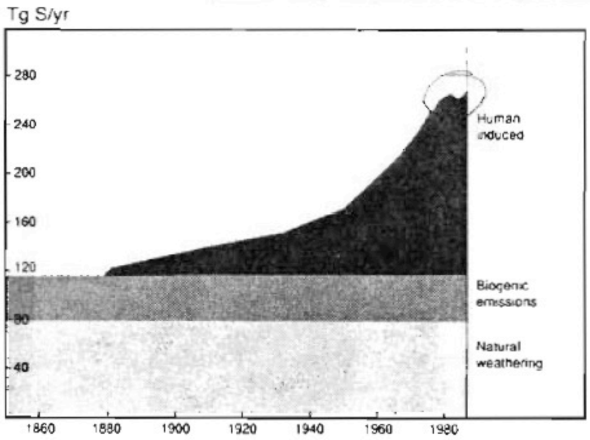


Figure 24.11 Global natural and human-induced sulfur mobilization.
Husar + Husar 1990

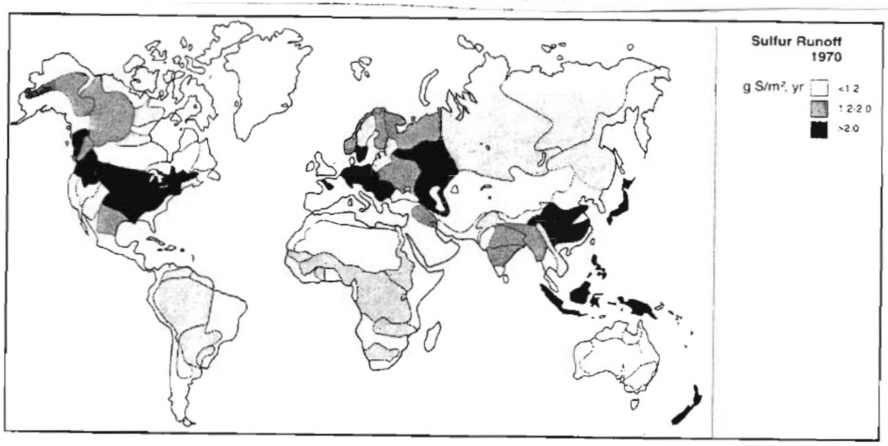


Figure 24.14 Sulfur runoff in the world rivers around 1970. Husar + Husar 1990

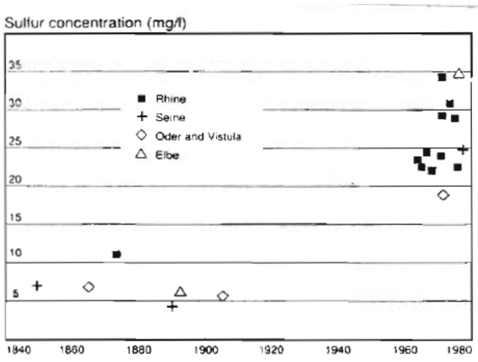


Figure 24.15 Trends in sulfur concentration in European rivers: Rhine (■), Seine (+), Oder and Vistula (◇), and Elbe (△). Sources: Meybeck 1979; Paces 1982; Steele 1980. Husar + Husar 199

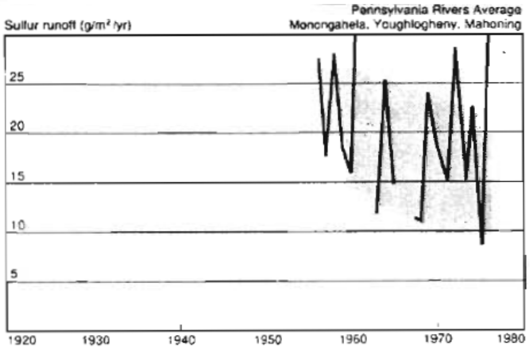


Figure 24.19 Trend of sulfur runoff in the Monongahela, Youghiogheny, and Mahoning rivers of the Pennsylvania–West Virginia mining district. Husar + Husar 1990

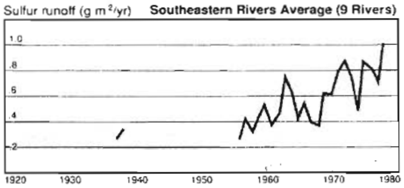


Figure 24.20 Trend of average sulfur runoff in nine rivers of the coastal plains in the eastern United States. Husar + Husar 1990

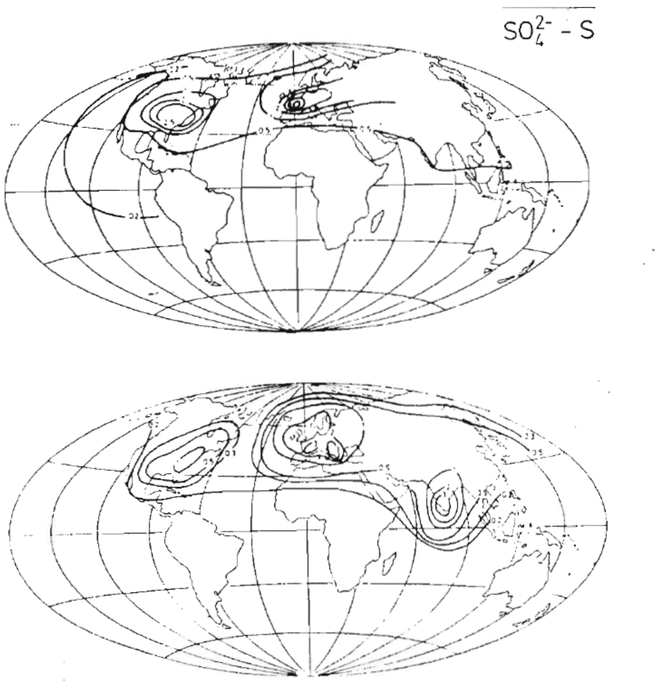
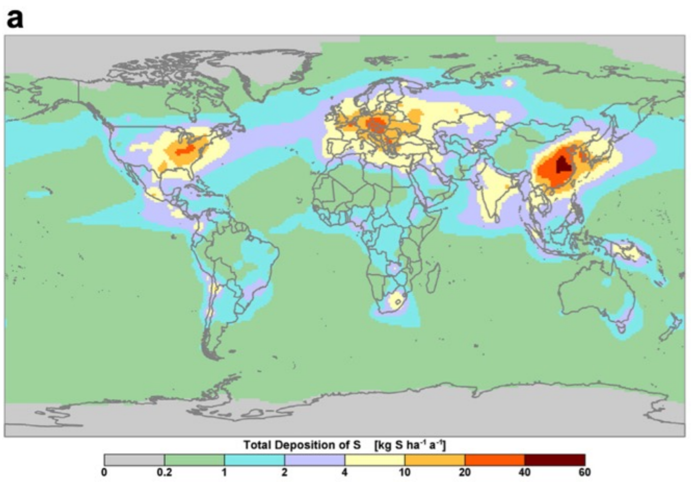
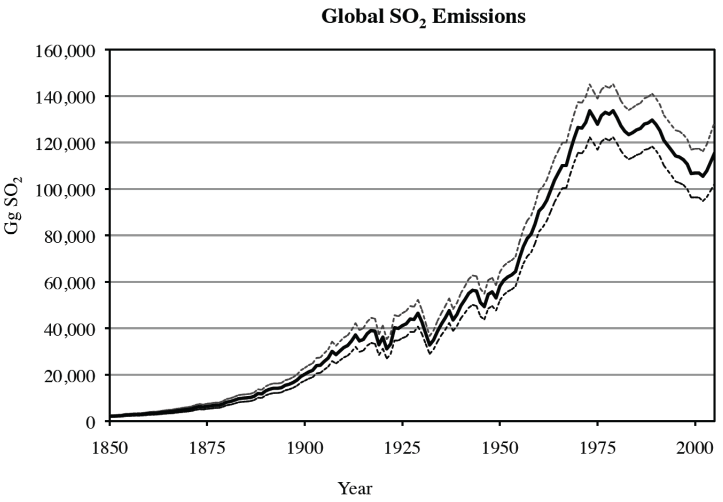
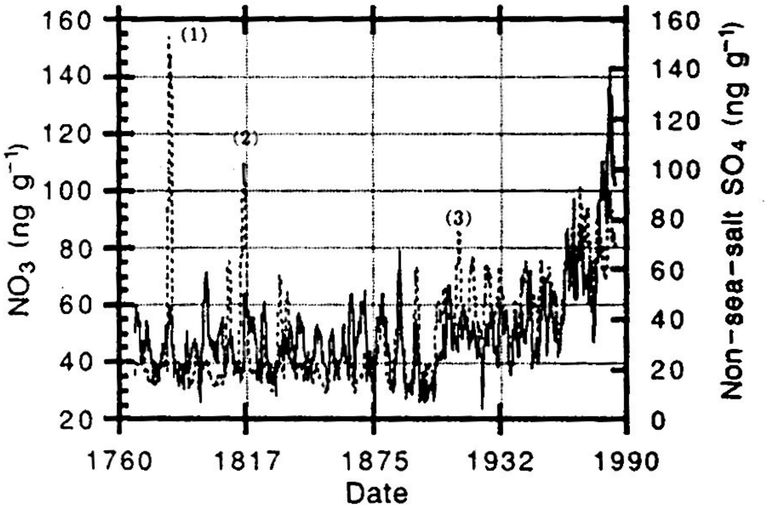


Fig. 10-7. Sulfate in rain water. Upper part: Global average distribution of concentration in units of mg S/liter. Lower part: Deposition rate in units of g S/m² yr. {From Georgii (1982), with permission.] Warneck 1988





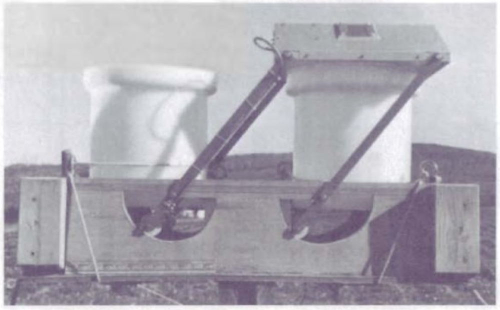
Smith et al. 2011

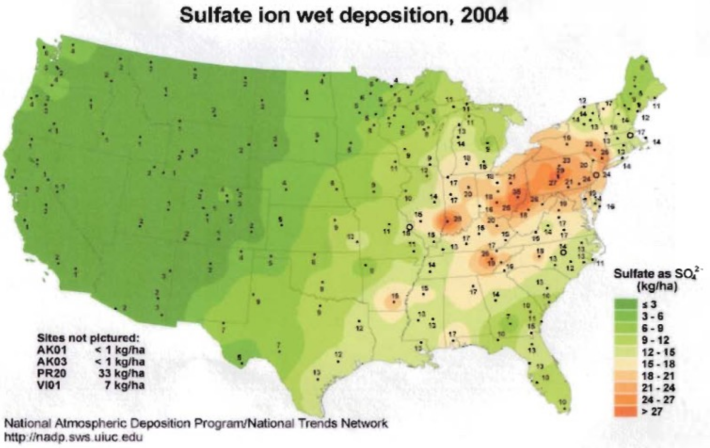


Mayewski et al. 1990

Atmospheric Deposition

Wet = rain + snow
Dry = particles + gases
Cloud = non-precipitating droplets





Sulfate ion wet deposition, 2004

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

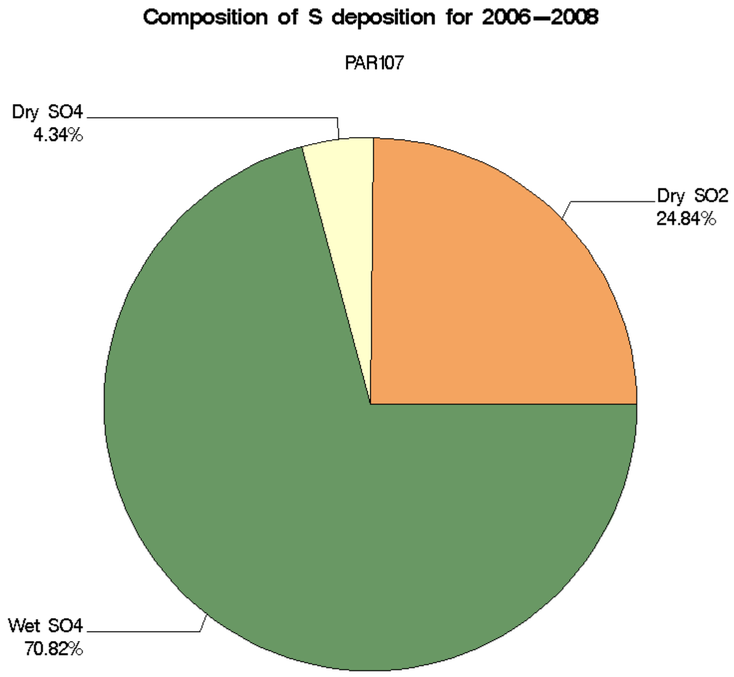
Acid deposition is more than acid rain

- Acid rain
- Acid snow

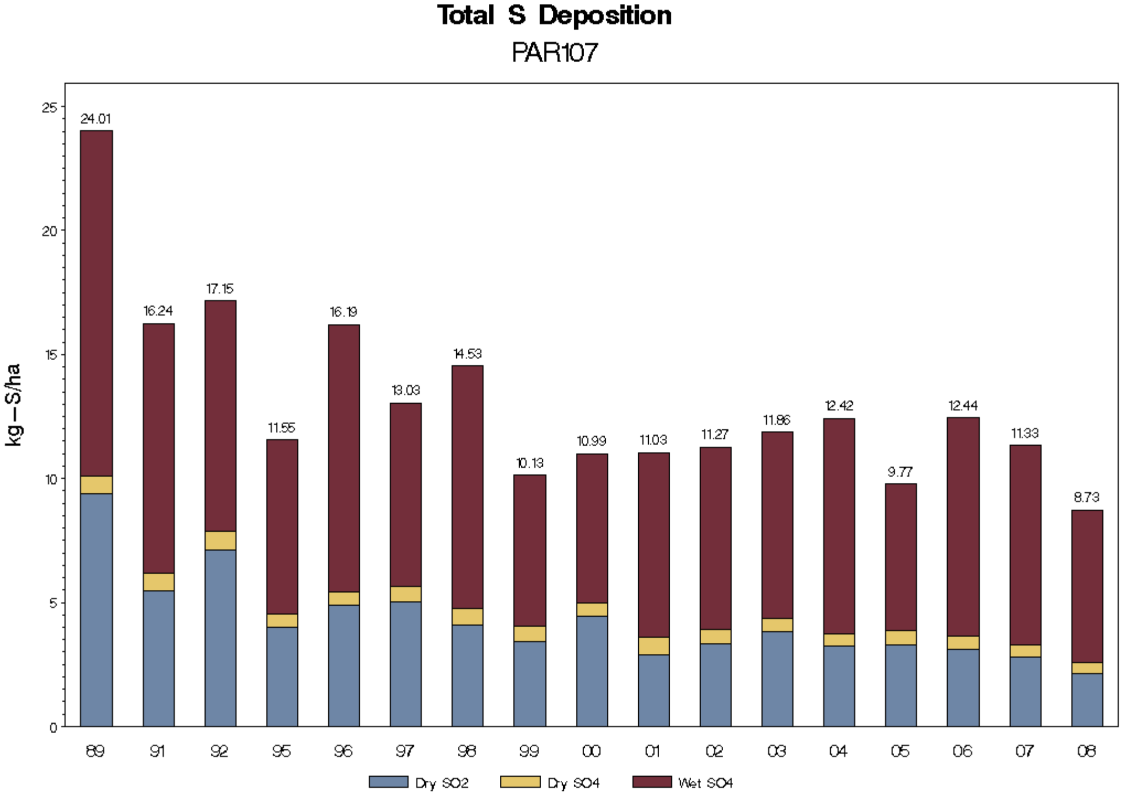
} **~80% of acid deposition**

- Acid fog
- Acid dry deposition
  - small particles (e.g. sulfate particles)
  - uptake of acid forming gases

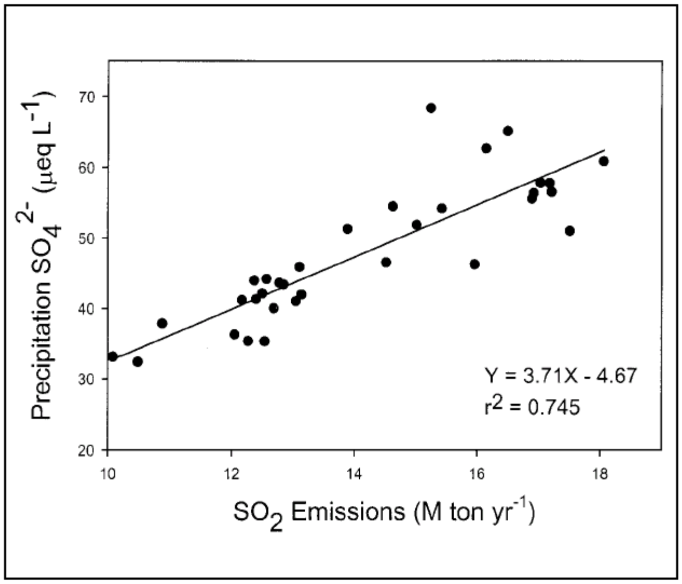
Dry & Wet Sulfur Deposition in WV

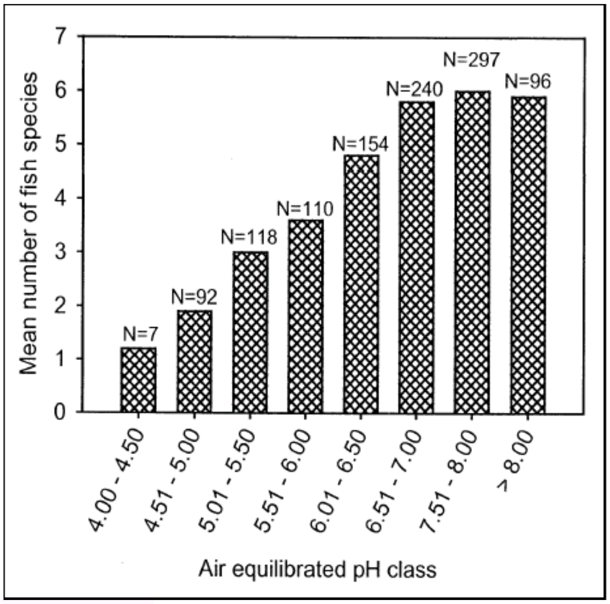


Source: CASTNET/NADP–NTN Only complete years are shown 30JUN10



Source: CASTNET/NADP–NTN Only complete years are shown 30JUN10





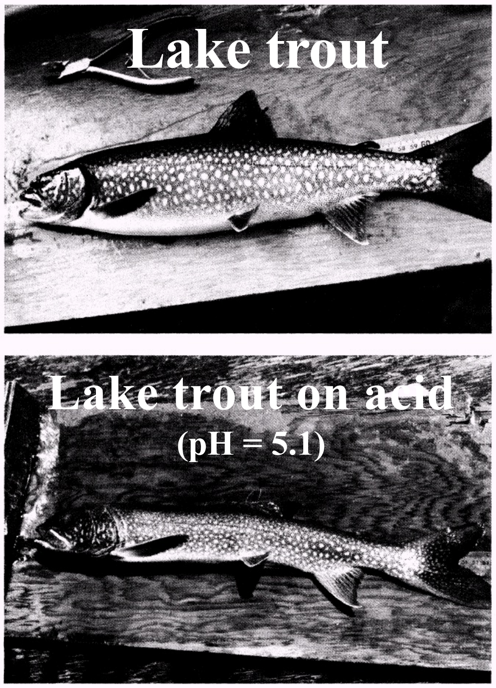
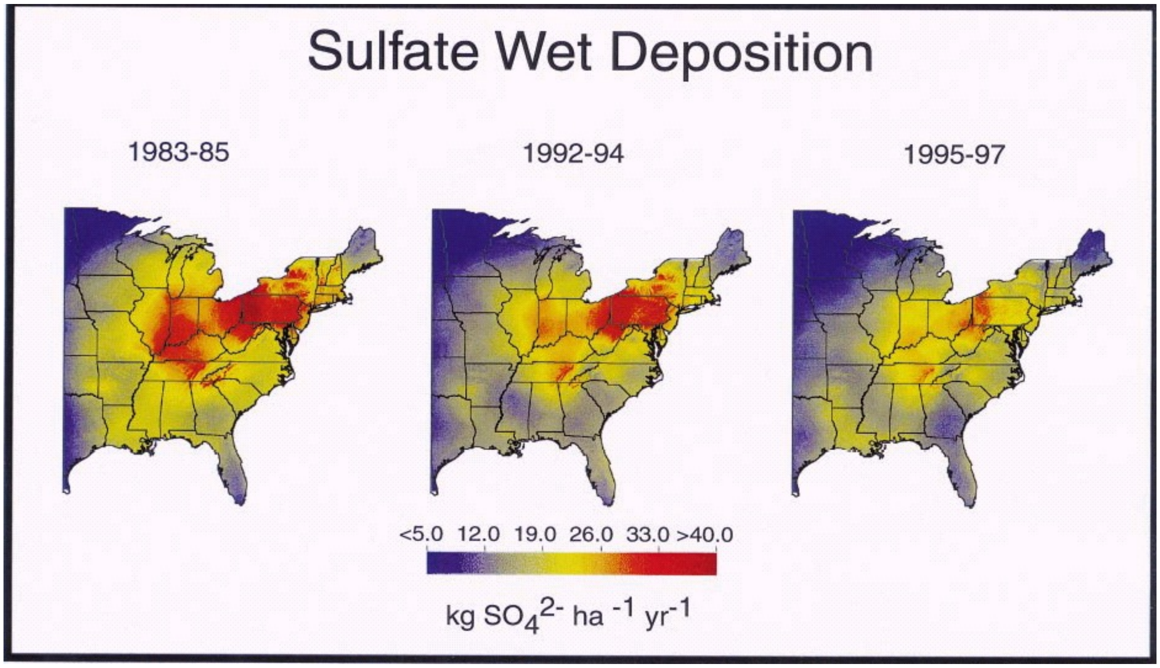
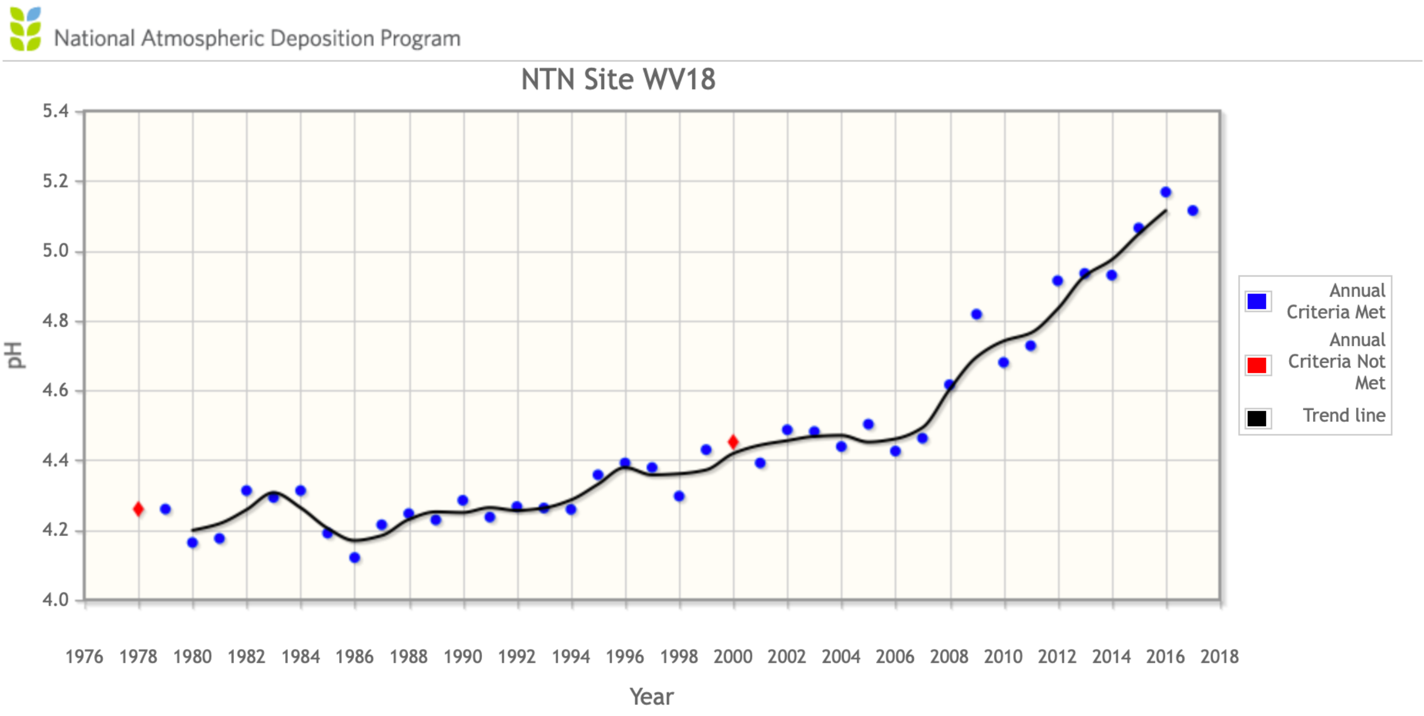
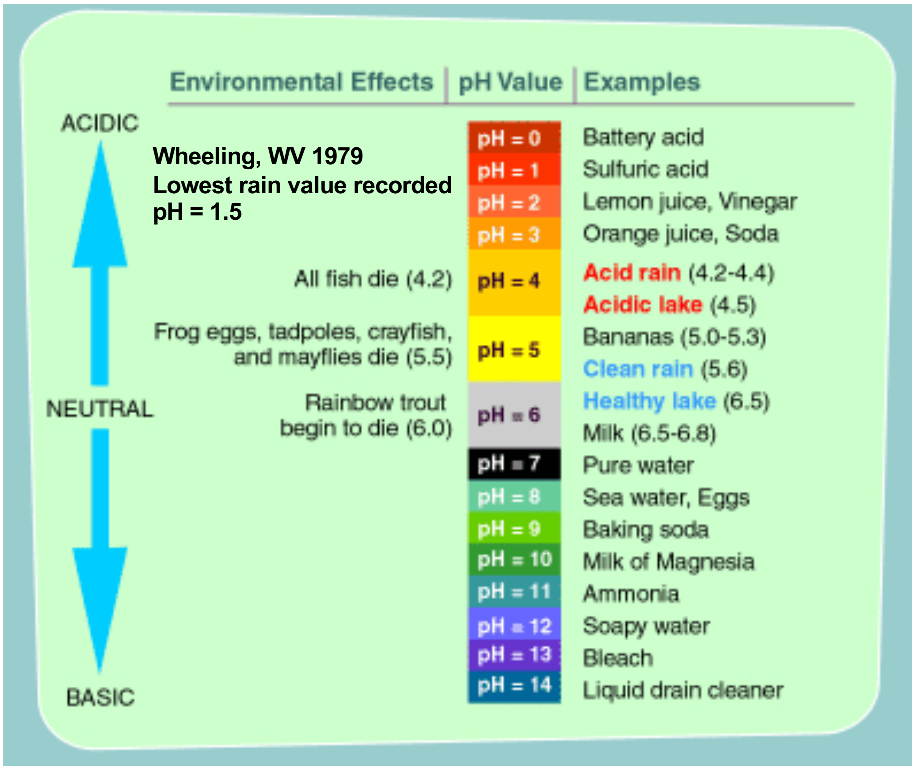


Fig. 2. Appearance of lake trout in Lake 223 in 1979 (*pH* 5.4) and 1982 (*pH* 5.1), clearly illustrating the loss of condition as indicated by the factor calculated as in Fig. 1G.



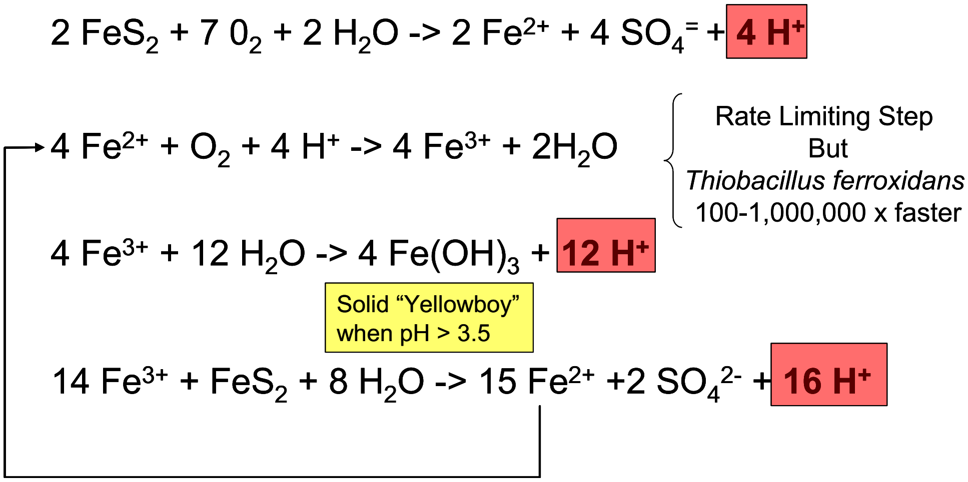




	Environmental Effects	pH Value	Examples
ACIDIC		pH = 0	Battery acid
	Wheeling, WV 1979 Lowest rain value recorded pH = 1.5	pH = 1	Sulfuric acid
		pH = 2	Lemon juice, Vinegar
		pH = 3	Orange juice, Soda
	All fish die (4.2)	pH = 4	Acid rain (4.2-4.4) Acidic lake (4.5)
	Frog eggs, tadpoles, crayfish, and mayflies die (5.5)	pH = 5	Bananas (5.0-5.3) Clean rain (5.6)
NEUTRAL	Rainbow trout begin to die (6.0)	pH = 6	Healthy lake (6.5) Milk (6.5-6.8)
		pH = 7	Pure water
		pH = 8	Sea water, Eggs
		pH = 9	Baking soda
		pH = 10	Milk of Magnesia
		pH = 11	Ammonia
		pH = 12	Soapy water
		pH = 13	Bleach
BASIC		pH = 14	Liquid drain cleaner

Surface reactions in mine spoil can lead to water acidification - acid mine drainage

AMD Formation



$2\ FeS_2 + 7\ 0_2 + 2\ H_2O \text{ -> } 2\ Fe^{2+} + 4\ SO_4^{=} + \boxed{\mathbf{4\ H^+}}$

$4\ Fe^{2+} + O_2 + 4\ H^+ \text{ -> } 4\ Fe^{3+} + 2H_2O$

Rate Limiting Step
But
Thiobacillus ferroxidans
100-1,000,000 x faster

$4\ Fe^{3+} + 12\ H_2O \text{ -> } 4\ Fe(OH)_3 + \boxed{\mathbf{12\ H^+}}$

Solid "Yellowboy"
when pH > 3.5

$14\ Fe^{3+} + FeS_2 + 8\ H_2O \text{ -> } 15\ Fe^{2+} + 2\ SO_4^{2-} + \boxed{\mathbf{16\ H^+}}$

Streams receiving this drainage could have a pH as low as 3.0!

Streams with Fisheries Impacted by Acid Mine Drainage in MD, OH, PA, VA, WV

(Based on EPA Fisheries Survey – 1995)

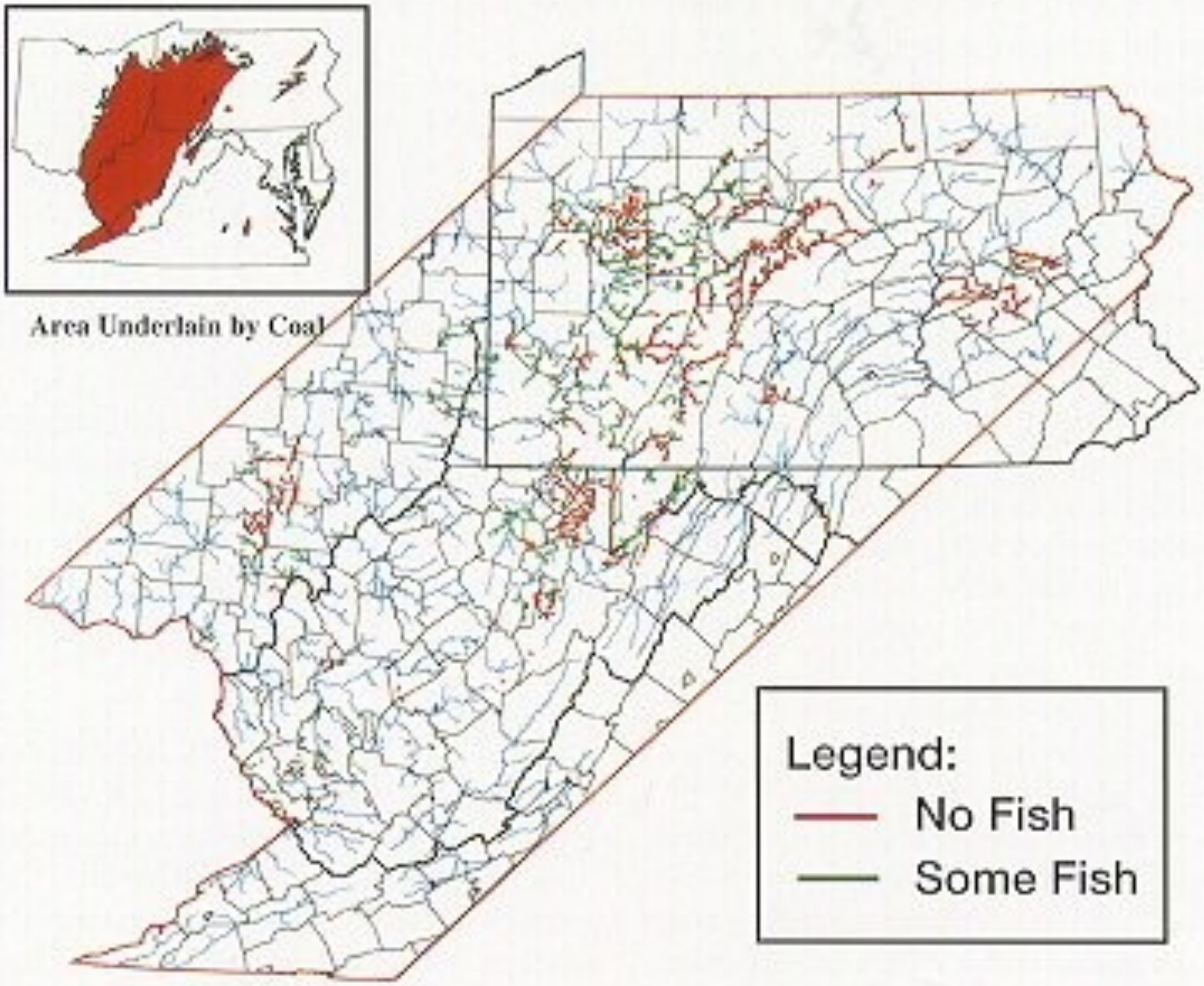
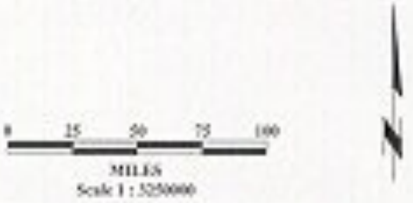


Figure 1

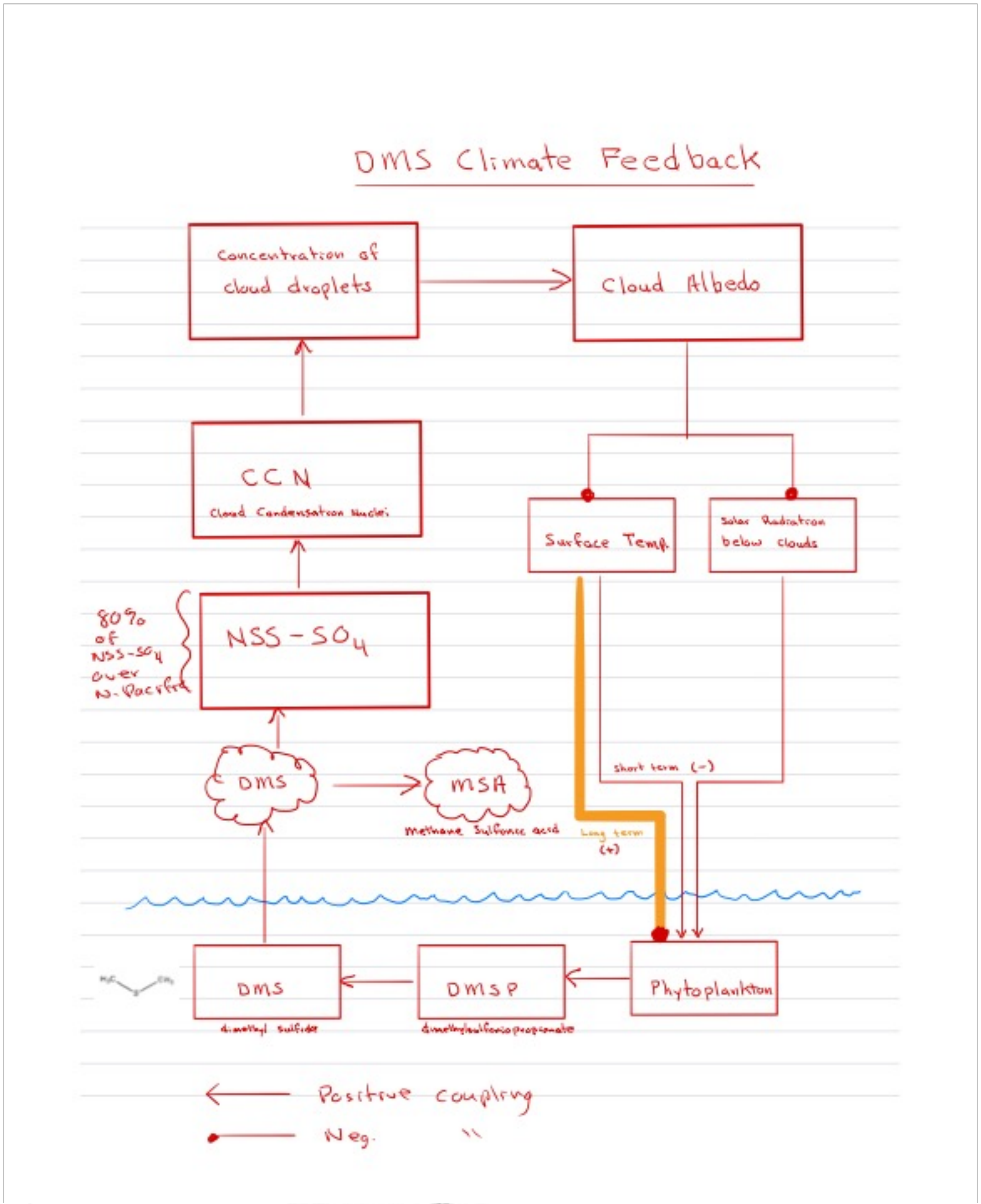


Stream Miles Impacted

State	No Fish	Some Fish	Total
OH	258	349	607
PA	1714	1525	3239
WV	488	612	1100
VA	17	0	17
MD	42	110	152
TOTAL	2519	2596	5115

Roger May @walkyourcamera · Jan 21

Acid mine drainage on Fifteenmile Fork (right) at the confluence of Cabi
Creek (left). Kanawha County, West Virginia.



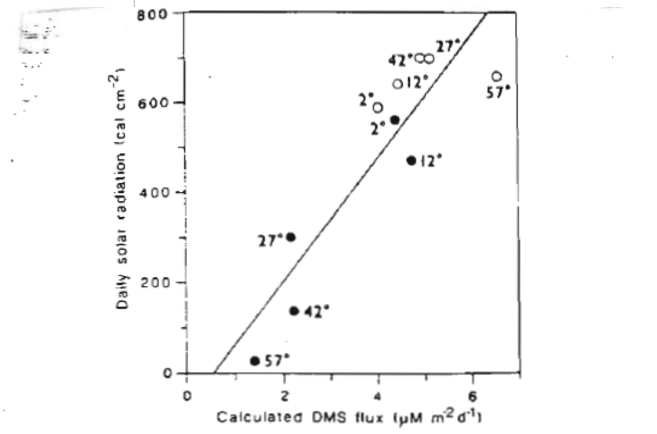


Fig. 3 Plot of calculated DMS flux[11] in μM m^{-2} d^{-1} against daily direct solar radiation reaching the surface of the Earth in cal cm^{-2}. The ten points represent five latitudinal regions in two seasons (summer, open circles; winter, filled circles). The equation of this line is radiation = 137 (flux) − 68 with a correlation coefficient, r, of 0.90.

Bates et al. 1987