



Acid Rain  
Week 10

## Cap and Trade Working Already

December 15, 2009 10:14 AM - *Roger Greenway, ENN*

The US already has years of experience with Cap and Trade. A sulfur dioxide (SO<sub>2</sub>) Cap and Trade program has proven an effective control strategy to lower SO<sub>2</sub> emissions. It provides elements of market incentives and provides flexibility to facilities that emit large quantities of the pollutant in several ways. One of the most important ways is that it permits older facilities which may need to operate for a limited number of years to purchase “emissions credits” to continue operating without installing un-economic emissions controls by purchasing credits. The credits are created by other sources which control their emissions MORE than required under regulations. There is also an overall reduction in the program to benefit the environment so we are not just transferring emission from one plant to another. A reflection of the effectiveness is that the U.S. Environmental Protection Agency announced that power plants across the country decreased emissions of SO<sub>2</sub>, a precursor to acid rain, to 7.6 million tons in 2008.

# Overview of Acid Rain Phenomenon

Reading – see Daniel Jacob Chapter 13

<http://acmg.seas.harvard.edu/publications/jacobbook/bookchap13.pdf>

Most common term for acidification of the environment, which can occur from a wide variety of processes, including precipitation, fog, dry deposition, aerosol sedimentation. Acids in the environment originate largely from pollutants such as nitrogen and sulfur oxides, which, in turn are generally by-products of combustion activities

# Overview of Acid Rain Phenomenon

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## Key points

- Research into environmental acidity started in the late 1800's in Britain and Scandinavia; widespread effects seen as early as the 1950's
- The first large-scale (multi-national) environmental issue, requiring cooperation among states and countries (e.g., US and Canada)
- Effects include "death" of many mountain lakes and severe damage to forests
- Good case study in regulation and international cooperation

## The Basics: Acidity and pH

Need a refresher on acid/base chemistry? Try this web based [tutorial!](#)

Recall that water dissociates weakly:  $\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$

What is an acid? - A substance that, when dissolved in water, increases the concentration of hydrogen ion ( $\text{H}^+$ ). Similarly a base is a substance that, when dissolved in water, increases the concentration of the hydroxide ion ( $\text{OH}^-$ ).

In an acidic solution,  $[\text{H}^+] > 1.00 \times 10^{-7} \text{ M}$  ( $M \equiv \text{moles L}^{-1}$ )

In a neutral solution,  $[\text{H}^+] = 1.00 \times 10^{-7} \text{ M}$

In a basic solution,  $[\text{H}^+] < 1.00 \times 10^{-7} \text{ M}$

## The pH scale

For convenience, the pH (potential hydrogen) scale was developed. This relates the  $[H^+]$  to an easier number to manipulate, via:

$$pH = -\log_{10}[H^+]$$

So, if the  $[H^+]$  of a solution is  $1 \times 10^{-4} M$ , the pH would be

$$pH = -\log_{10}(1 \times 10^{-4}) = 4$$

If the  $[H^+]$  of a solution is  $1 \times 10^{-3} M$ , the pH would be

$$pH = -\log_{10}(1 \times 10^{-3}) = 3$$

If the  $[H^+]$  is  $3 \times 10^{-4} M$ , the pH would be somewhere in between:

$$pH = -\log_{10}(3 \times 10^{-3}) = 3.52$$

## Acids (and Bases) in Water

Called aqueous solutions; ions given subscript (aq)

Let's take a generic acid, HA:



$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}_2\text{O}][\text{HA}]}$$

Since the water concentration does not change (it is 55.5 moles L<sup>-1</sup>. since there is 1 kg of water in 1 L), it can be combined with K:

$$K_a = K[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The chemical equation is typically shortened to  $\text{HA}_{(\text{aq})} \leftrightarrow \text{H}^+_{(\text{aq})} + \text{A}^-_{(\text{aq})}$

$$\text{so } K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

## What about [OH]<sup>-</sup>?

Called the self-ionization of water, to some small degree, water will break down into ions as well. So water has its own equilibrium constant:



$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ M}^2$$

So if pH = 7

$$[\text{H}^+] = 1 \times 10^{-7} \text{ M}$$

$$[\text{OH}^-] = 1 \times 10^{-14} \text{ M}^2 / (1 \times 10^{-7} \text{ M}) = 1 \times 10^{-7} \text{ M}$$

$$\text{pOH} = -\log_{10}[\text{OH}^-] = 7$$

This result is nice, because we can always calculate [OH<sup>-</sup>] if we know [H<sup>+</sup>].



Sample Problem: The pH of blood is 7.40. What is the hydrogen ion concentration? What is the hydroxide ion concentration?

$$\text{pH} = -\log[\text{H}^+], \text{ so } [\text{H}^+] = 10^{-\text{pH}}$$

$$[\text{H}^+] = 10^{-7.4} = 3.98 \times 10^{-8} \text{ M}$$

To determine the  $[\text{OH}^-]$ , one can take either of two paths:

(a)  $\text{pH} + \text{pOH} = 14.0$ , so  $\text{pOH} = 14.0 - \text{pH} = 6.6$

$$\text{Then } [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-6.6} = 2.51 \times 10^{-7} \text{ M}$$

(b)  $[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$ , so  $[\text{OH}^-] = 1 \times 10^{-14}/[\text{H}^+]$

$$\text{Then } [\text{OH}^-] = 1 \times 10^{-14}/3.98 \times 10^{-8} = 2.51 \times 10^{-7} \text{ M}$$

We typically deal with two classes of acids.

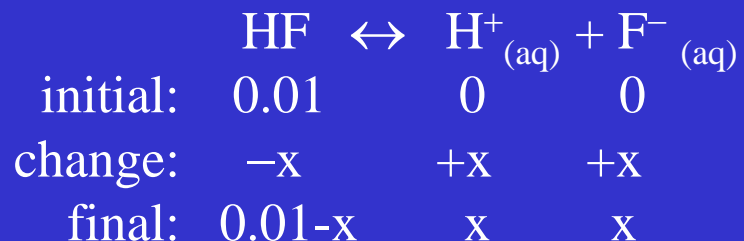
For strong acids,  $K_a \gg 1$  (can even assume infinity!)

So that the demoninator is so small that essentially the acid completely dissociates into ions.

For weak acids,  $K_a$  is finite, and there will be some undissolved parent acid (HA) in solution. We can use the equilibrium (or acidity) constant to determine the ions in solution, although the math may be a bit cumbersome (involving a quadratic expression).

## Sample of a Weak Acid Problem

A 0.01 M solution of hydrofluoric acid (HF) is used in an experiment. If  $K_a = 6.8 \times 10^{-4}$ , what is the pH of this solution?



Then,

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

$$6.8 \times 10^{-4} = \frac{x^2}{(0.01-x)}$$

If  $x$  is small compared to 0.01, we can disregard it in the denominator.

$$x^2 = 6.8 \times 10^{-6}$$

$$x = 2.61 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [2.61 \times 10^{-3}] = 2.58$$

Note that we can solve this exactly by using the quadratic equation:

$$6.8 \times 10^{-4} = x^2/(0.01-x)$$

$$x^2 + 6.8 \times 10^{-4} x - 6.8 \times 10^{-6} = 0$$

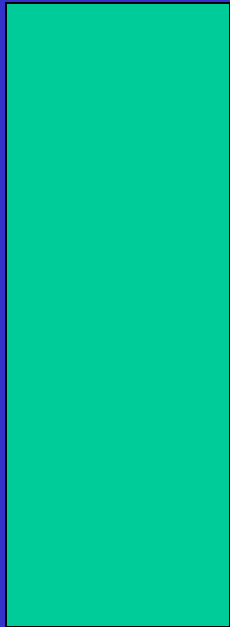
$$\text{Solve for } x = 2.29 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.64$$

the answer on the previous pages off by only a little – about 12%

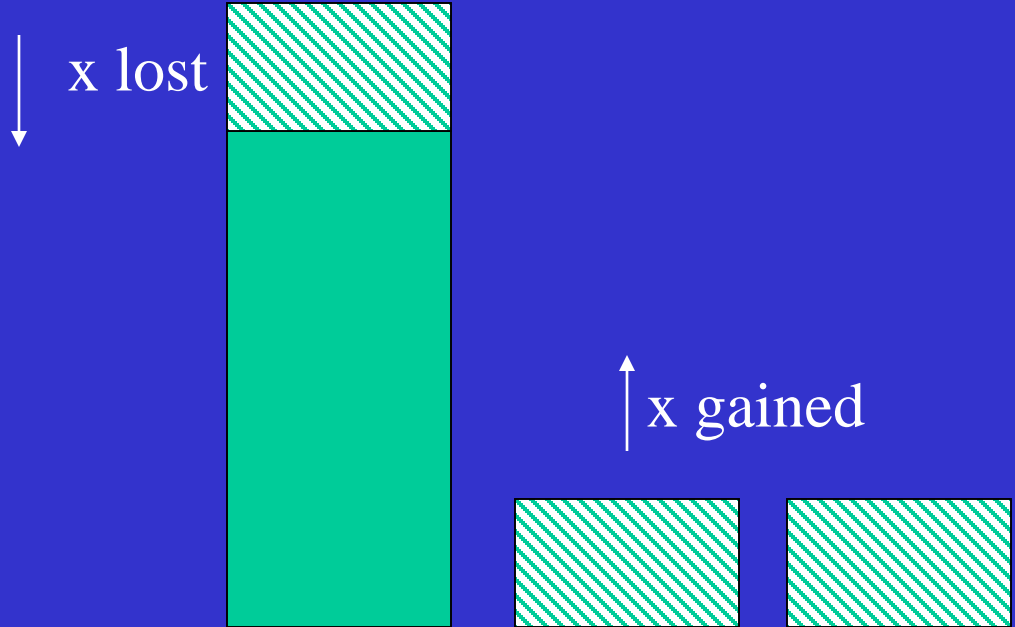
# Symbolically

Before



[HA]

After



[H<sup>+</sup>]

[A<sup>-</sup>]

[HA]<sub>(aq)</sub>

[H<sup>+</sup>]

[A<sup>-</sup>]

# Atmospheric Aqueous Chemistry

Atmospherically relevant aqueous chemistry usually involves interactions between gases and water, in addition to the liquid-phase reactions.

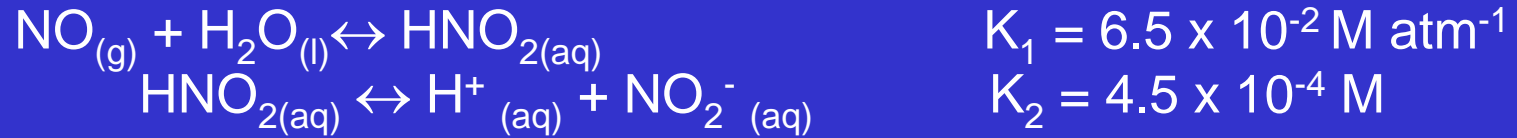
When a gas is involved, we use its partial pressure rather than concentration:



$K_h$  for this type of situation is called the “Henry’s Law Constant”

Note that this equilibrium is a bit different than our analysis of heterogeneous reactions from last lecture. Here, we assume that a gas is partitioned between the gas and aqueous phases. In the atmosphere, acids typically stick to water droplets, so we are mainly interested in how many of those molecules come back out of solution once they are dissolved. Most strong acids don’t return to the gas phase (i.e.,  $K \gg 1$ ), but some (like  $\text{CO}_2$ ) do.

Example: Nitrogen oxides can interact with water to produce nitrous acid:



Suppose there were a raindrop in contact with these gases; what would its pH be? [NO =  $1 \times 10^{-9}$  atm]

First, set up equilibrium expressions for the two processes:

$$K_1 = [\text{HNO}_2]/P_{\text{NO}} \quad K_2 = [\text{H}^+][\text{NO}_2^-]/[\text{HNO}_2]$$

Both expressions contain  $[\text{HNO}_2]$ , so we can solve one and substitute into the other:

$$[\text{HNO}_2] = K_1 P_{\text{NO}} \quad \text{then } K_2 = [\text{H}^+][\text{NO}_2^-]/K_1 P_{\text{NO}}$$

However, this still leaves us with an equation with two unknowns. From the second chemical reaction, we can see that for every  $\text{H}^+$ , we must have an  $\text{NO}_2^-$ . In other words,  $[\text{H}^+] = [\text{NO}_2^-]$ . This allows us to simplify the equation for  $K_2$  to:

$$K_2 = [\text{H}^+][\text{H}^+]/K_1 P_{\text{NO}}$$

Solving for  $[\text{H}^+]$ :

$$[\text{H}^+]^2 = K_2 K_1 P_{\text{NO}}$$

$$[\text{H}^+] = (K_2 K_1 P_{\text{NO}})^{1/2}$$

$$[\text{H}^+] = [(6.5 \times 10^{-2} \text{ M atm}^{-1})(4.5 \times 10^{-4} \text{ M})(1 \times 10^{-9} \text{ atm})]^{1/2} = 1.7 \times 10^{-7} \text{ M}$$

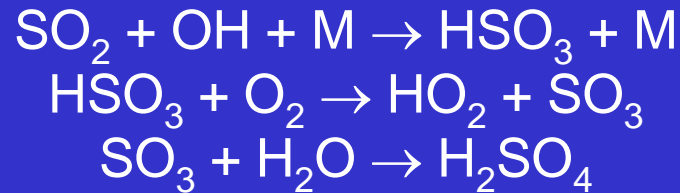
$$\text{pH} = -\log[\text{H}^+] = -\log[1.7 \times 10^{-7}] = 6.77$$



## What are the acids in the atmosphere?

### Inorganic acids

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ): Source – sulfur-containing gases such as  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $(\text{CH}_3)_2\text{S}$  (dimethyl sulfide)



Nitric acid ( $\text{HNO}_3$ ): Source – nitrogen oxide emissions from combustion and soils



Hydrochloric acid ( $\text{HCl}$ ): Source – Volcanoes, industry

Carbonic acid ( $\text{H}_2\text{CO}_3$ ): Source – carbon dioxide, mostly natural, but has increased due to fossil fuel burning



Sulfurous acid ( $\text{H}_2\text{SO}_3$ ): Source – sulfur dioxide (as above)



Organic acids – Origins can be biologic or fossil-fuel emissions

Formic acid ( $\text{HCOOH}$ ): Source – by-product of oxidation of complex hydrocarbons; also made by ants

Acetic acid ( $\text{CH}_3\text{COOH}$ ): Also a by-product of oxidation

So “clean” water in the atmosphere is made slightly acidic through contact with CO<sub>2</sub>, which forms an acid when it dissolves in water.



For the atmosphere, we can typically stop at the second step above in order to get a good estimate for the pH of water in contact with CO<sub>2</sub>. The first step, dissolution of CO<sub>2</sub> in water, can be calculated using the expression:

$$K_1 = [\text{H}_2\text{CO}_3] / p_{\text{CO}_2} = 3.45 \times 10^{-2} \text{ moles L}^{-1} \text{ atm}^{-1}$$

Where  $p_{\text{CO}_2}$  is the partial pressure of CO<sub>2</sub>, which is basically the mixing ratio, or 0.000400 atm for “400 ppm”

$$\begin{aligned} \text{So } [\text{H}_2\text{CO}_3] &= 3.45 \times 10^{-2} \times 0.000400 \text{ moles L}^{-1} \\ &= 1.38 \times 10^{-5} \text{ moles L}^{-1} \end{aligned}$$

Based on the equilibrium for the second step:



$$K_2 = [\text{HCO}_3^-] [\text{H}^+] / [\text{H}_2\text{CO}_3] = 4.45 \times 10^{-7} \text{ moles L}^{-1}$$

But each time  $\text{H}_2\text{CO}_3$  dissolves, it makes one  $\text{HCO}_3^-$  and one  $\text{H}^+$ , so  $[\text{HCO}_3^-] = [\text{H}^+]$

$$[\text{H}^+]^2 / [\text{H}_2\text{CO}_3] = 4.45 \times 10^{-7} \text{ moles L}^{-1}$$

$$[\text{H}^+]^2 = [\text{H}_2\text{CO}_3] \times 4.45 \times 10^{-7} \text{ moles L}^{-1}$$

$$= 1.38 \times 10^{-5} \text{ moles L}^{-1} \times 4.45 \times 10^{-7} \text{ moles L}^{-1}$$

$$= 6.14 \times 10^{-12} (\text{moles L}^{-1})^2$$

Taking square root,  $[\text{H}^+] = 2.48 \times 10^{-6} \text{ moles L}^{-1}$

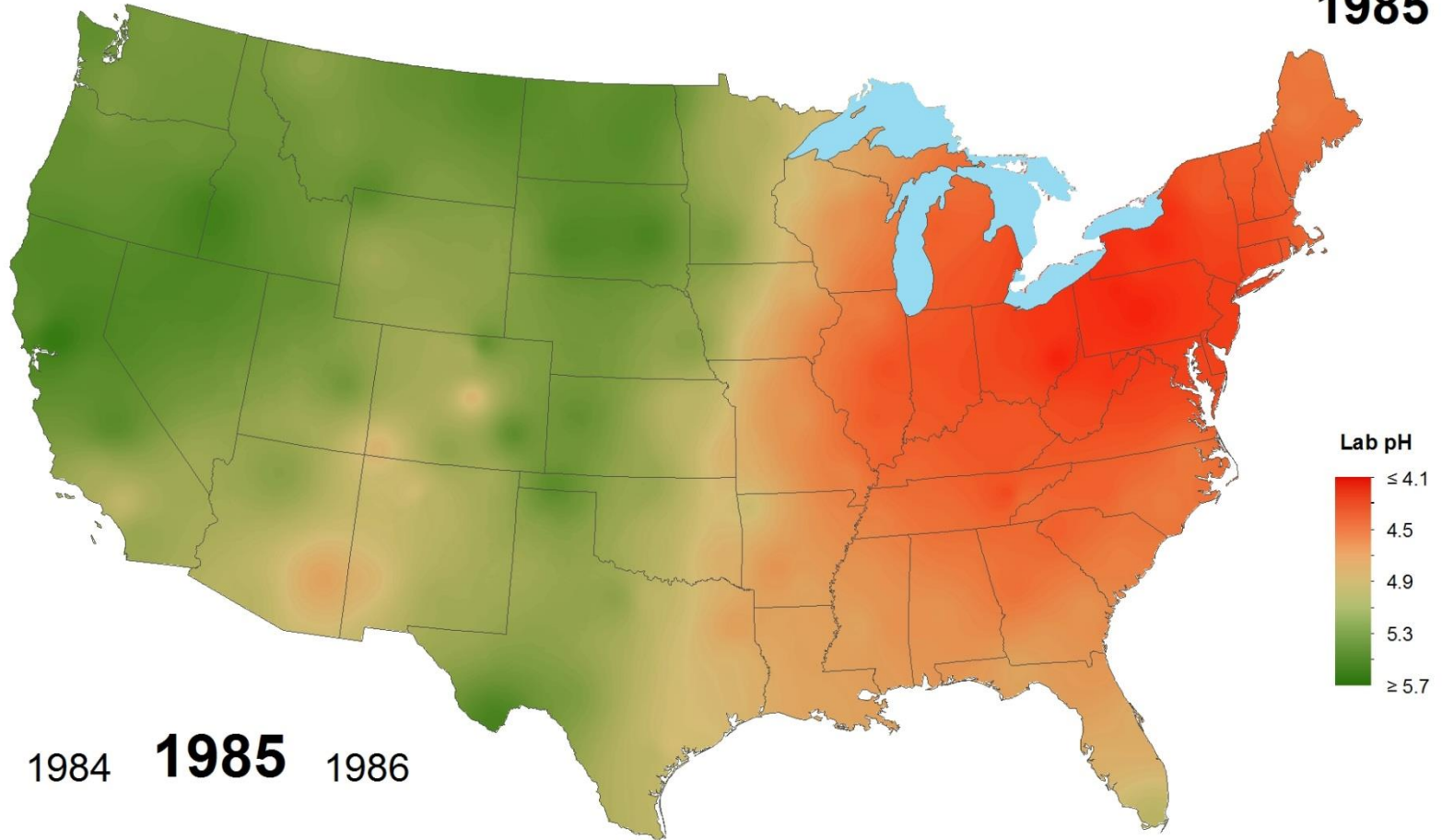
$$\text{pH} = 5.61$$

The following slides represent a time series of important parameters related to wet deposition (i.e., rain). The first is pH, which is acidity. This is followed by the major ions in water that determine that pH, sulfate (from sulfuric acid), nitrate (from nitric acid), and ammonium (which is basic, and acts to neutralize the acidity).

More details can be found here:

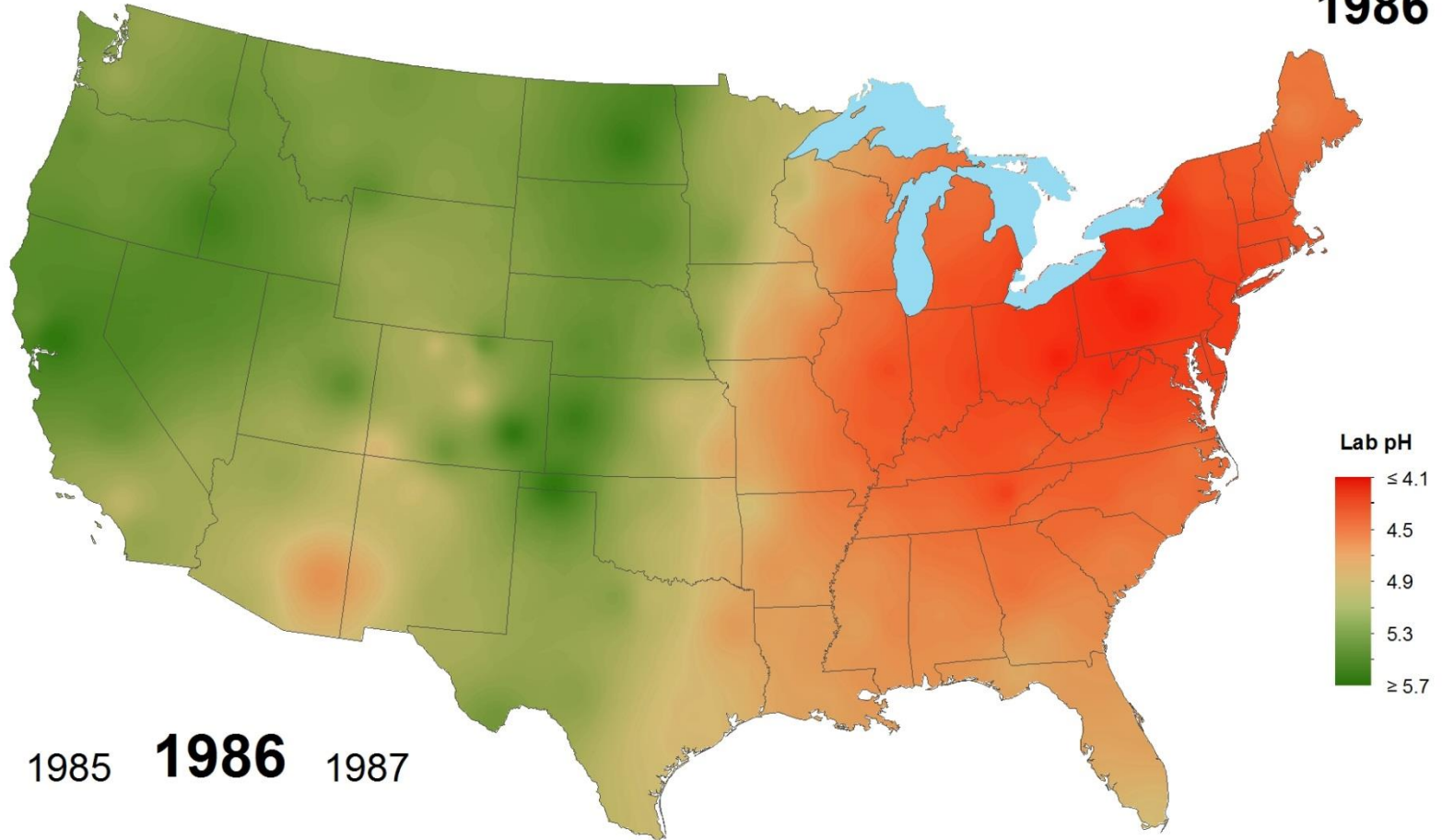
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# Hydrogen ion concentration as pH 1985



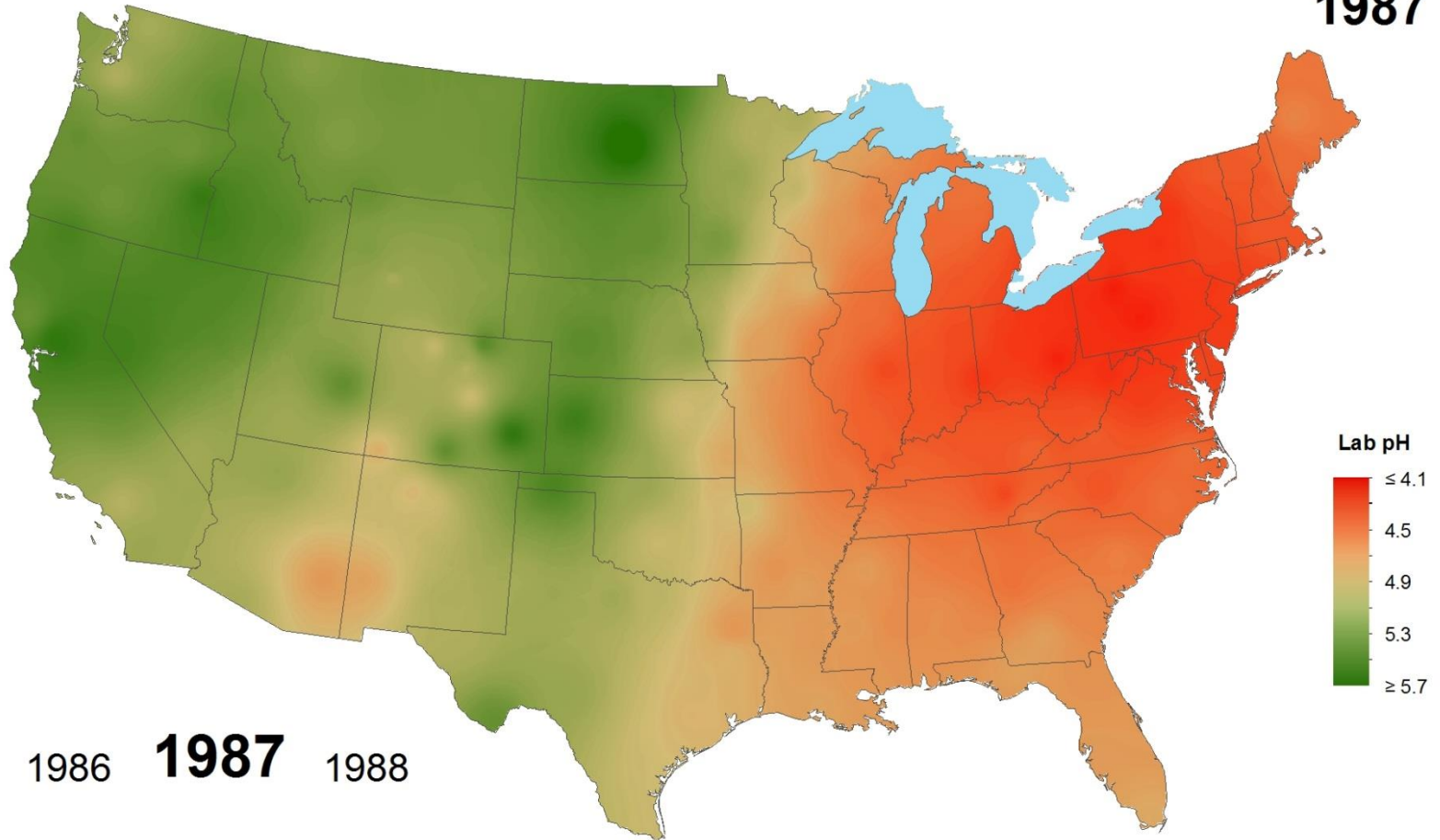
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# Hydrogen ion concentration as pH 1986



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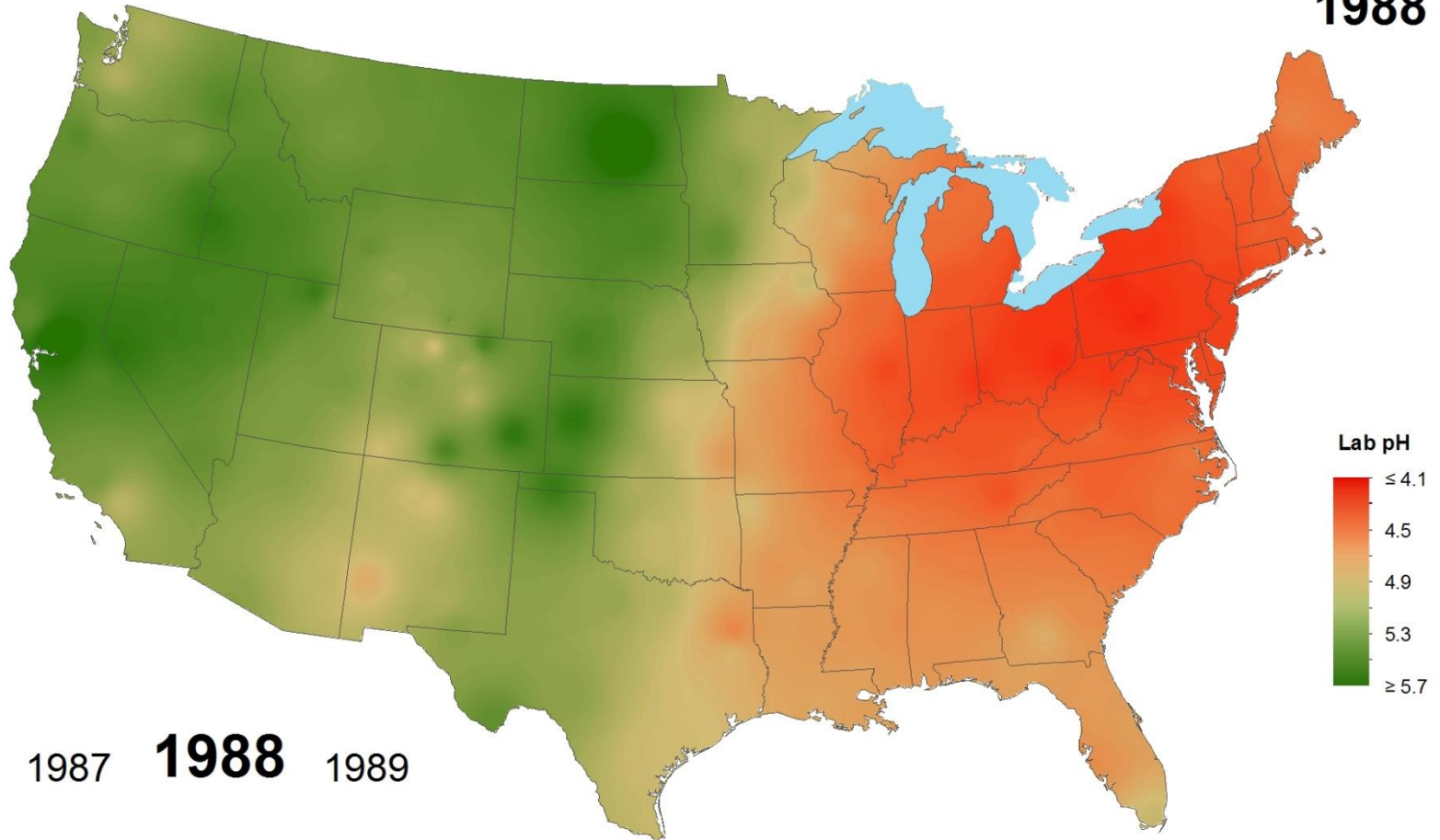
# Hydrogen ion concentration as pH 1987



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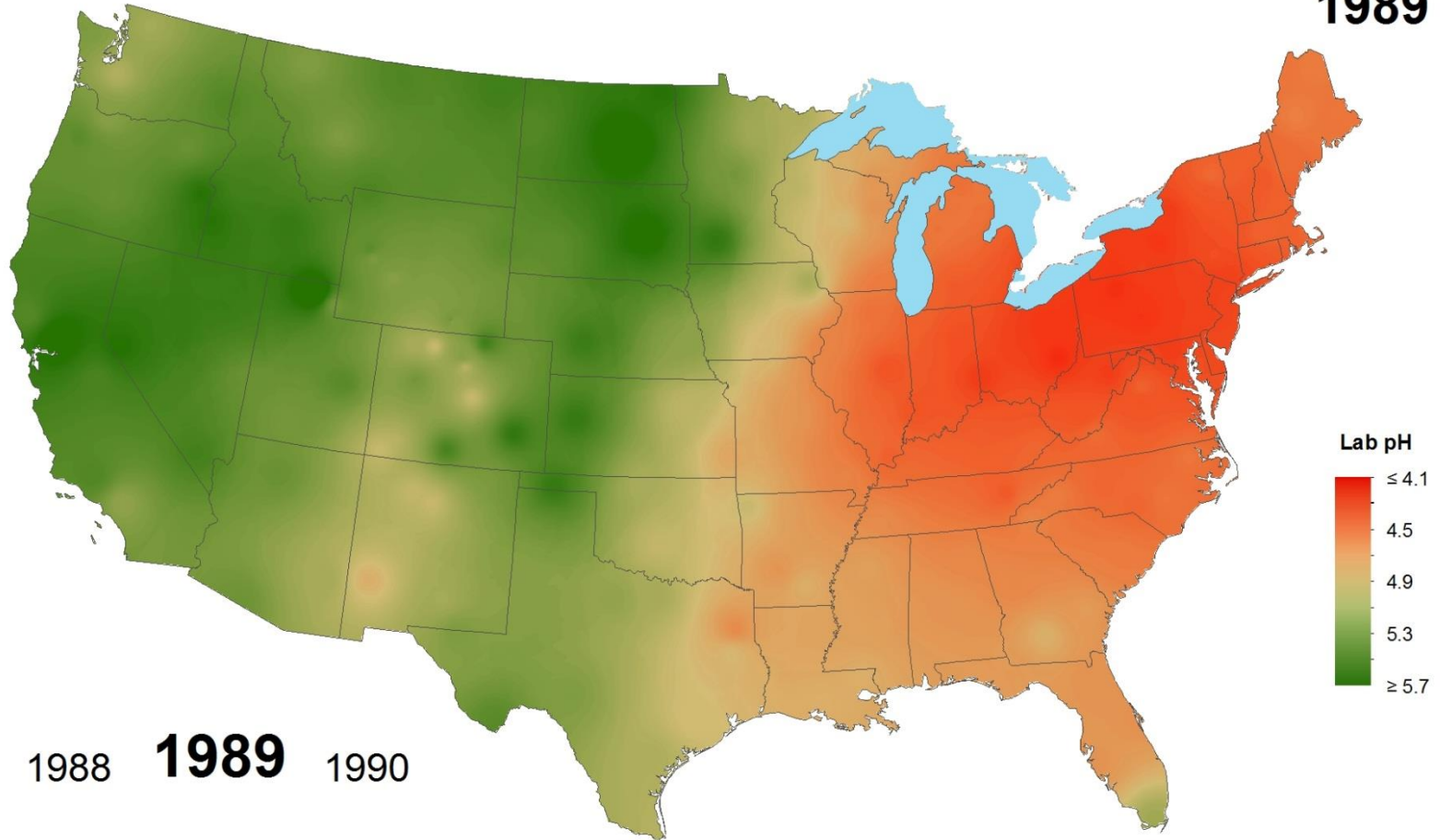


# Hydrogen ion concentration as pH 1988



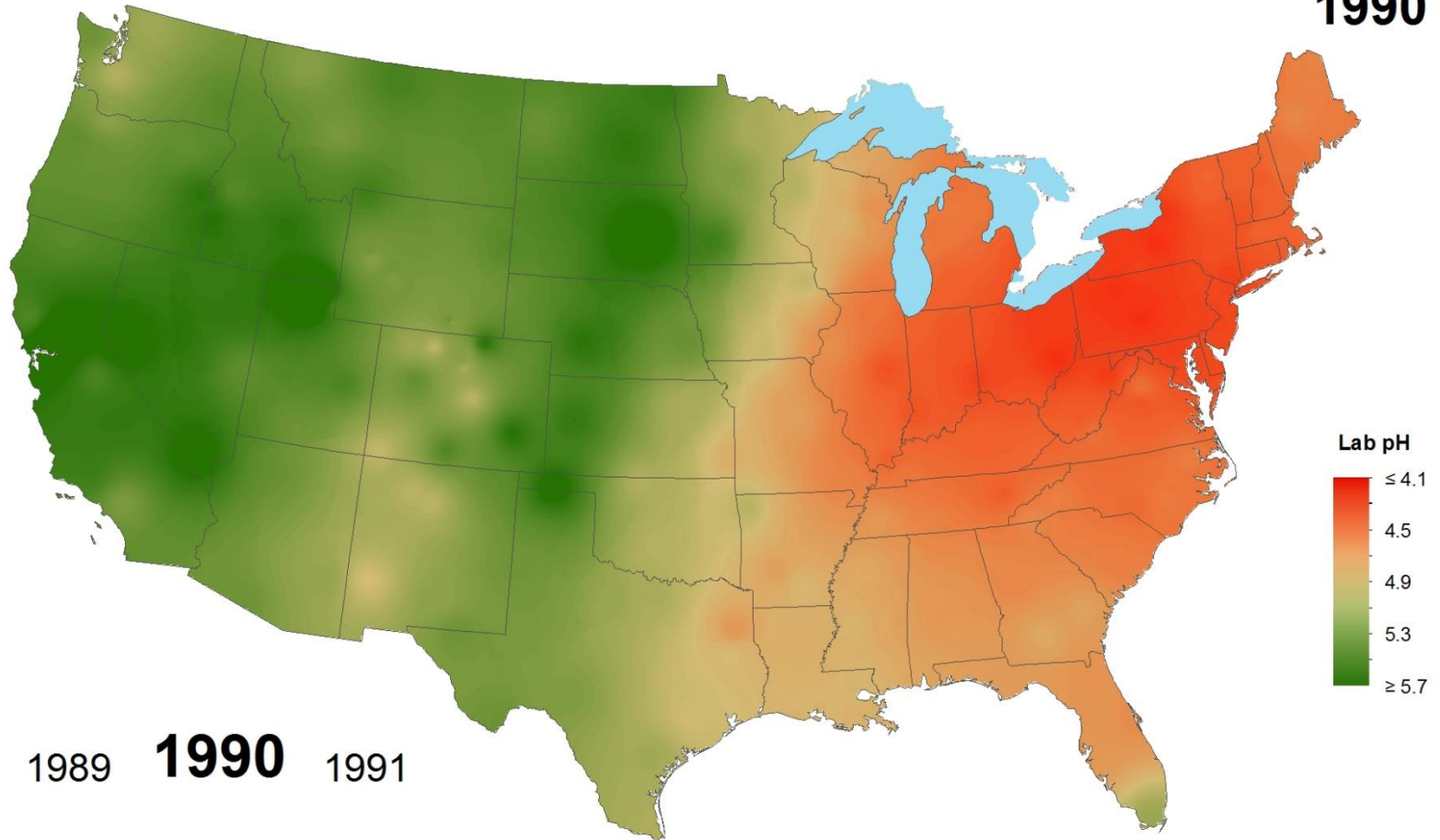
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# Hydrogen ion concentration as pH 1989



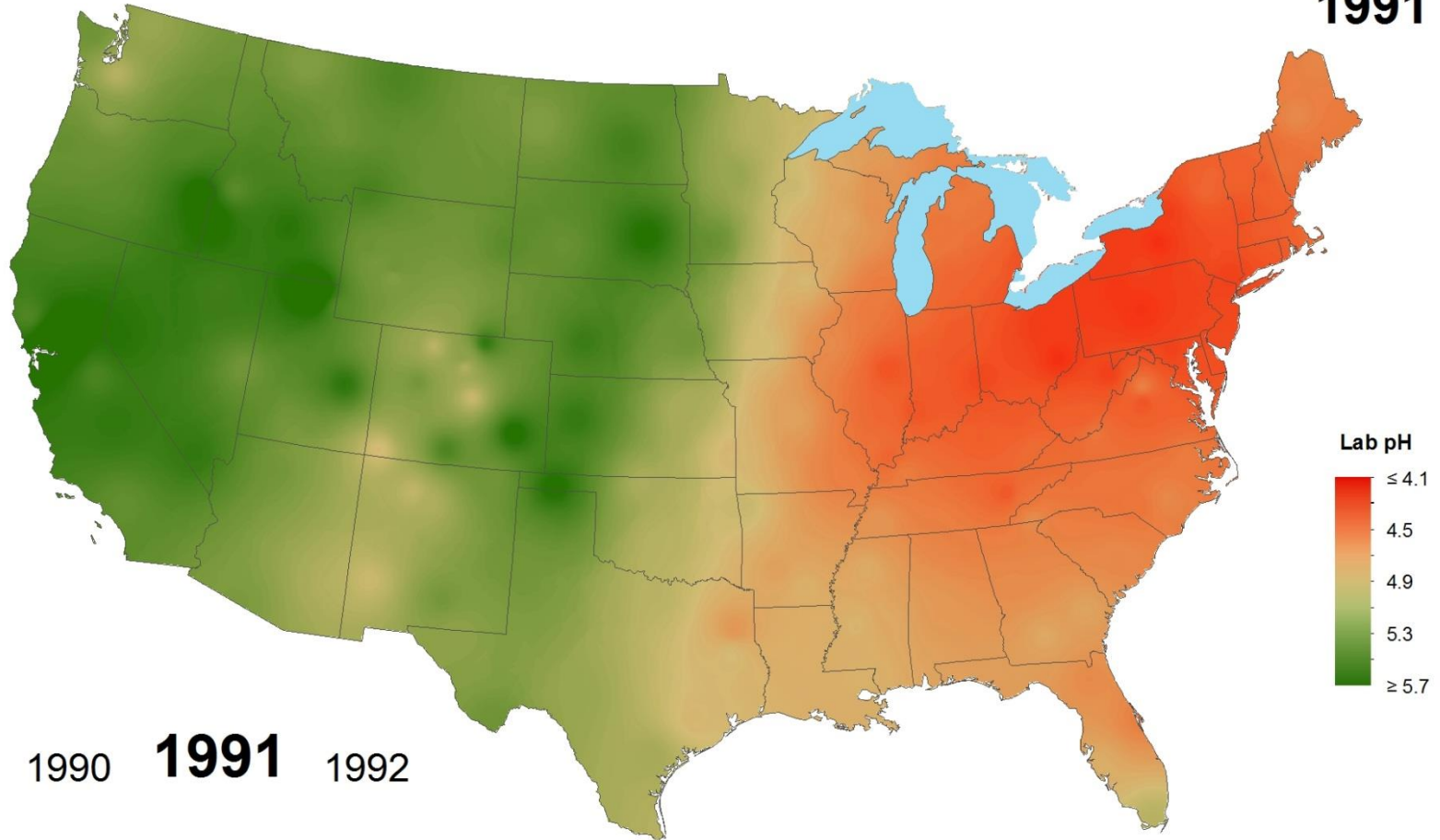
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# Hydrogen ion concentration as pH 1990



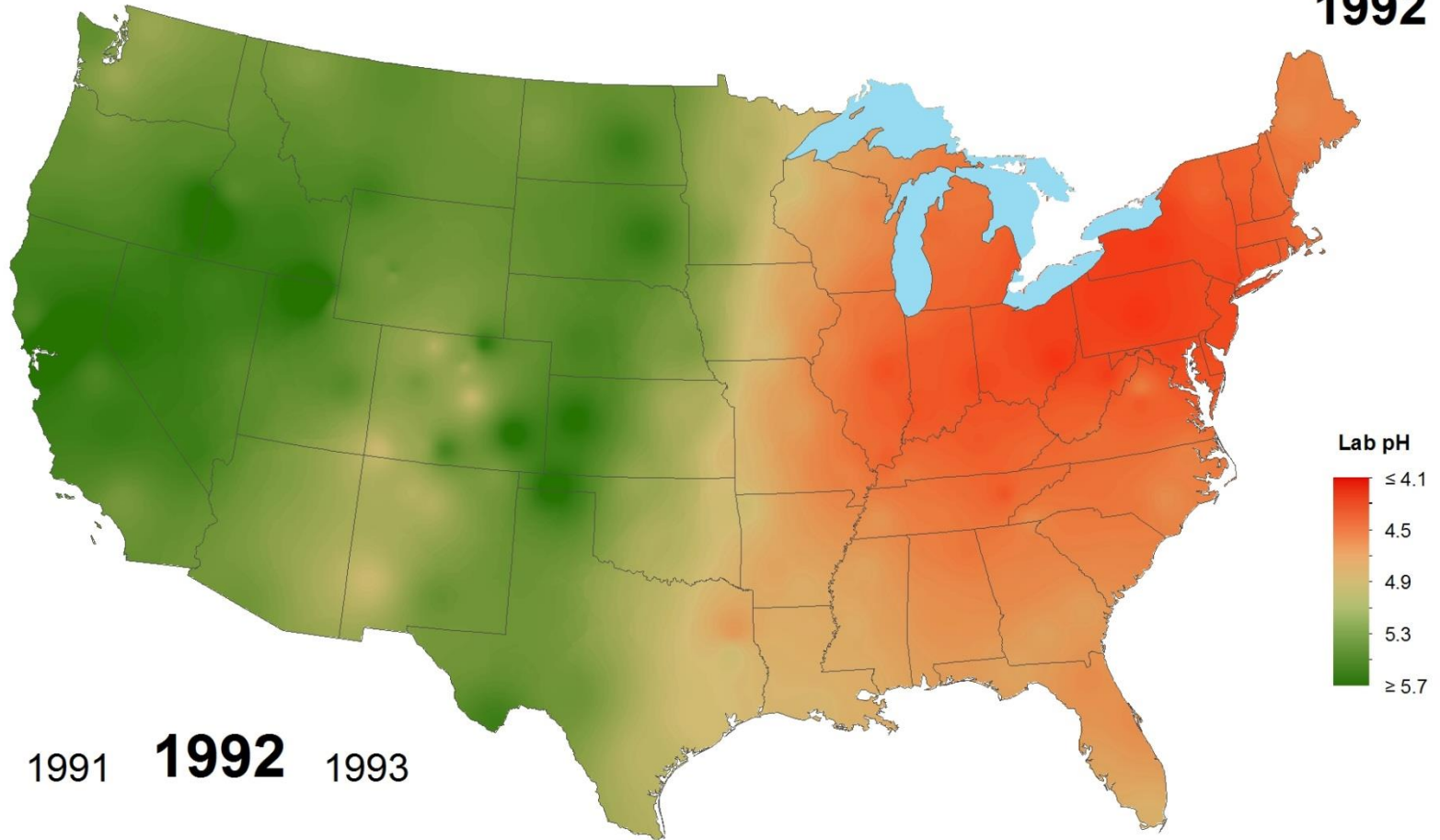
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# Hydrogen ion concentration as pH 1991



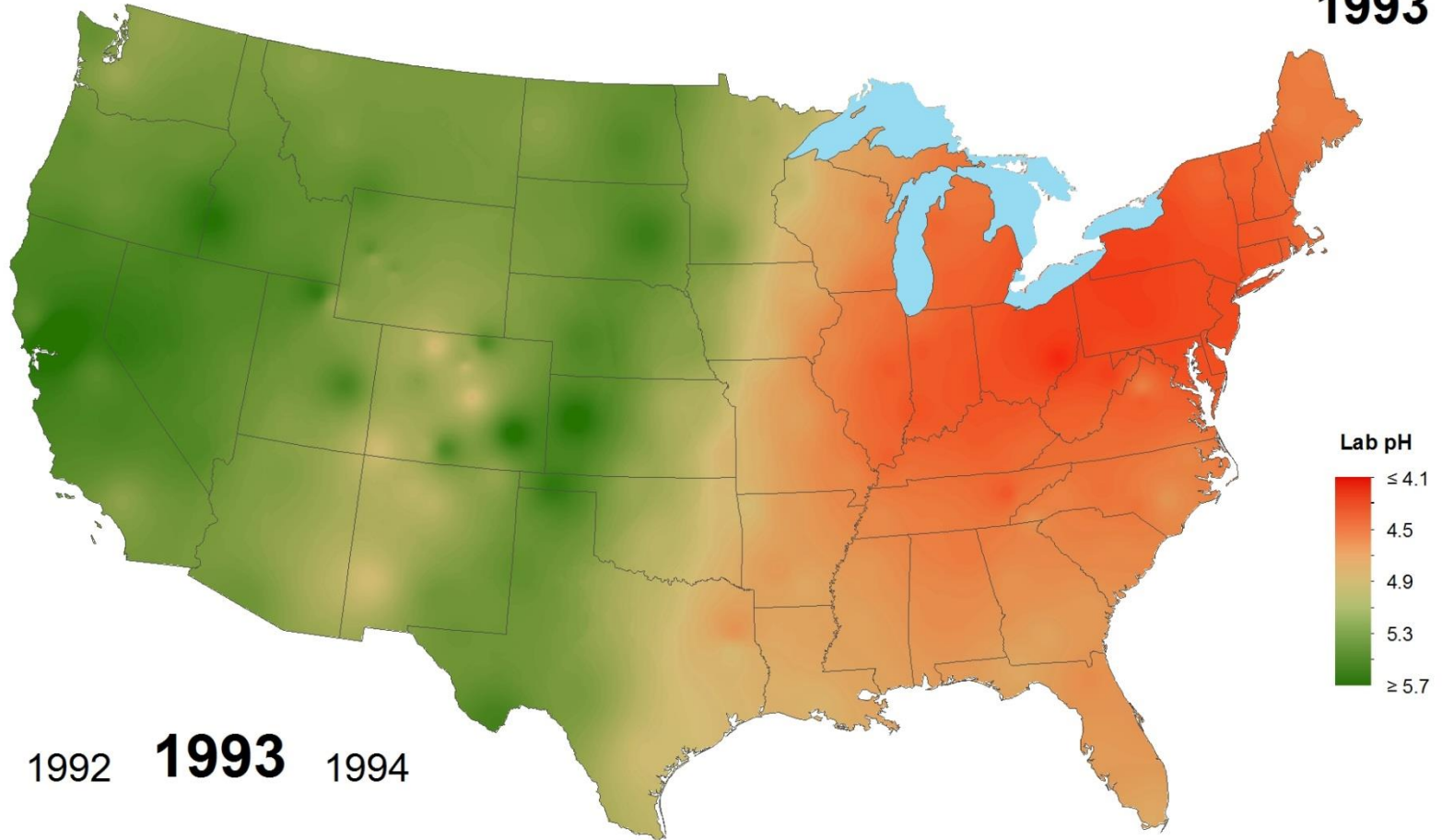
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# Hydrogen ion concentration as pH 1992



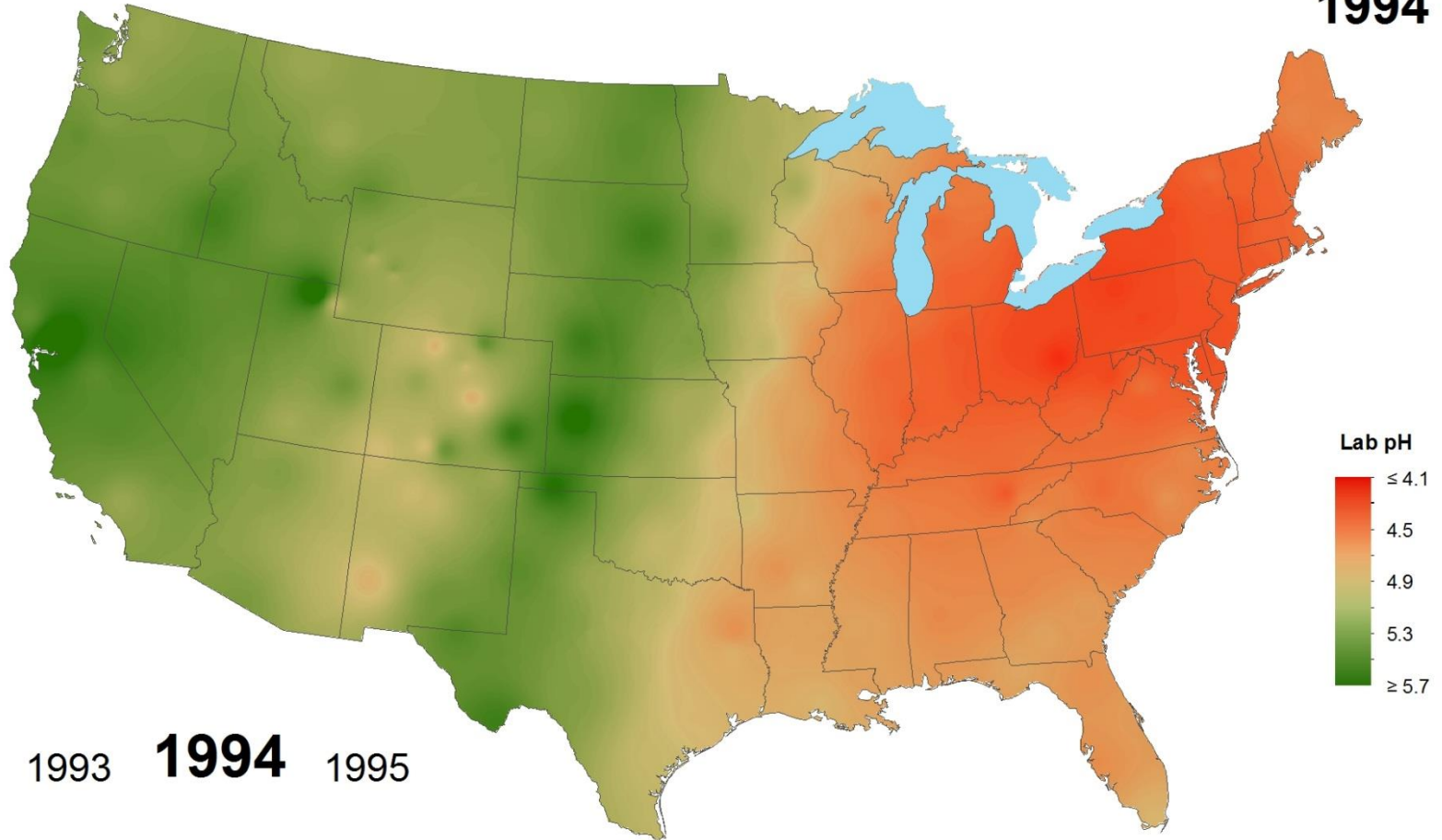
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# Hydrogen ion concentration as pH 1993



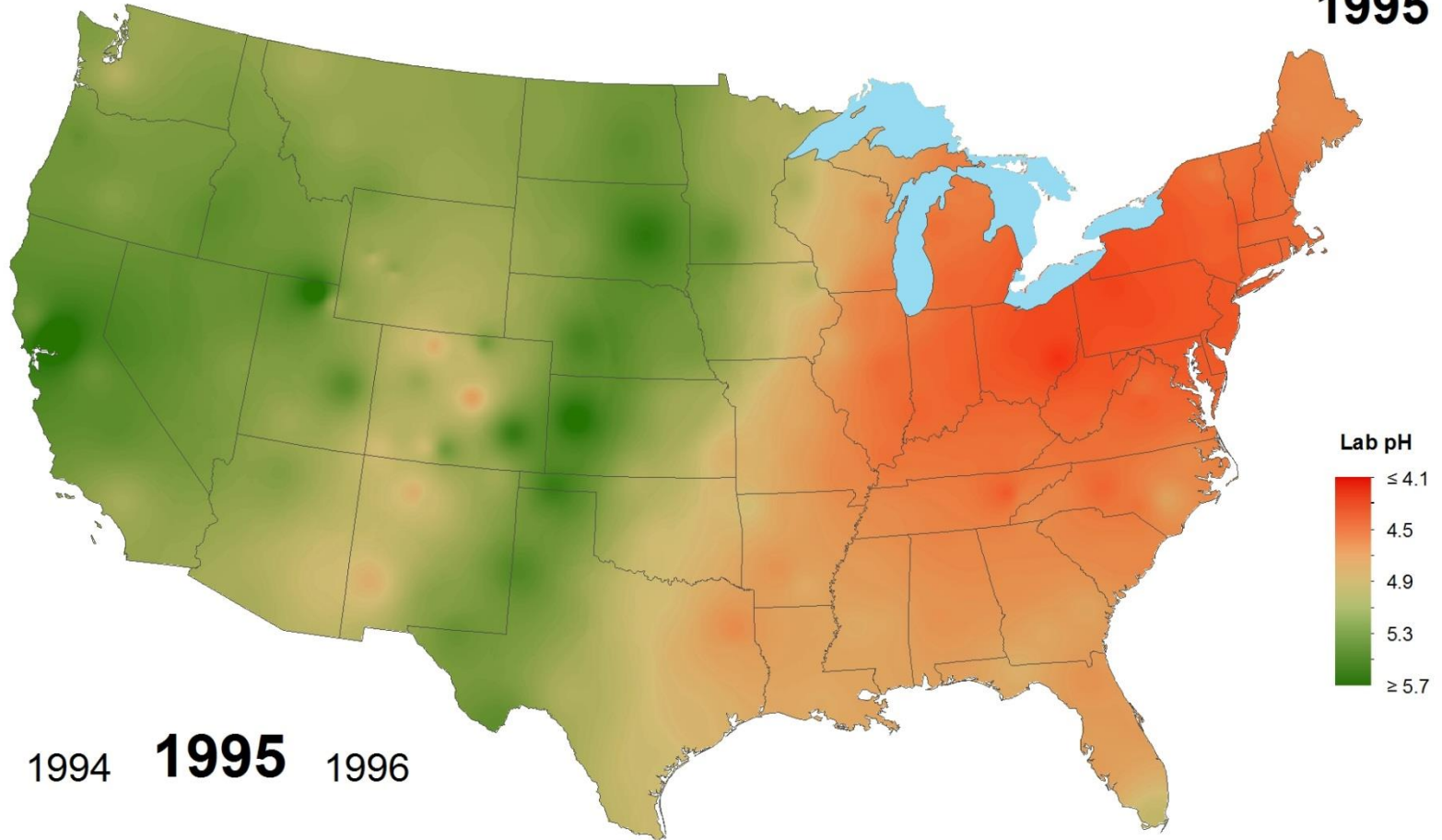
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# Hydrogen ion concentration as pH 1994



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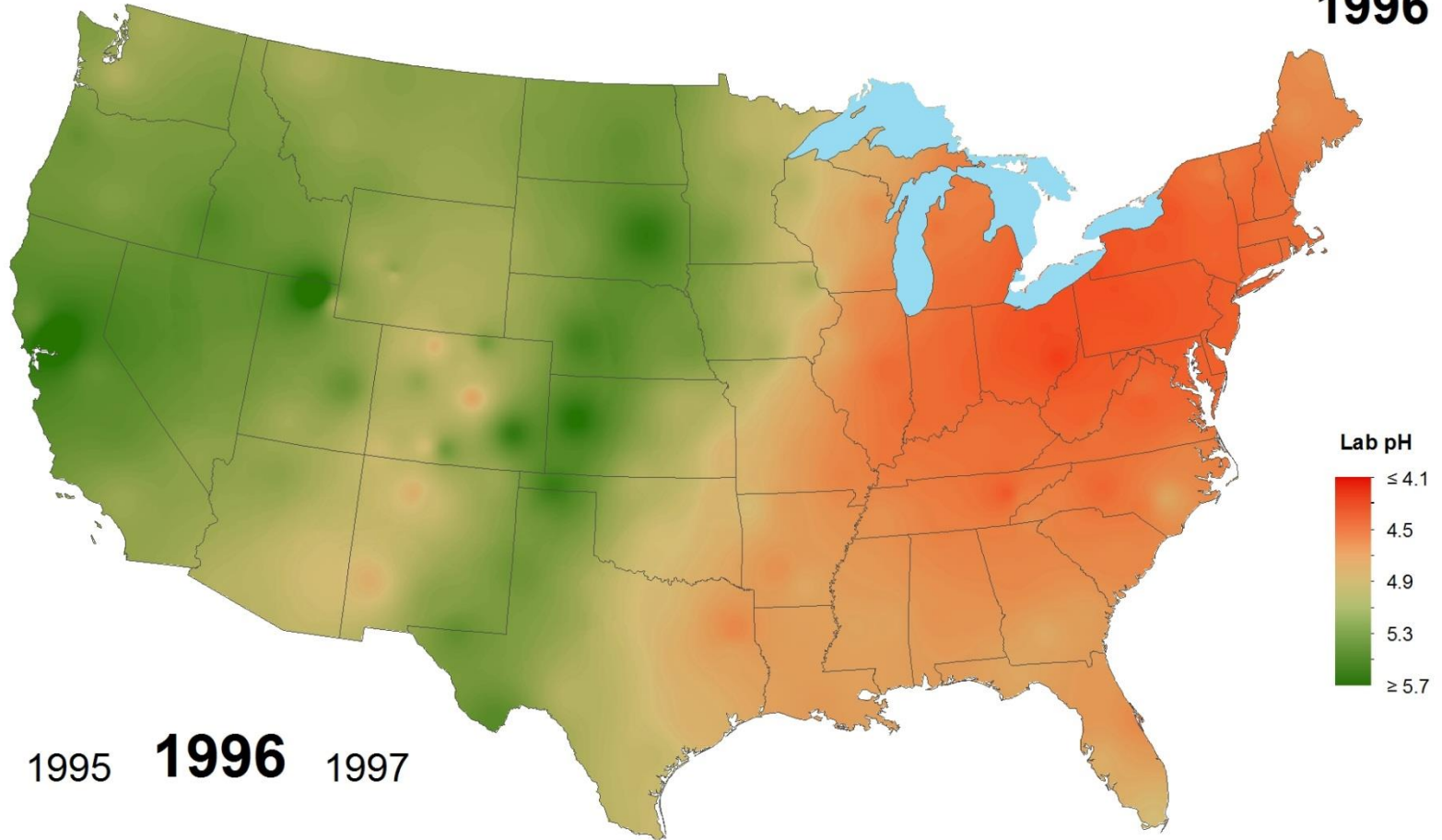
# Hydrogen ion concentration as pH 1995



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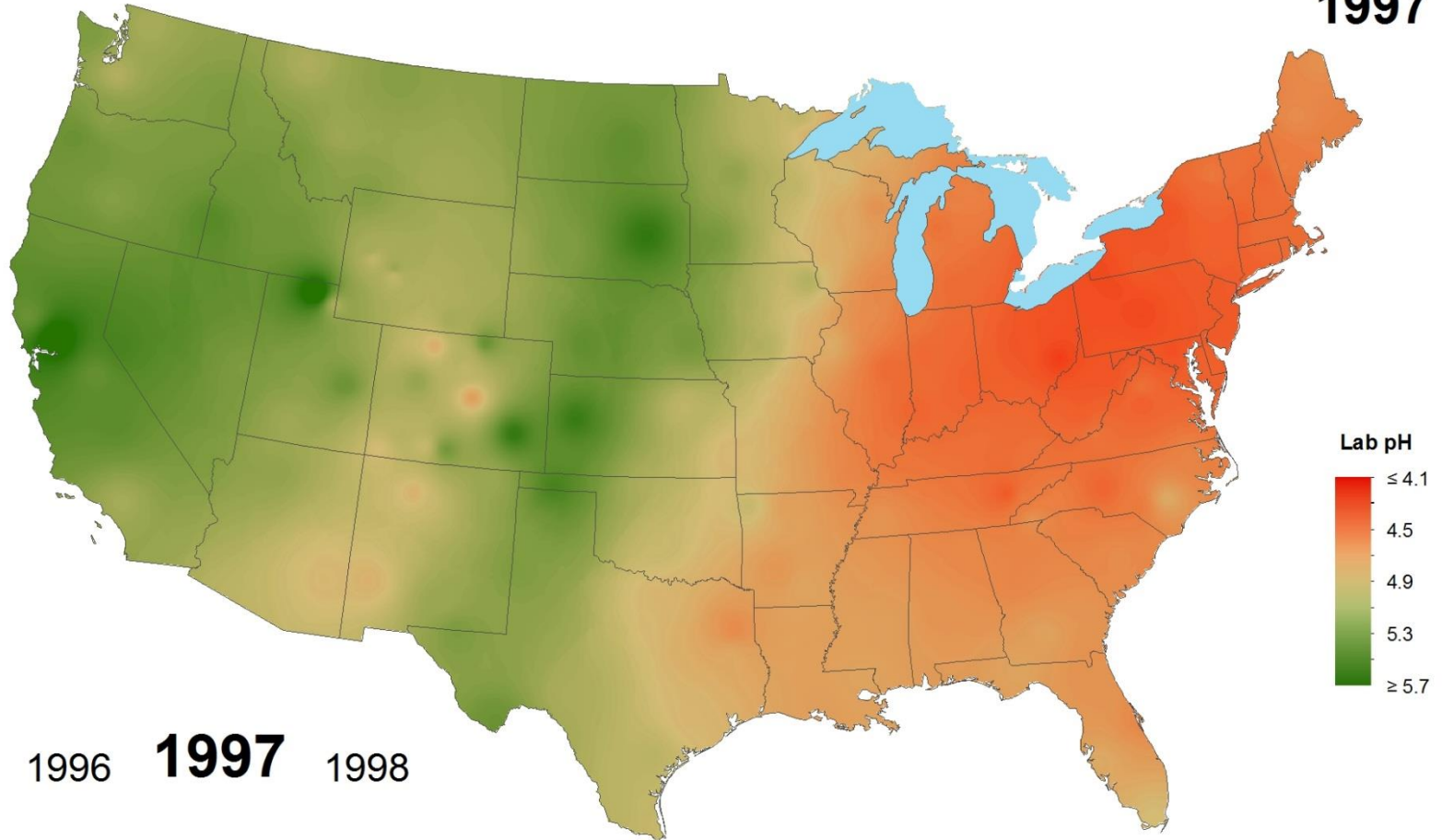


# Hydrogen ion concentration as pH 1996



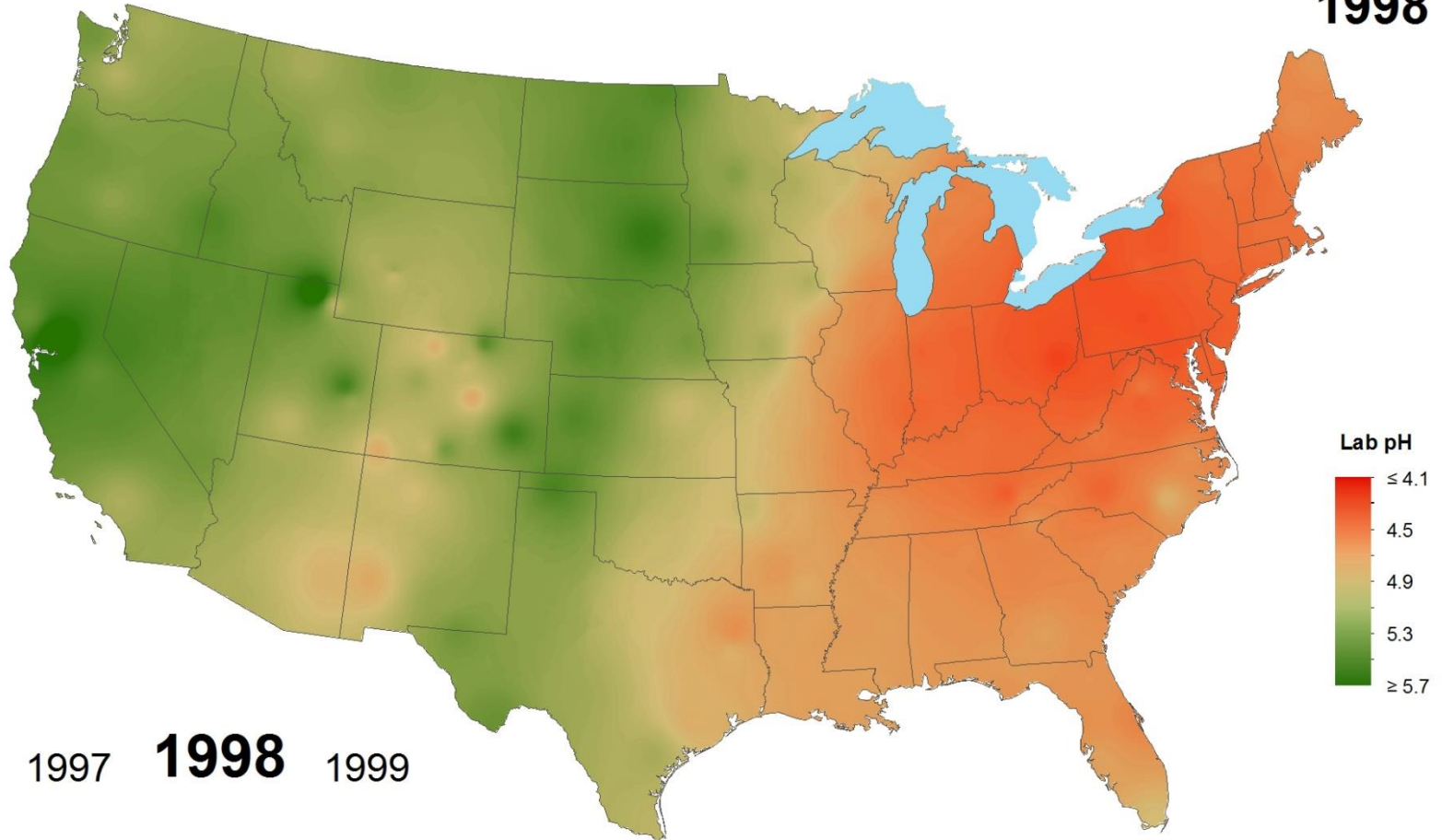
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# Hydrogen ion concentration as pH 1997



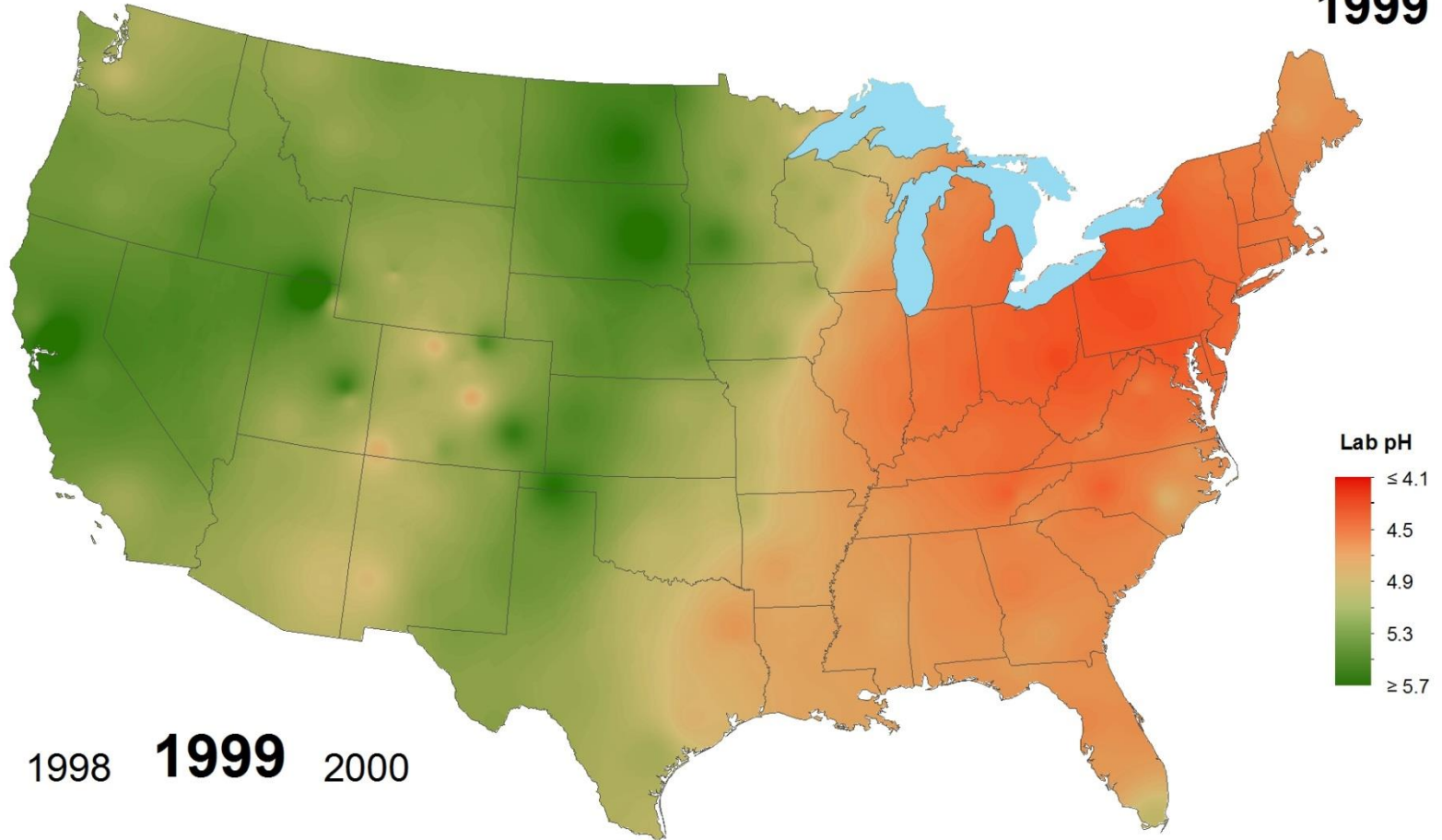
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# Hydrogen ion concentration as pH 1998



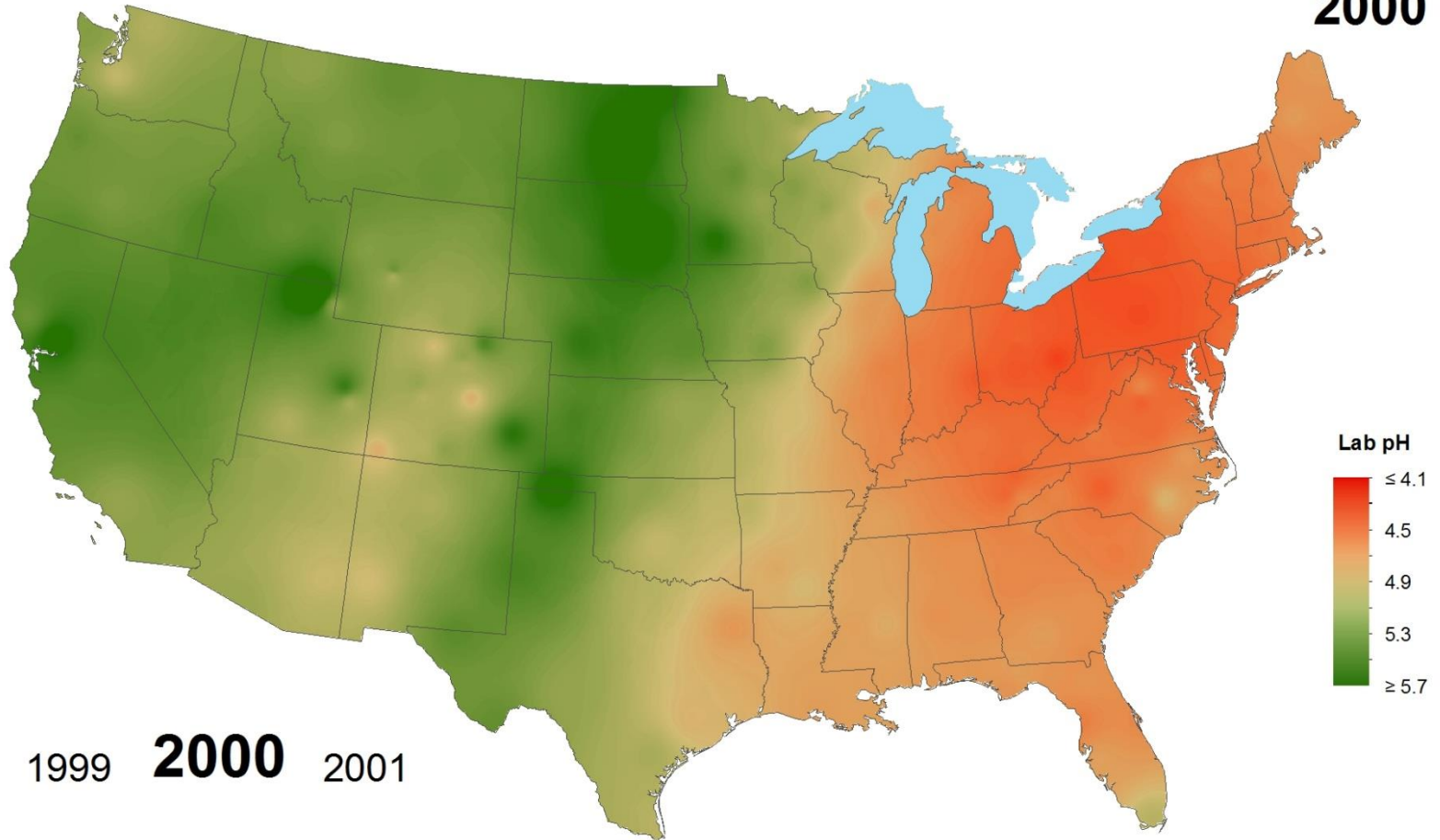
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# Hydrogen ion concentration as pH 1999



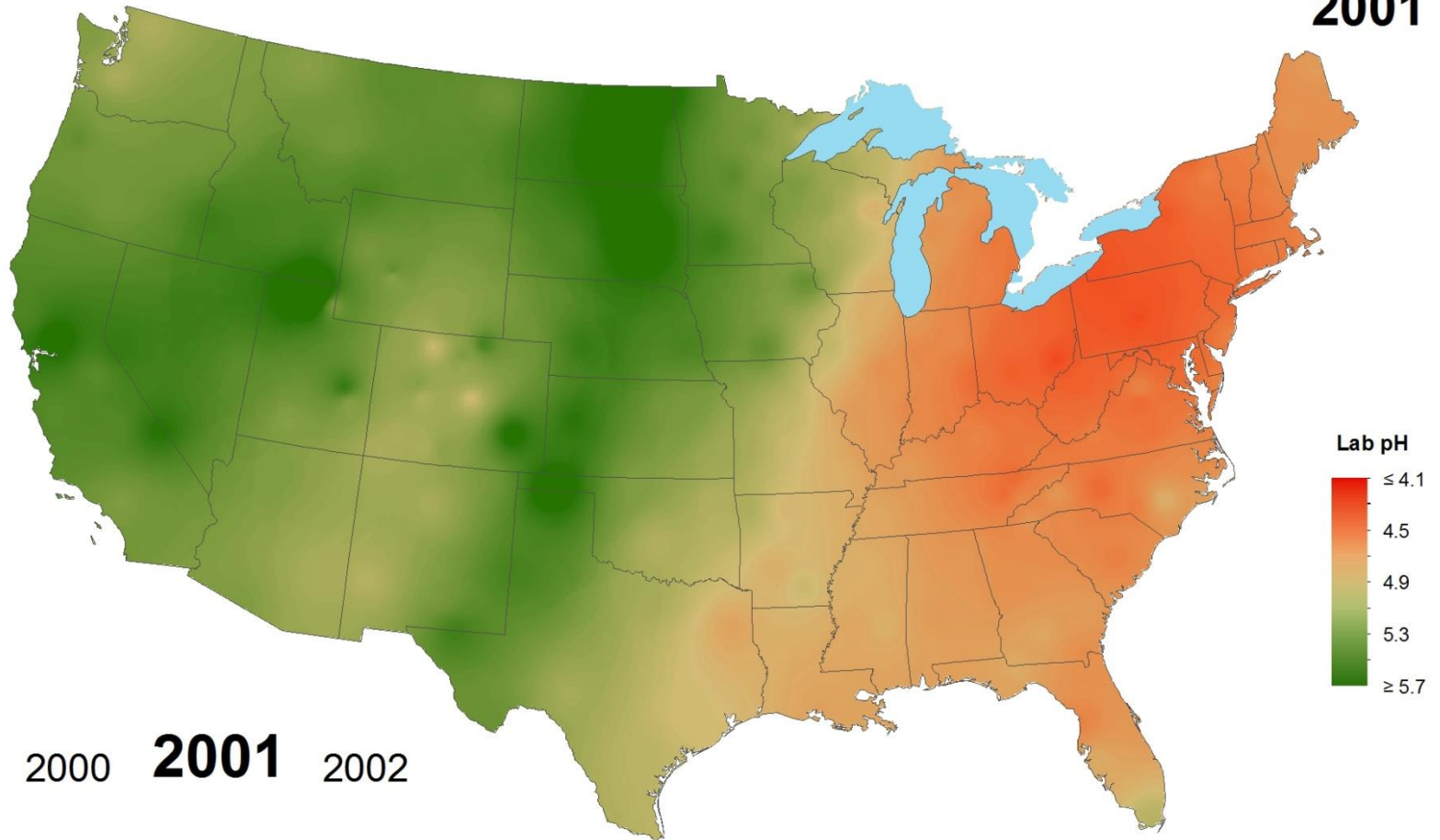
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# Hydrogen ion concentration as pH 2000



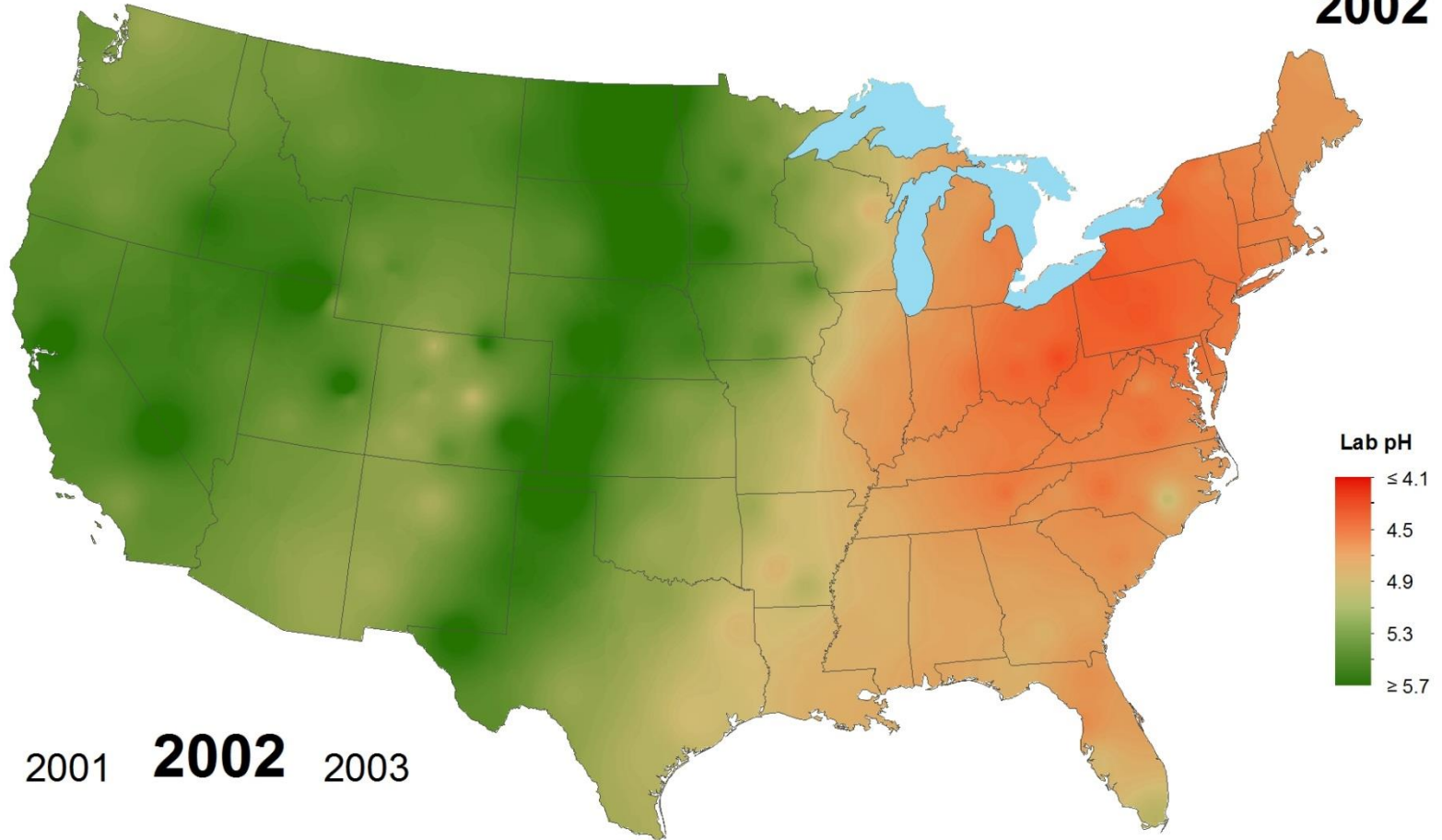
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# Hydrogen ion concentration as pH 2001



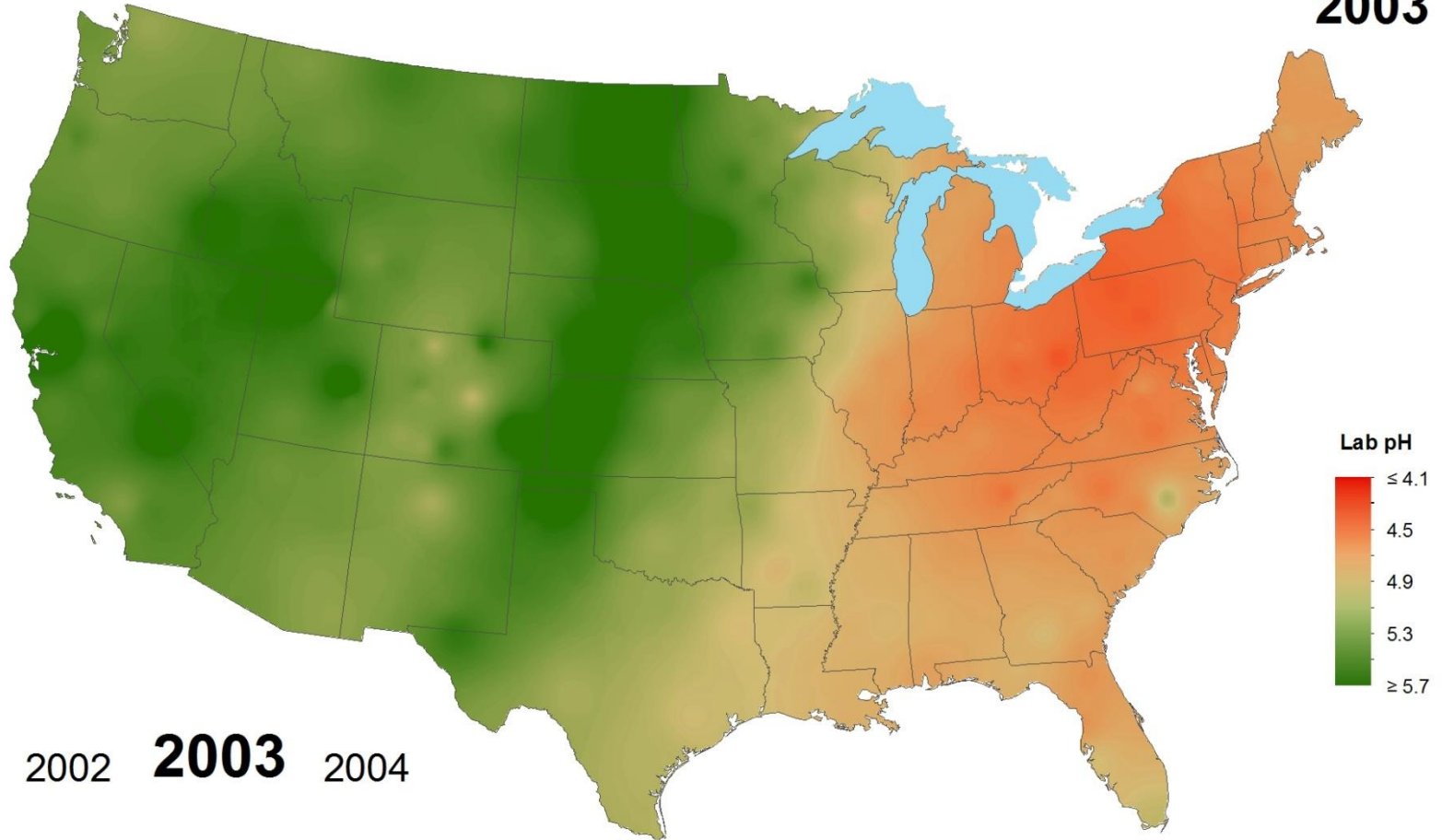
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# Hydrogen ion concentration as pH 2002



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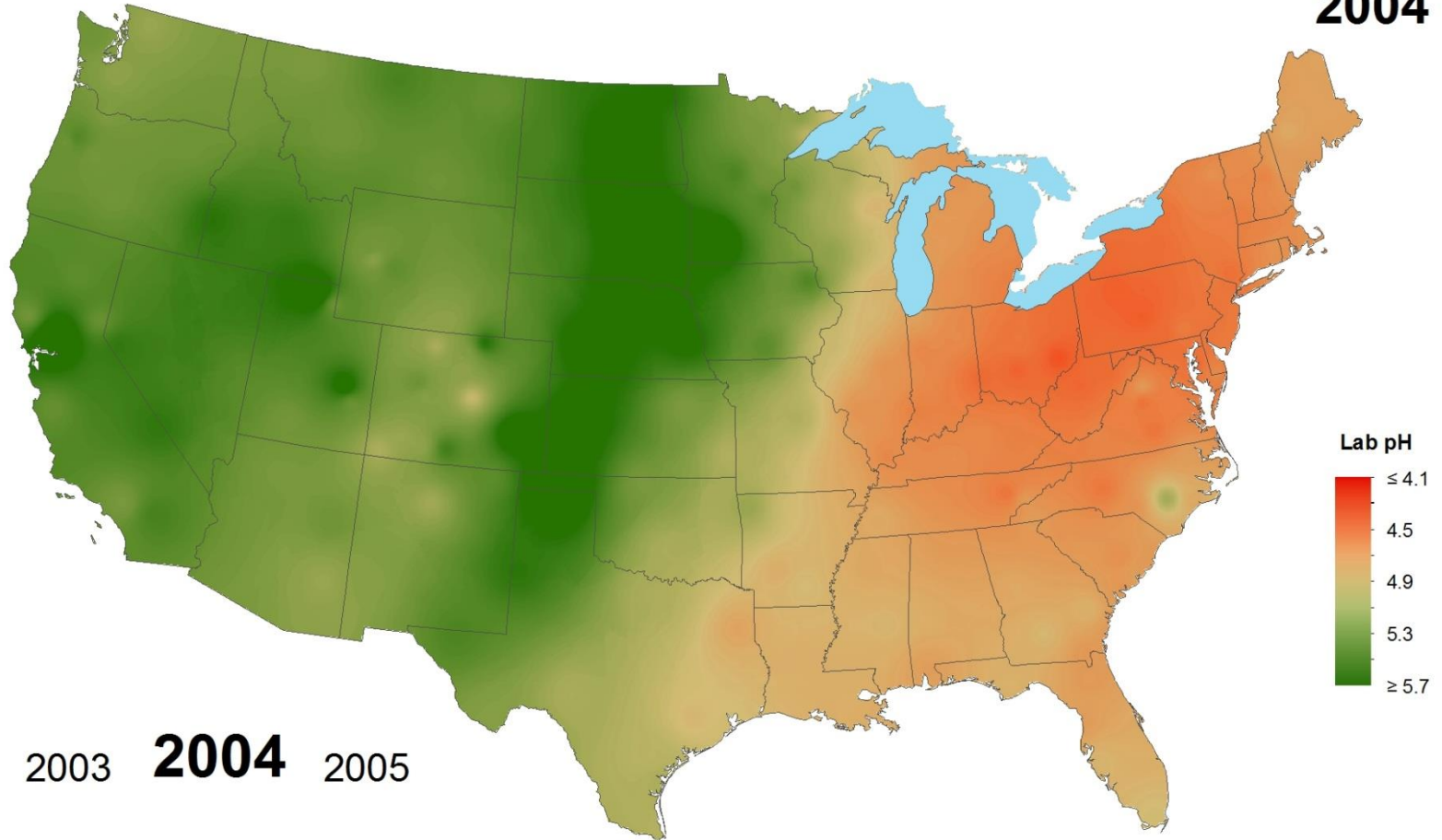
# Hydrogen ion concentration as pH 2003



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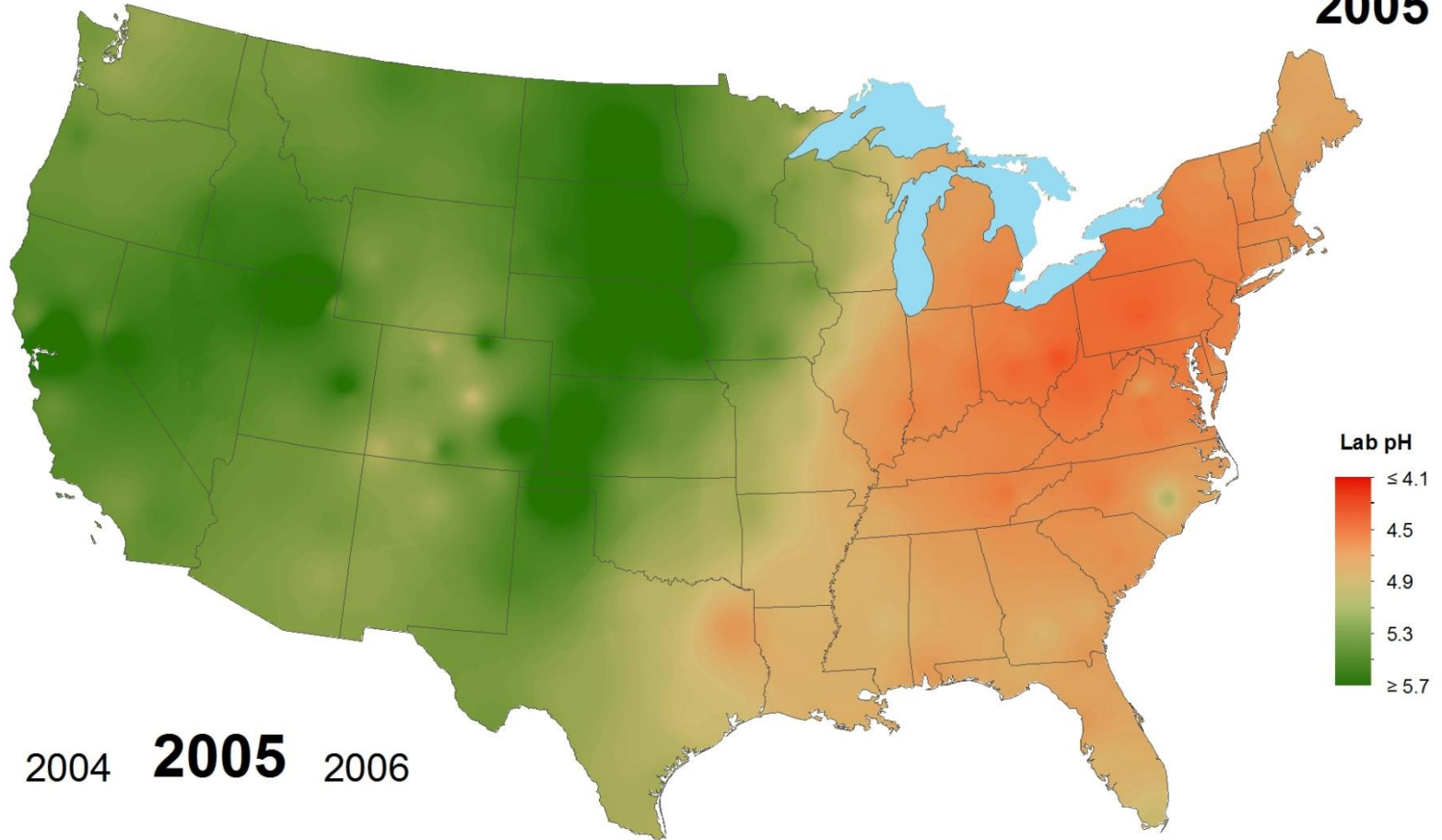


# Hydrogen ion concentration as pH 2004



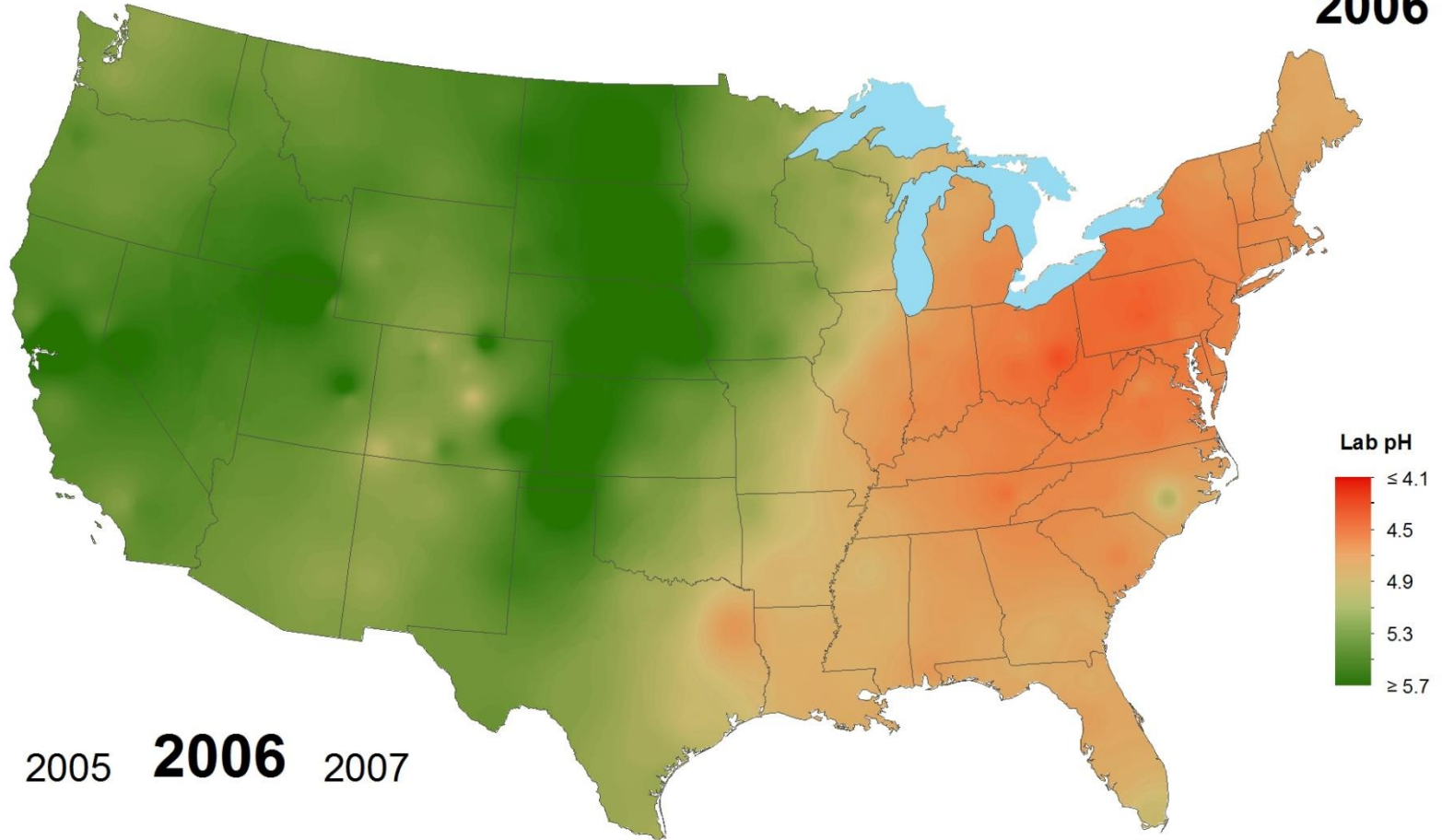
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# Hydrogen ion concentration as pH 2005



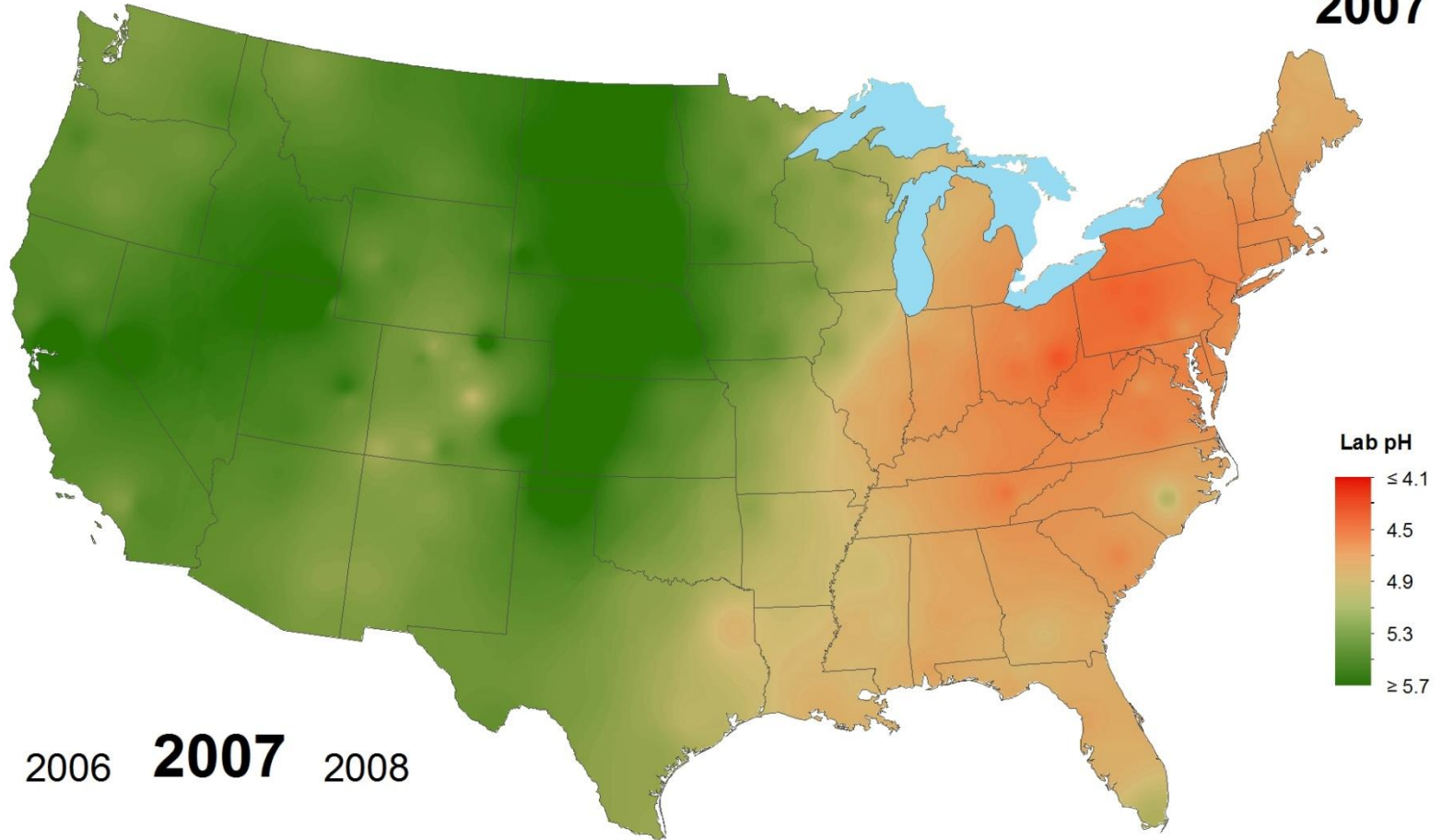
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# Hydrogen ion concentration as pH 2006



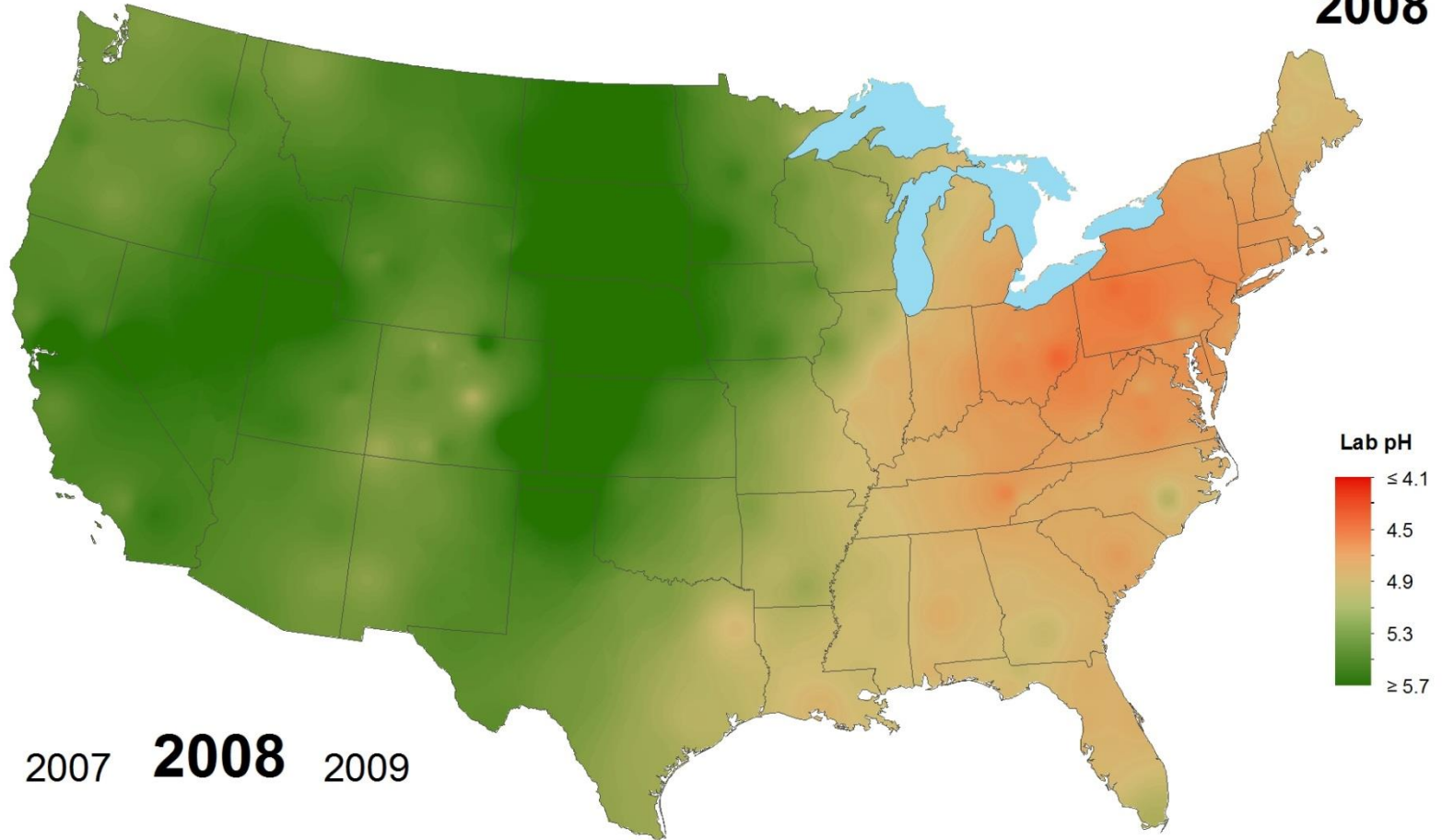
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# Hydrogen ion concentration as pH 2007



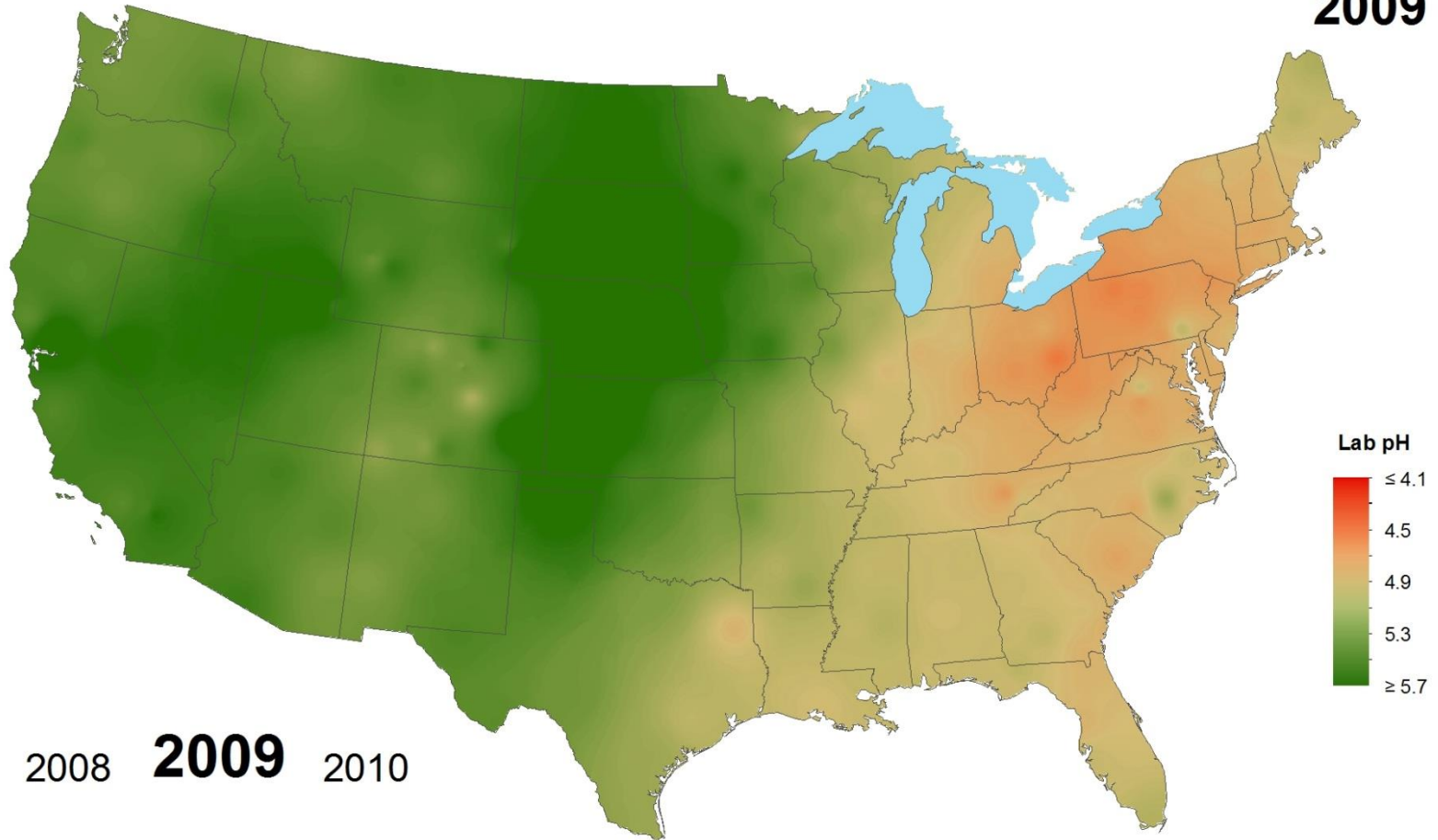
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# Hydrogen ion concentration as pH 2008



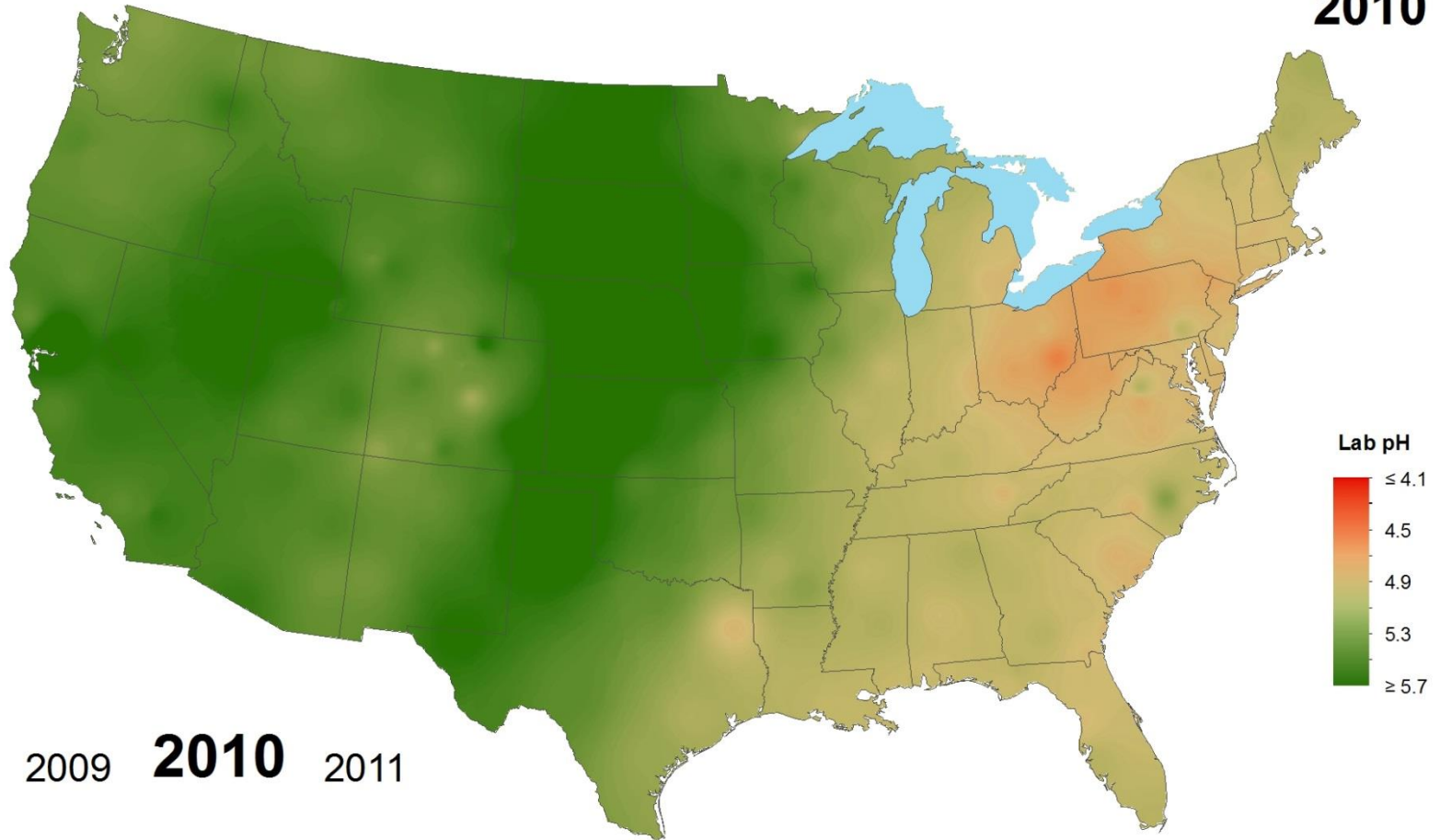
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# Hydrogen ion concentration as pH 2009



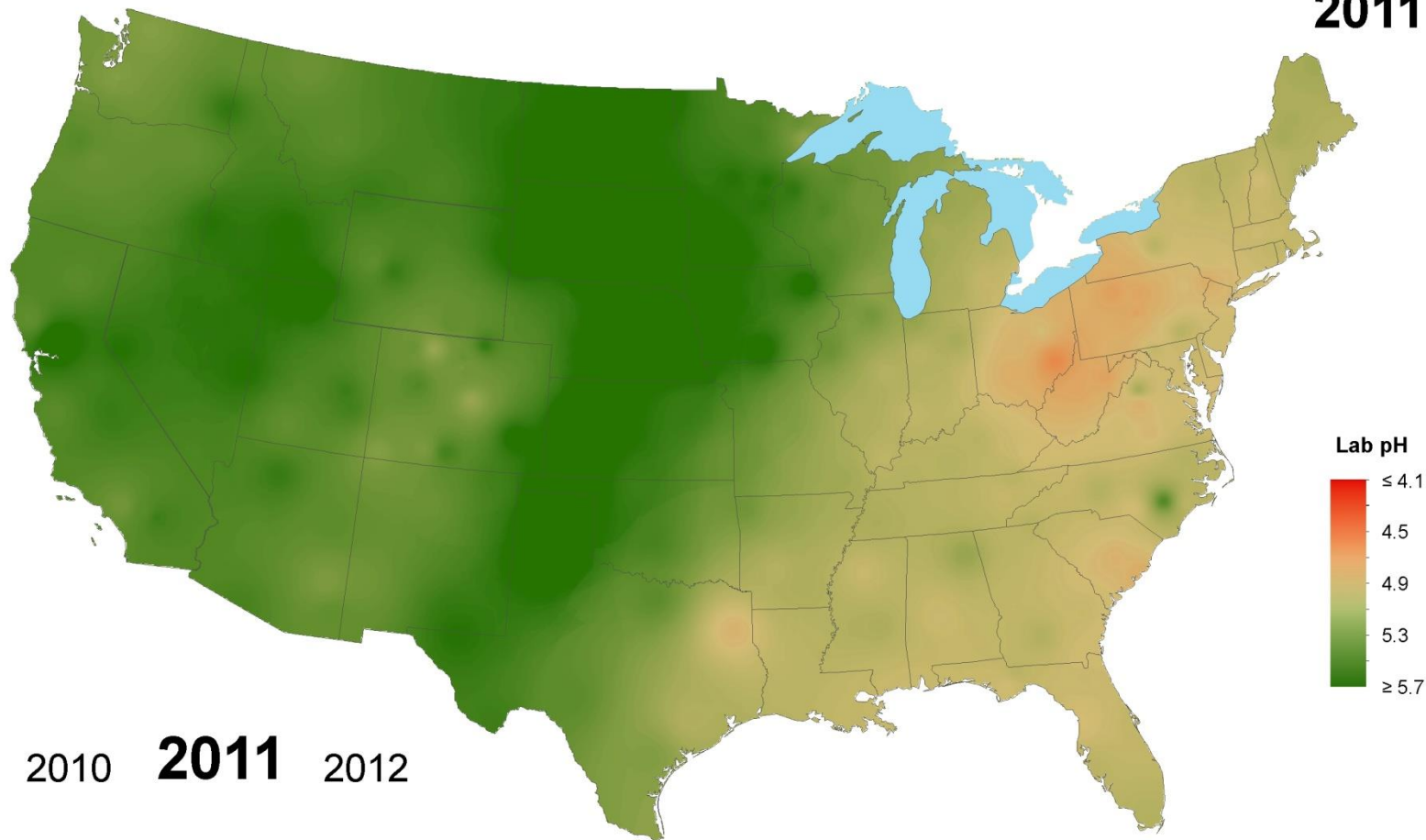
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# Hydrogen ion concentration as pH 2010



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# Hydrogen ion concentration as pH 2011

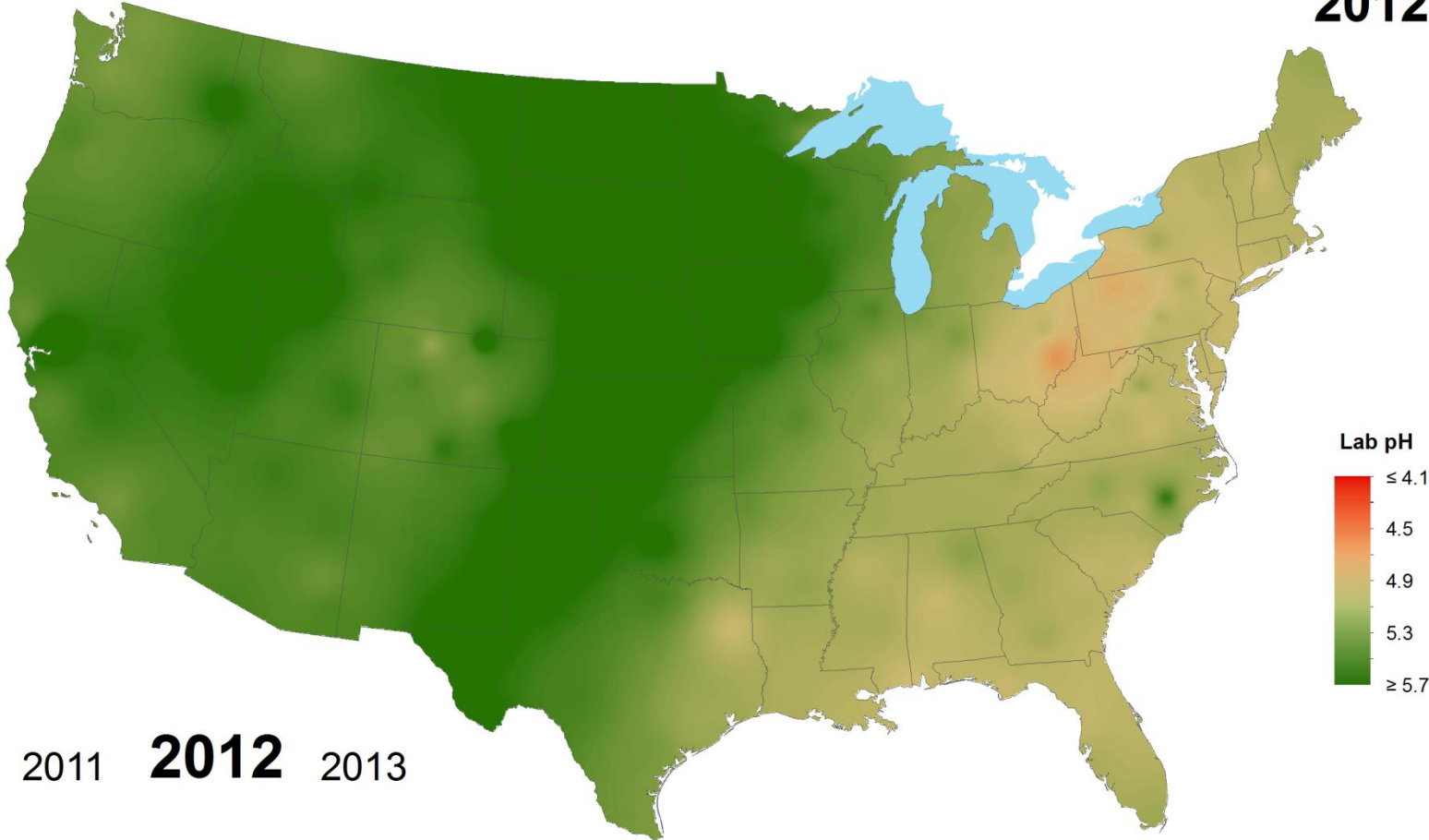


2010 **2011** 2012

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# Hydrogen ion concentration as pH 2012



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**What's in acid rain?** Short answer – it depends on the location!!

North America:

Mostly sulfate ( $\text{SO}_4^{2-}$ ), followed by nitrate ( $\text{NO}_3^-$ ) and chloride ( $\text{Cl}^-$ ).  
Some regional dependence – more chloride near coasts, more nitrate in heavily polluted areas (such as LA)  
Cations (to balance charge):  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$

Europe:

Similar to the US

China:

In some regions, acidity neutralized by alkaline dusts from the central desert.  
Otherwise, afflicted with the same problems as industrialized areas.

Remote regions: (northern Canada, central Australia)

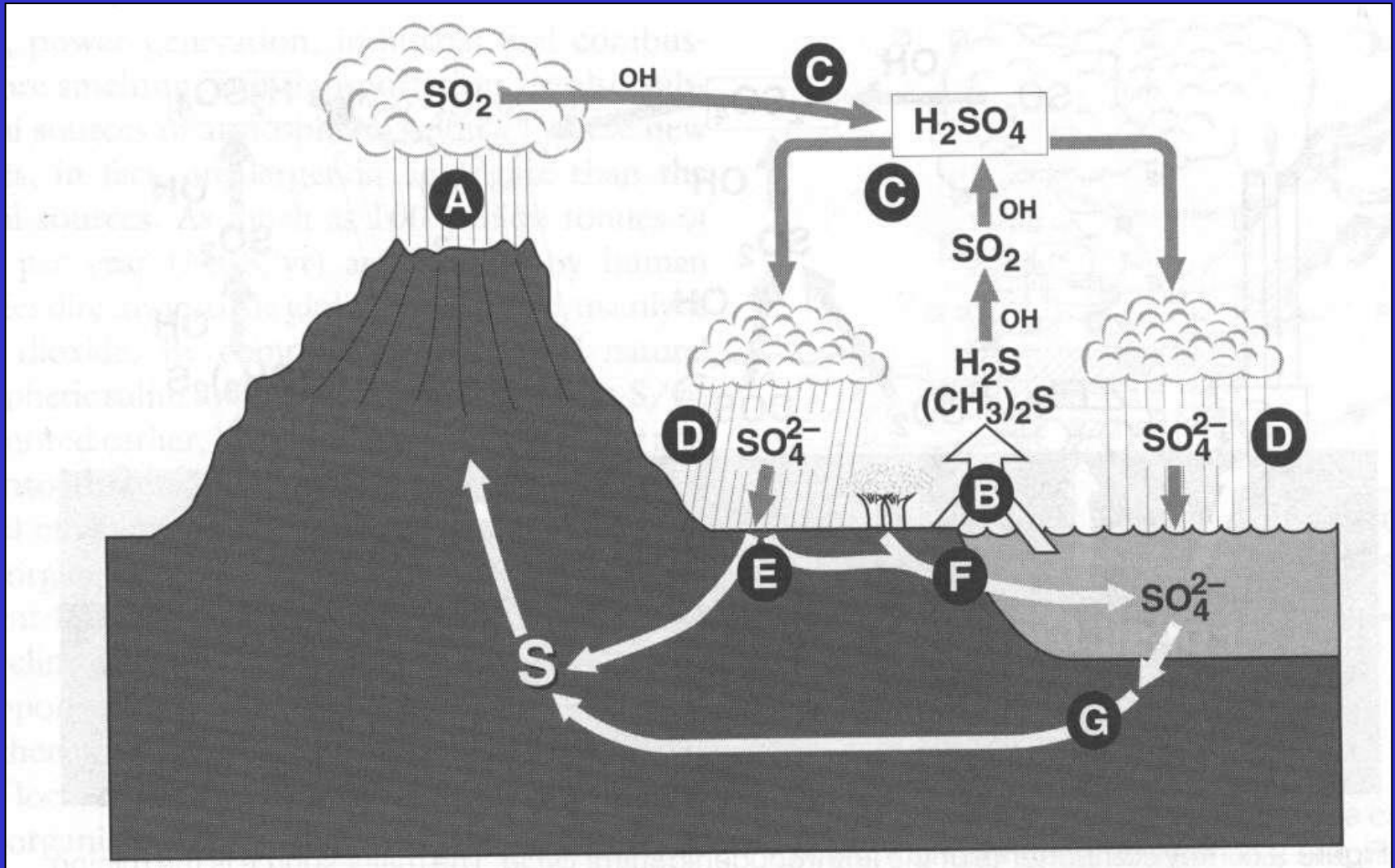
Dominant acid is sulfuric, but source is biological, not industrial (tested with isotope studies).

# The Sulfur Cycle

## Major emitted compounds

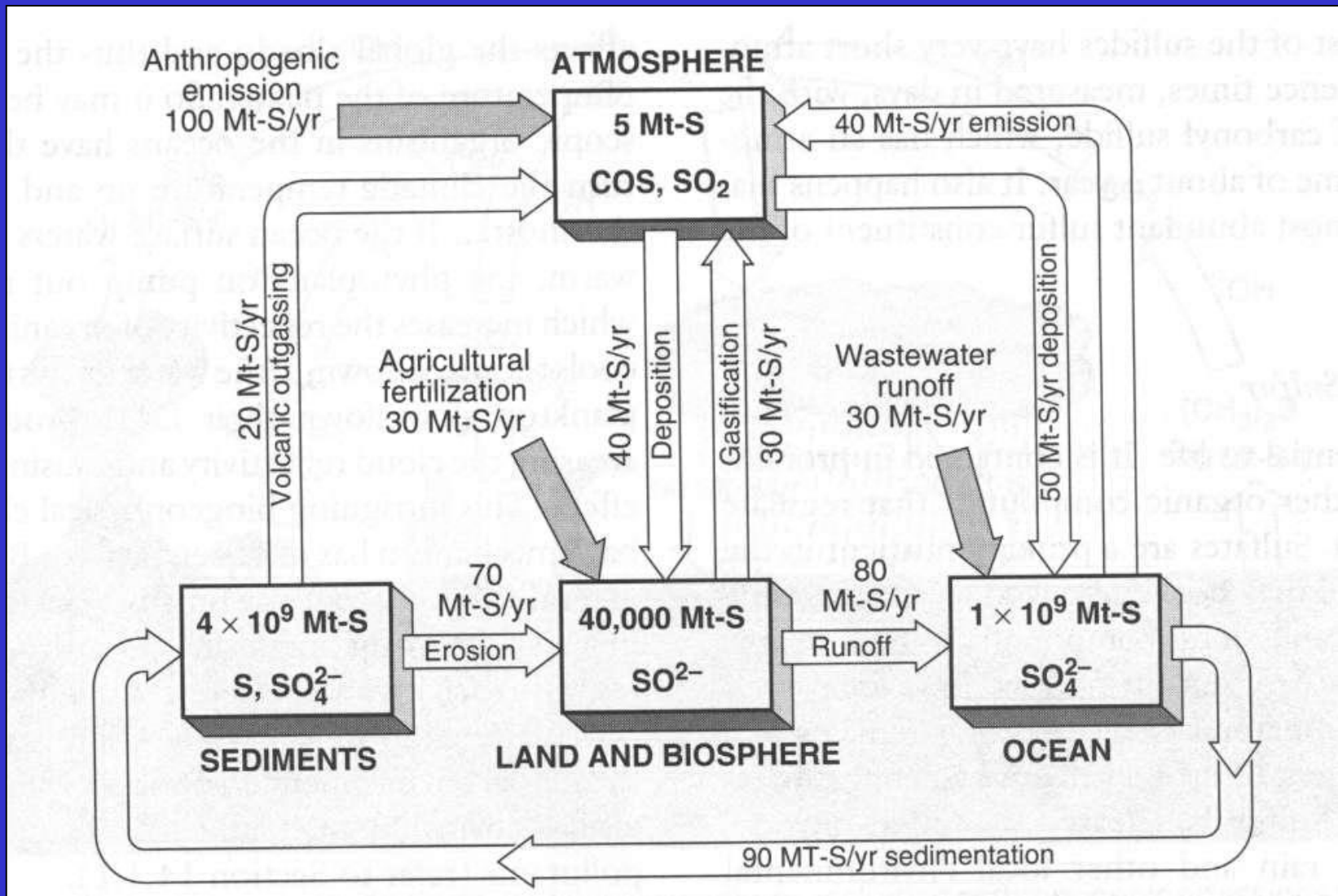
- Sulfur dioxide ( $\text{SO}_2$ ): volcanos, fumaroles, etc.; *fossil fuel burning*
- Hydrogen sulfide ( $\text{H}_2\text{S}$ ): biogenic emissions from anoxic soils and waters
- Carbonyl sulfide ( $\text{OCS}$ ): oceanic biology; *industrial by-product*
- Dimethyl sulfide ( $(\text{CH}_3)_2\text{S}$ ): oceanic biology

# The Natural Sulfur Cycle - Schematically



# Reservoirs and Fluxes

(We'll look at these 'box diagrams' in detail next week)



## Magnitudes

1 tonne (metric ton) = 1000 kg =  $1 \times 10^6$  g

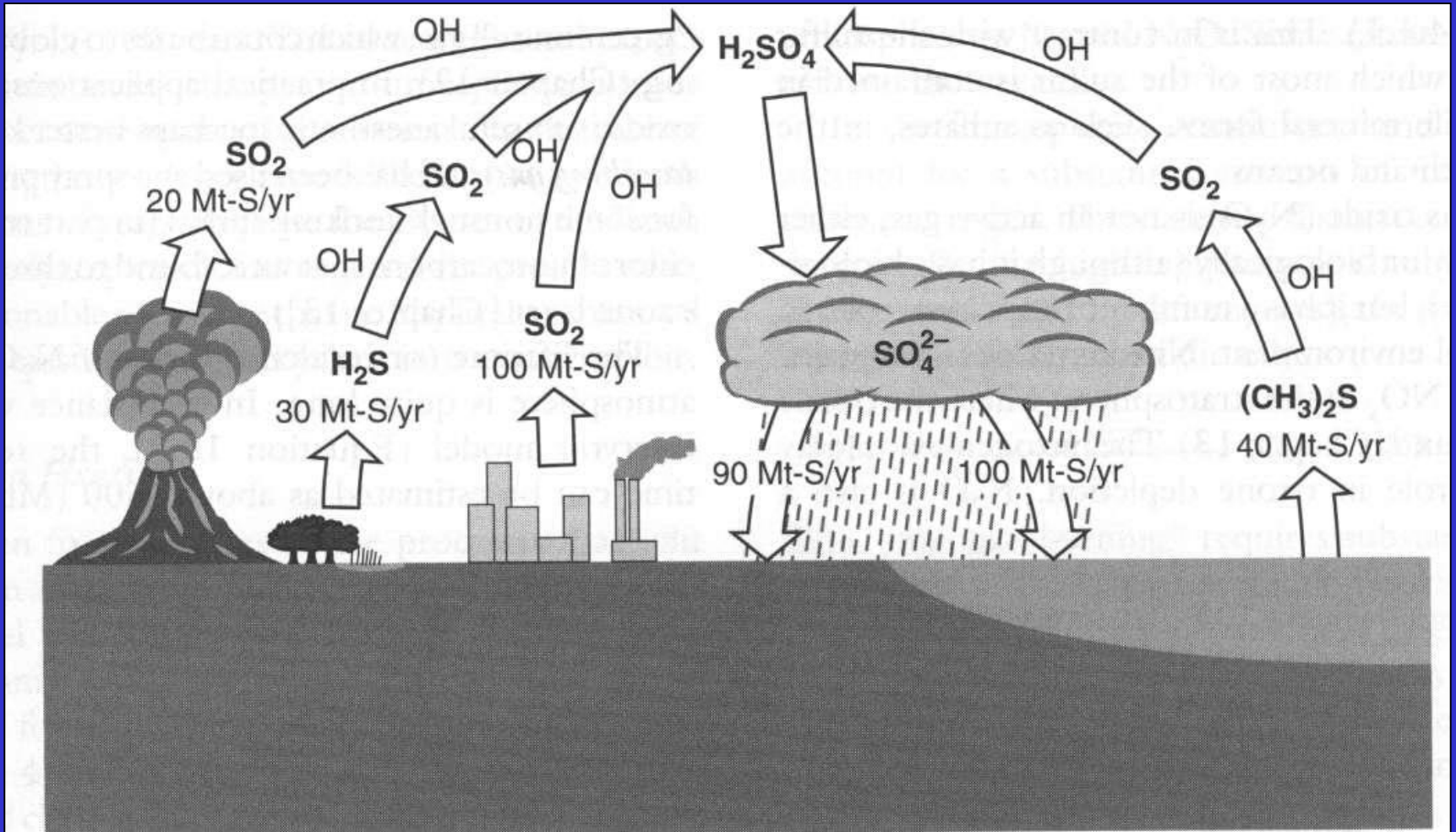
1 Megatonne (Mt) =  $1 \times 10^6$  tonne =  $1 \times 10^{12}$  g

1 Gigatonne (Gt) =  $1 \times 10^9$  tonne =  $1 \times 10^{15}$  g

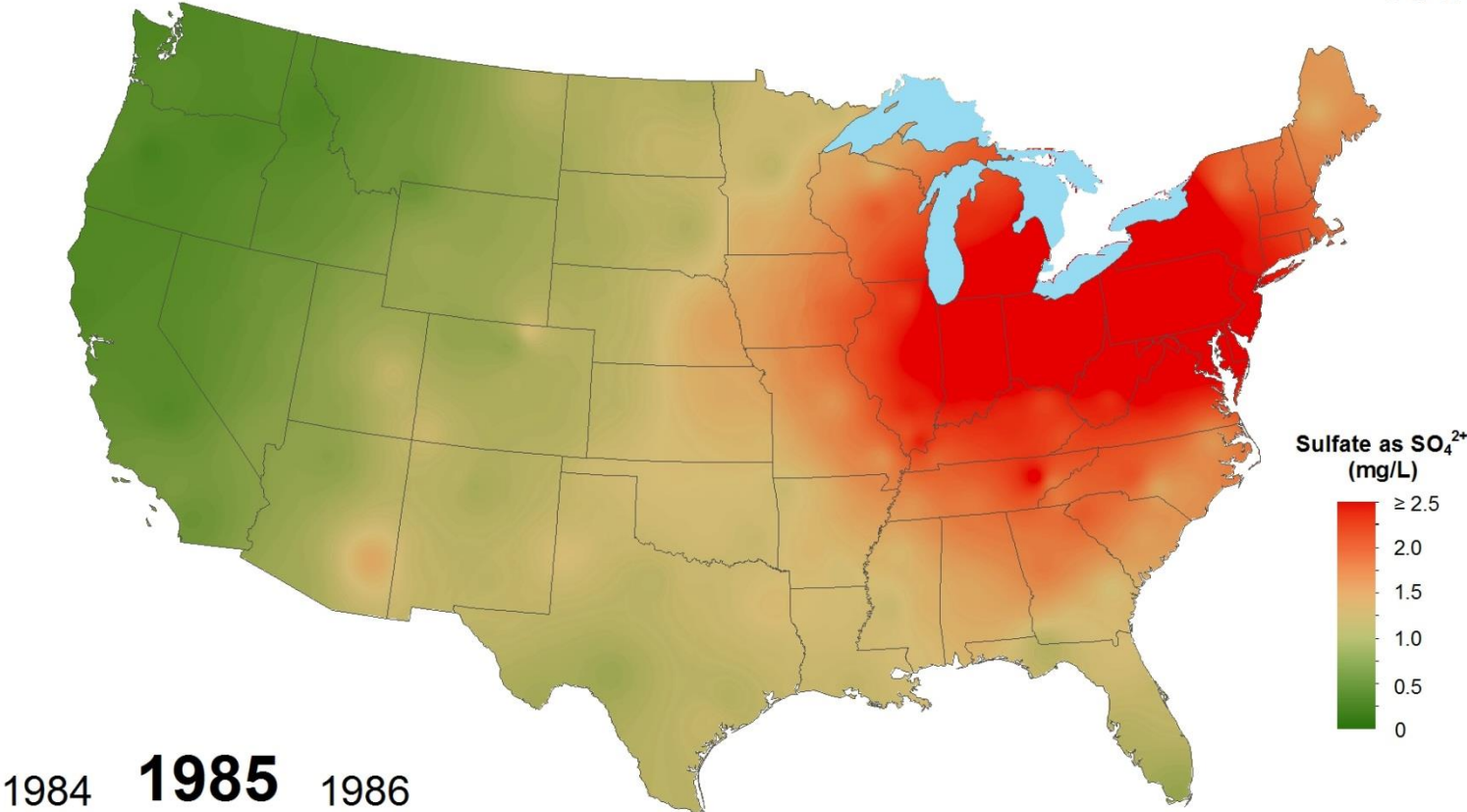
1 Teragram (Tg) =  $1 \times 10^{12}$  g

|                        |          |
|------------------------|----------|
| Natural sources:       | 90 Mt S  |
| Anthropogenic sources: | 100 Mt S |
| Sinks:                 | 190 Mt S |

# Anthropogenic Components and Fluxes



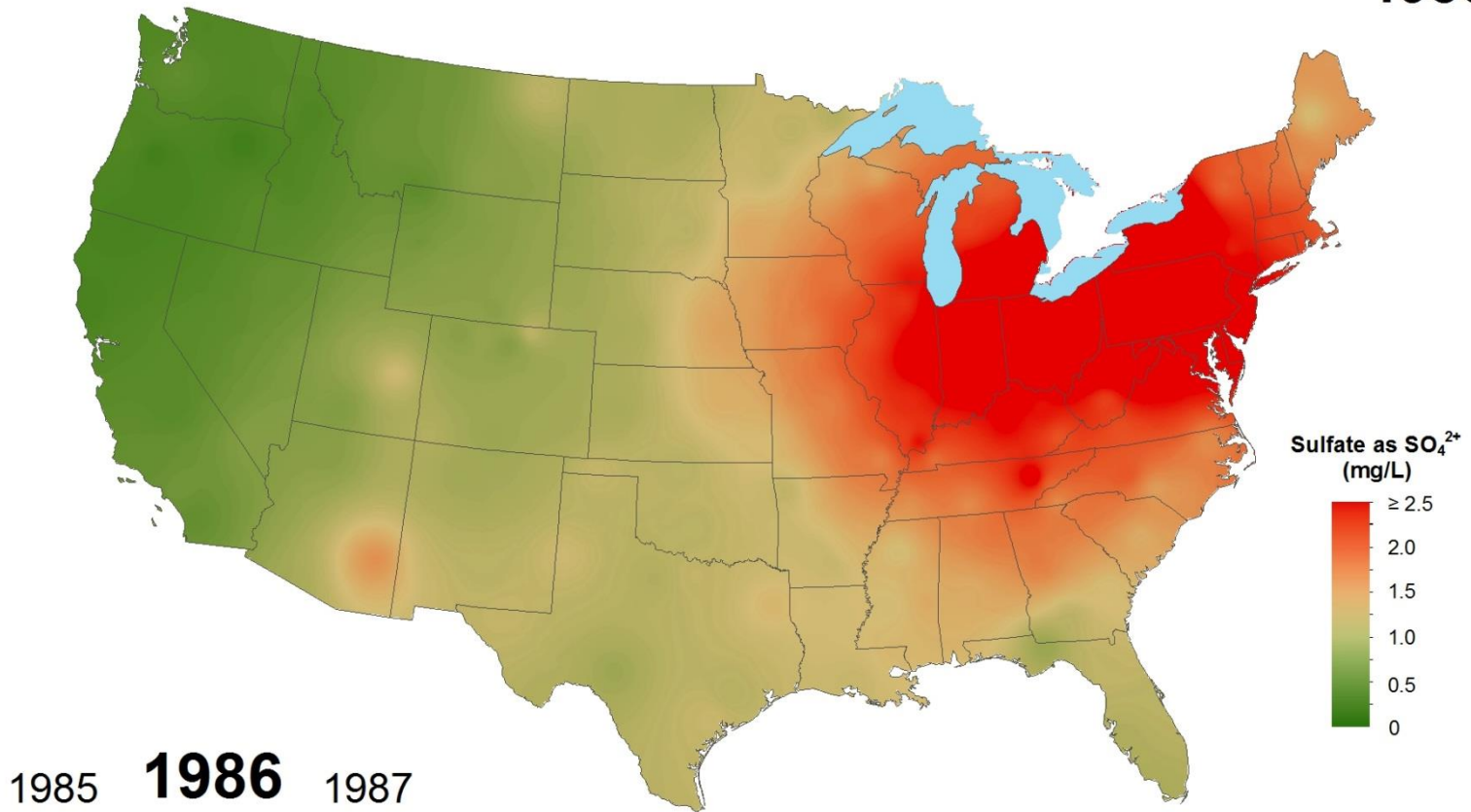
# Sulfate ion concentration 1985



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

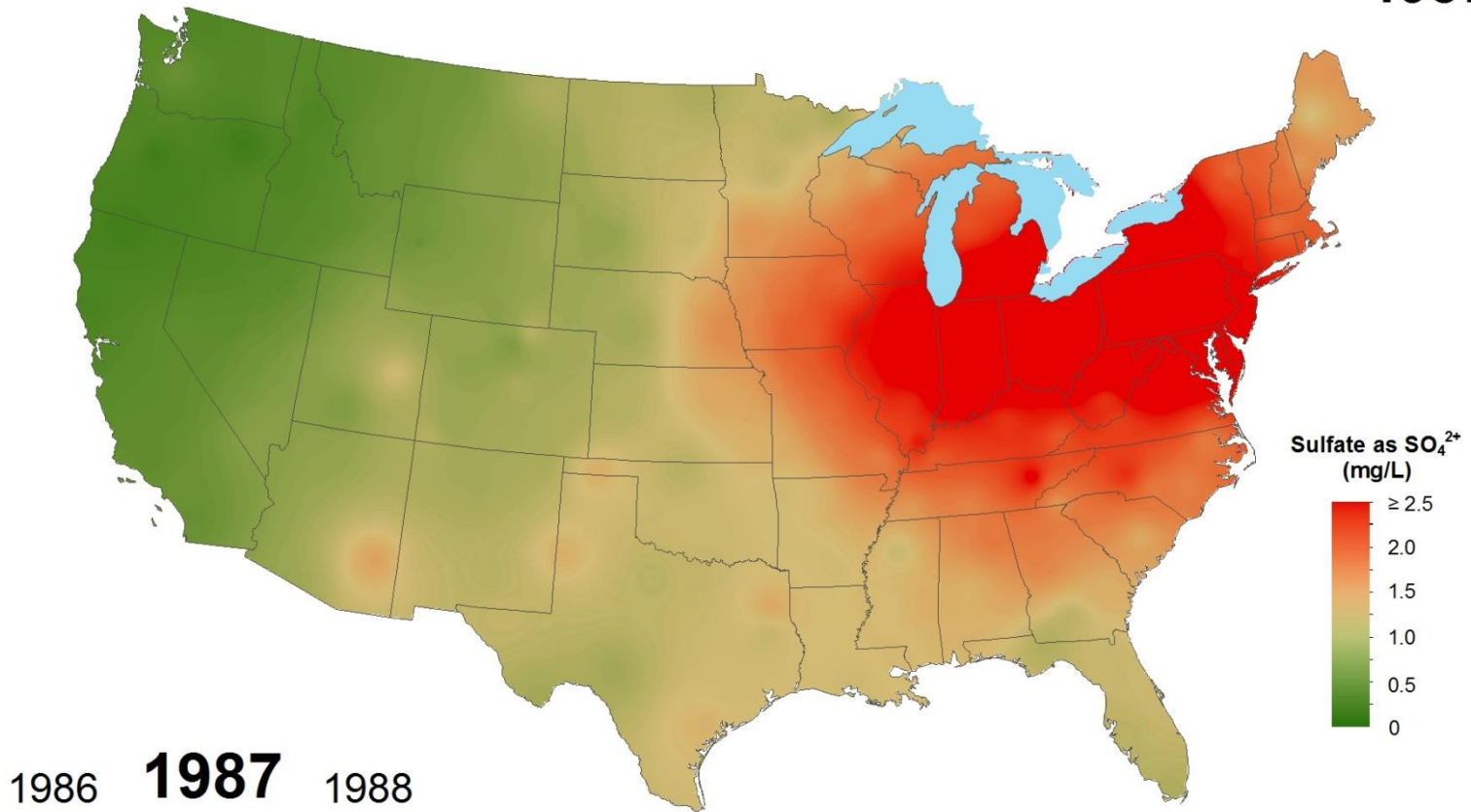


# Sulfate ion concentration 1986

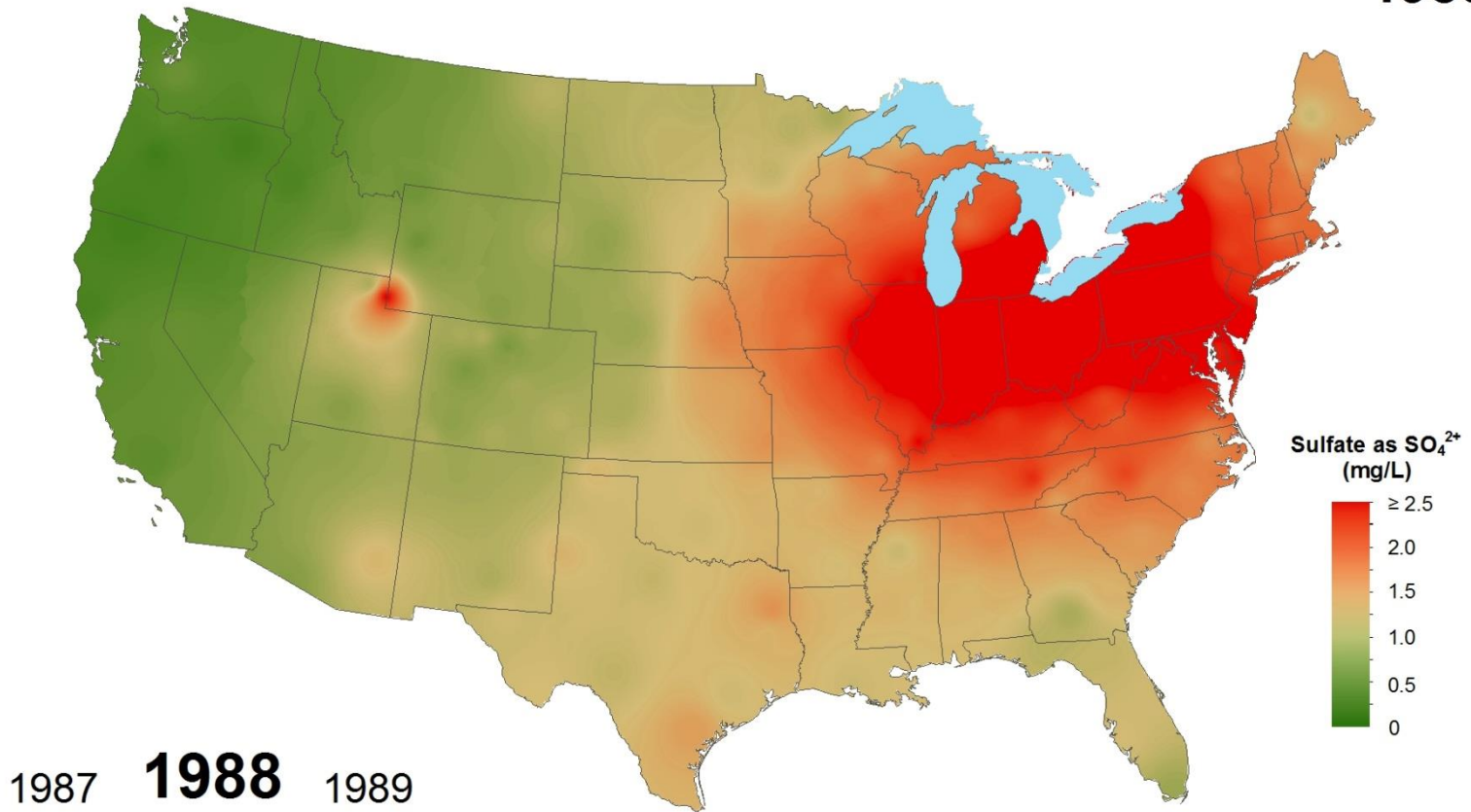


National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

# Sulfate ion concentration 1987

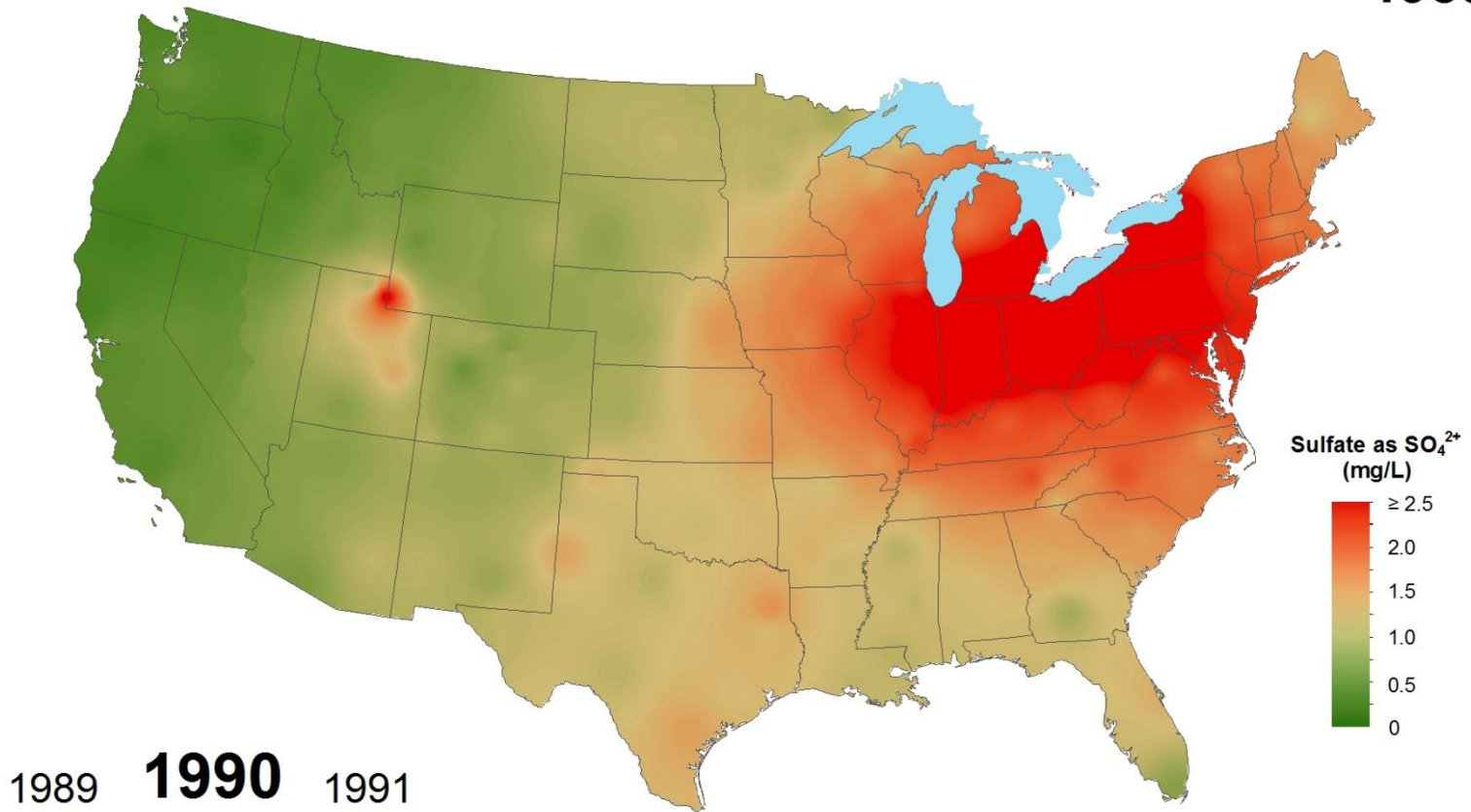


# Sulfate ion concentration 1988



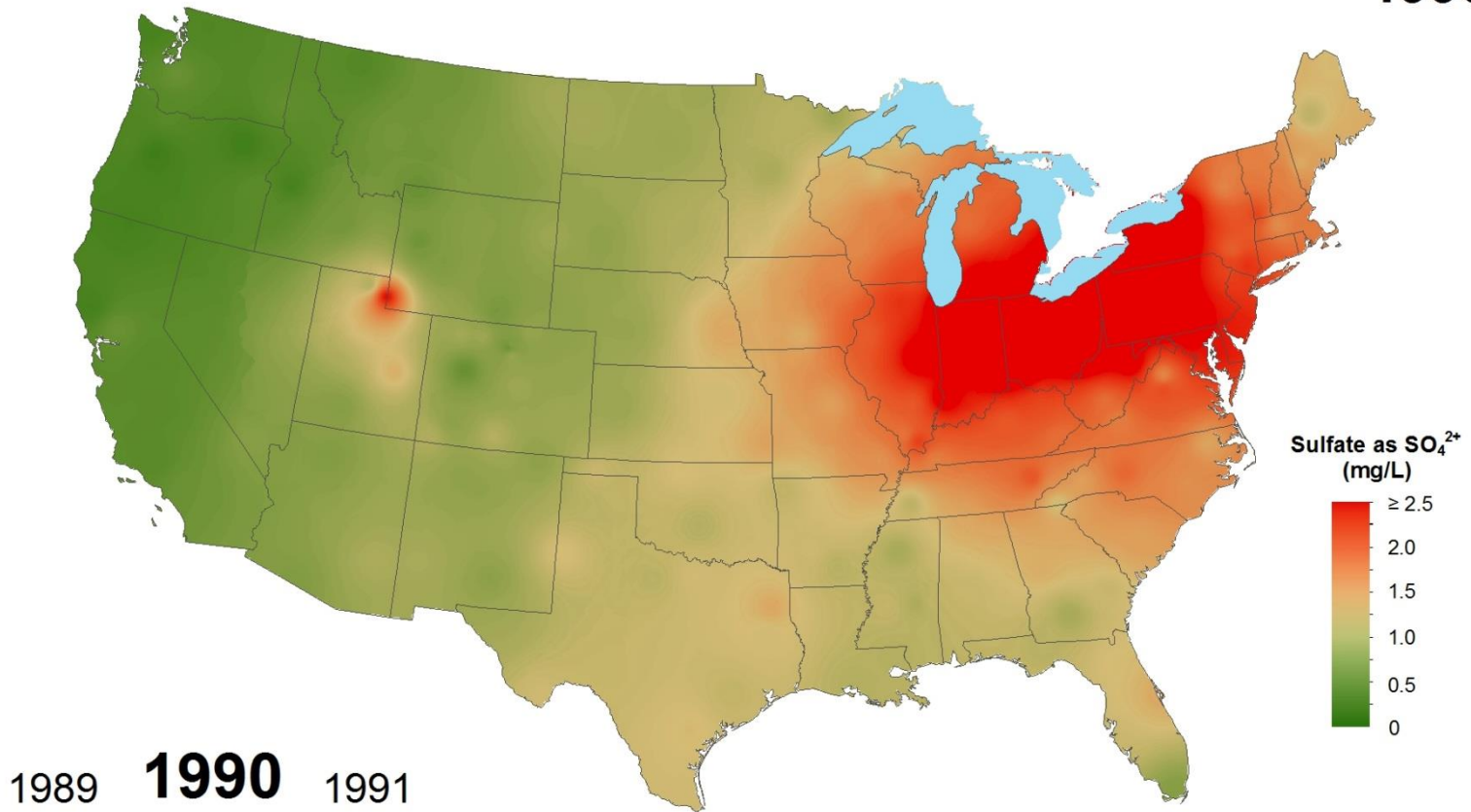
National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

# Sulfate ion concentration 1989



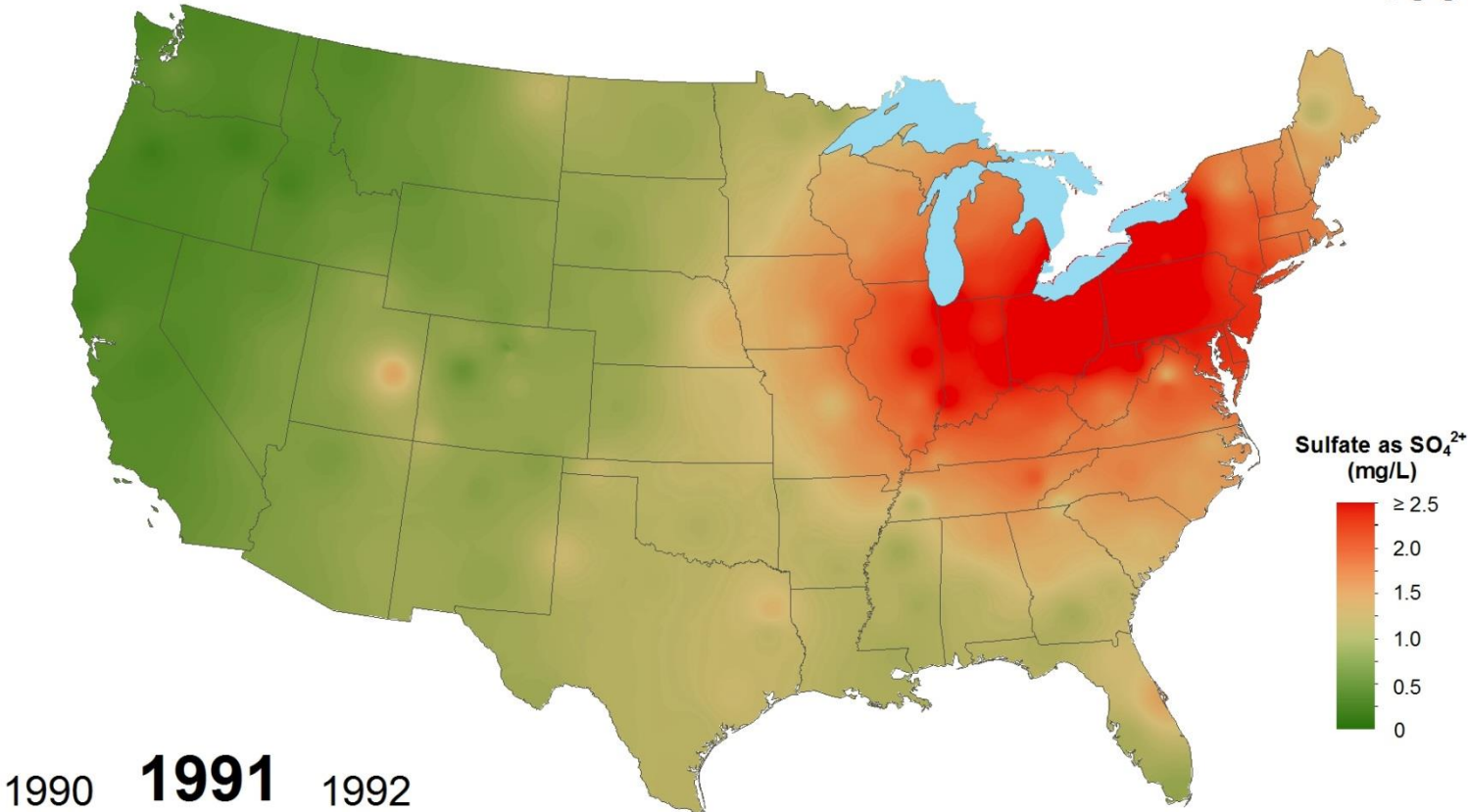
National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

# Sulfate ion concentration 1990



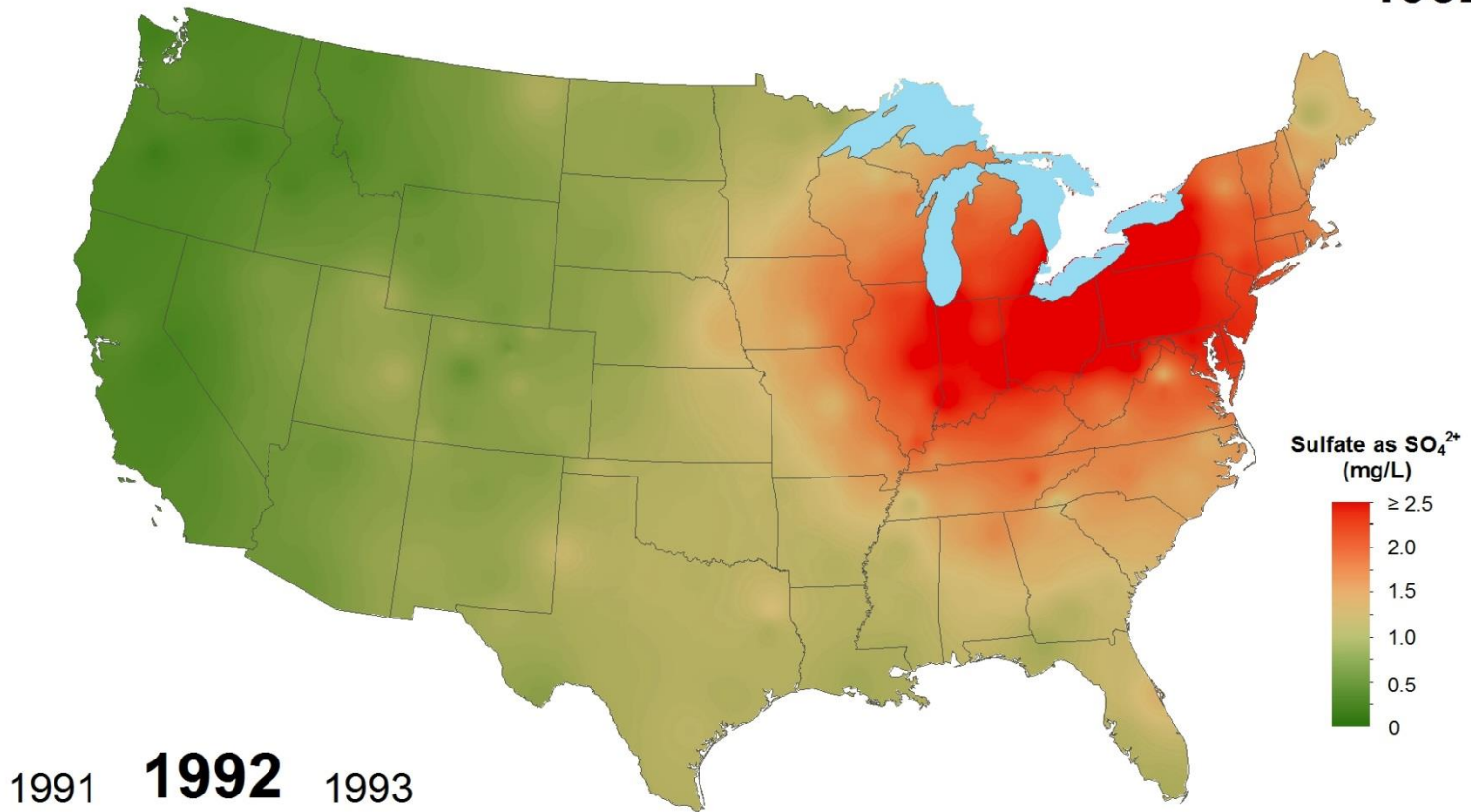
National Atmospheric Deposition Program/National Trends Network  
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# Sulfate ion concentration 1991

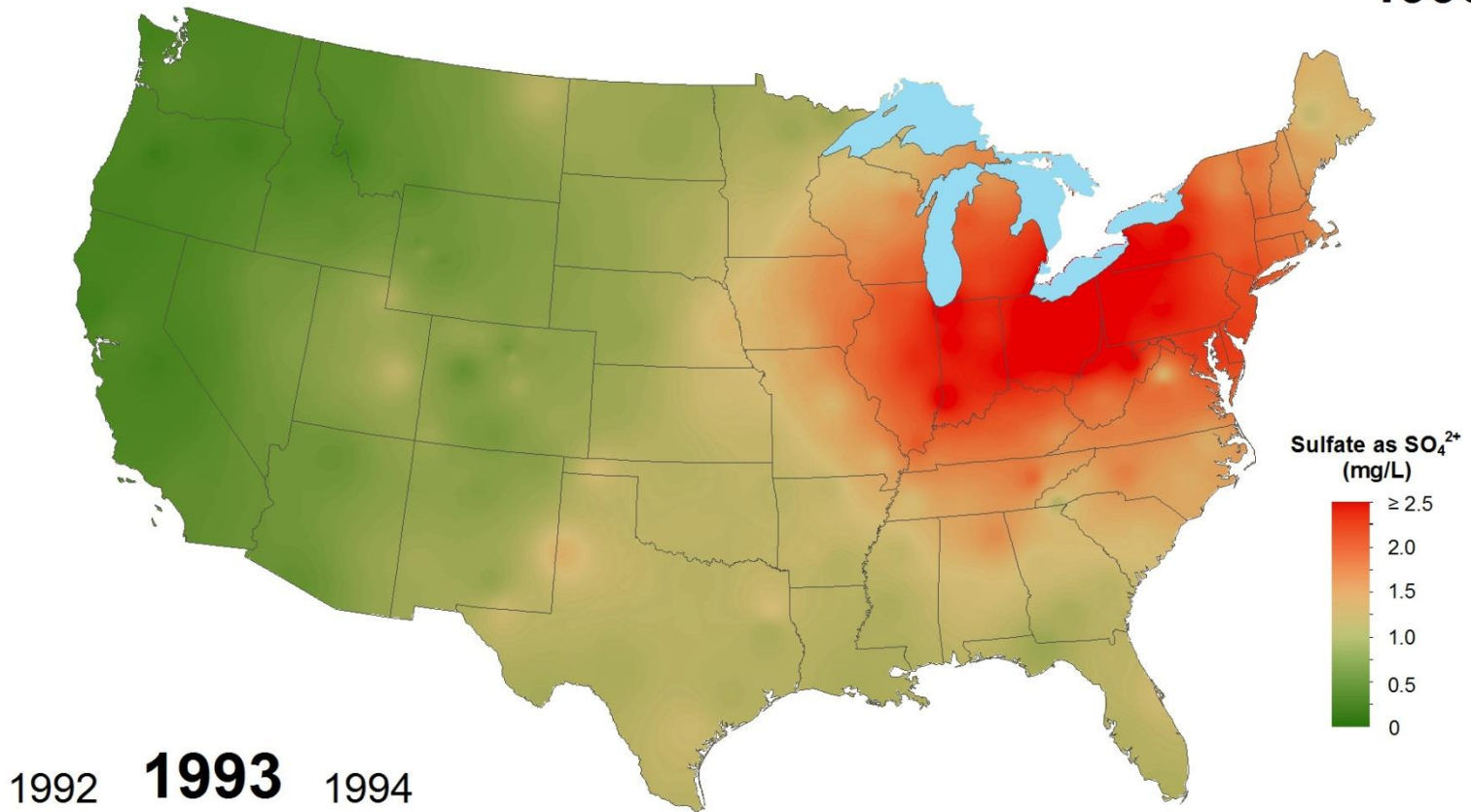


National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

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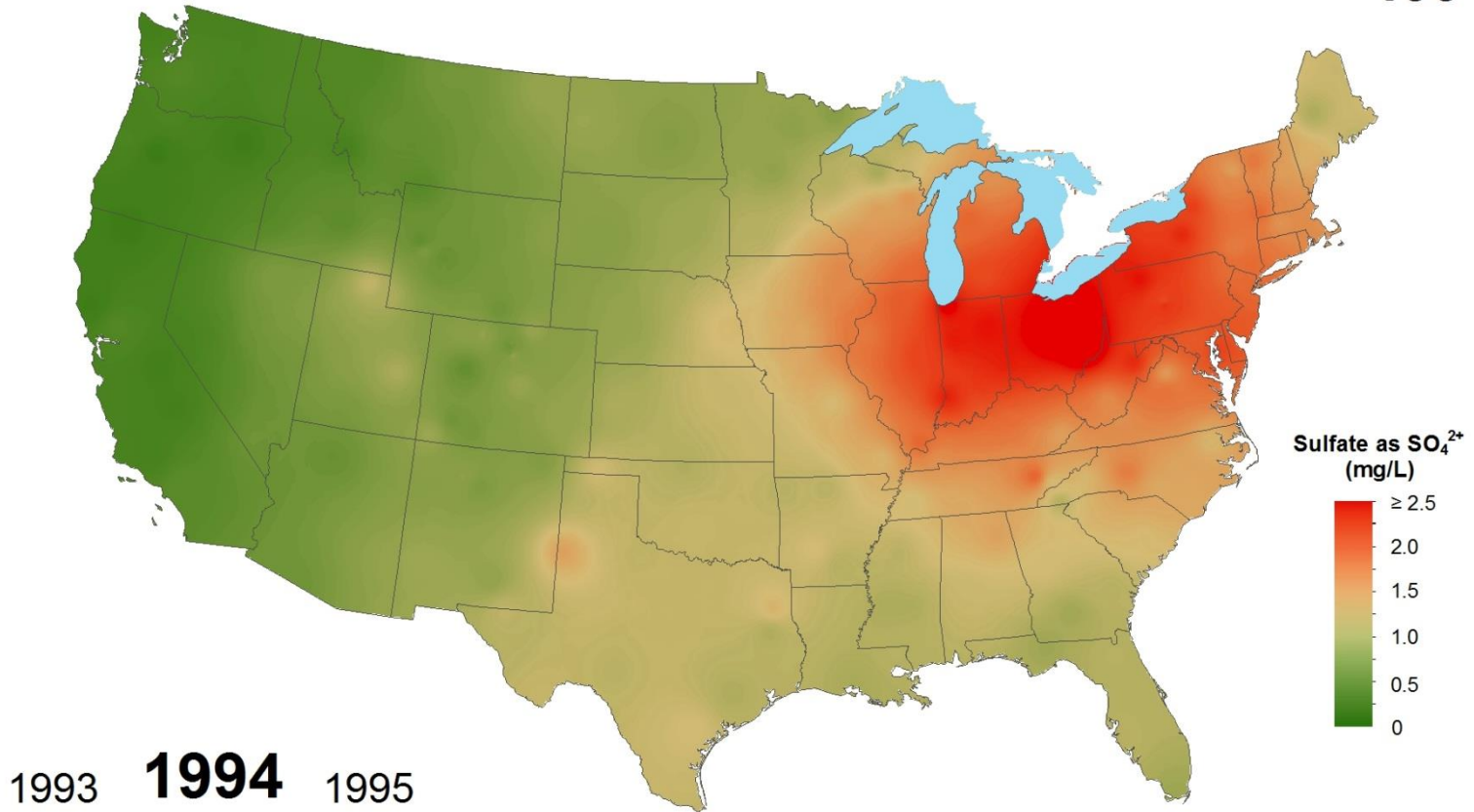


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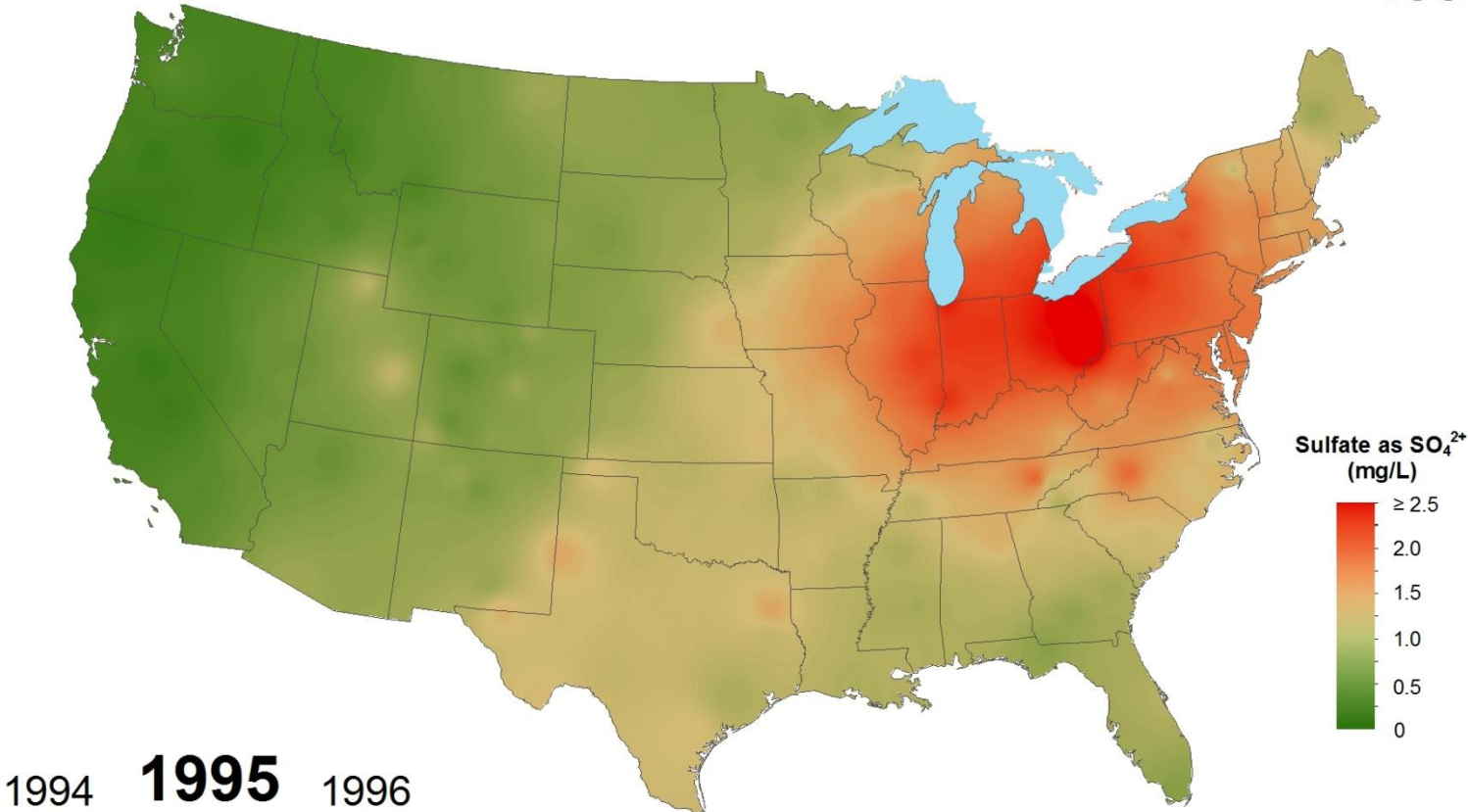




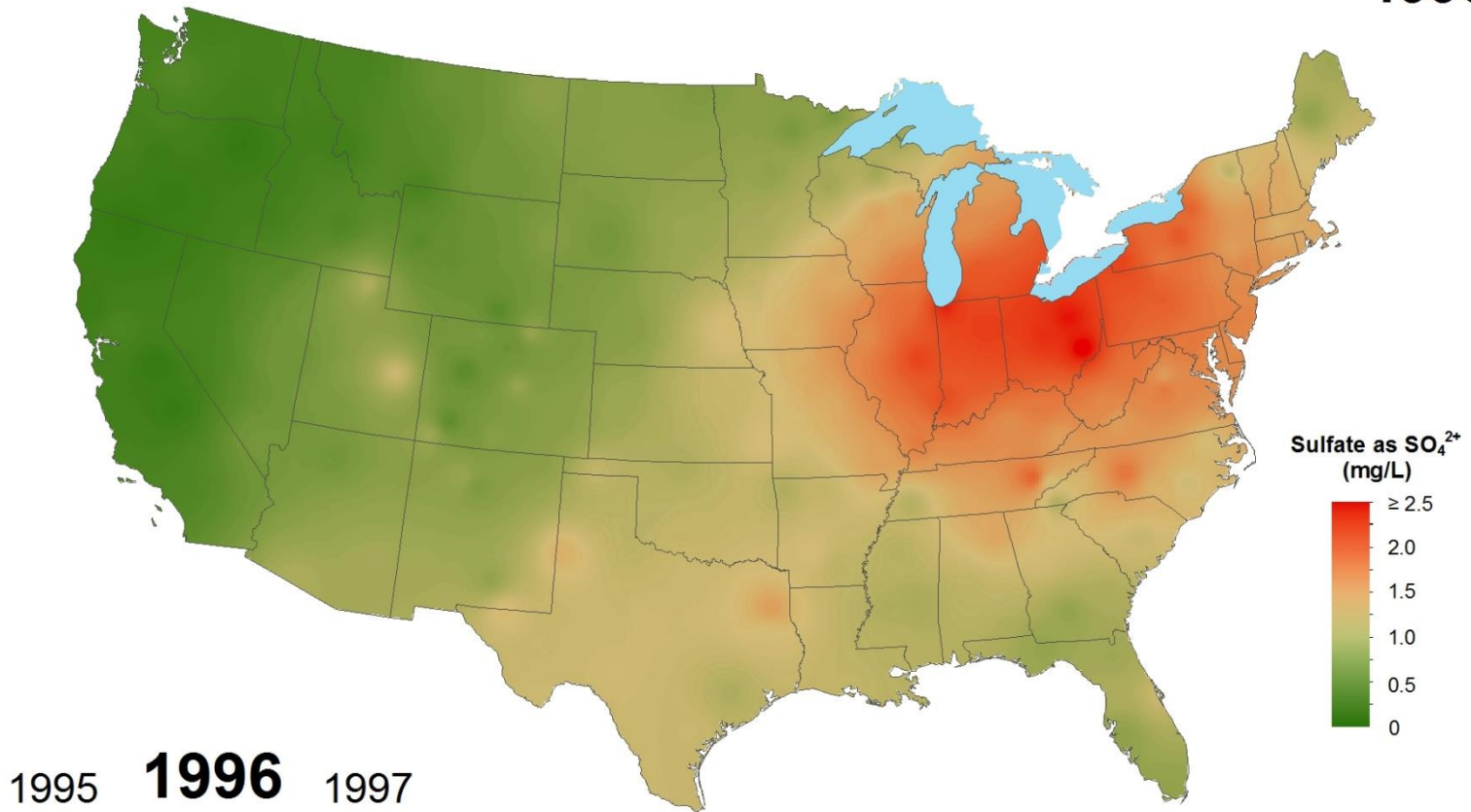
# Sulfate ion concentration 1994



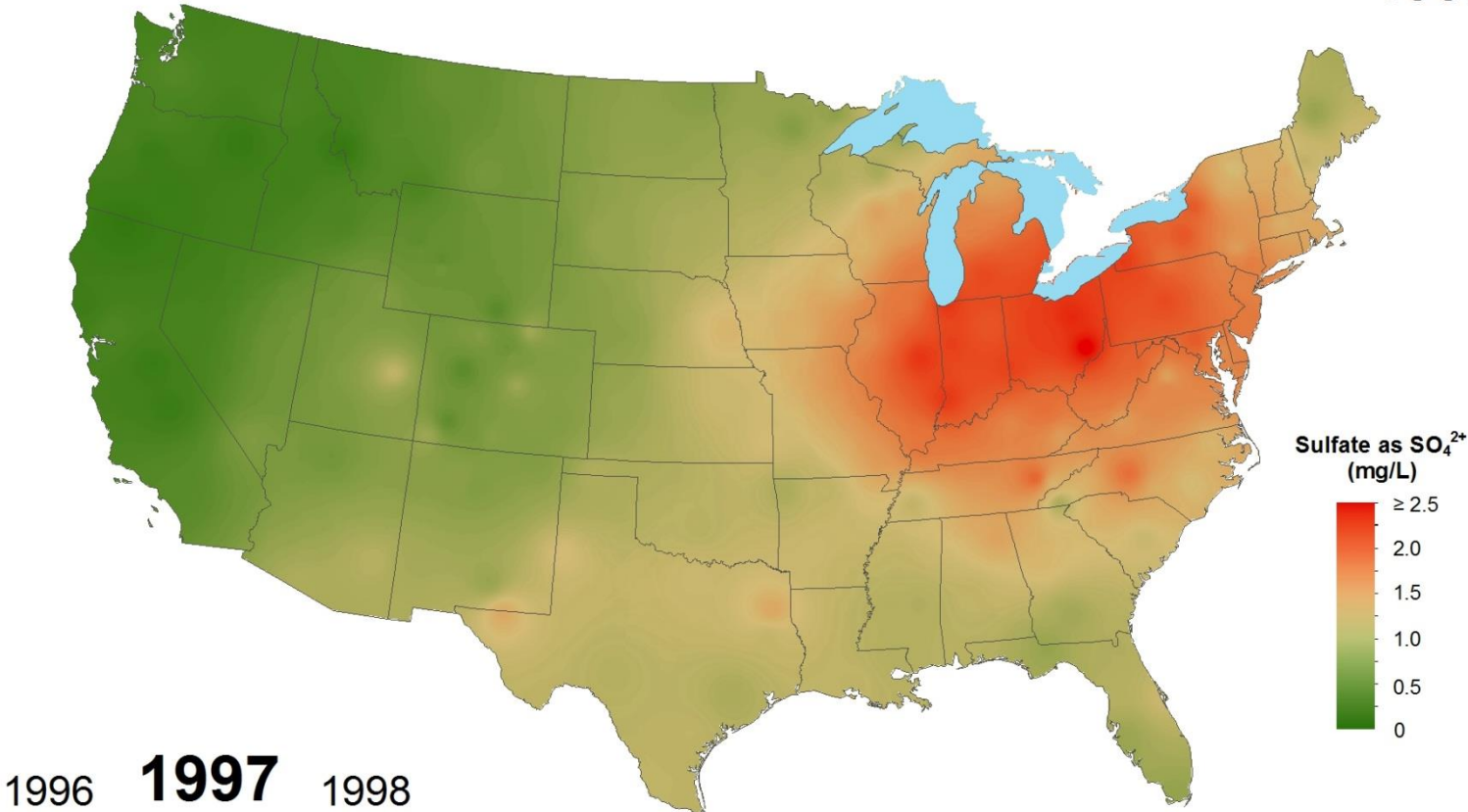
# Sulfate ion concentration 1995



# Sulfate ion concentration 1996

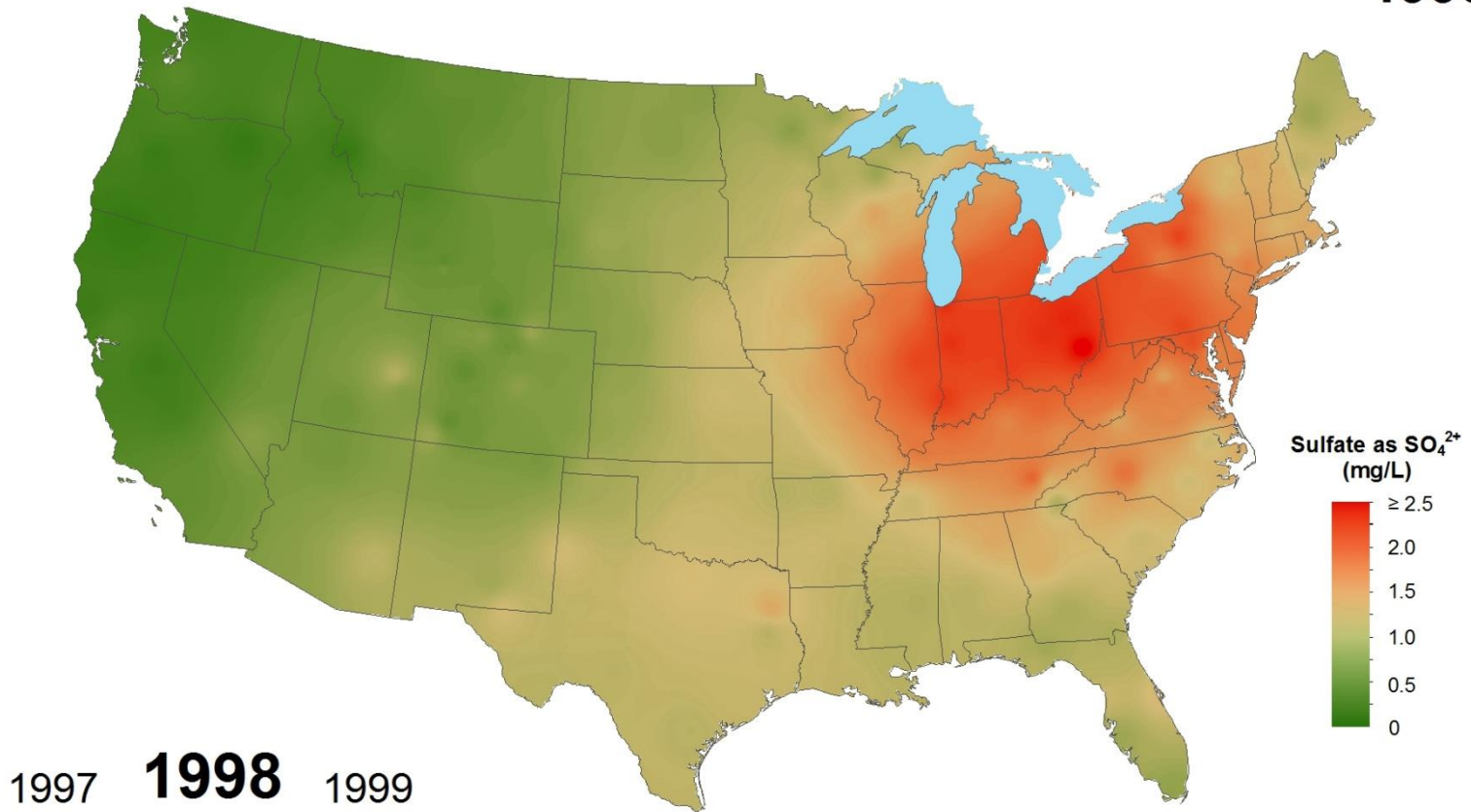


# Sulfate ion concentration 1997

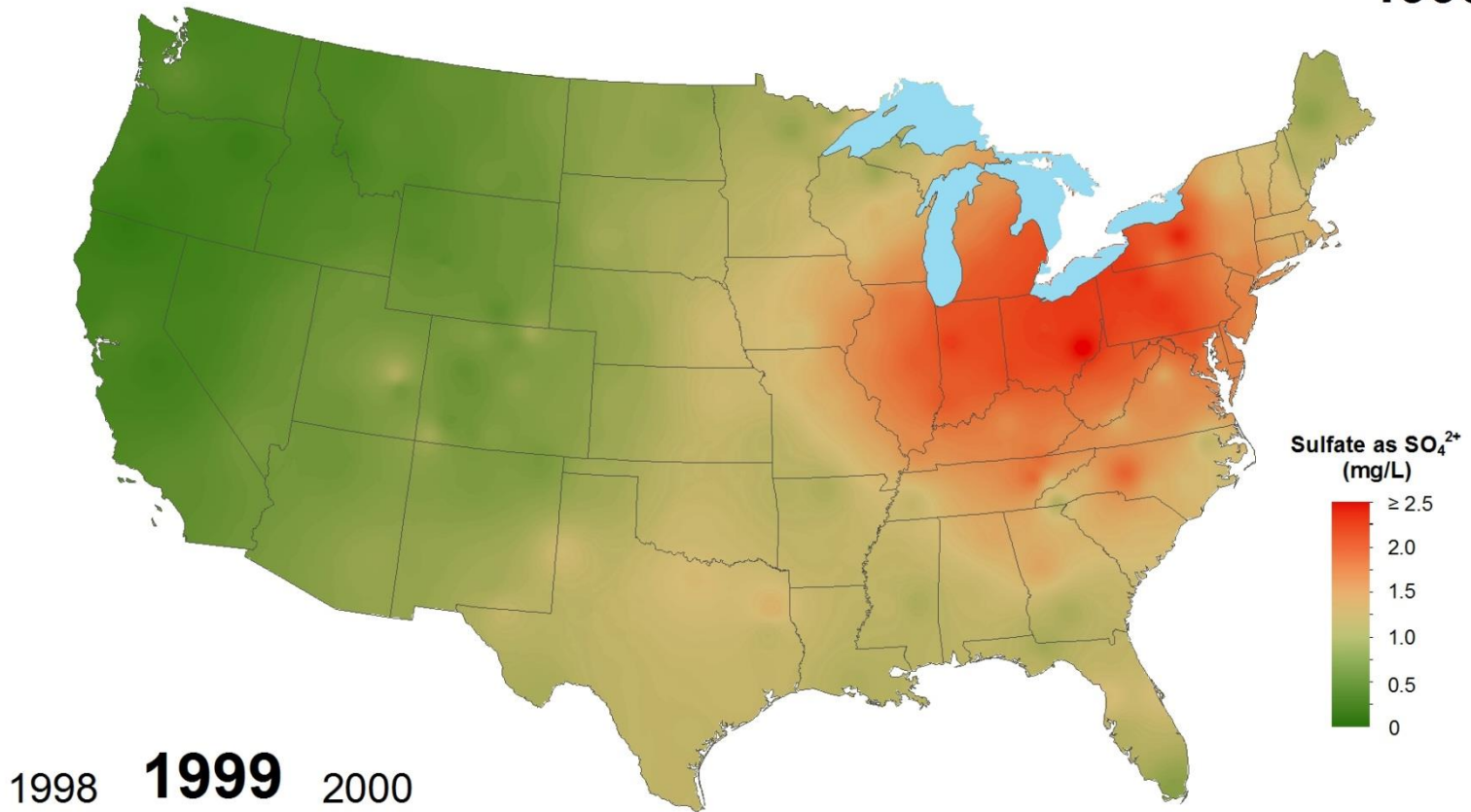


National Atmospheric Deposition Program/National Trends Network  
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# Sulfate ion concentration 1998

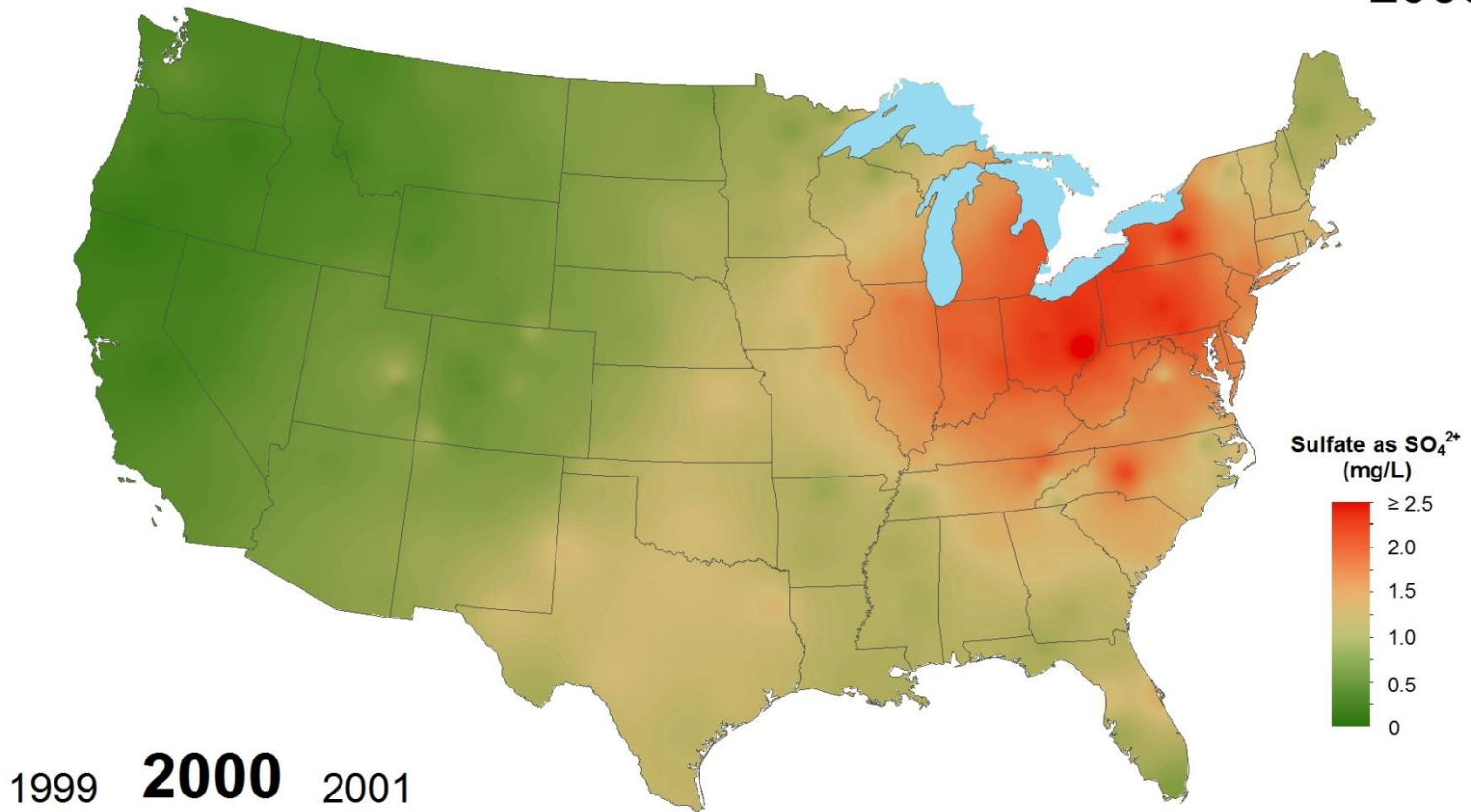


# Sulfate ion concentration 1999

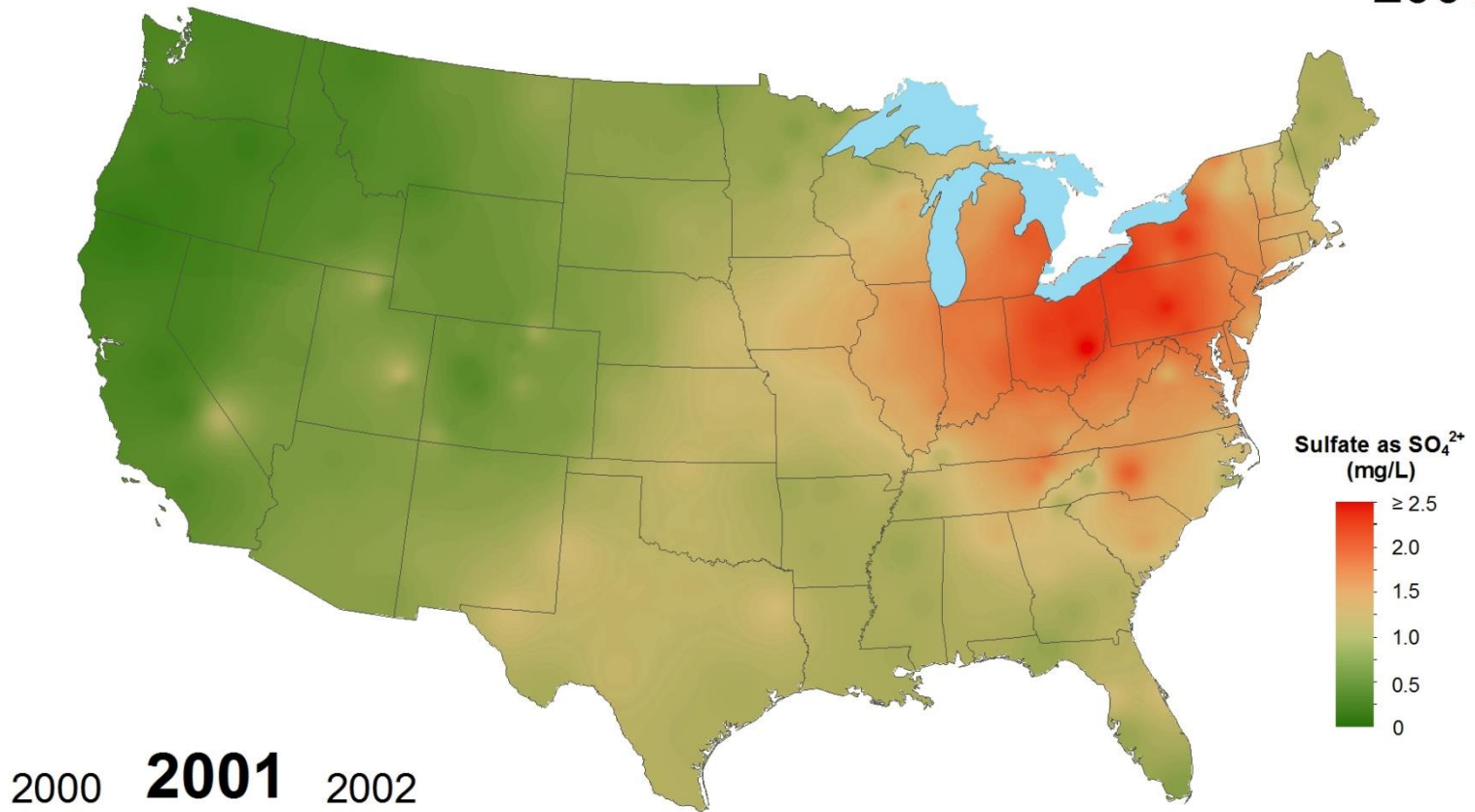


National Atmospheric Deposition Program/National Trends Network  
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# Sulfate ion concentration 2000

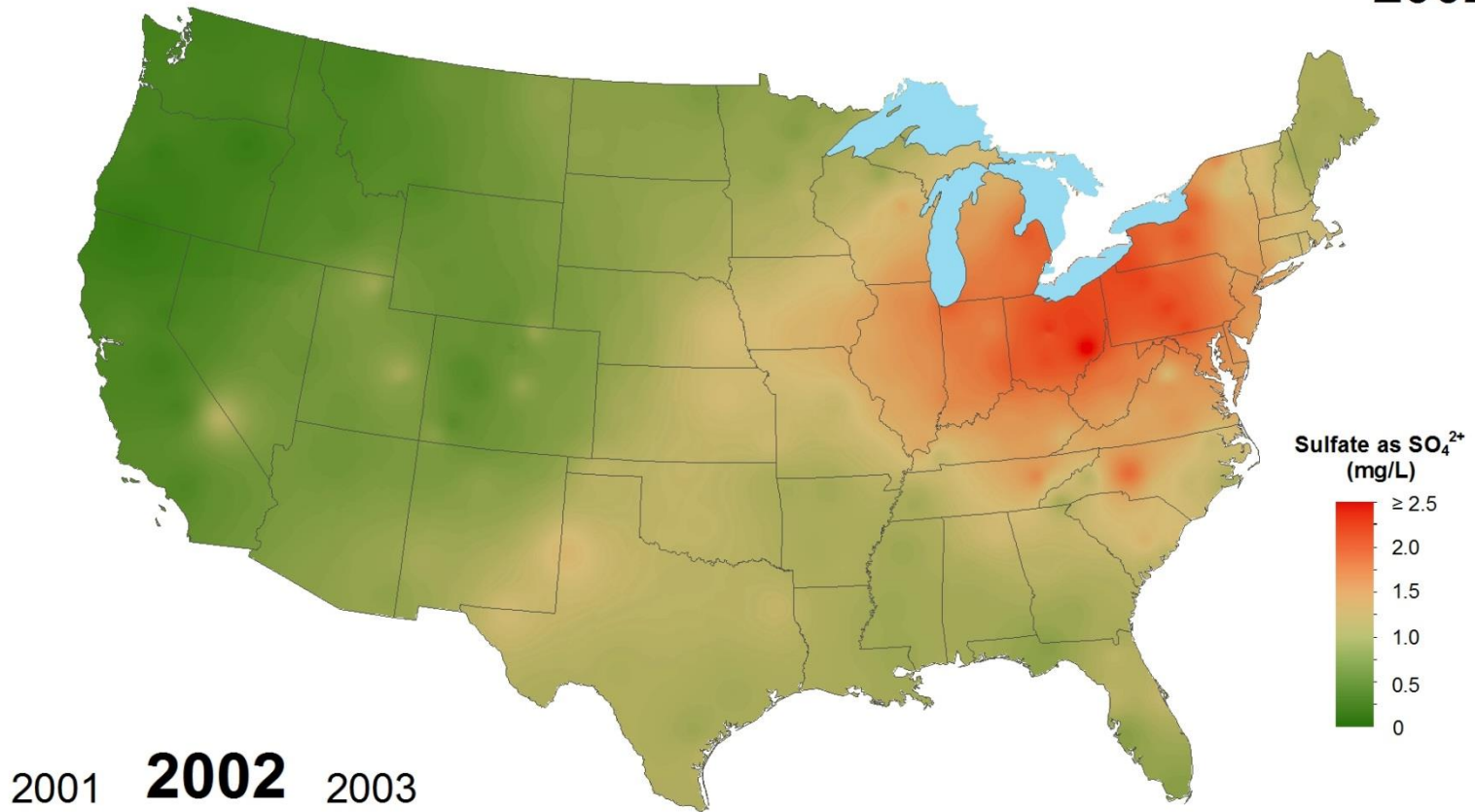


# Sulfate ion concentration 2001

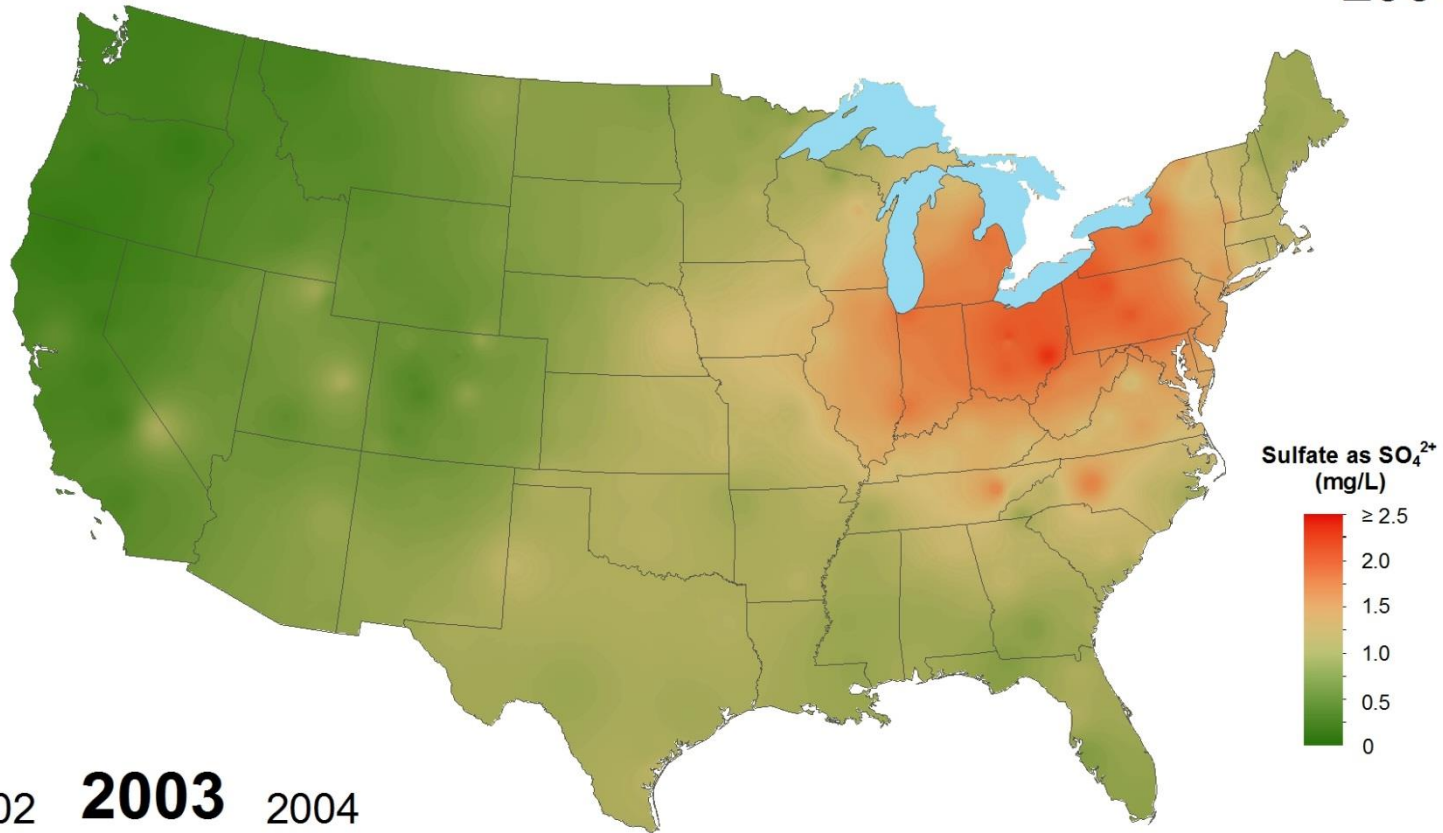




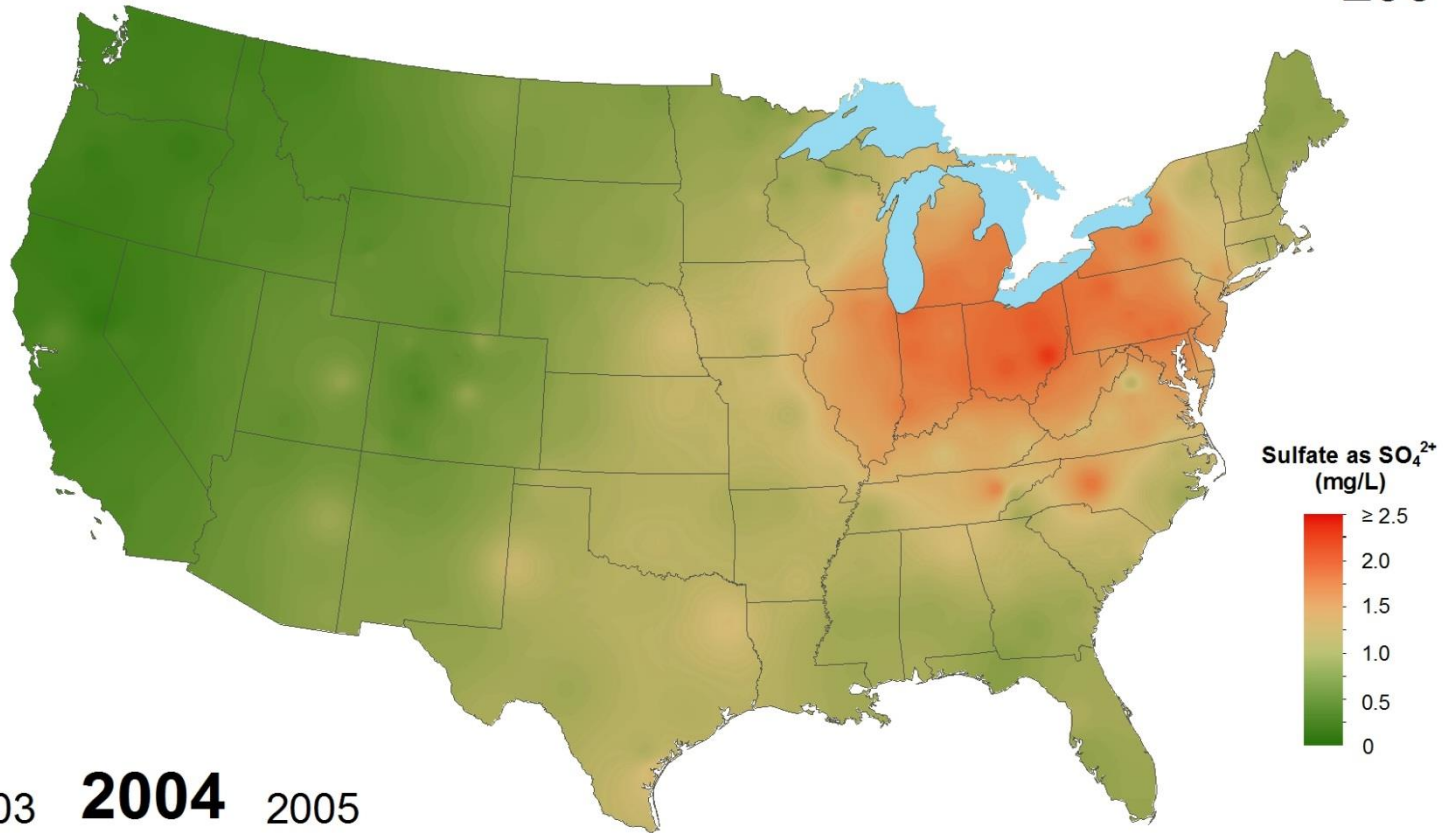
# Sulfate ion concentration 2002



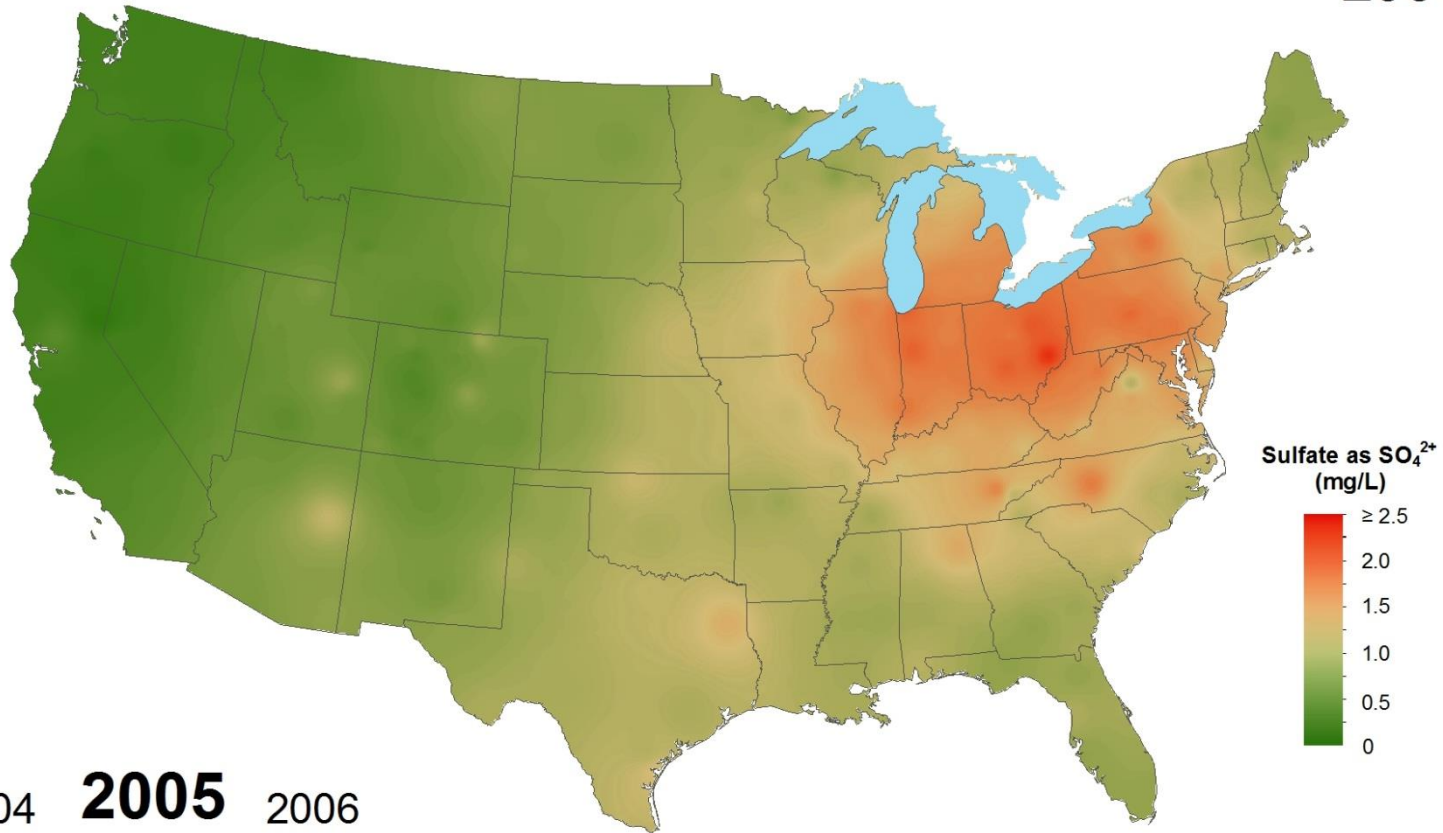
# Sulfate ion concentration 2003



# Sulfate ion concentration 2004

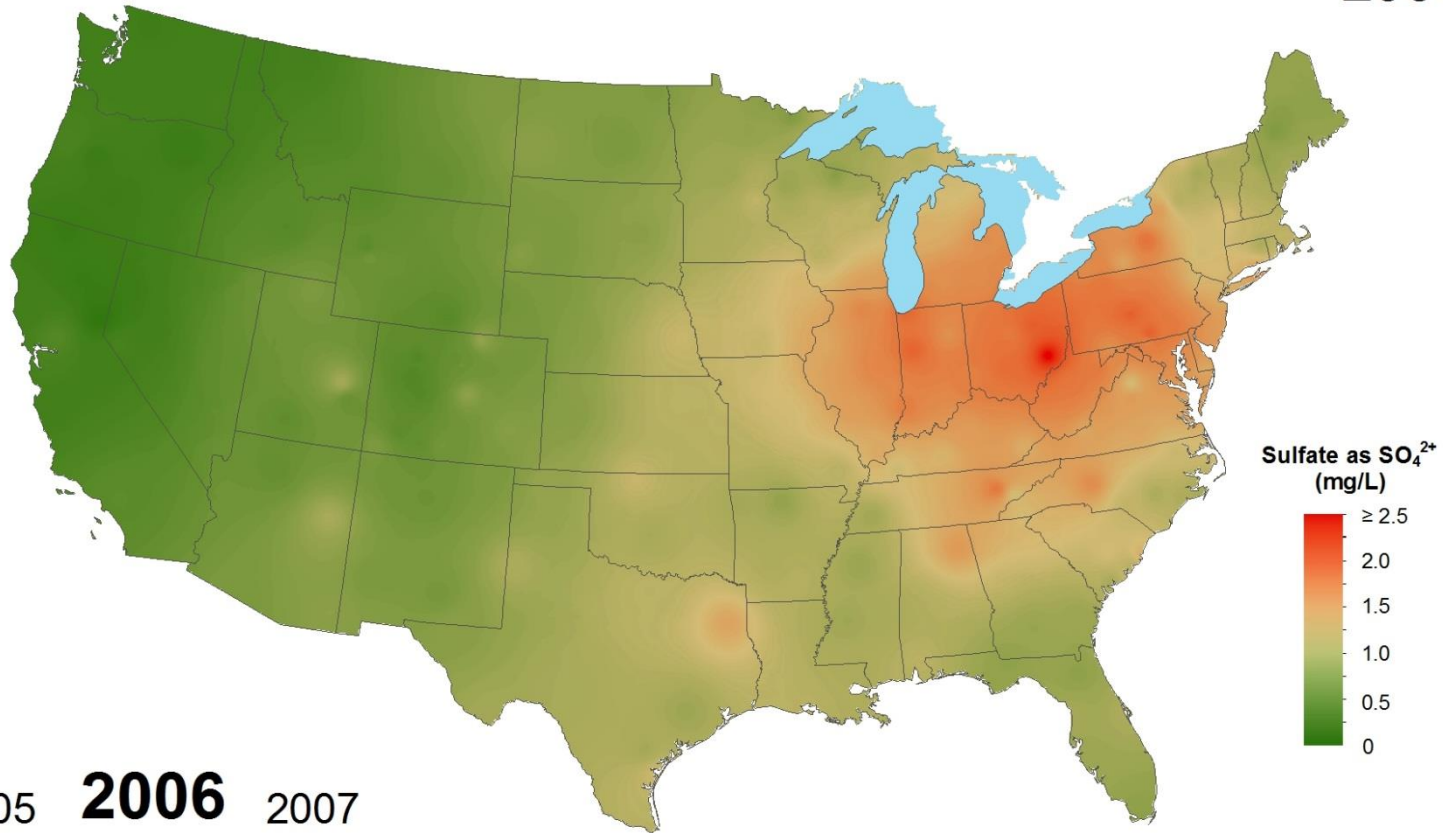


# Sulfate ion concentration 2005

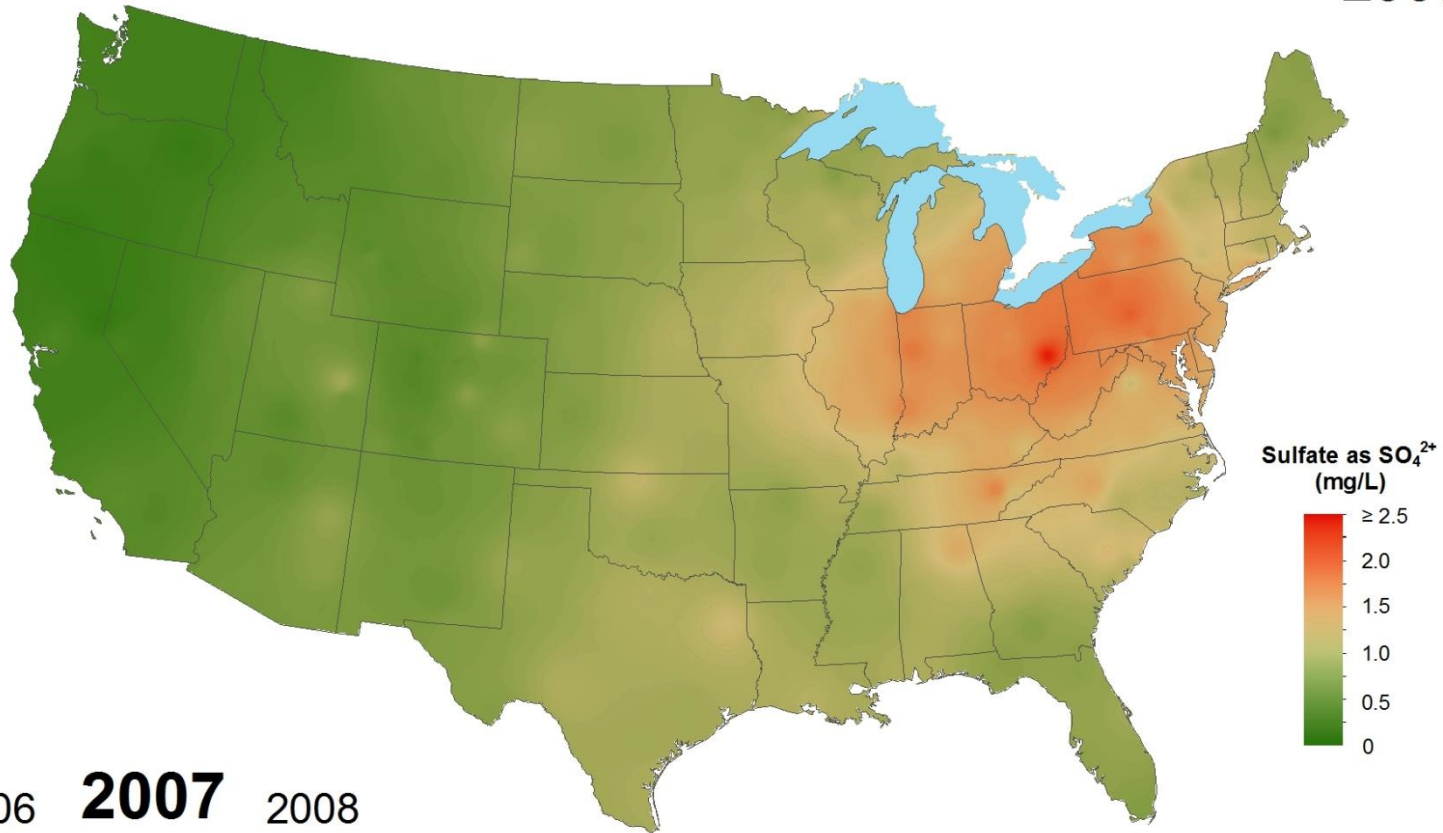


National Atmospheric Deposition Program/National Trends Network  
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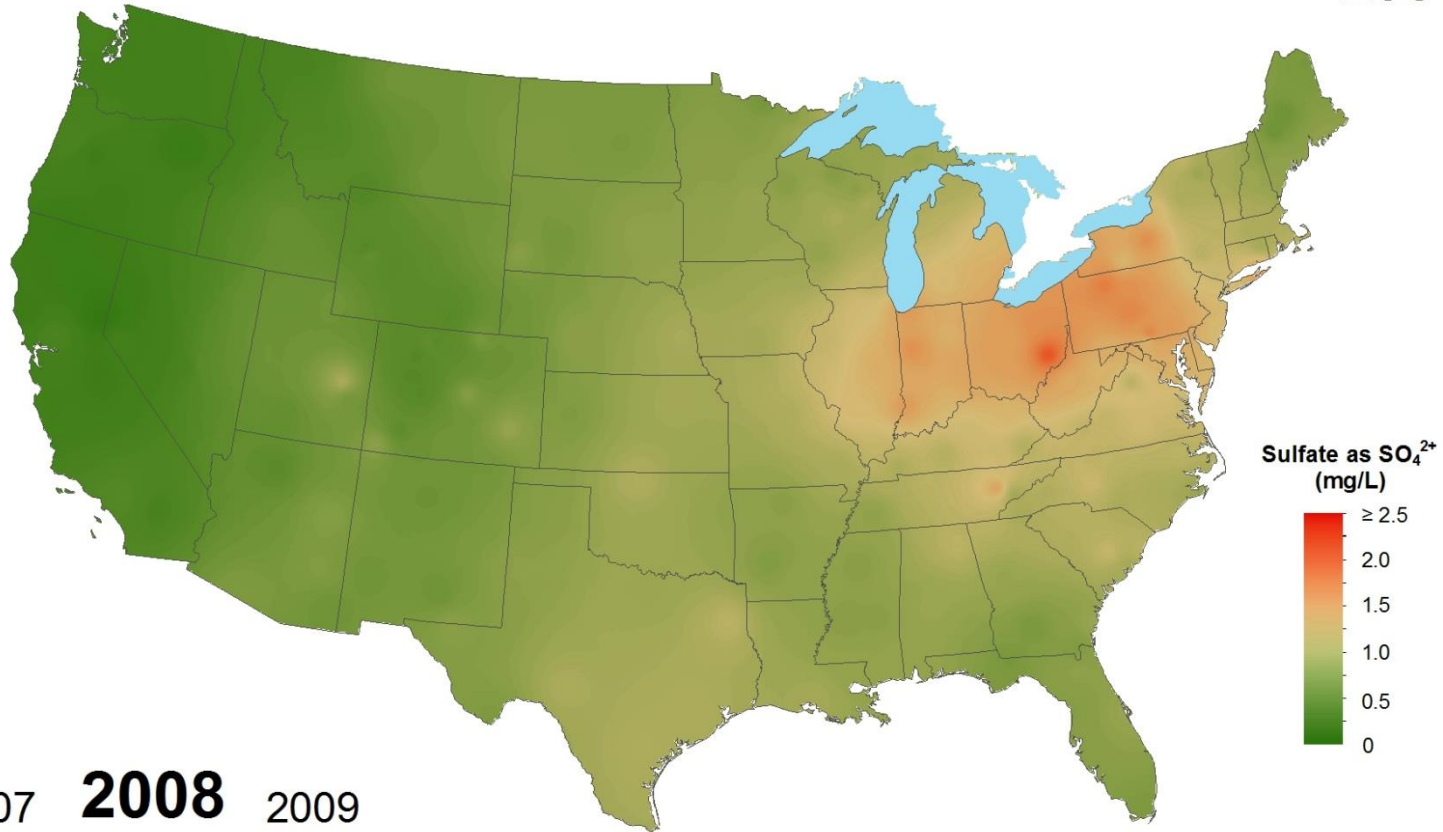
# Sulfate ion concentration 2006



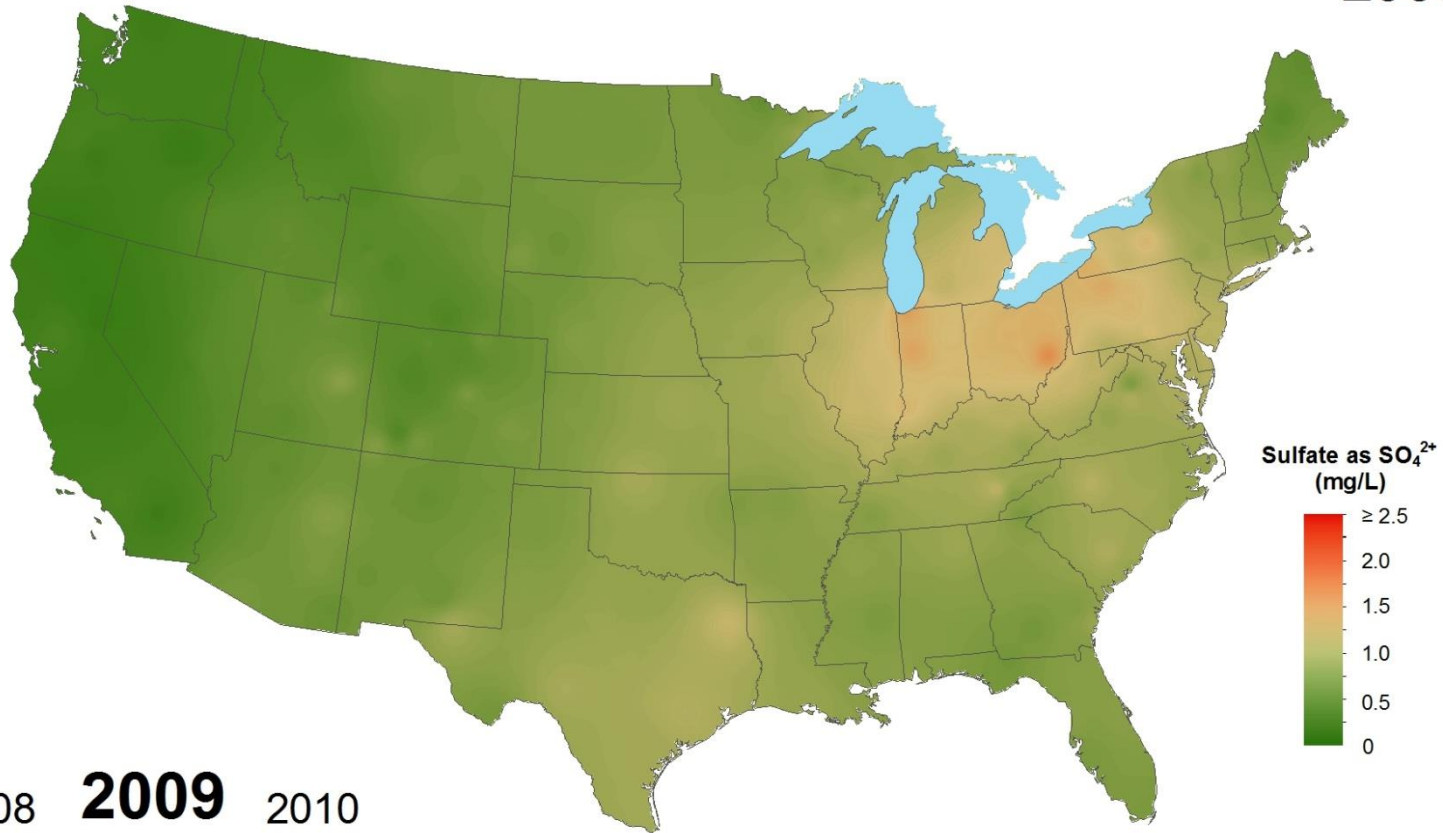
# Sulfate ion concentration 2007



# Sulfate ion concentration 2008



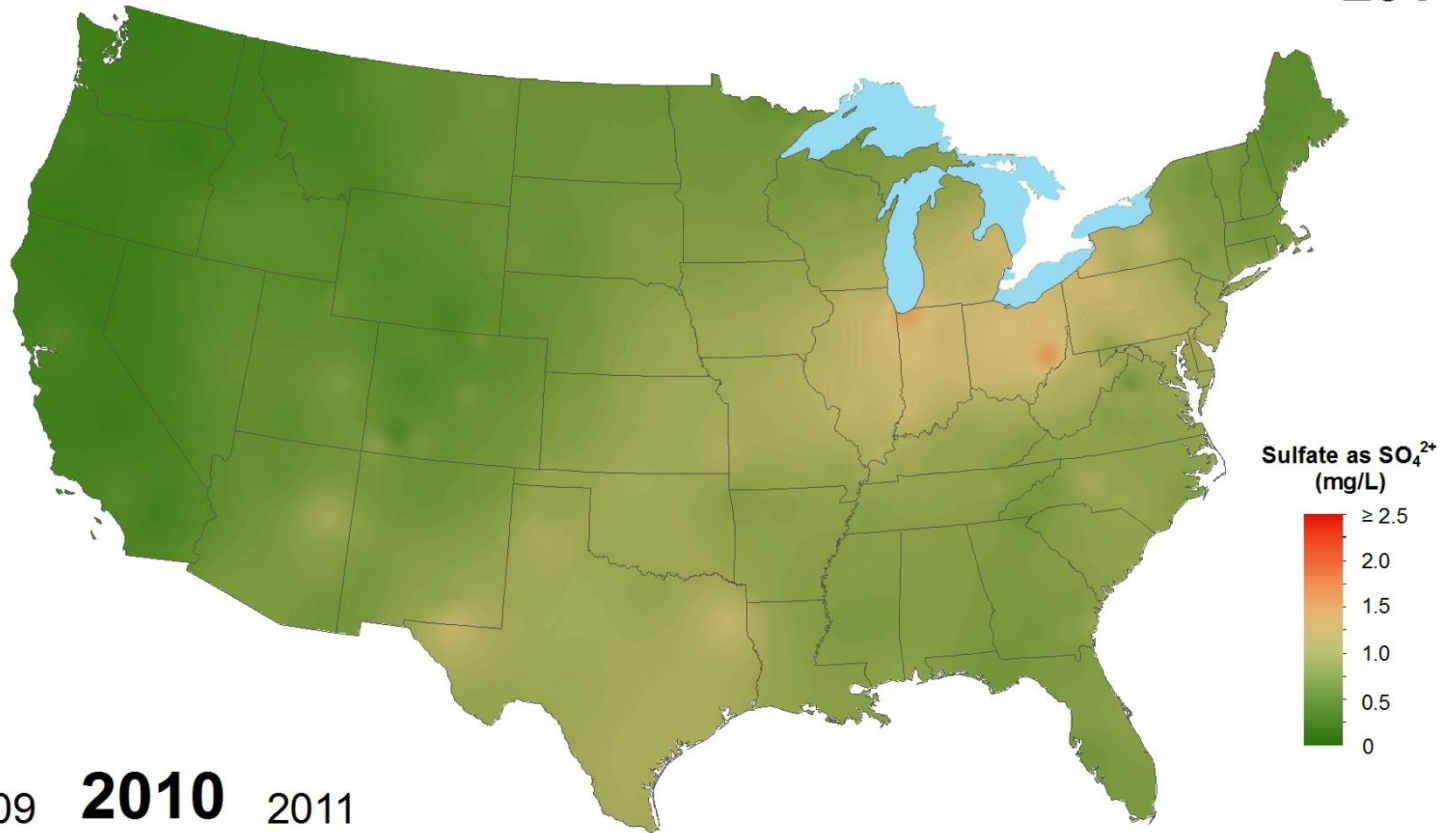
# Sulfate ion concentration 2009



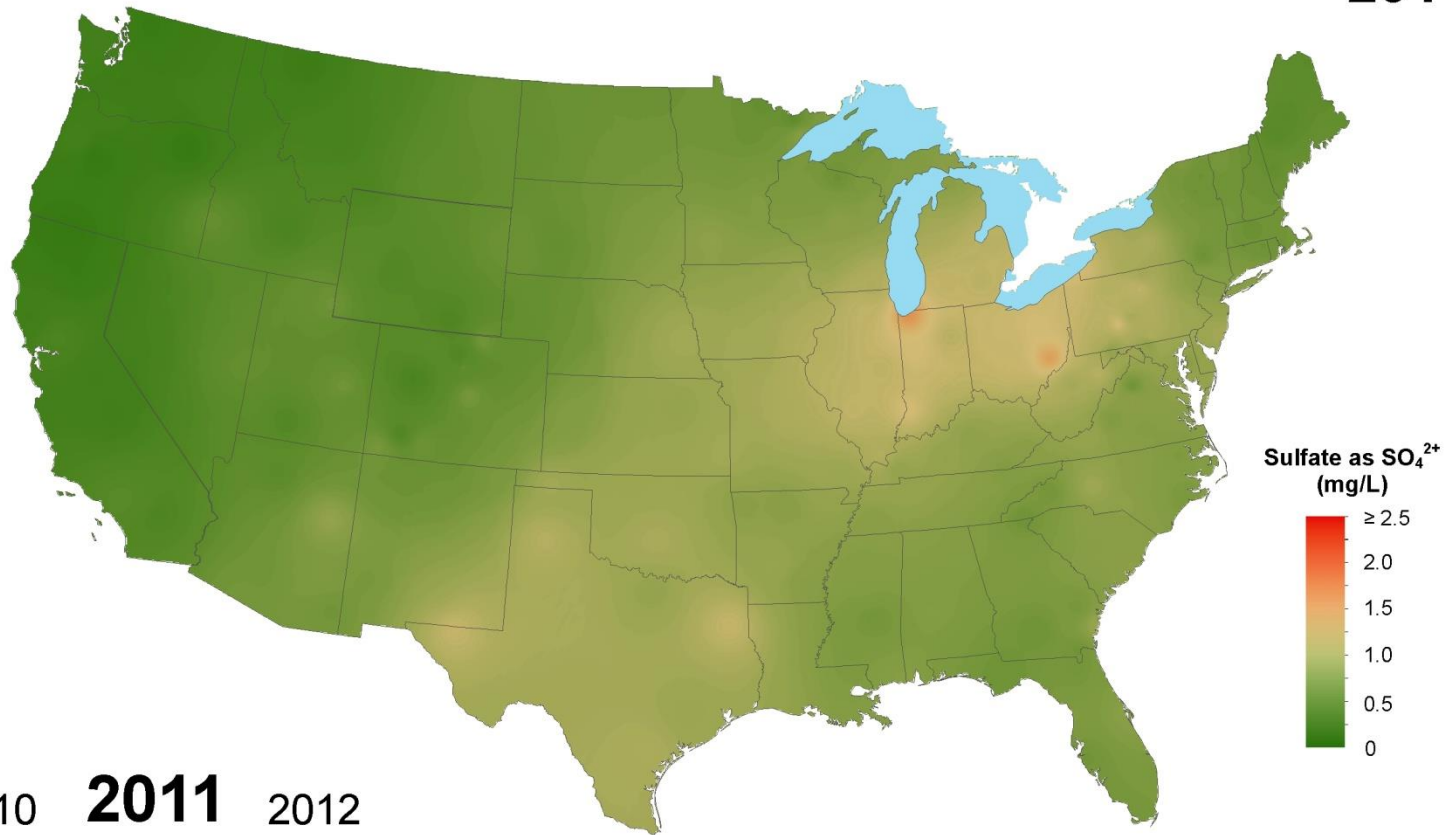
National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>



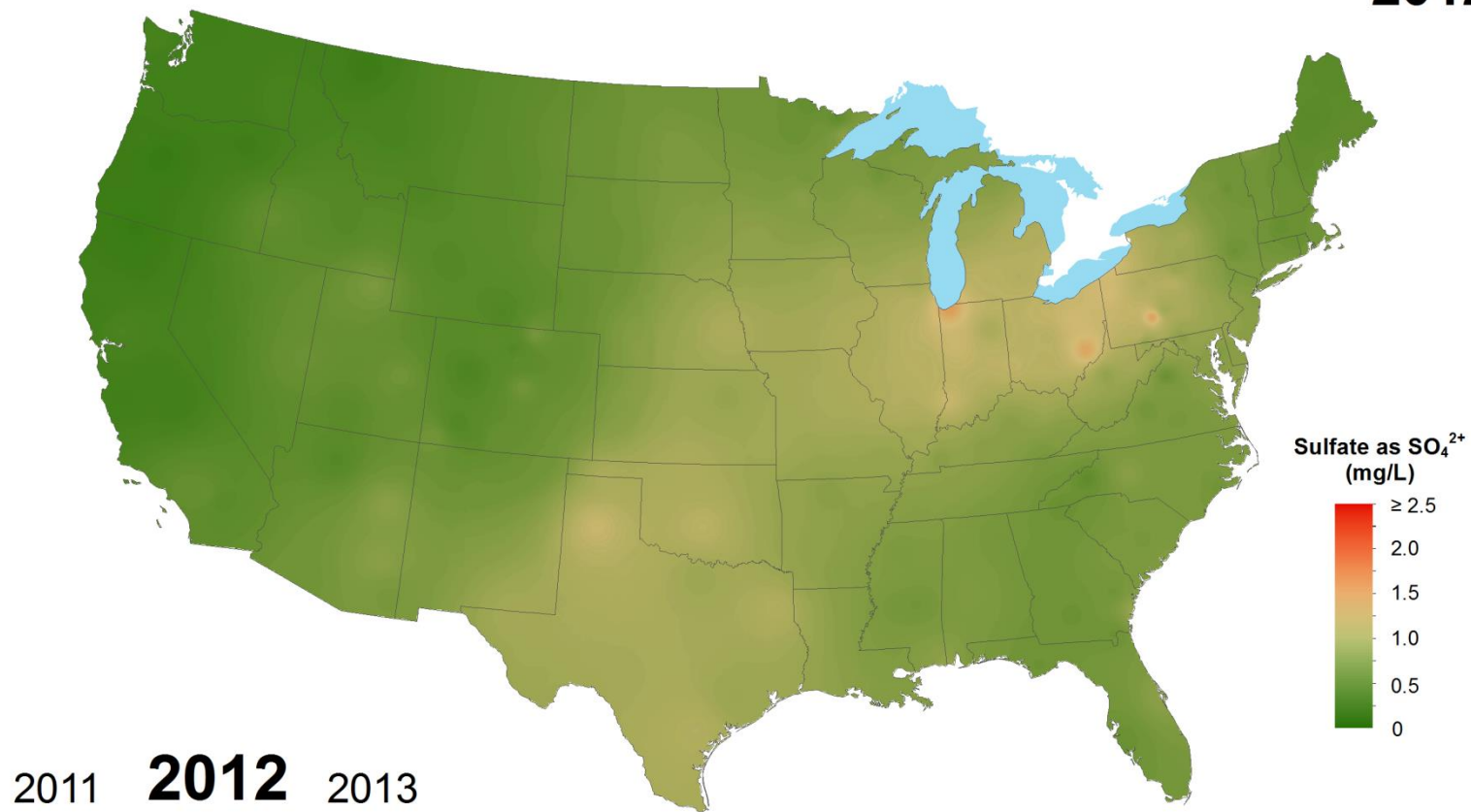
# Sulfate ion concentration 2010



# Sulfate ion concentration 2011



# Sulfate ion concentration 2012

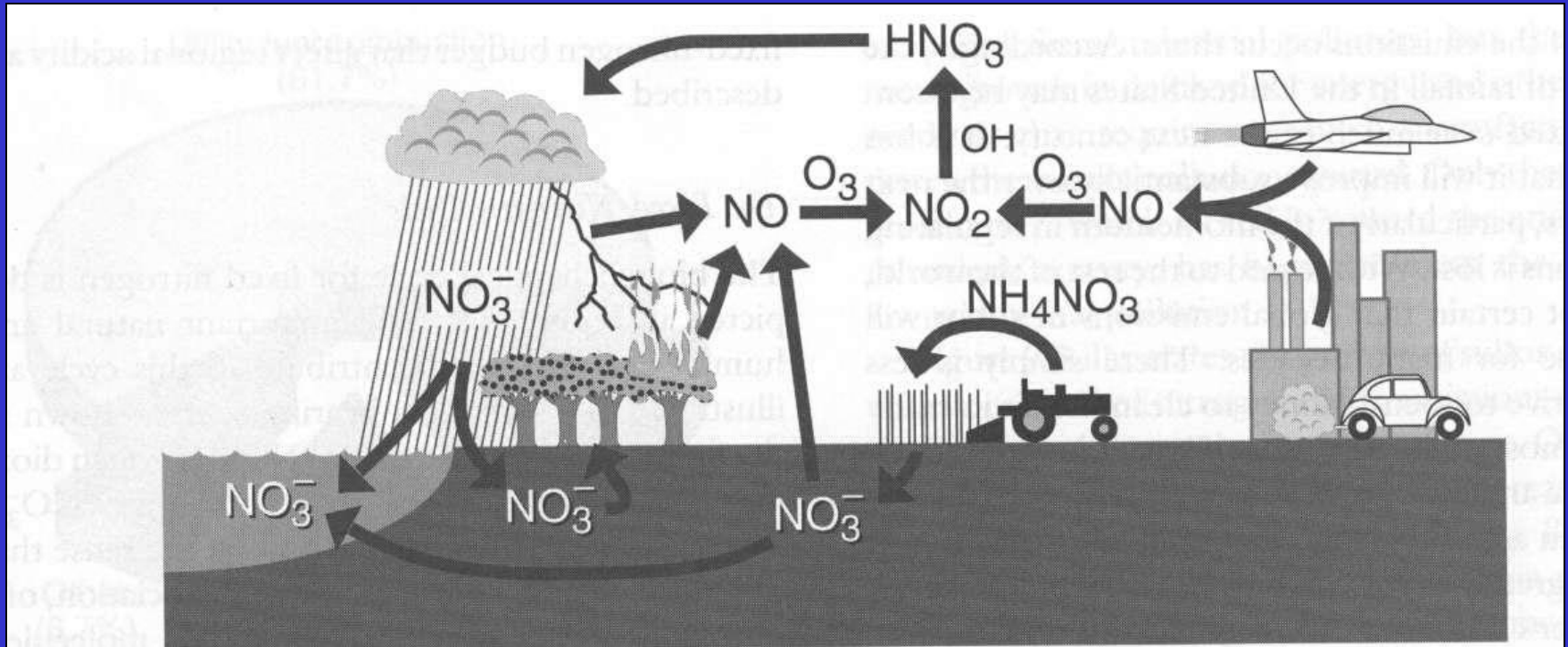


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# The Nitrogen Cycle

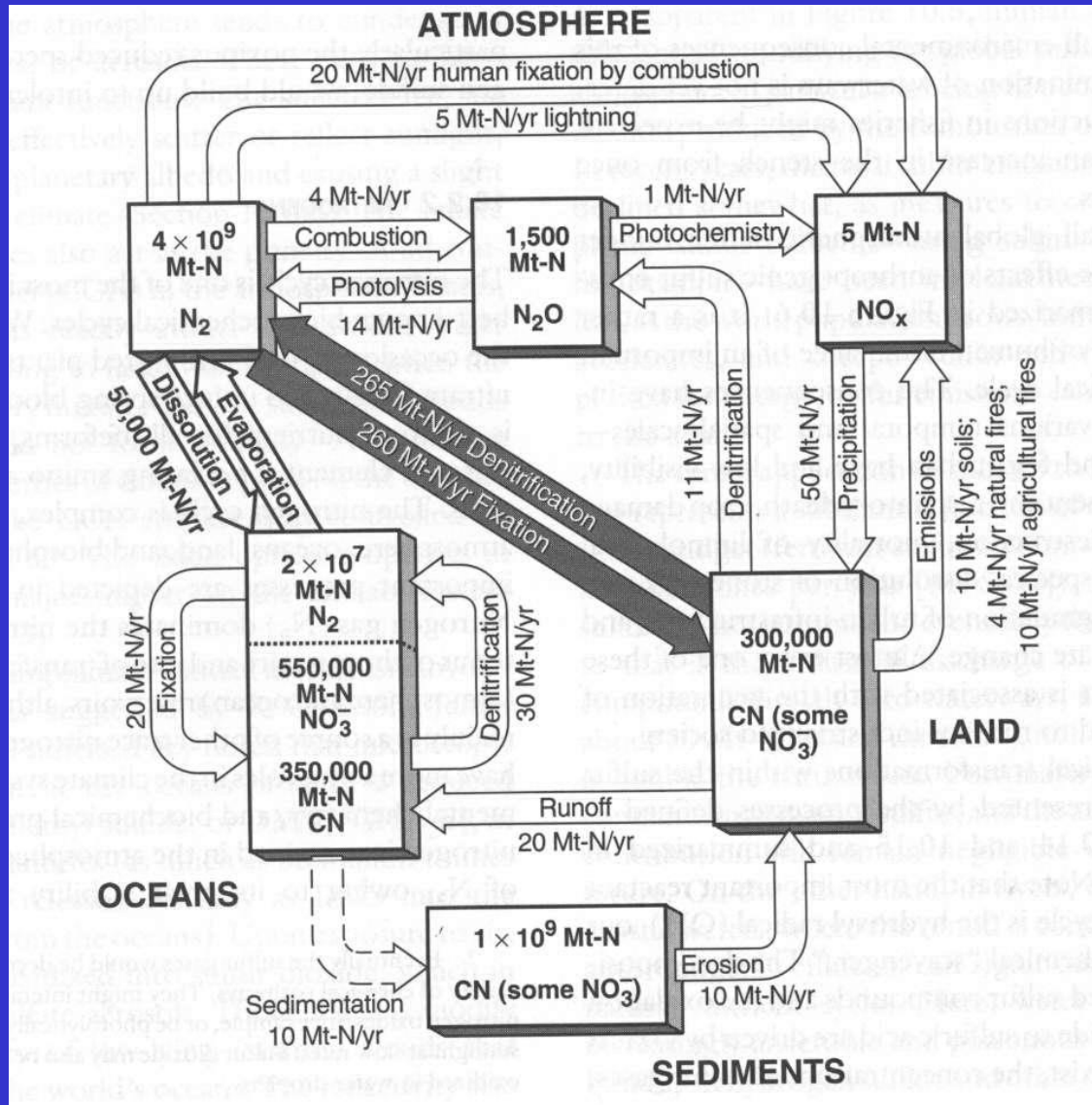
## Major emitted compounds

- Nitrous oxide ( $N_2O$ ): denitrifying bacteria in soils; *industry*
- Nitric oxide (NO): soils, biomass burning; *combustion*
- Ammonia ( $NH_3$ ): decay processes; *fertilizers, animal wastes*

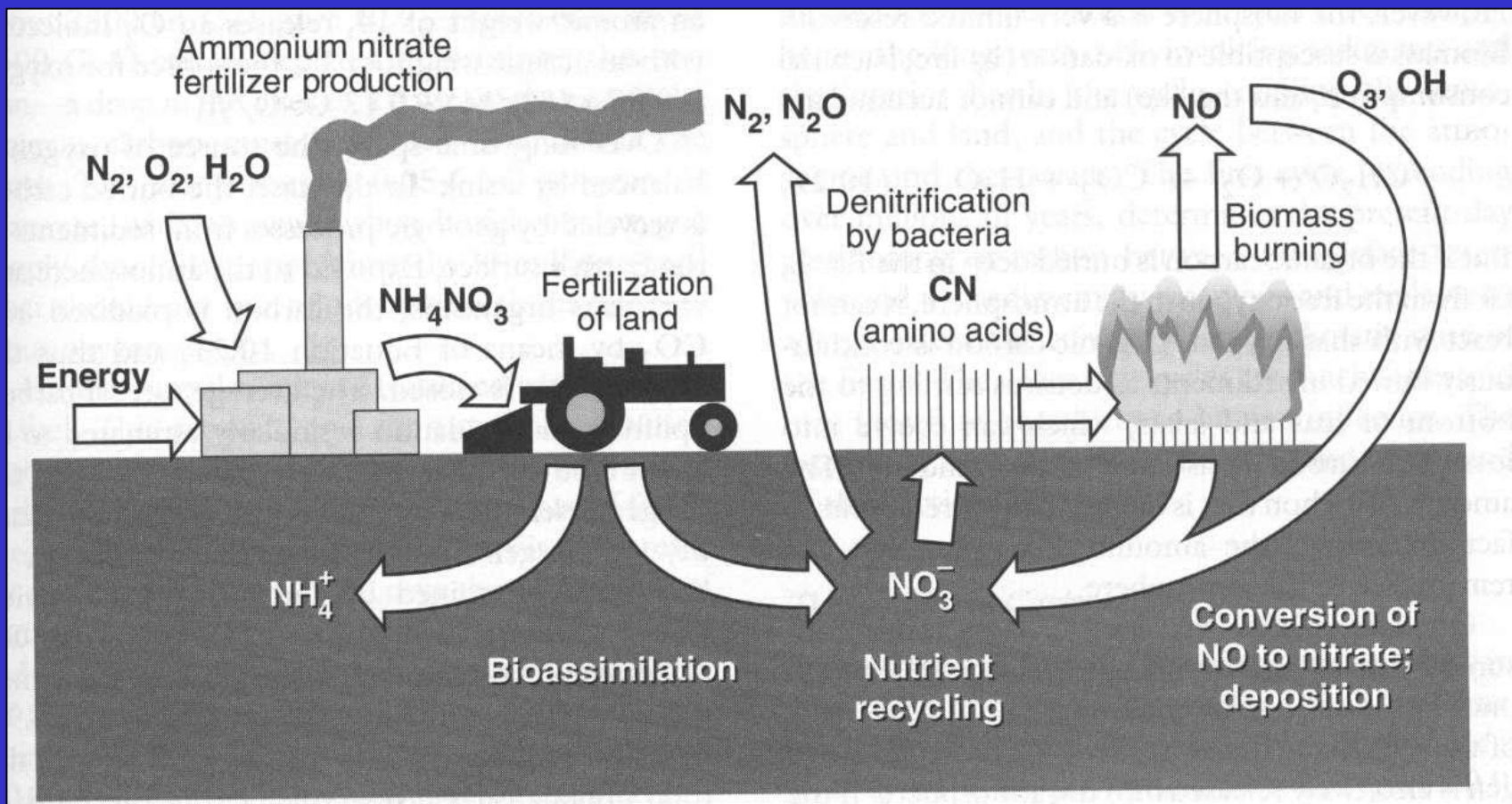


Natural:  $\sim 20 \text{ Mt N yr}^{-1}$

Anthropogenic:  $\sim 30 \text{ Mt N yr}^{-1}$

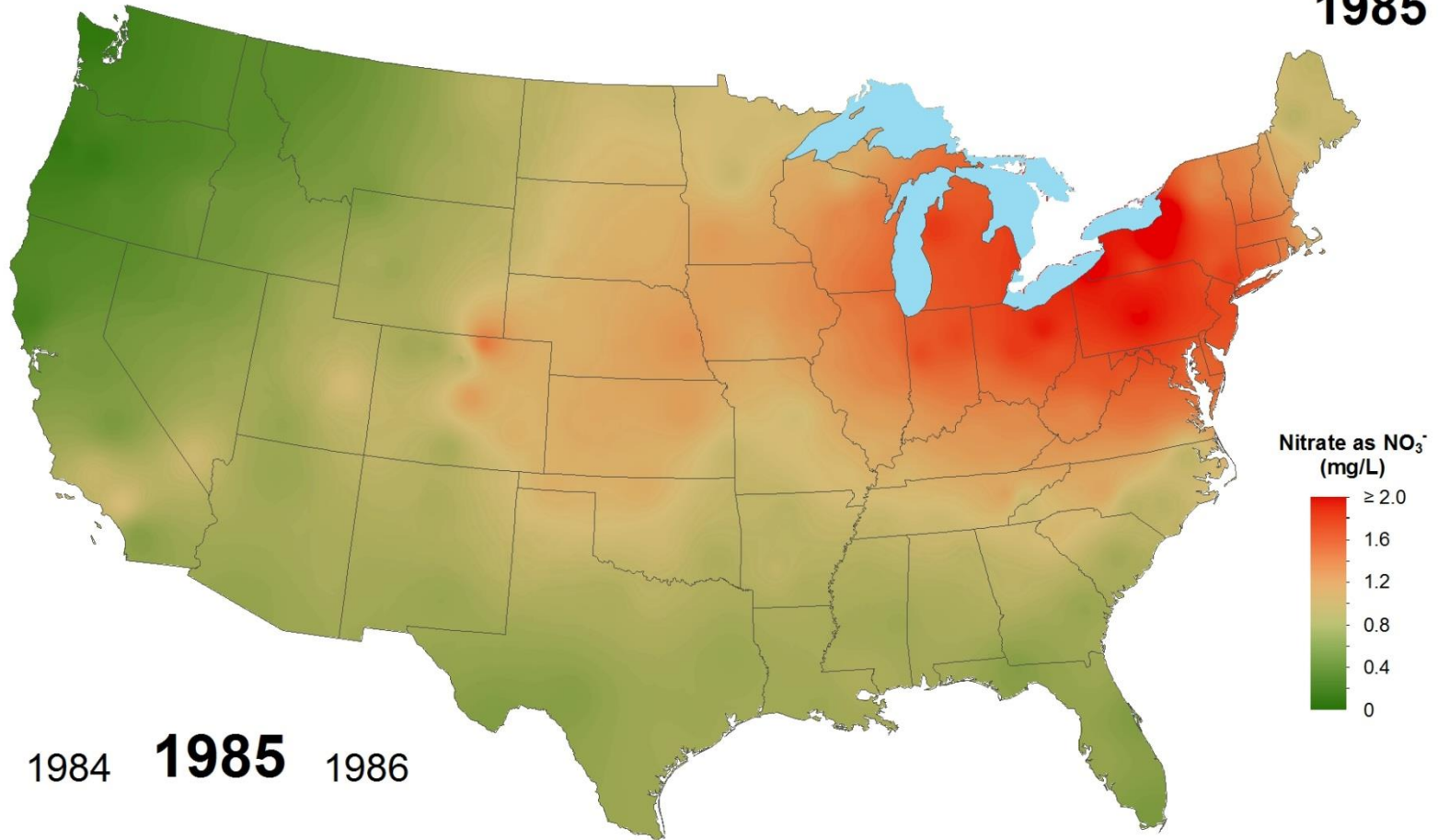


# Anthropogenic components (fertilizer-related)



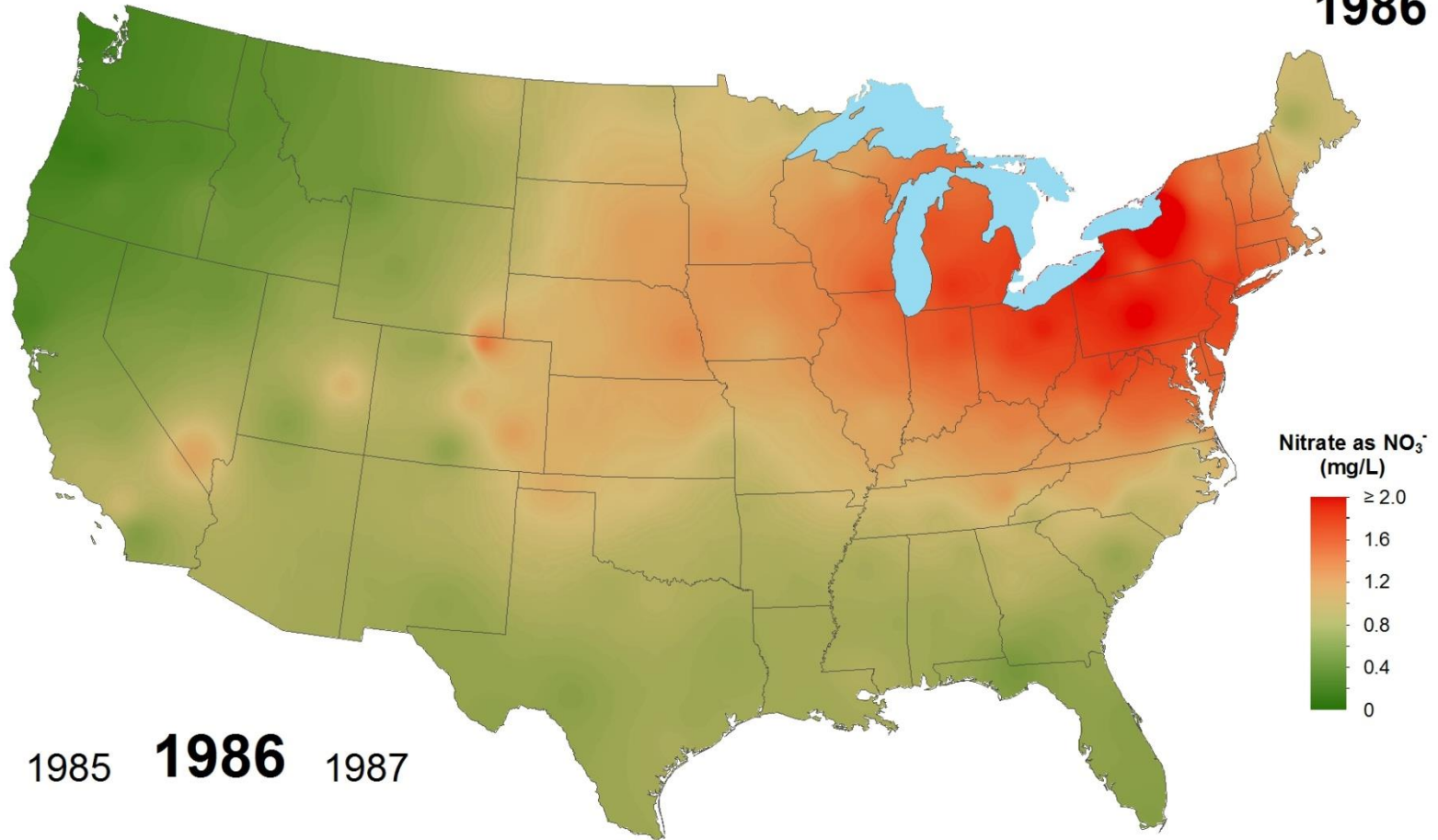
Natural:  $\sim 20 \text{ Mt N yr}^{-1}$   
 Anthropogenic:  $\sim 30 \text{ Mt N yr}^{-1}$

# Nitrate ion concentration 1985



National Atmospheric Deposition Program/National Trends Network  
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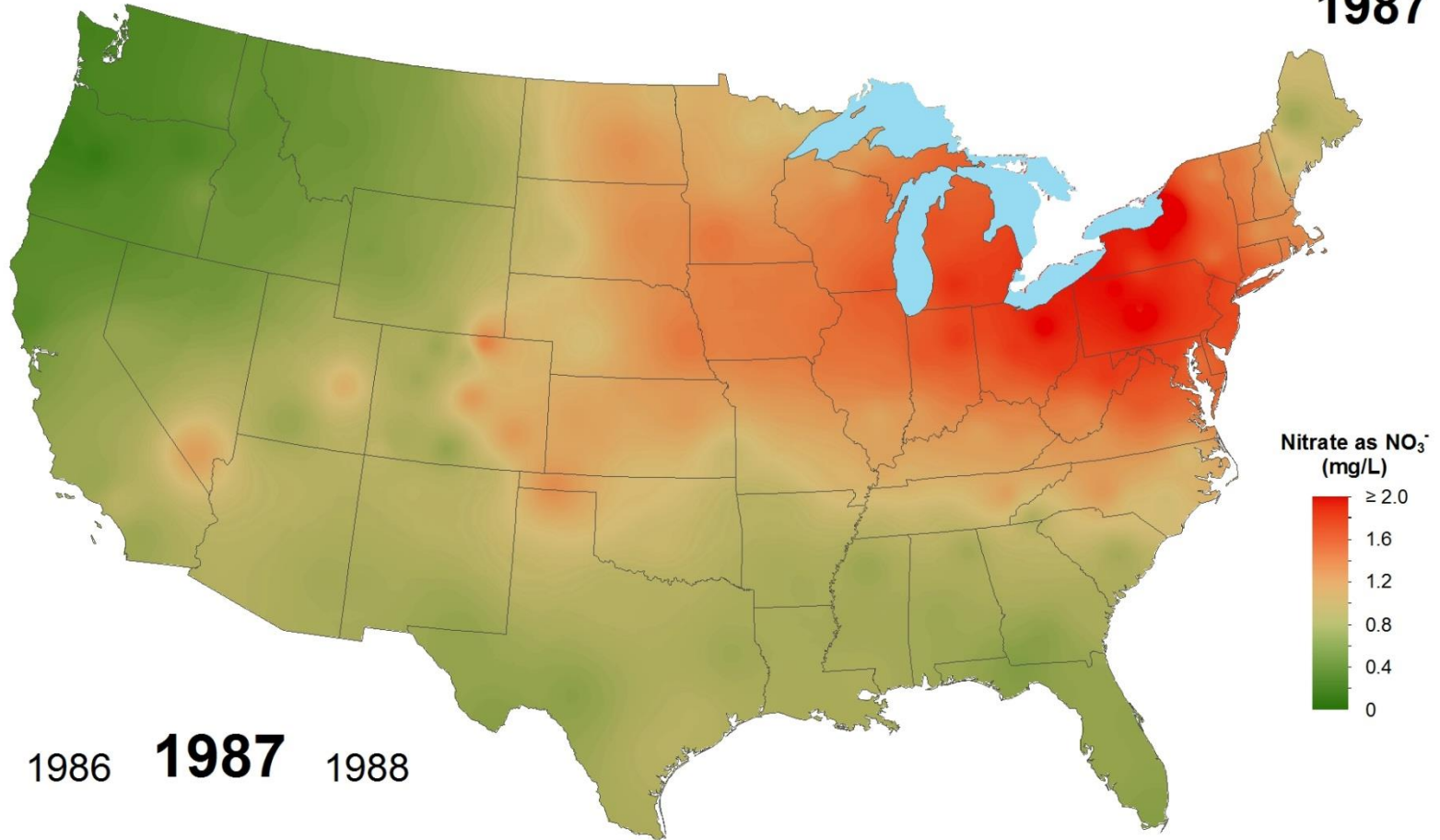
# Nitrate ion concentration 1986



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<http://nadp.isws.illinois.edu>

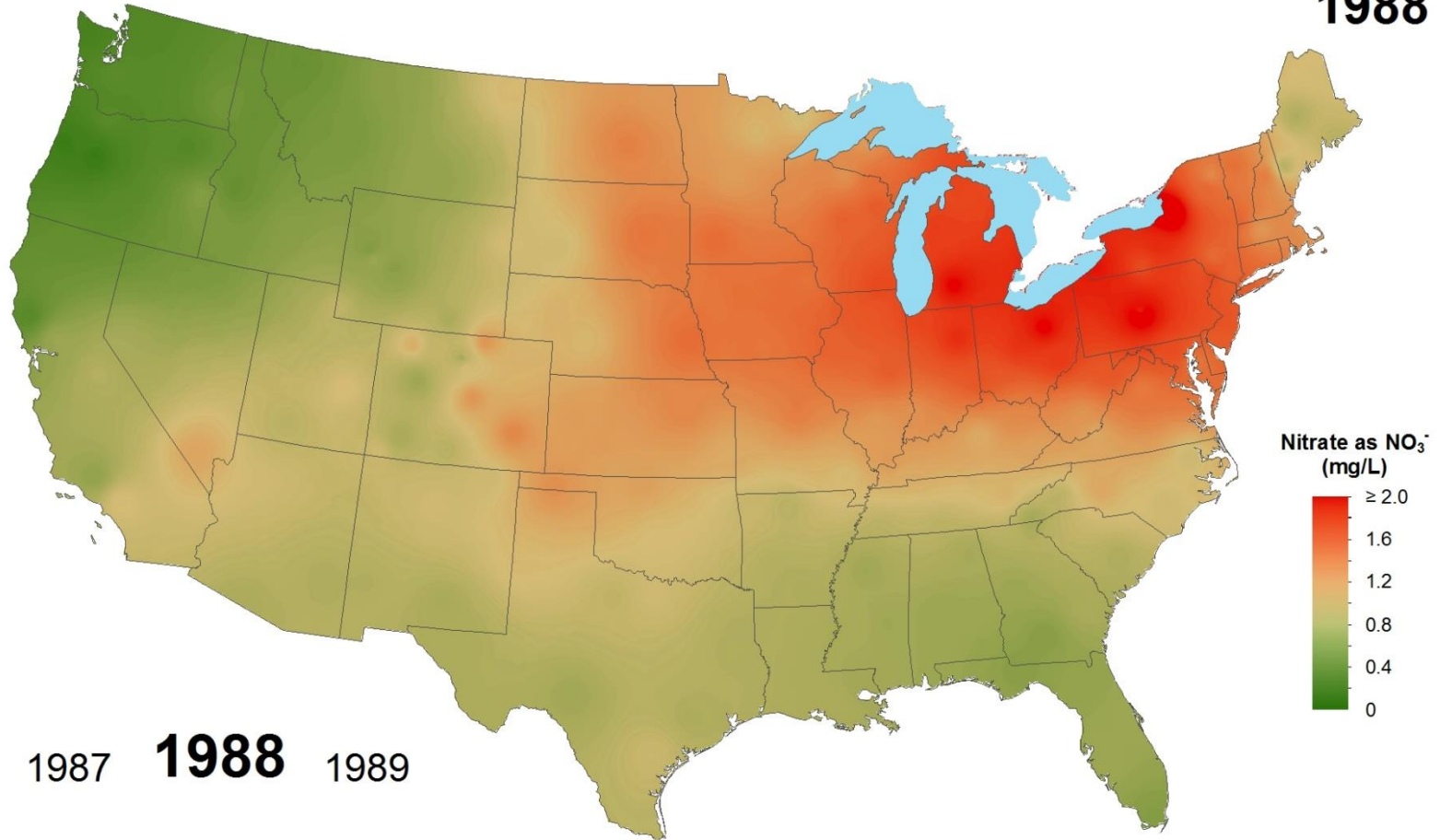


# Nitrate ion concentration 1987



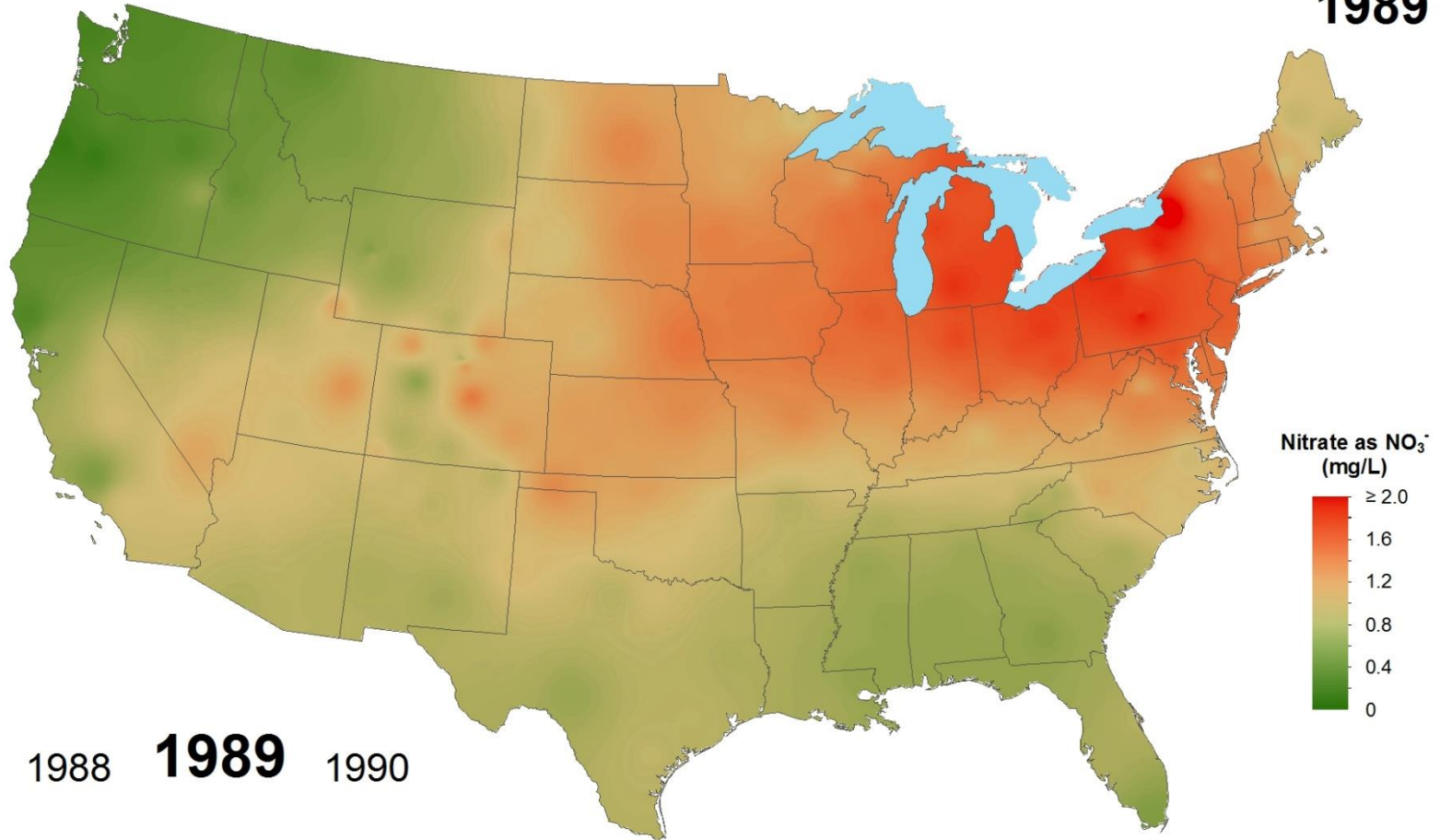
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# Nitrate ion concentration 1988



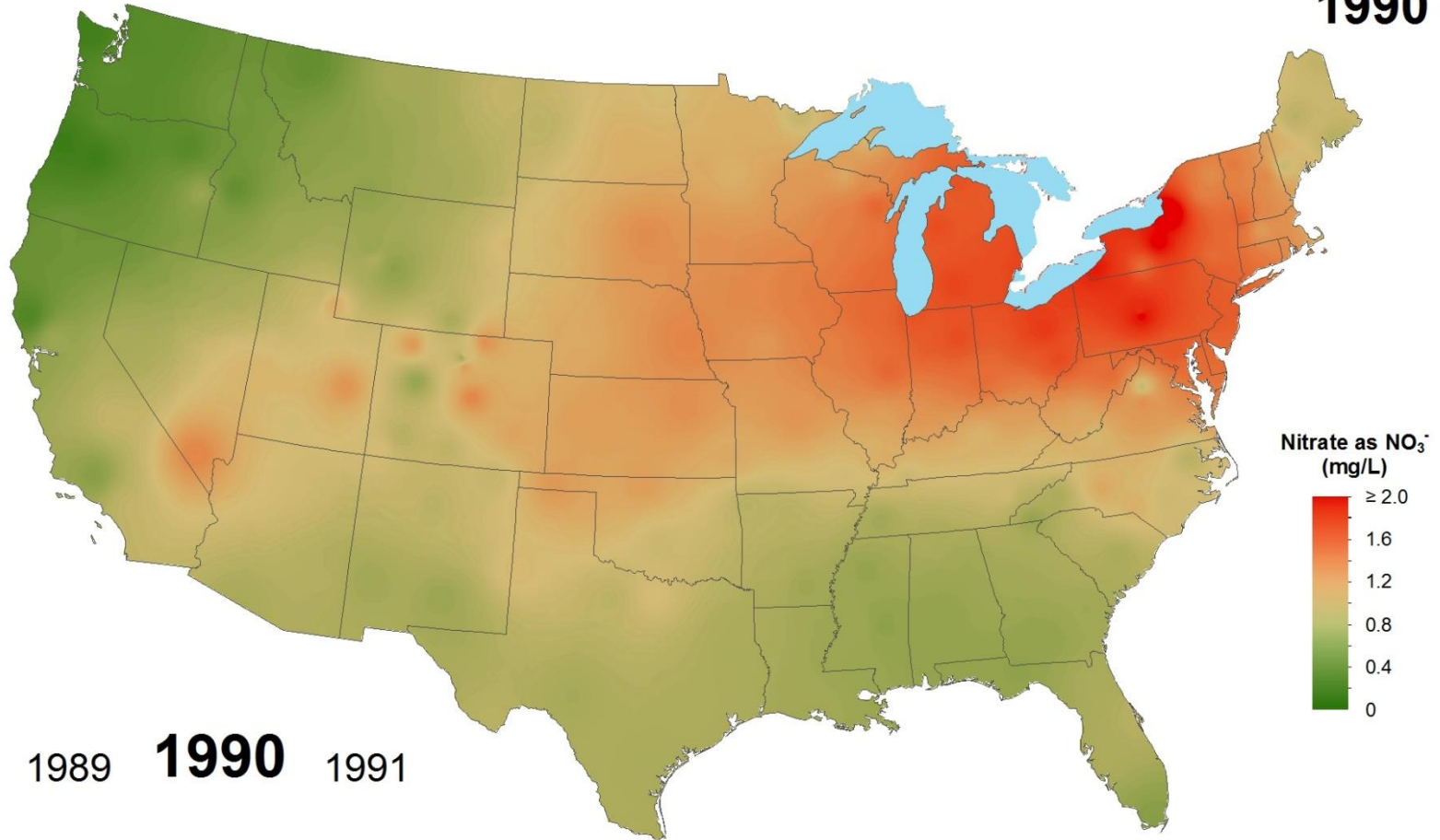
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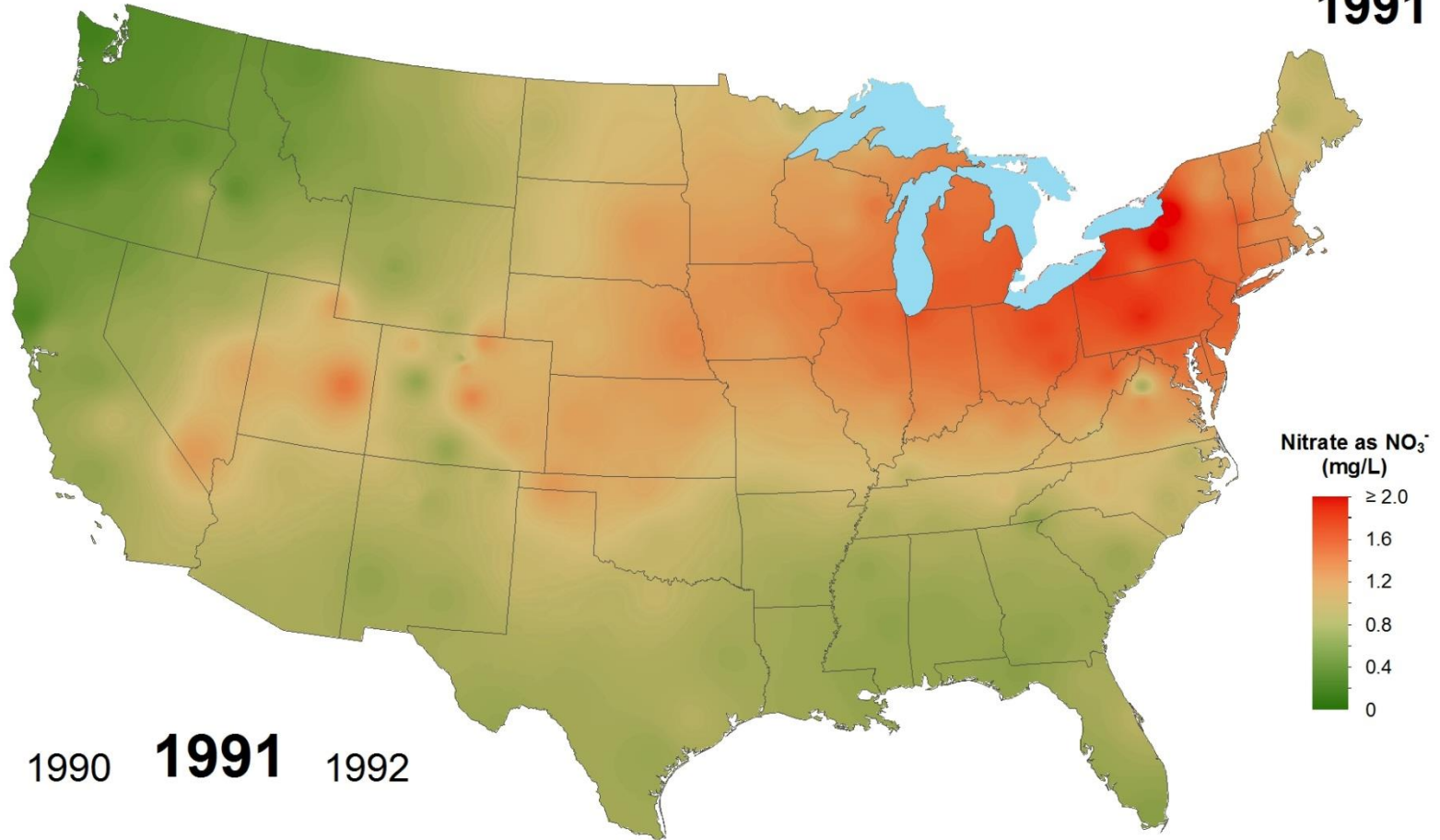
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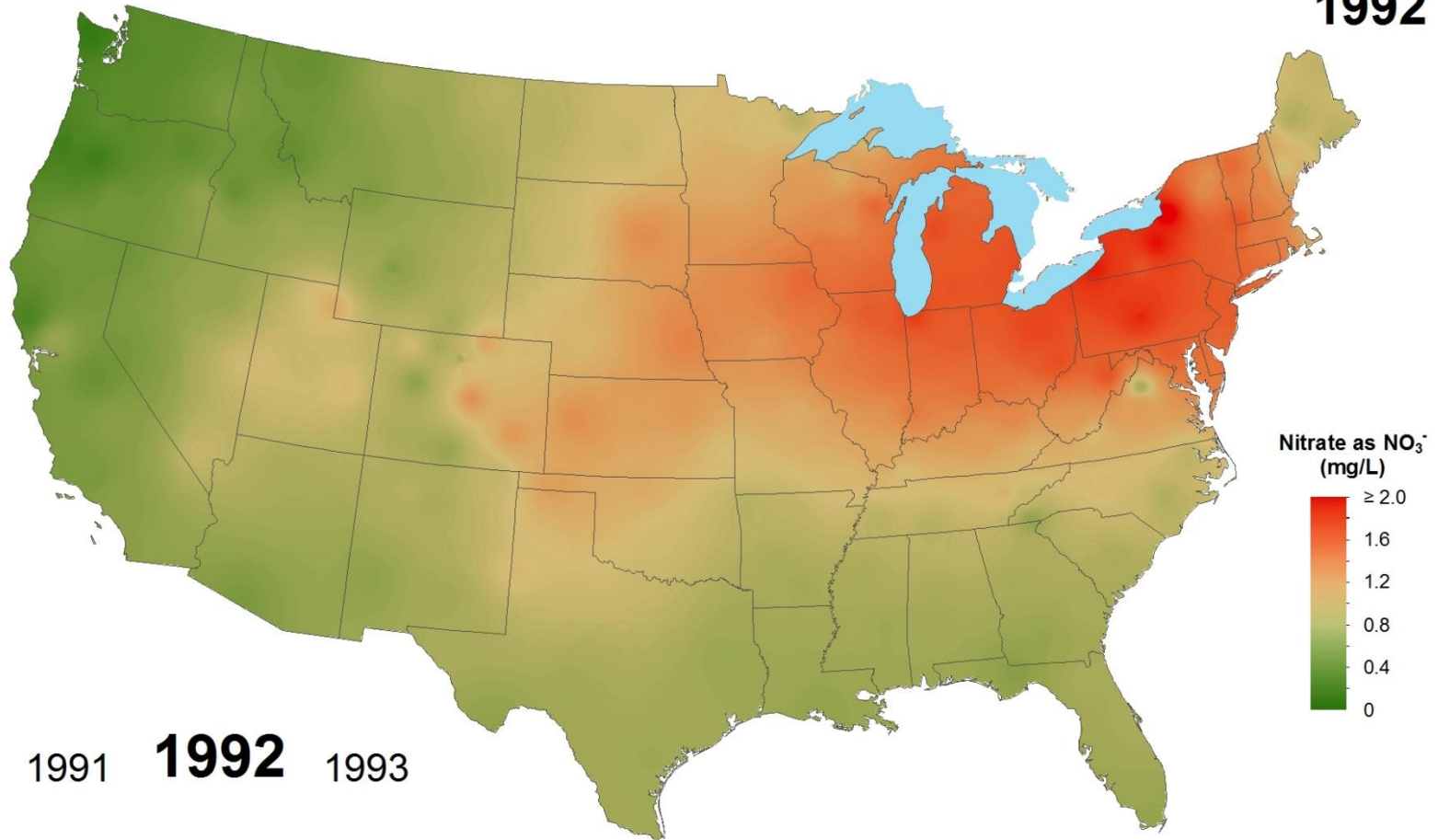
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# Nitrate ion concentration 1991



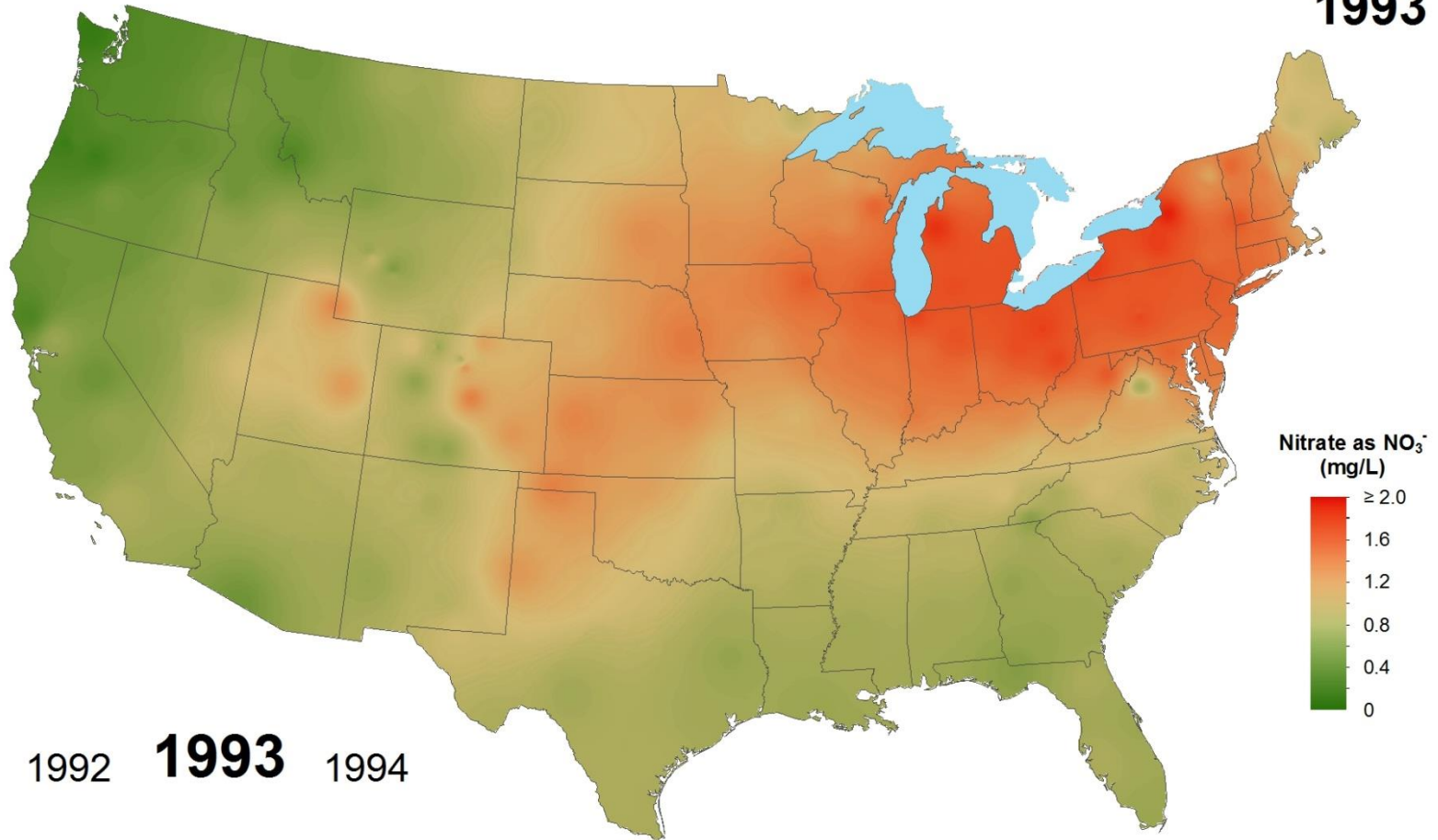
National Atmospheric Deposition Program/National Trends Network  
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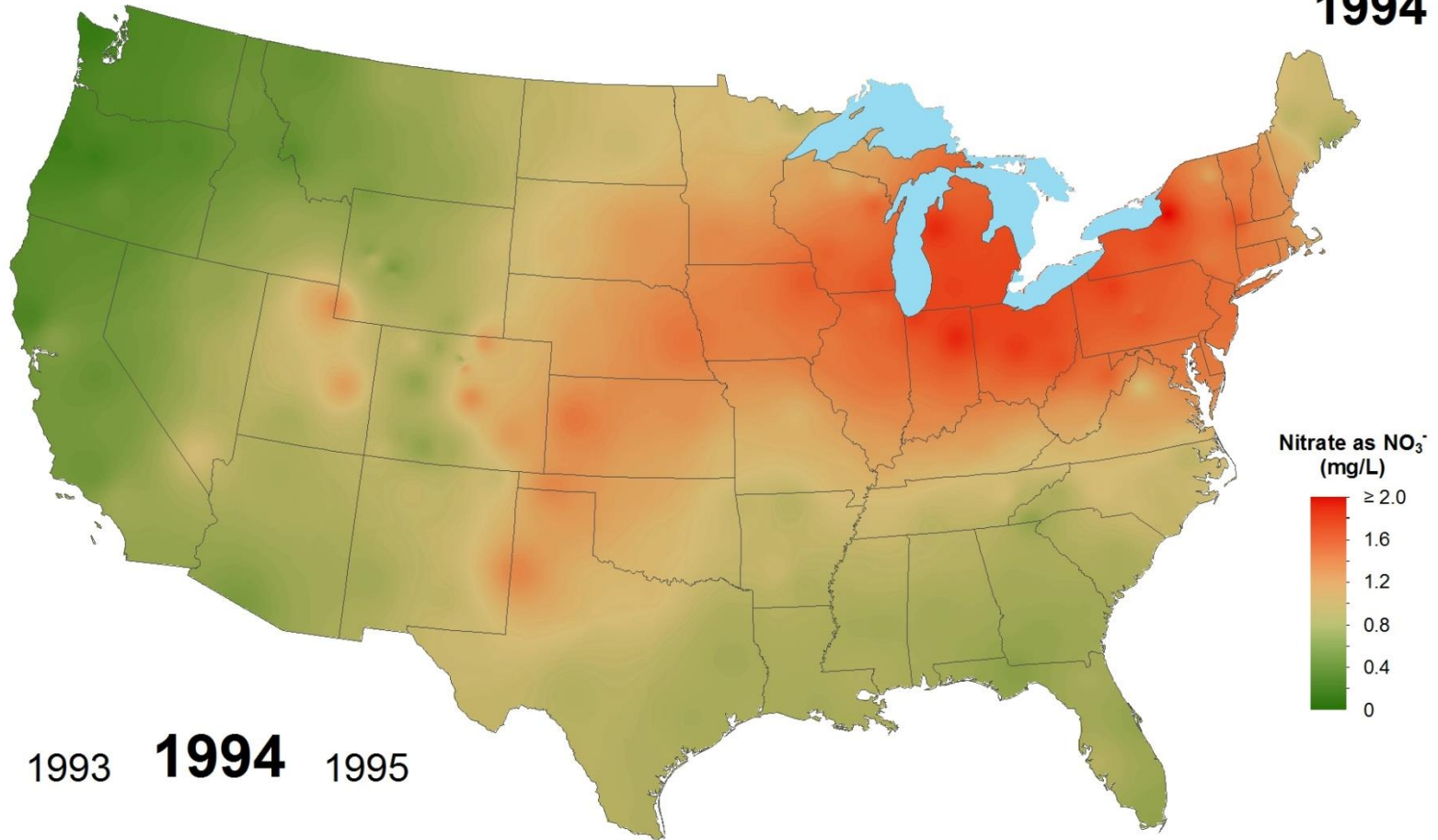
National Atmospheric Deposition Program/National Trends Network  
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# Nitrate ion concentration 1993



National Atmospheric Deposition Program/National Trends Network  
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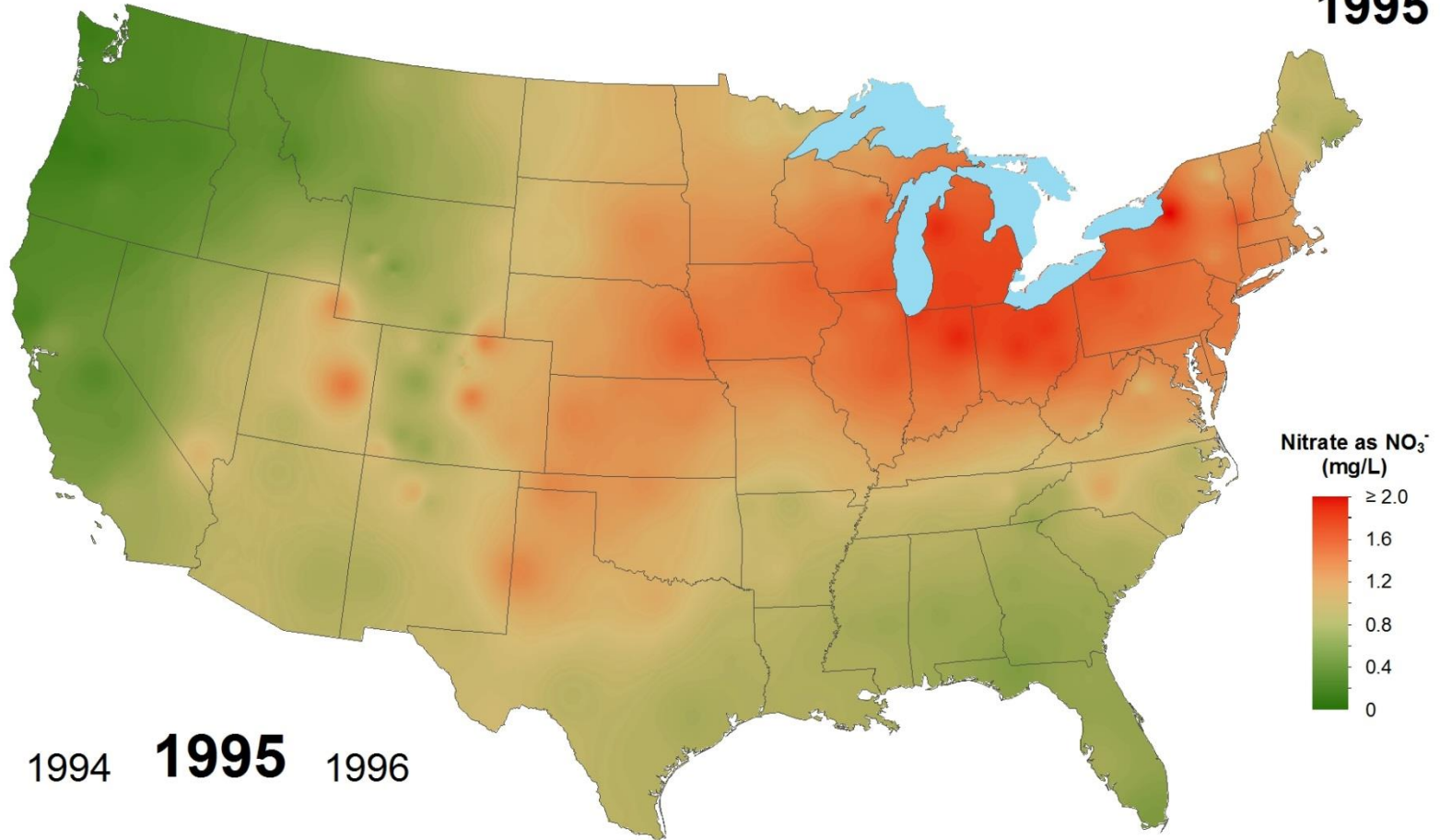
# Nitrate ion concentration 1994



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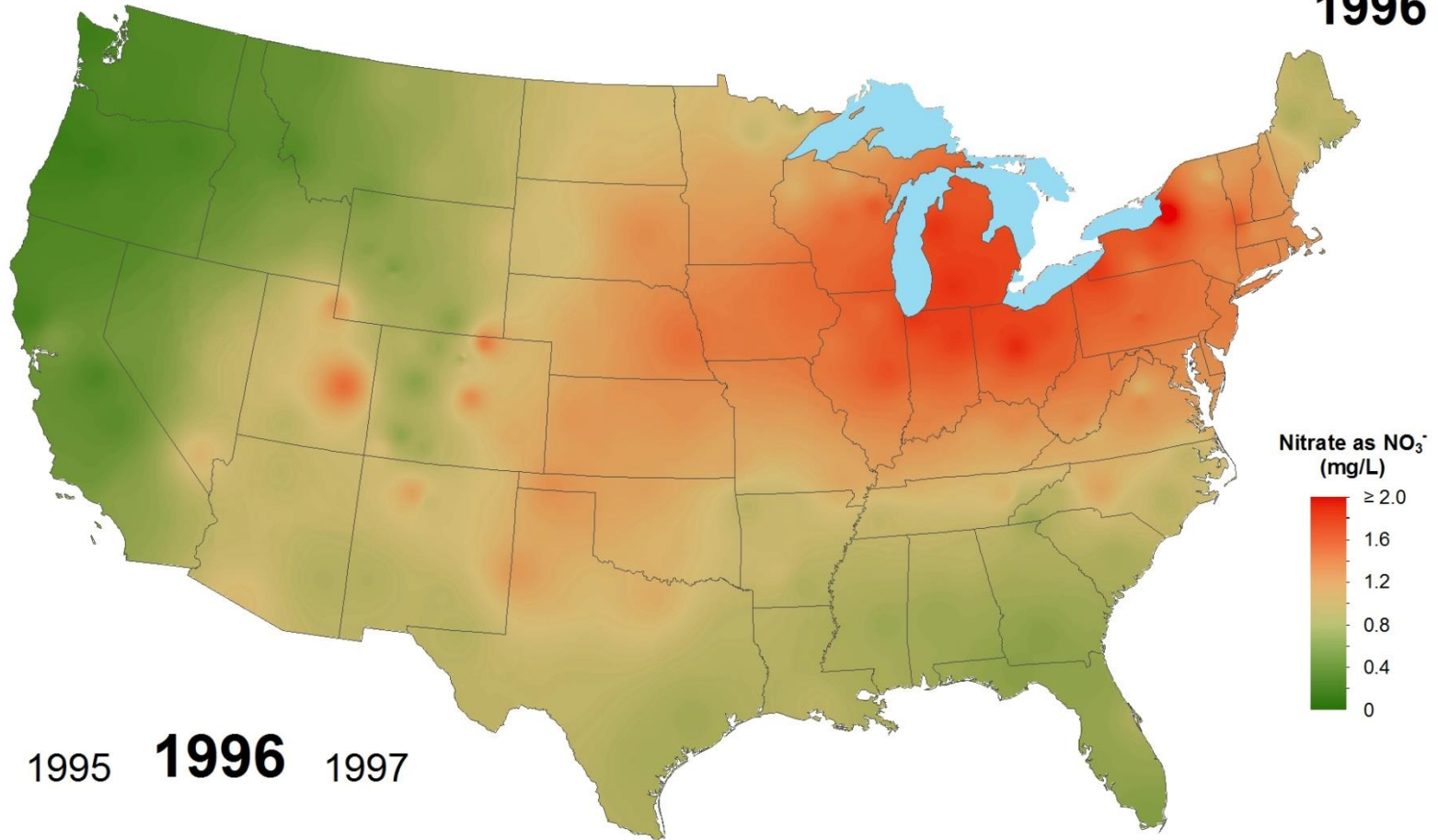


# Nitrate ion concentration 1995



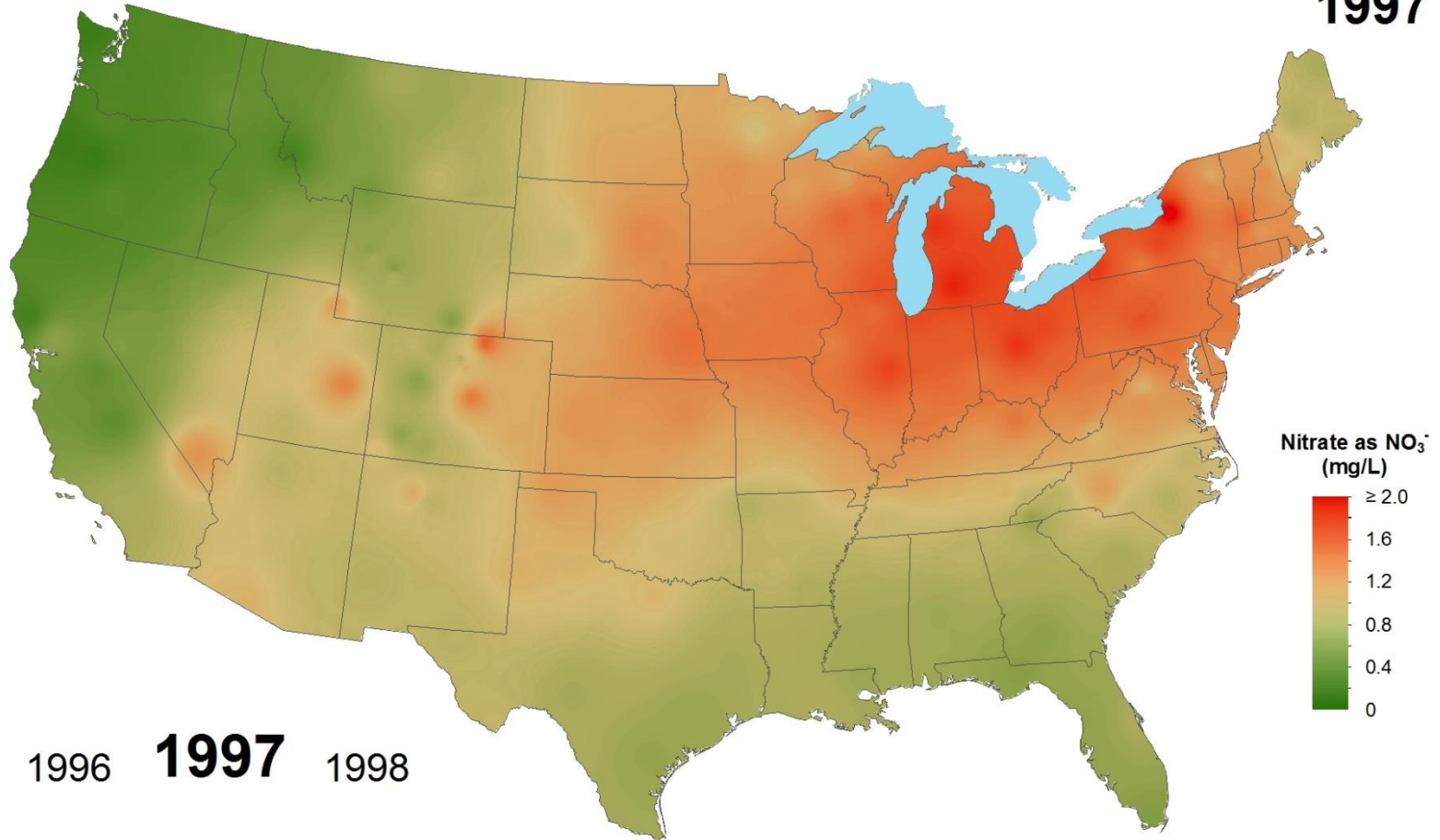
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# Nitrate ion concentration 1996



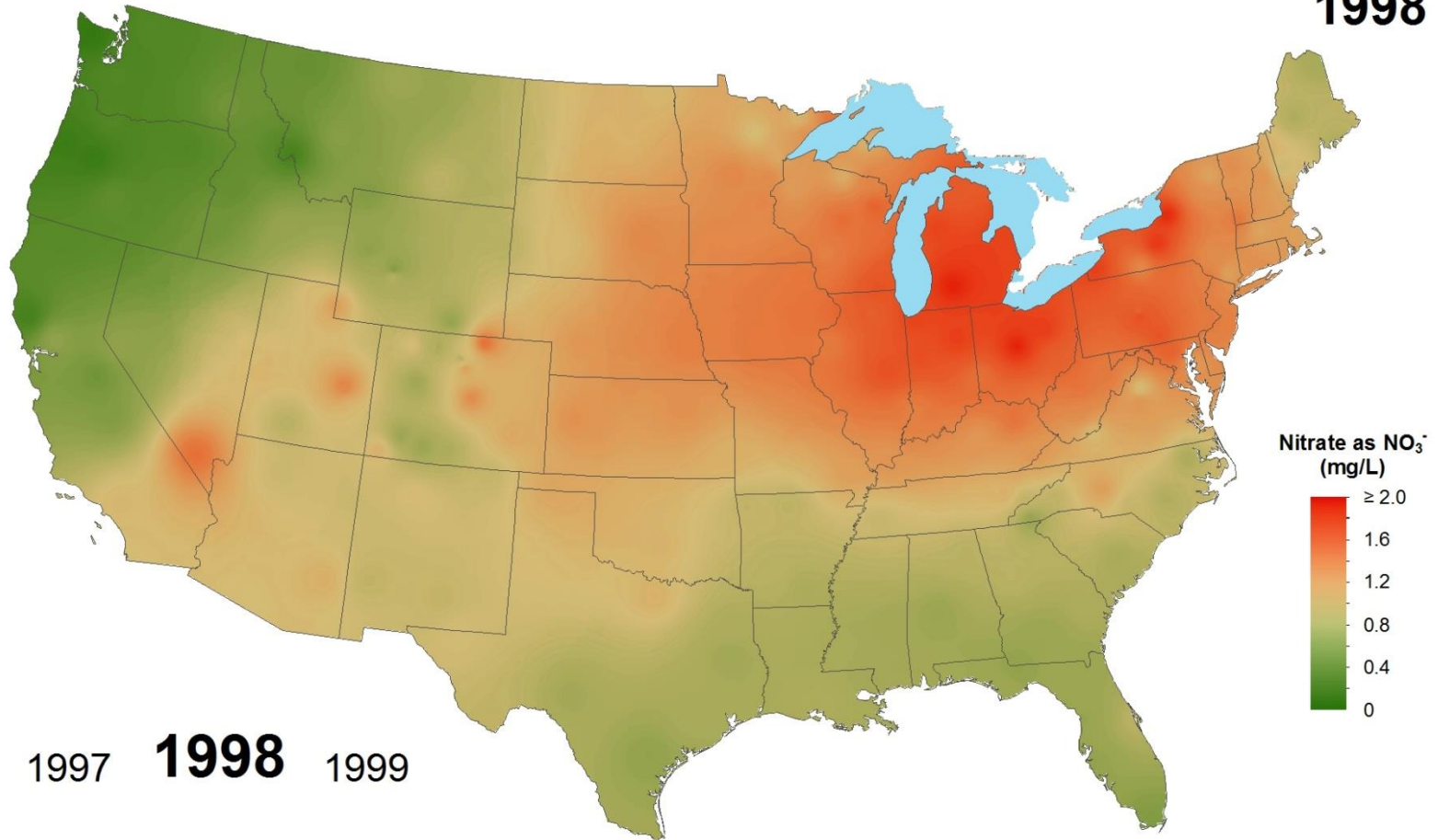
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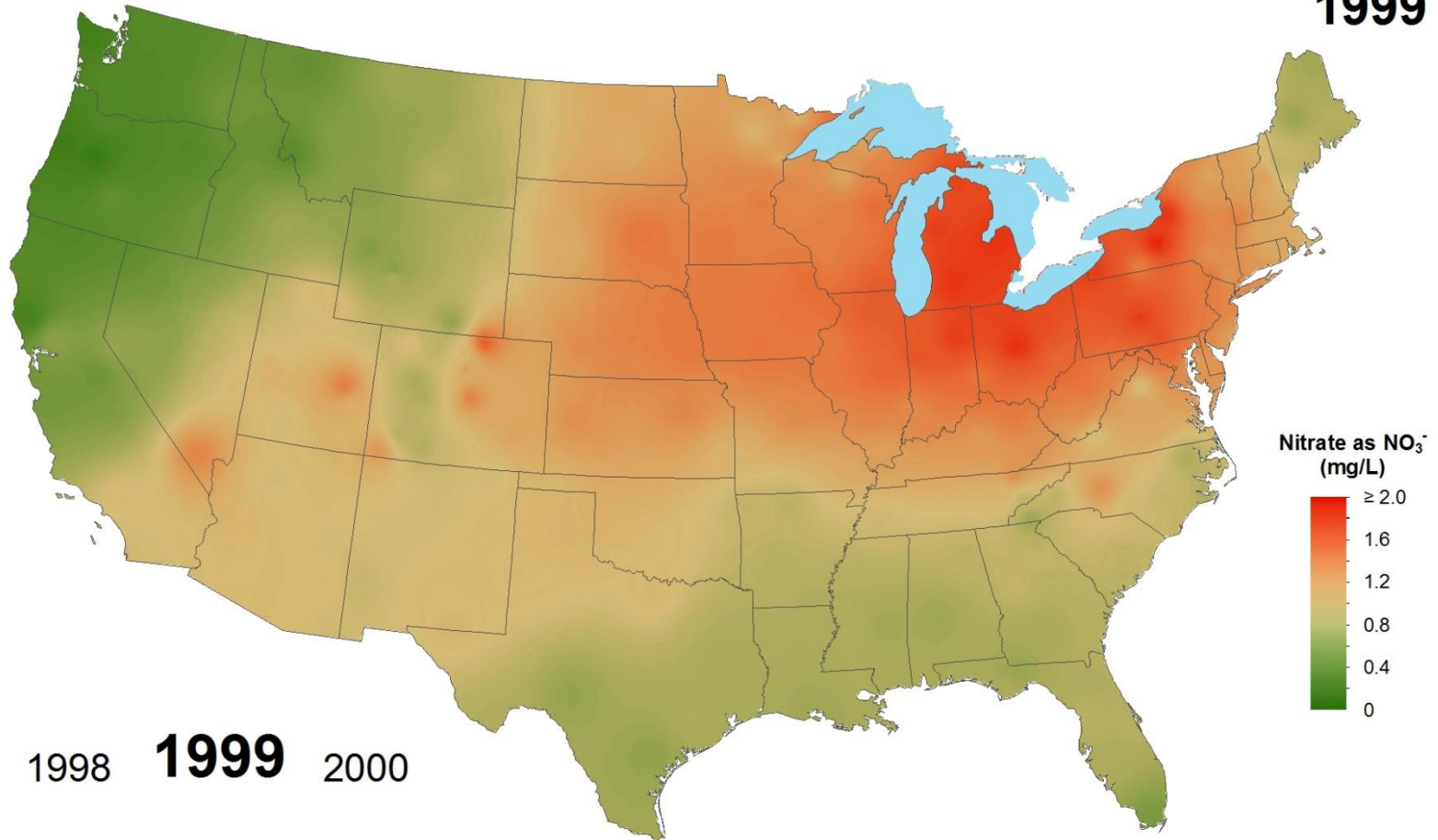
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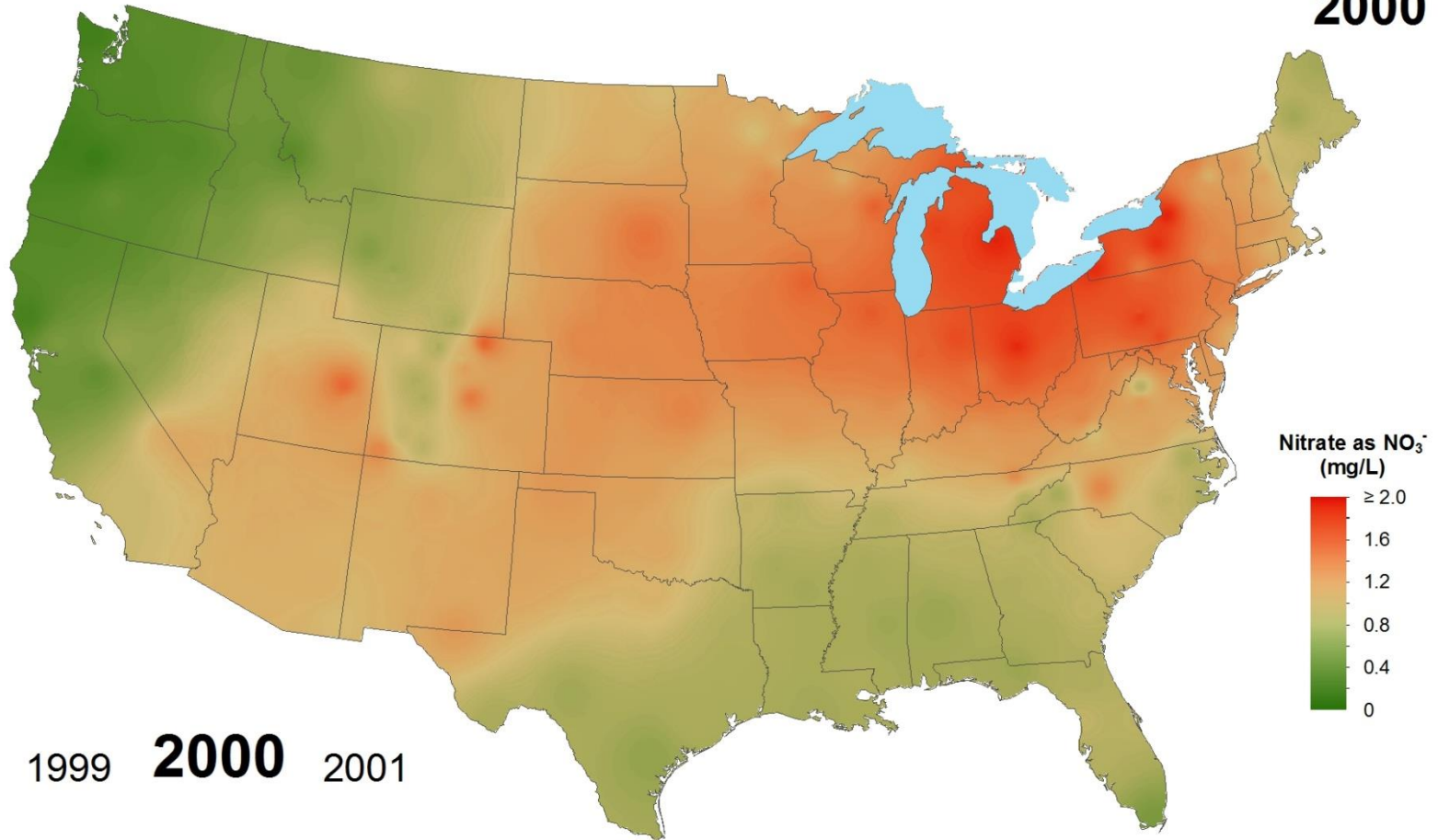
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# Nitrate ion concentration 1999



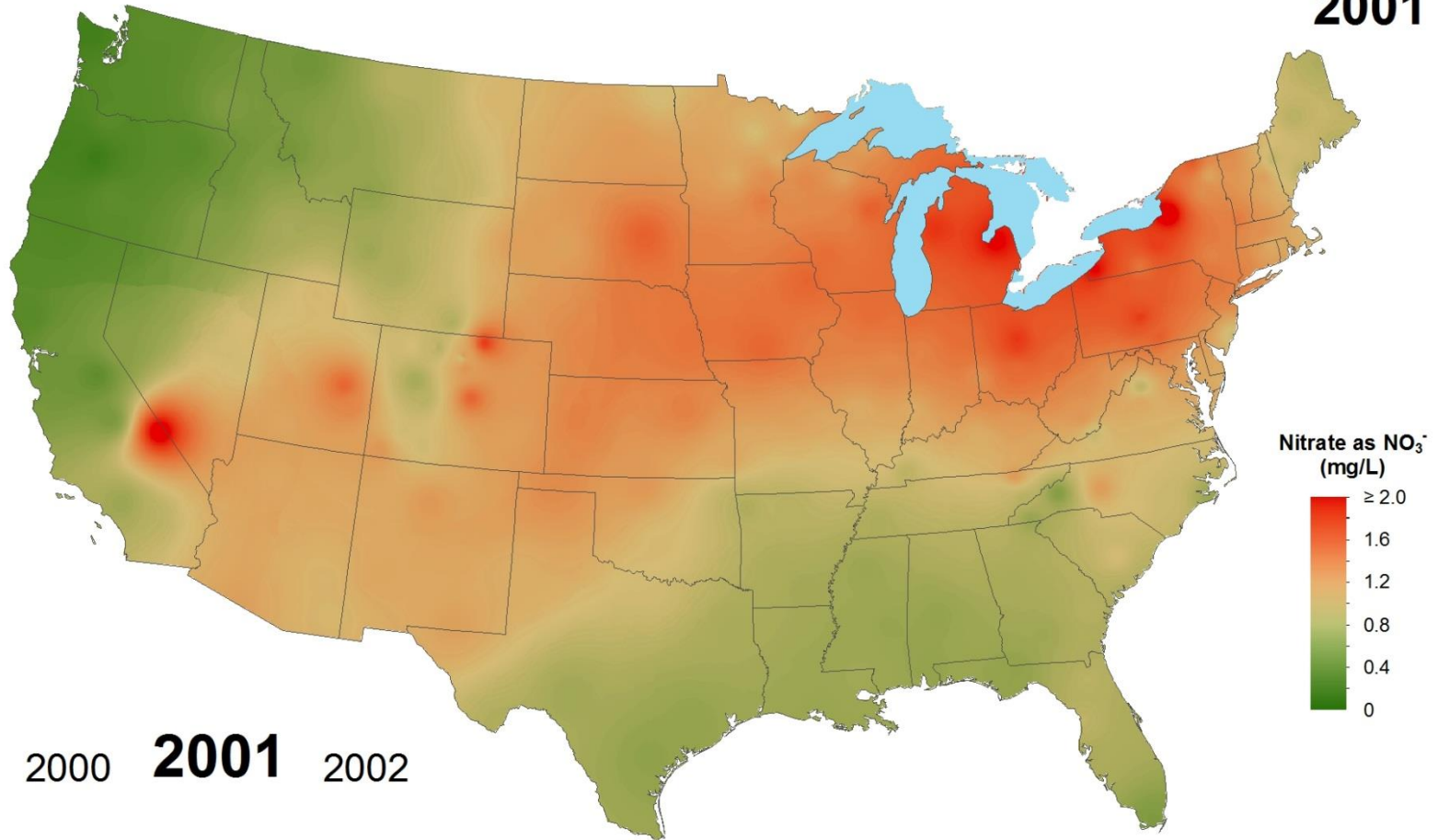
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# Nitrate ion concentration 2000



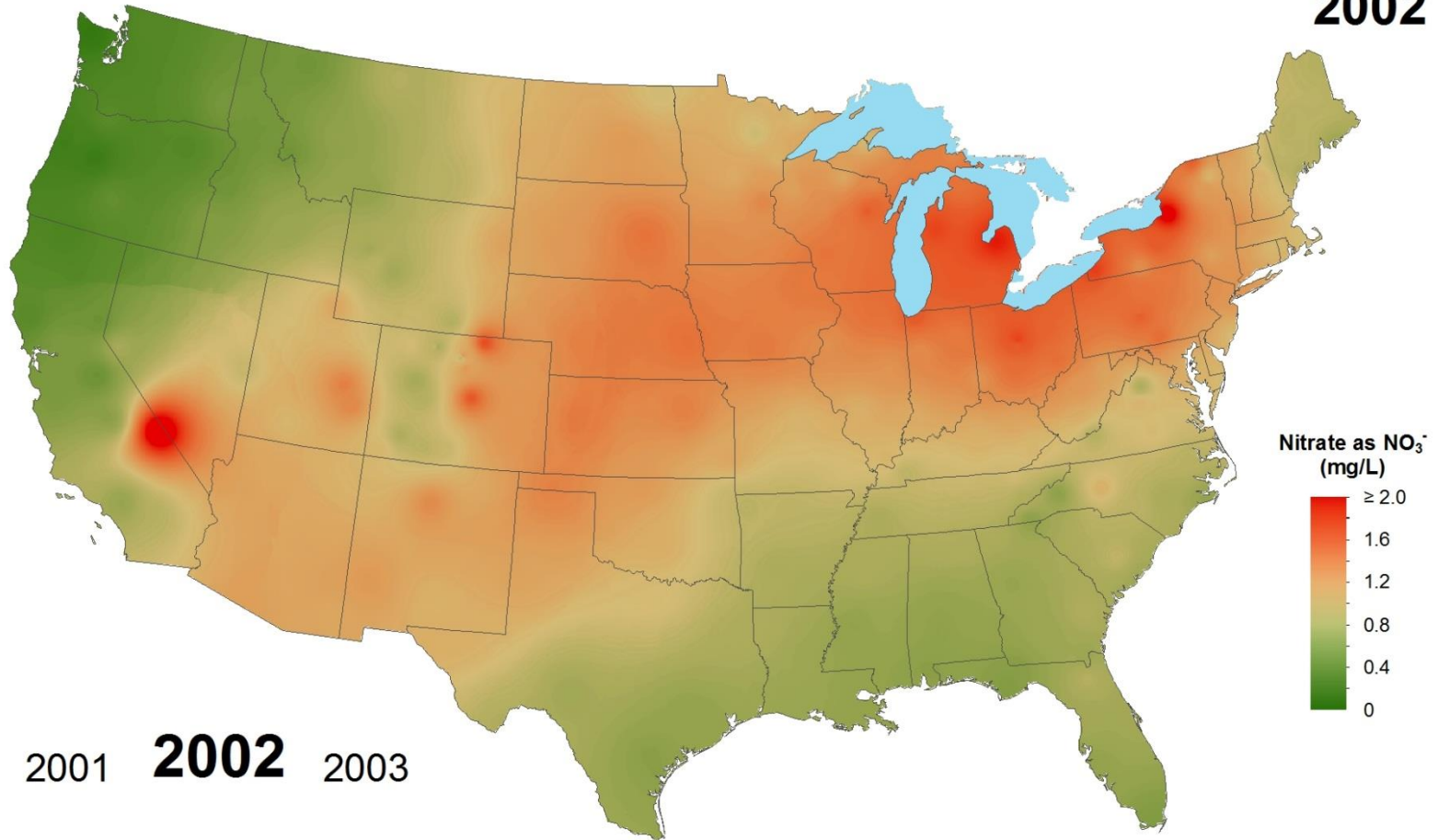
National Atmospheric Deposition Program/National Trends Network  
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# Nitrate ion concentration 2001



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

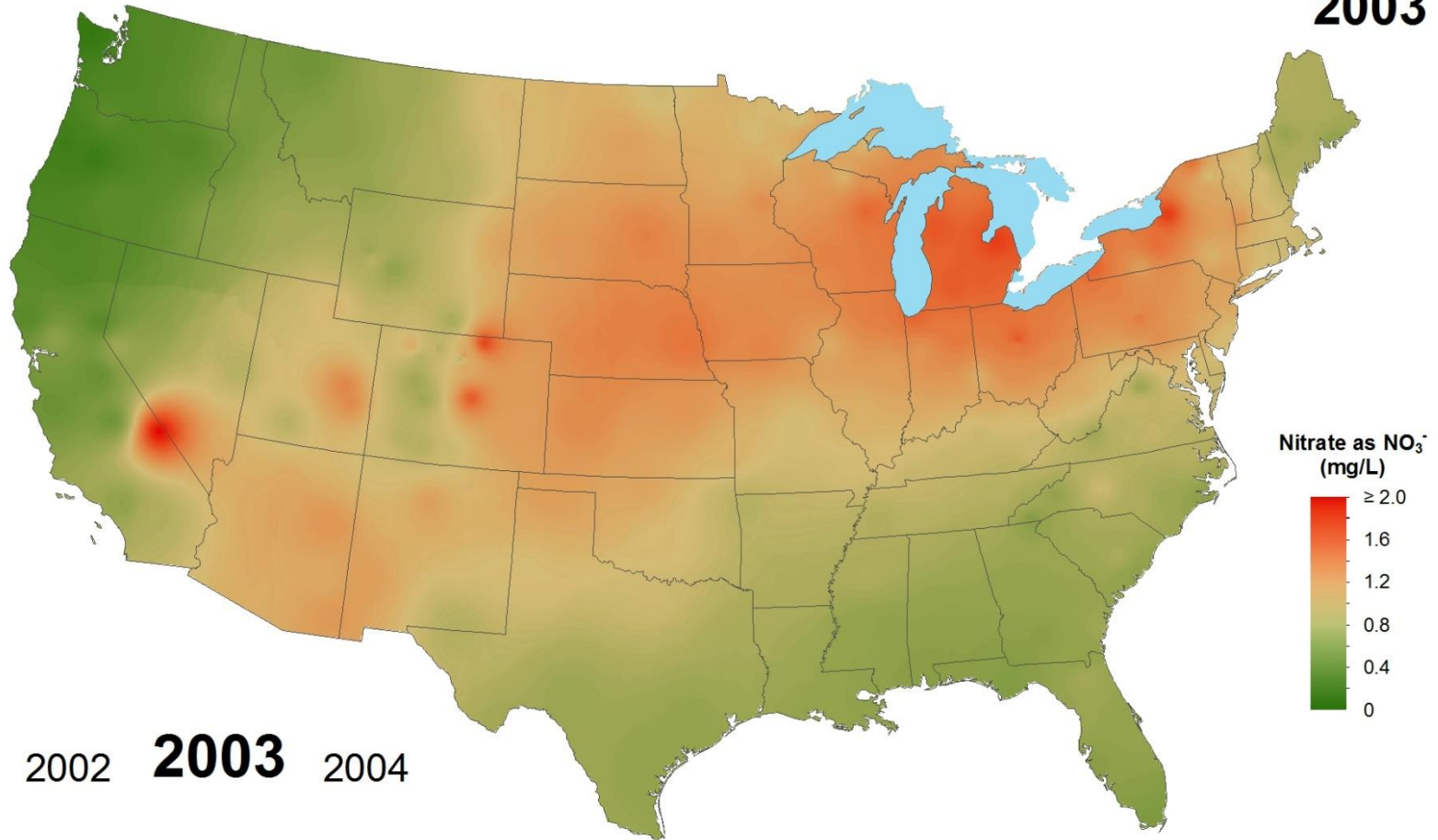
# Nitrate ion concentration 2002



National Atmospheric Deposition Program/National Trends Network  
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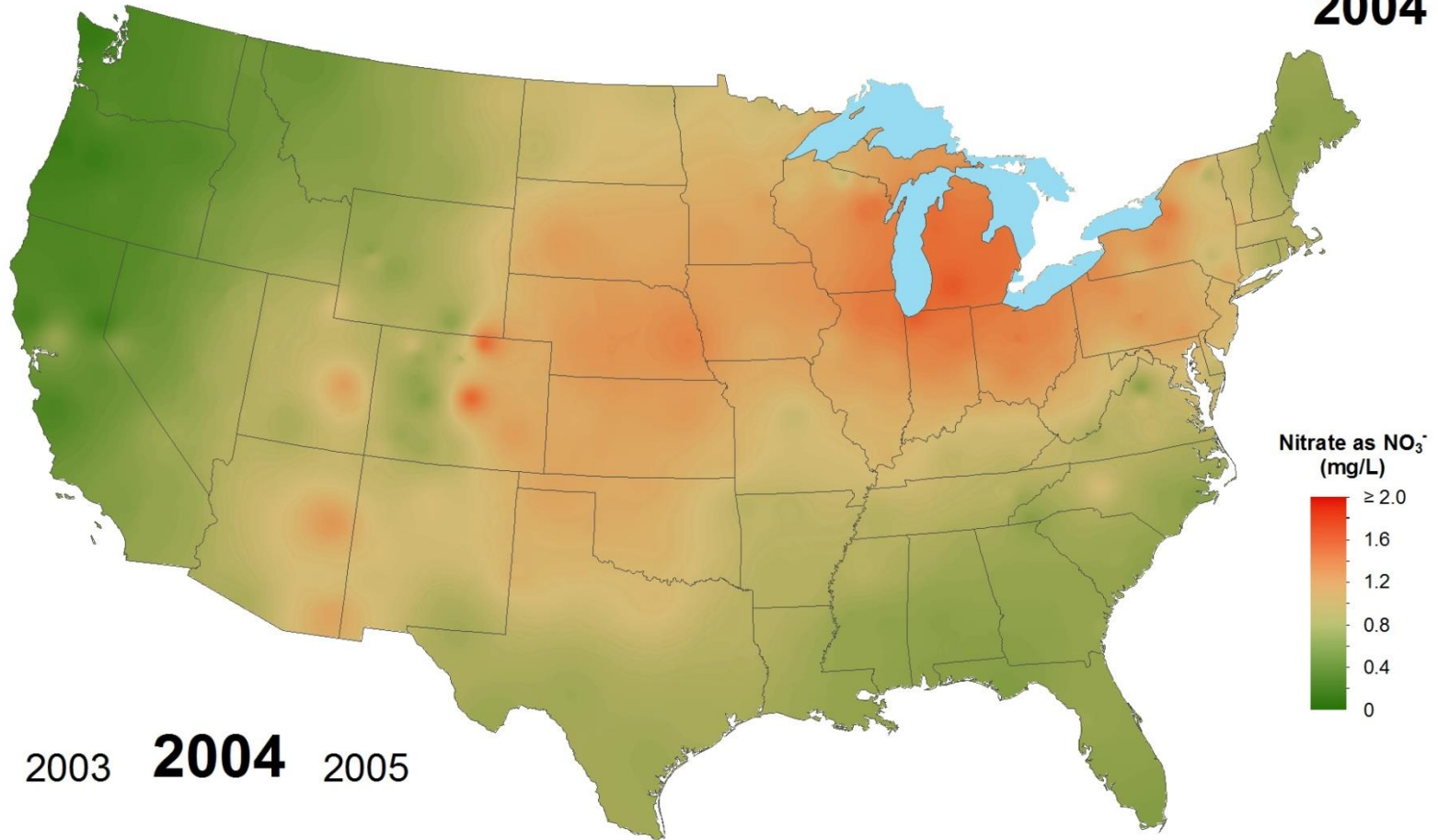


# Nitrate ion concentration 2003



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

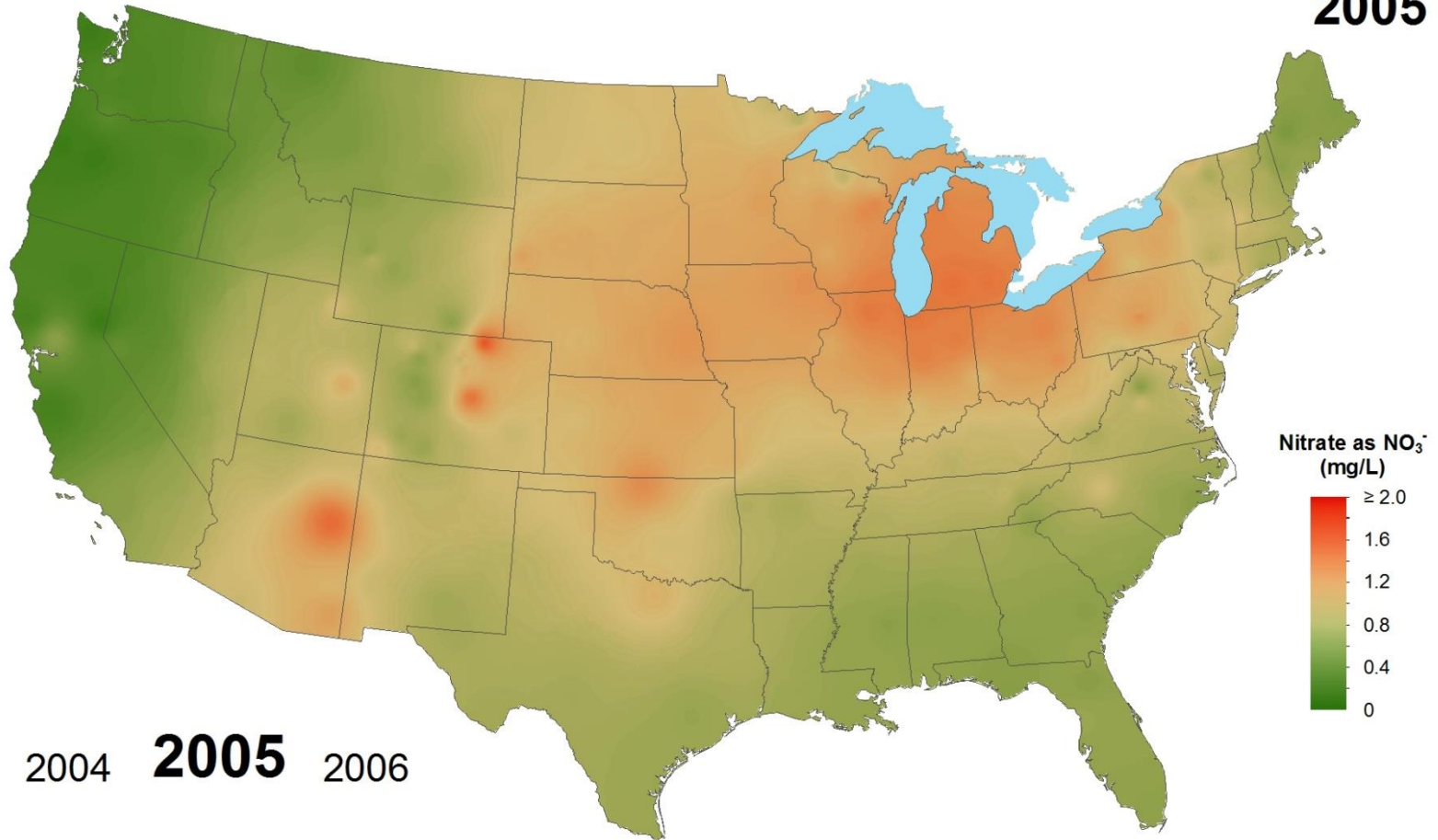
# Nitrate ion concentration 2004



2003 **2004** 2005

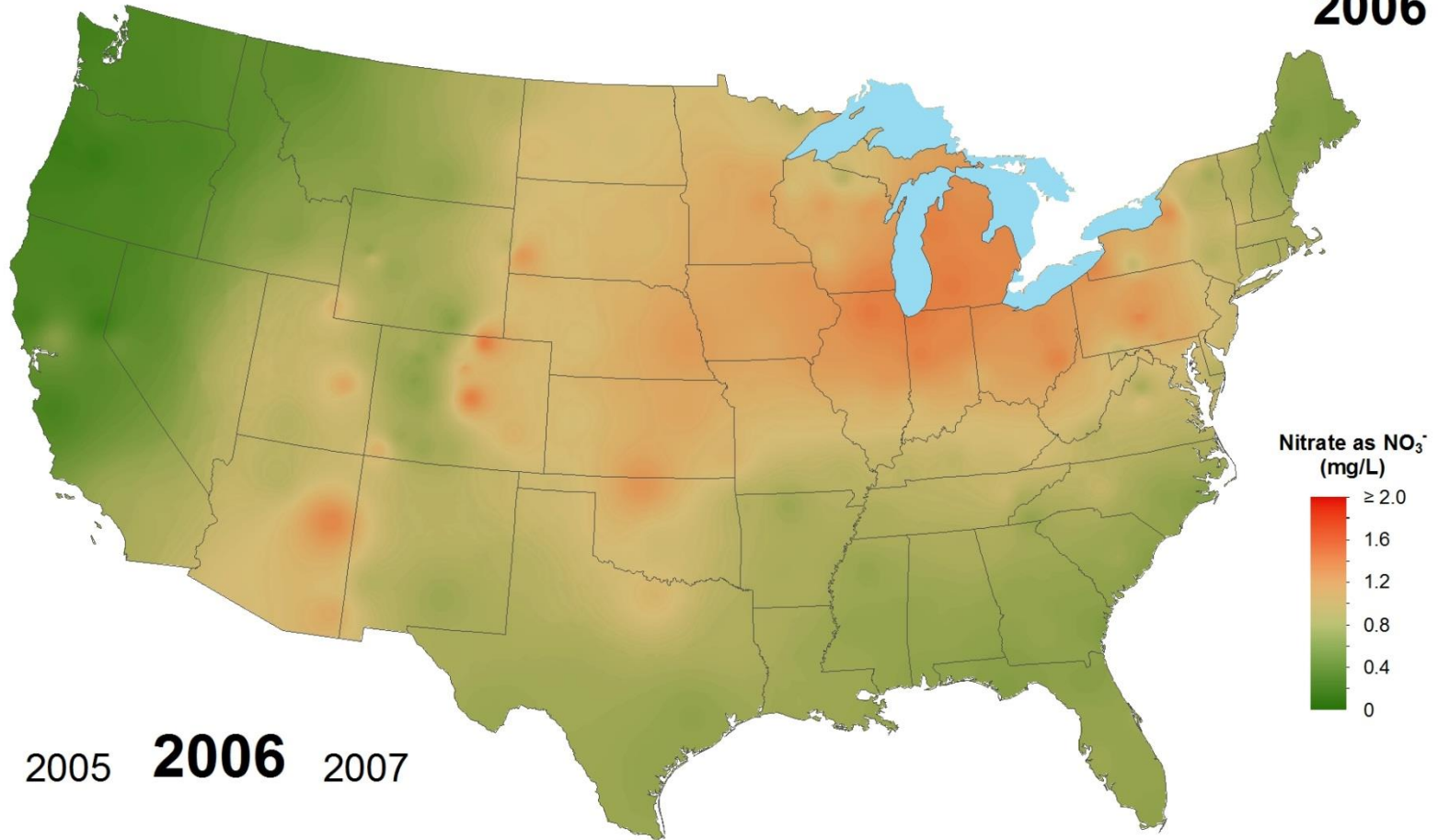
National Atmospheric Deposition Program/National Trends Network  
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# Nitrate ion concentration 2005



National Atmospheric Deposition Program/National Trends Network  
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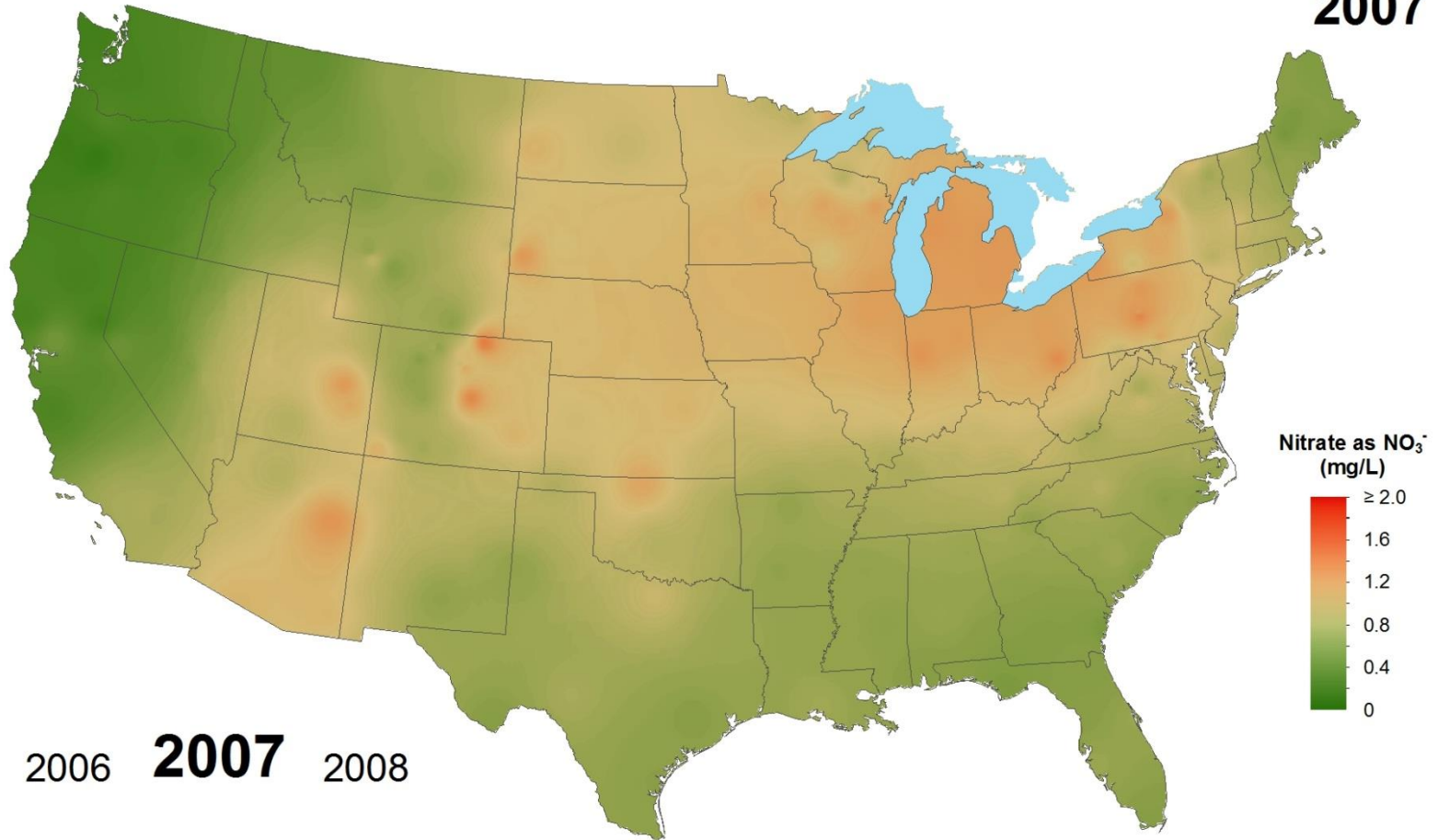
# Nitrate ion concentration 2006



2005 **2006** 2007

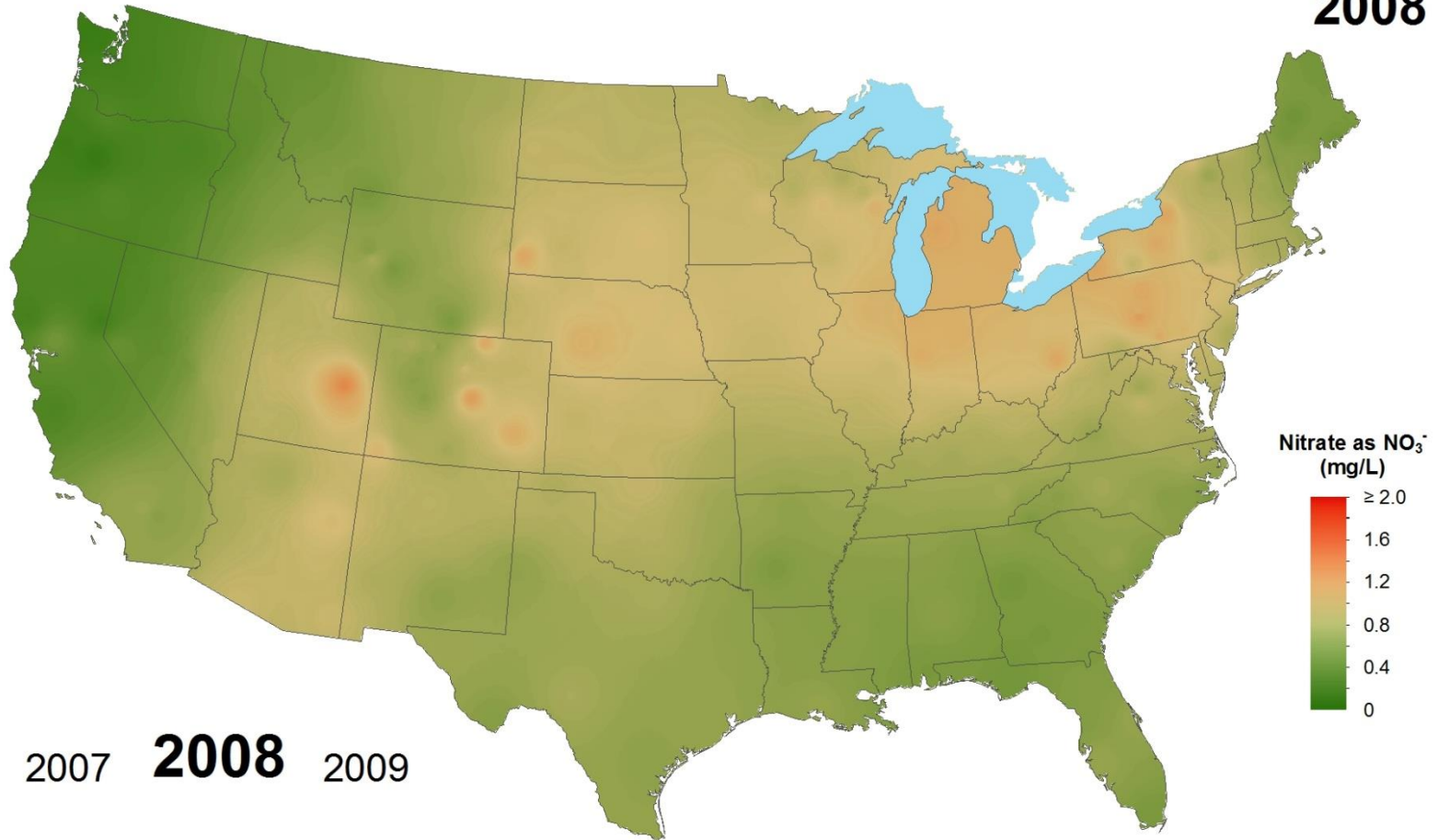
National Atmospheric Deposition Program/National Trends Network  
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# Nitrate ion concentration 2007



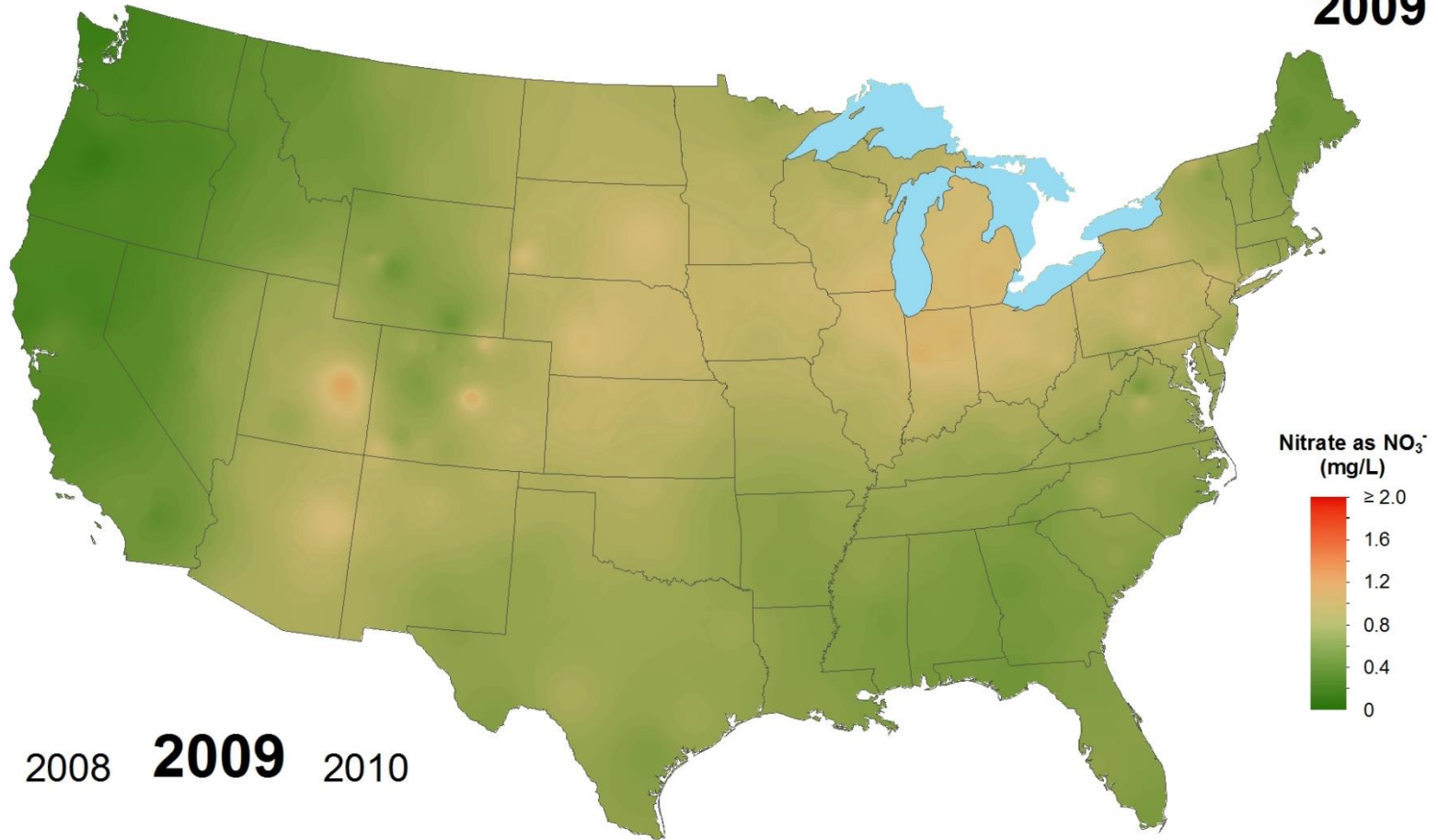
National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

# Nitrate ion concentration 2008



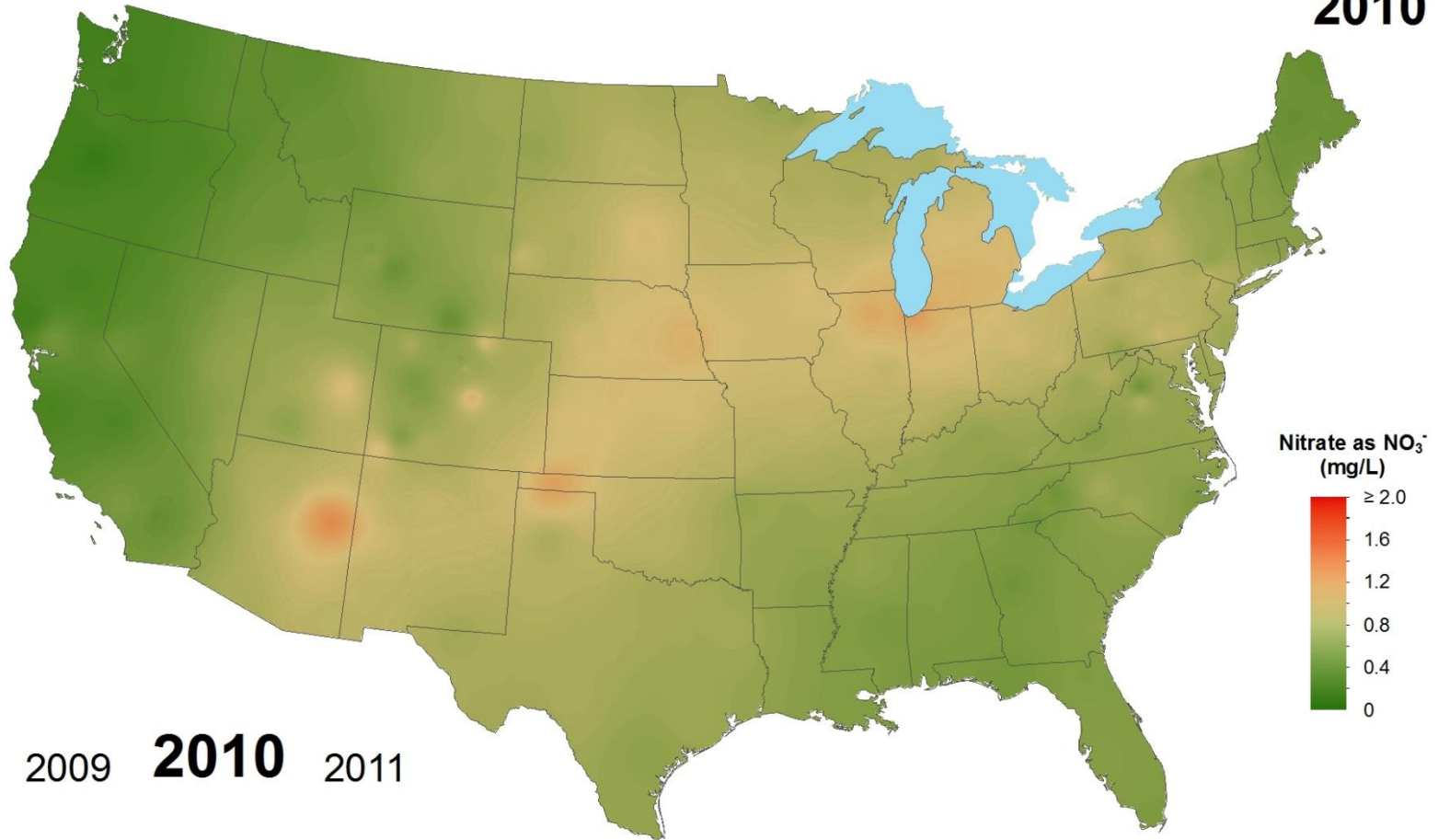
National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

# Nitrate ion concentration 2009



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

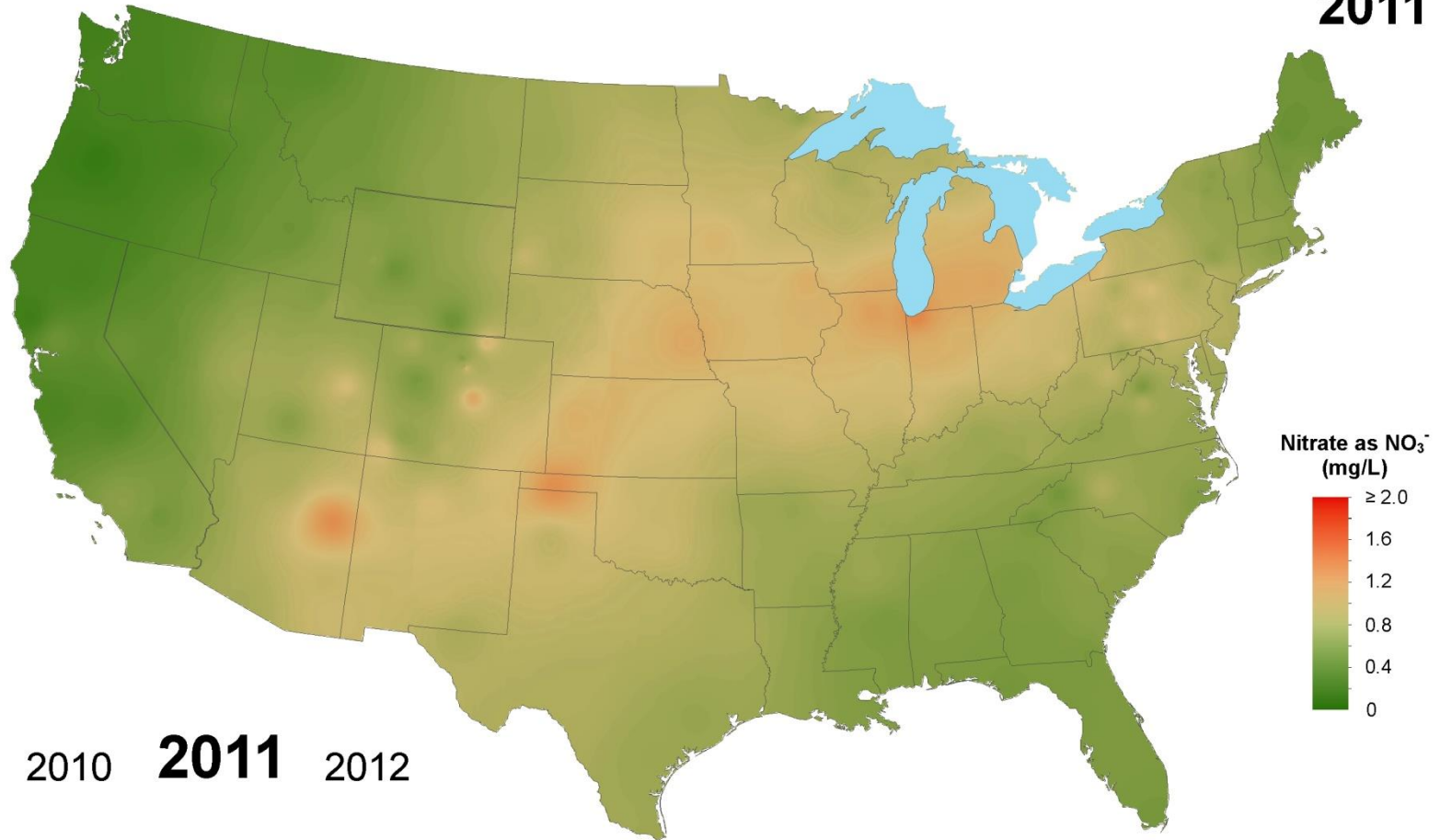
# Nitrate ion concentration 2010



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

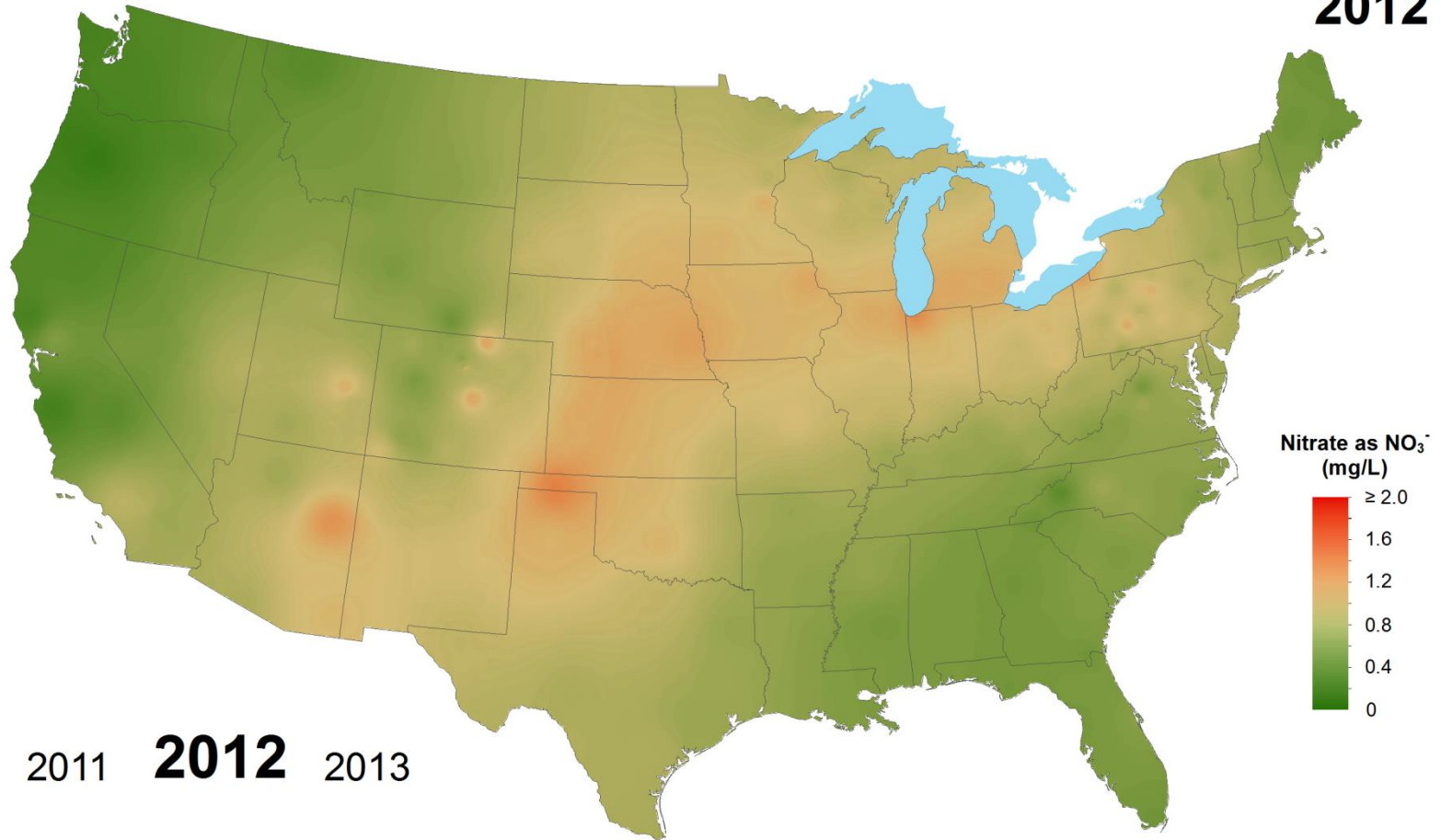


# Nitrate ion concentration 2011



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

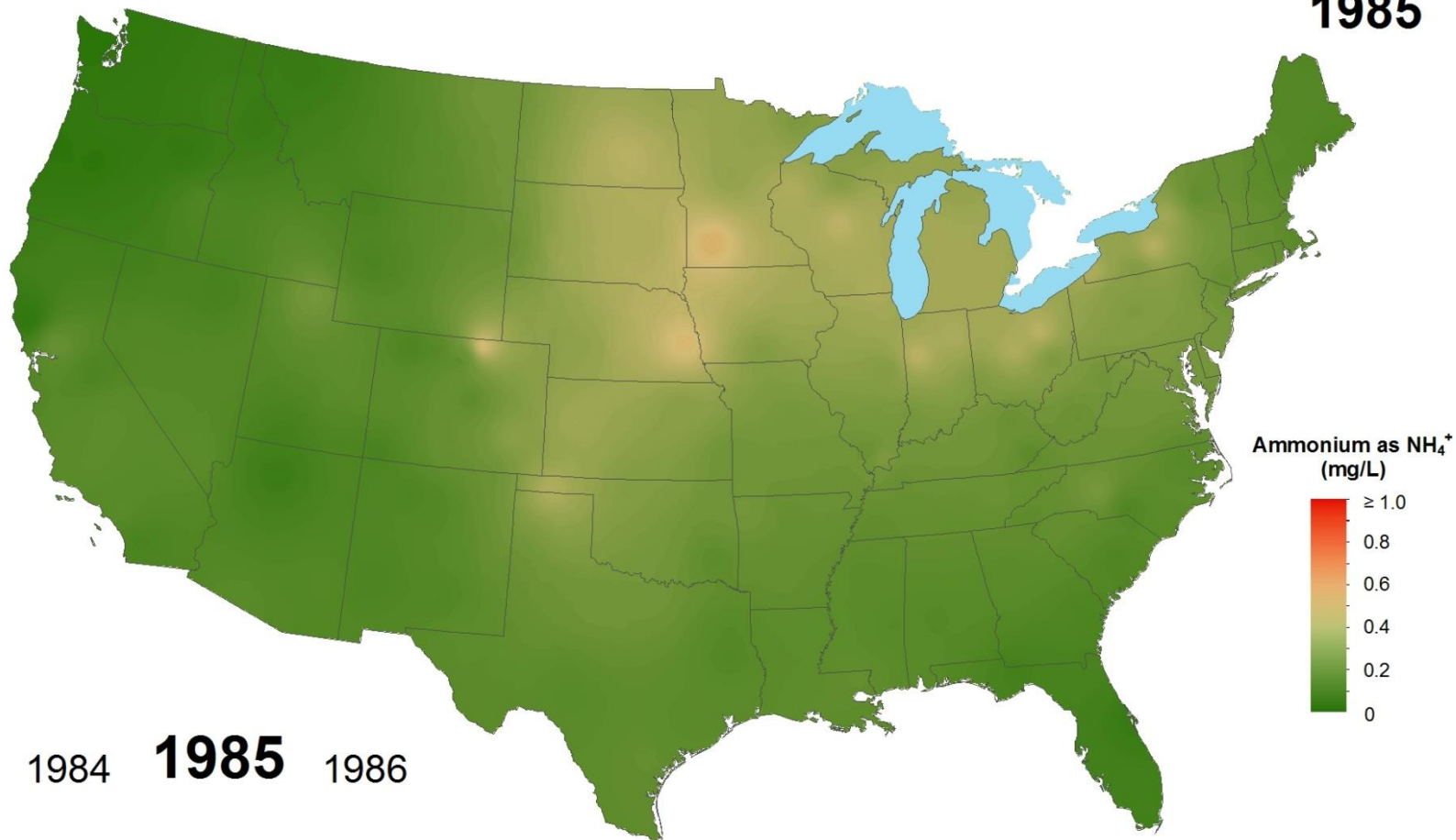
# Nitrate ion concentration 2012



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

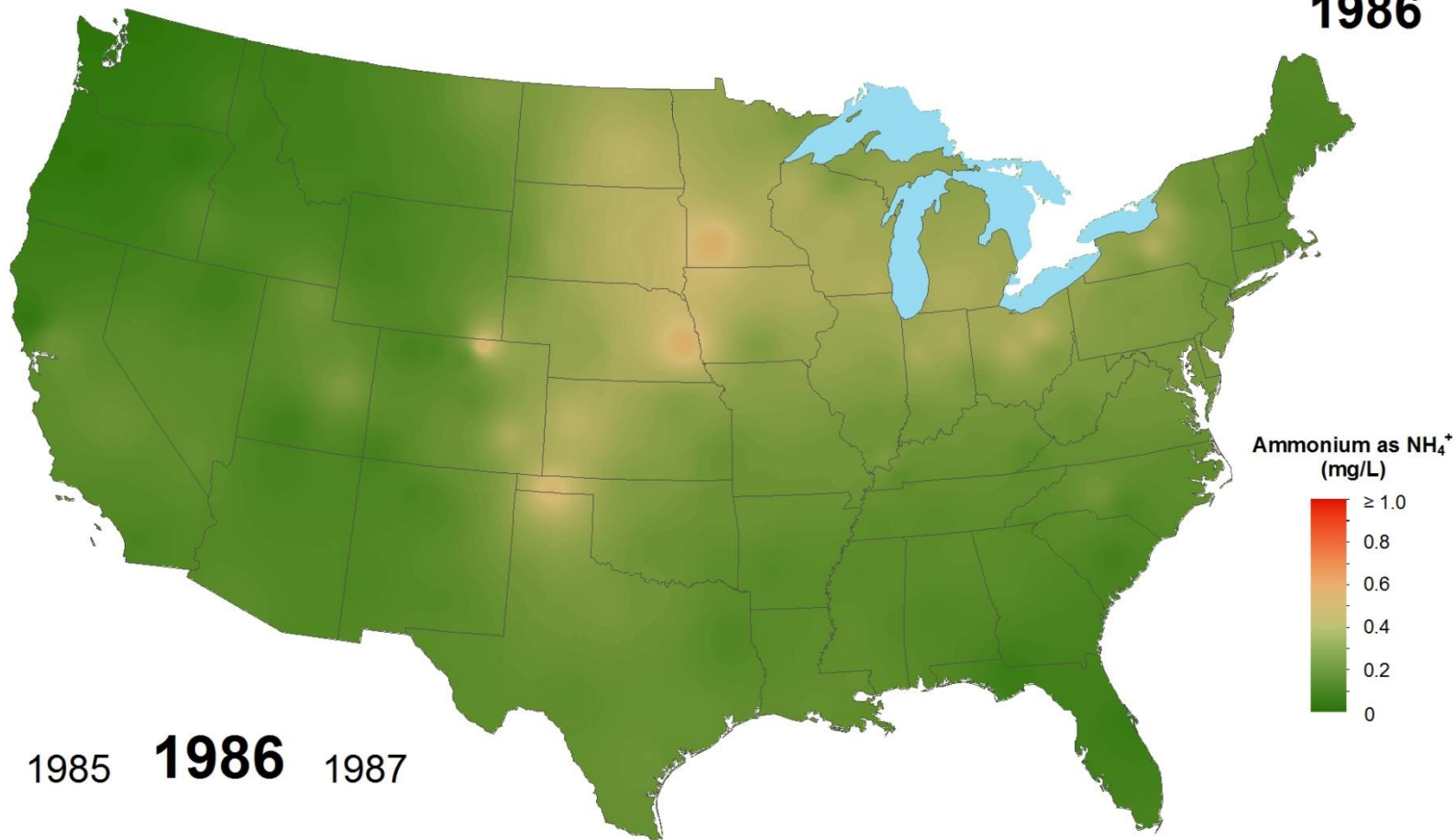


# Ammonium ion concentration 1985



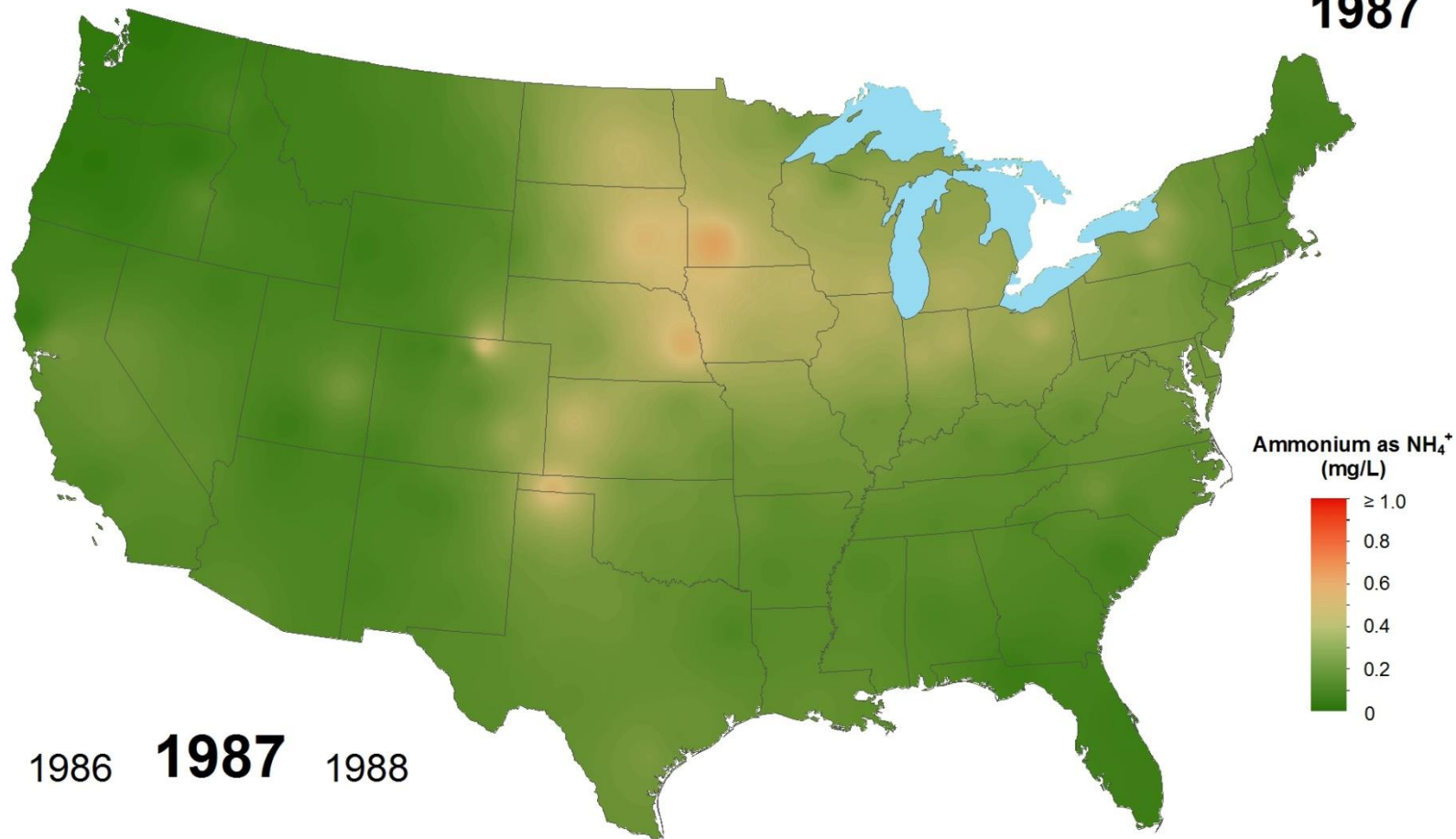
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<http://nadp.isws.illinois.edu>

# Ammonium ion concentration 1986



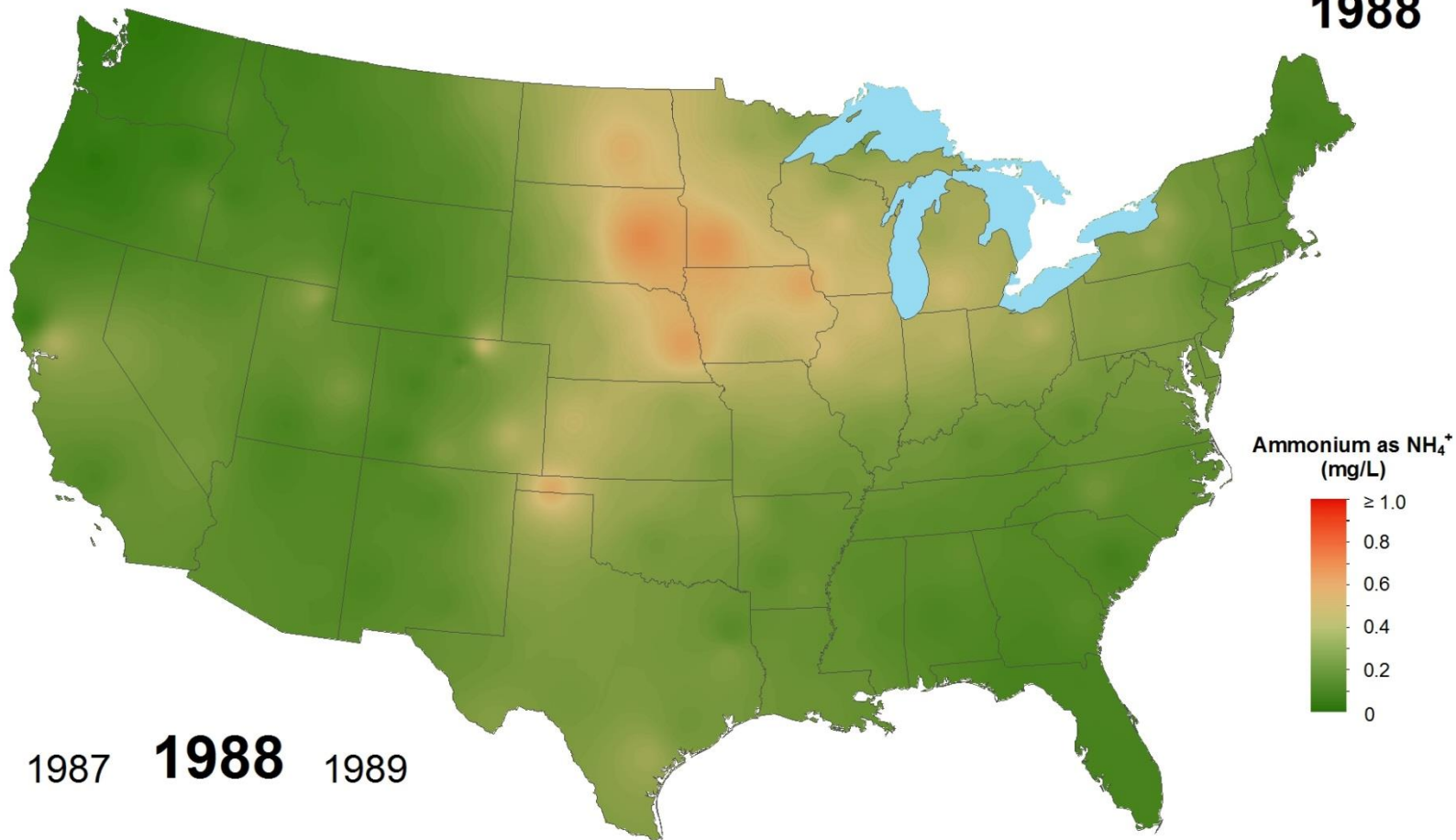
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# Ammonium ion concentration 1987



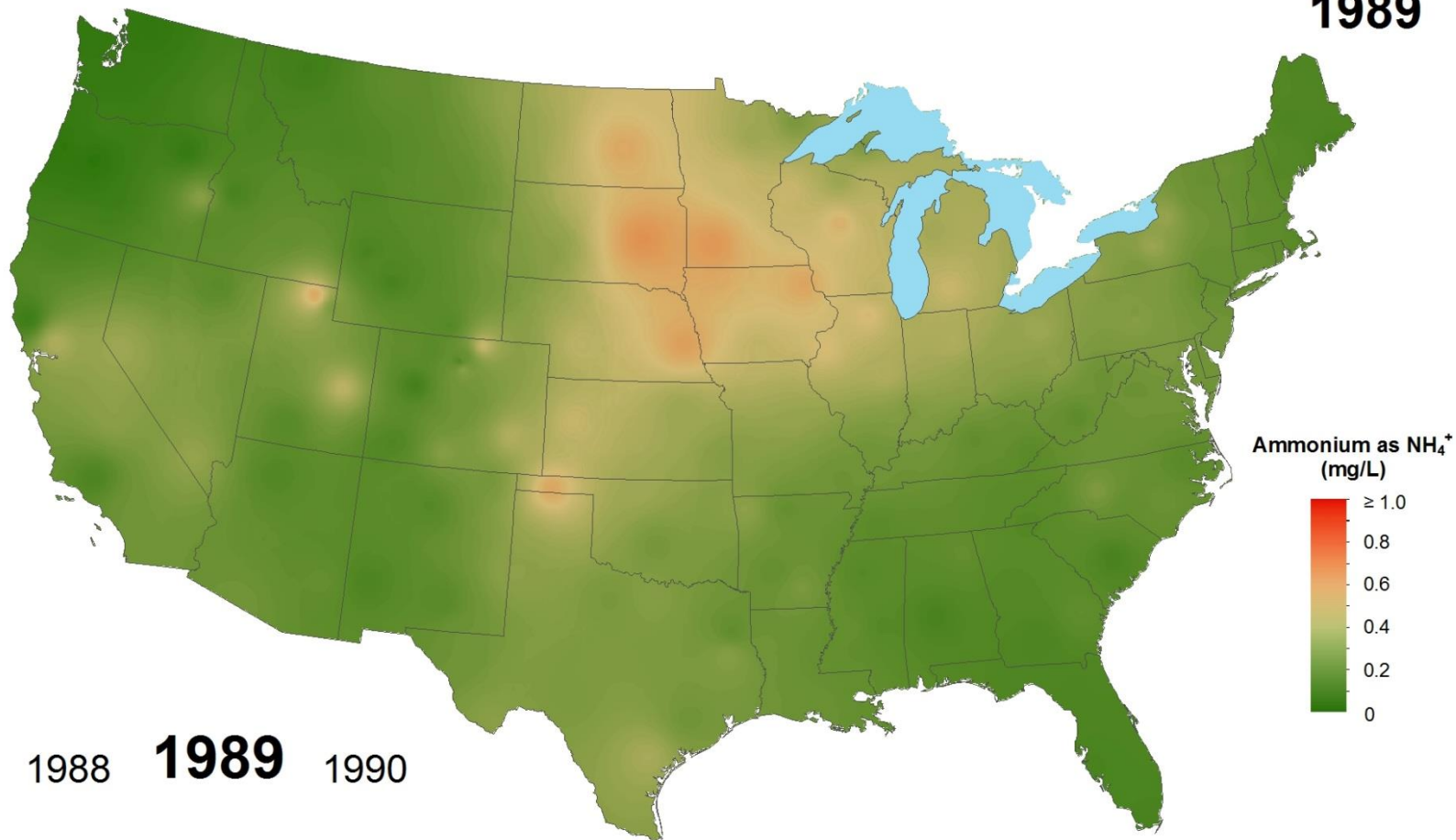
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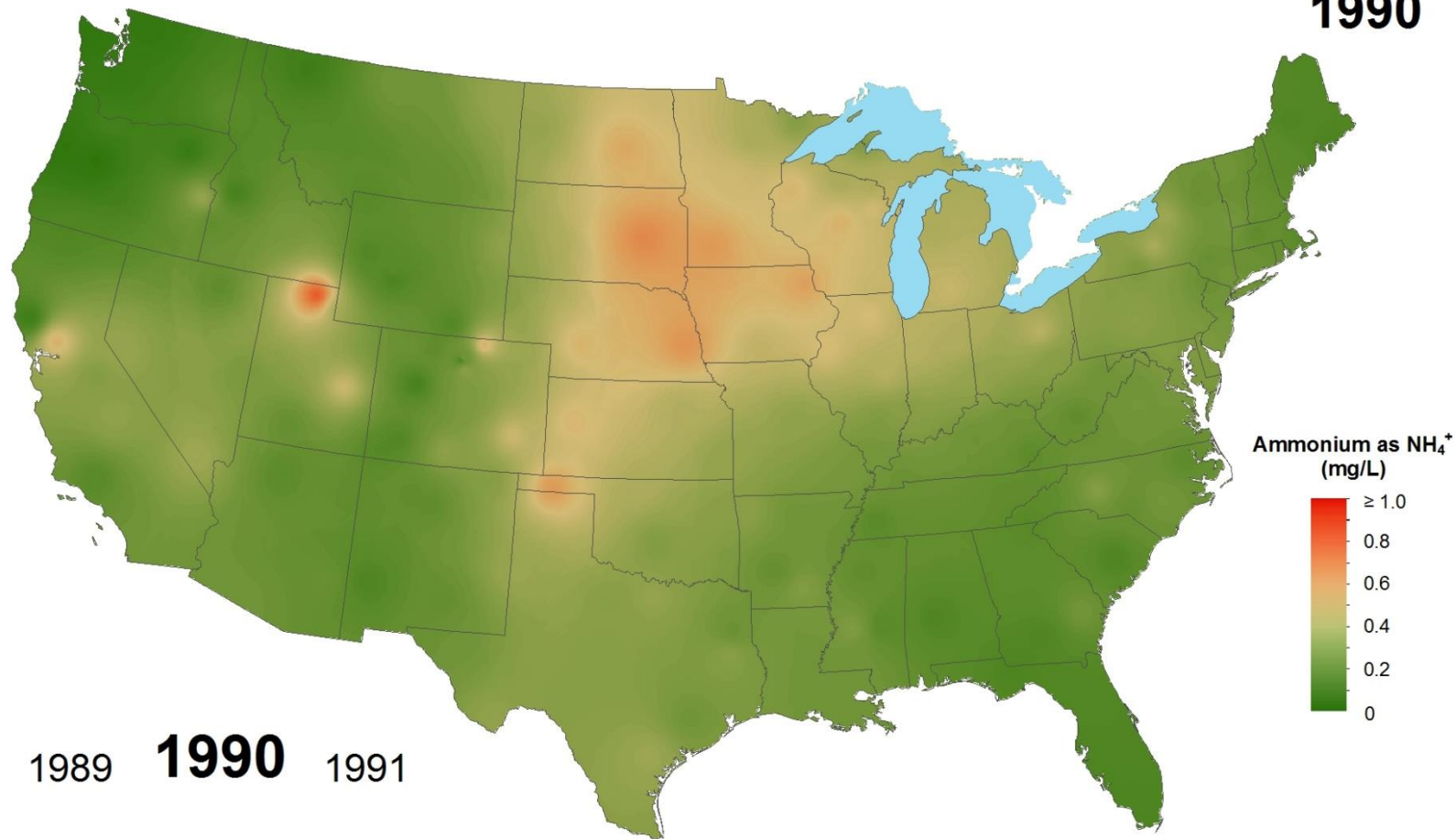
# Ammonium ion concentration 1989



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.isws.illinois.edu>

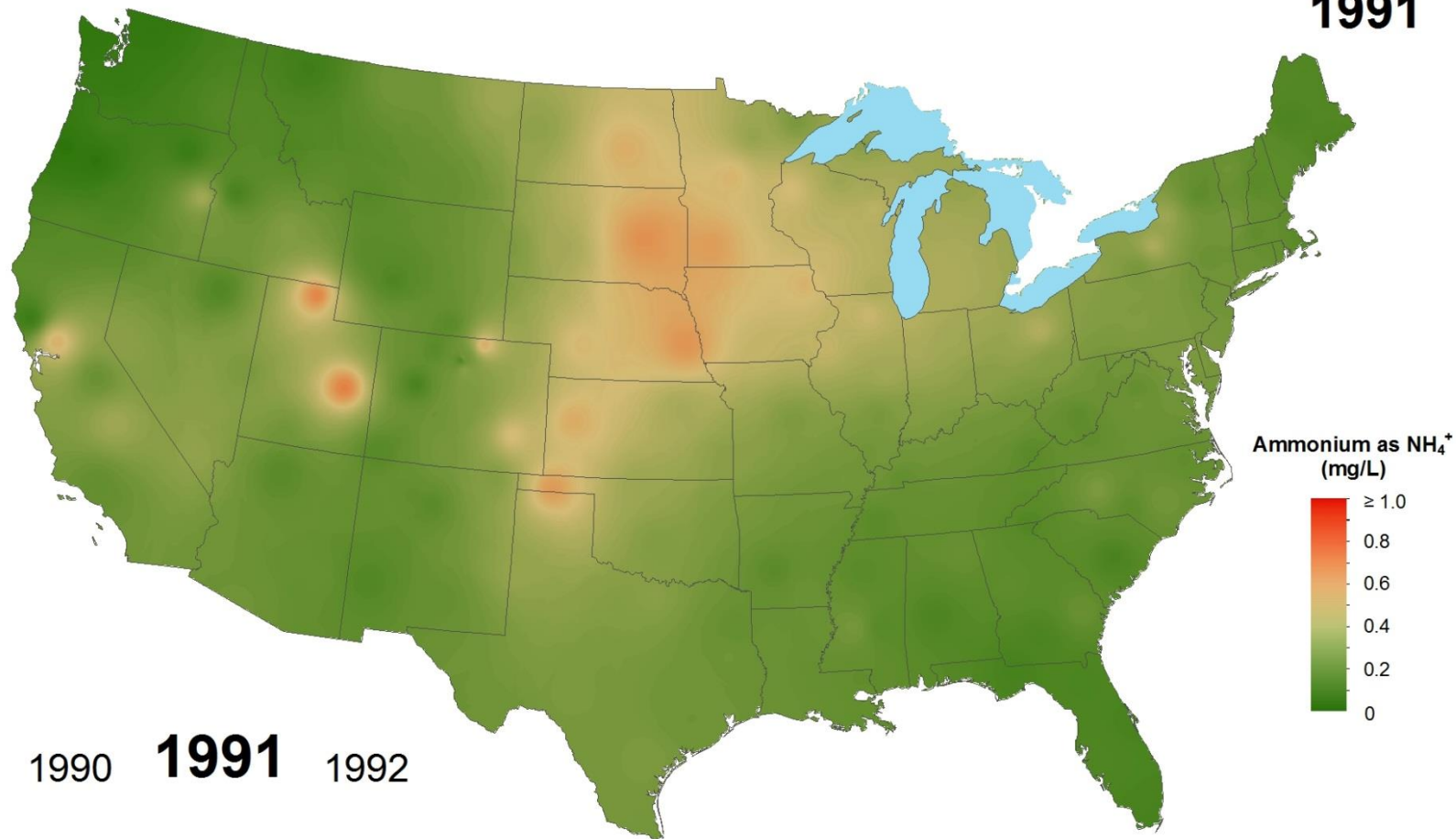


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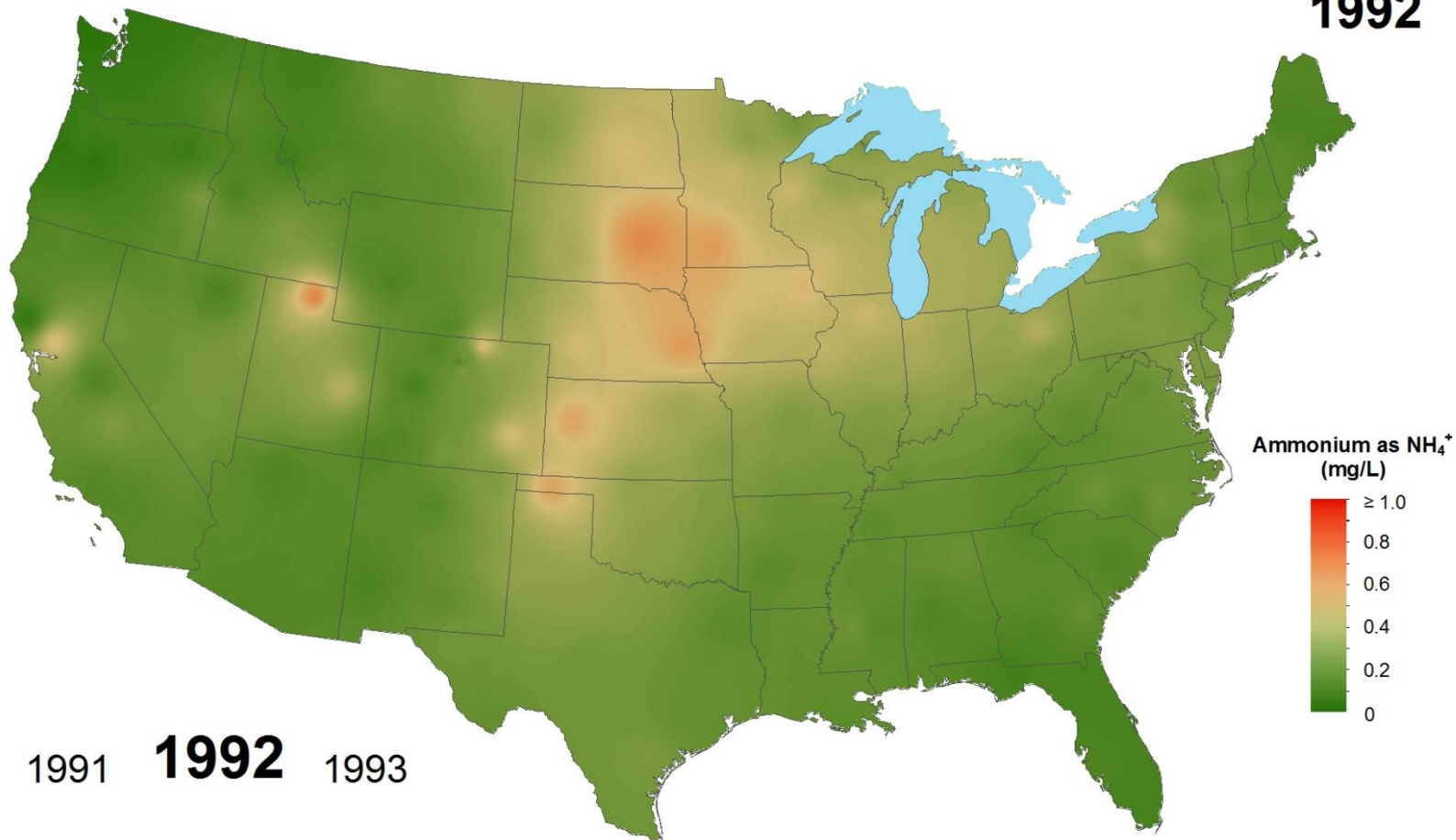
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# Ammonium ion concentration 1991



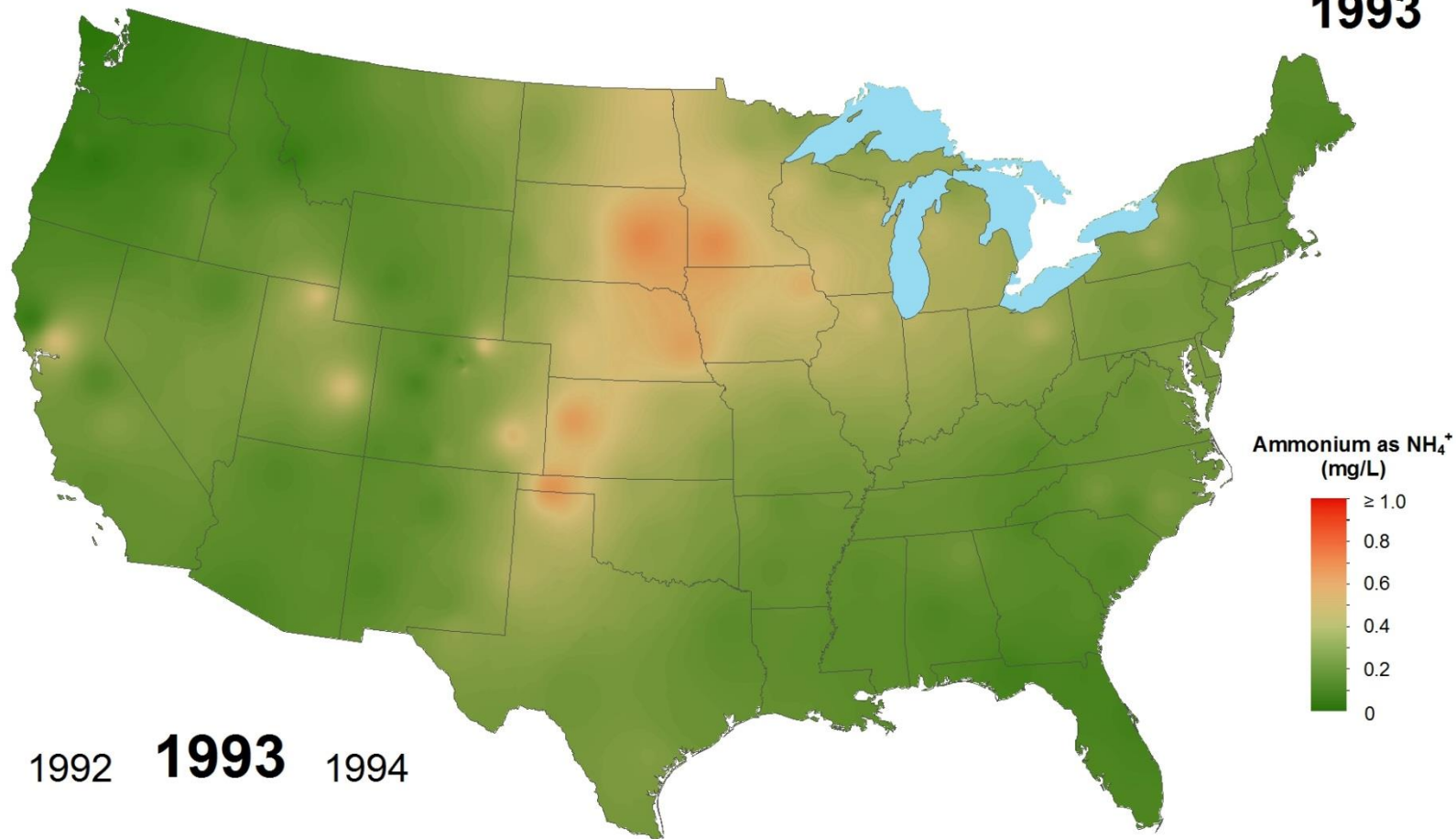
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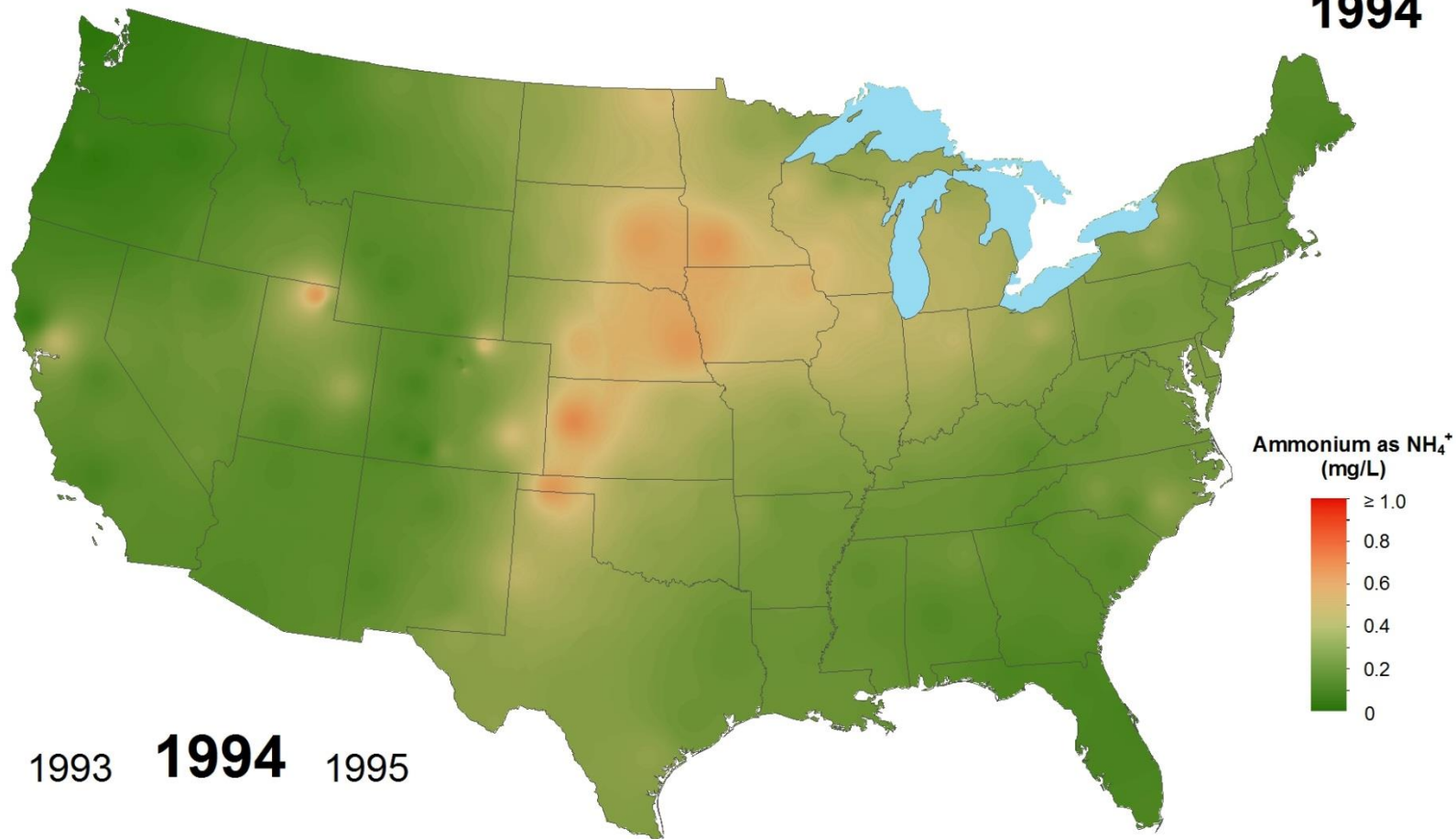
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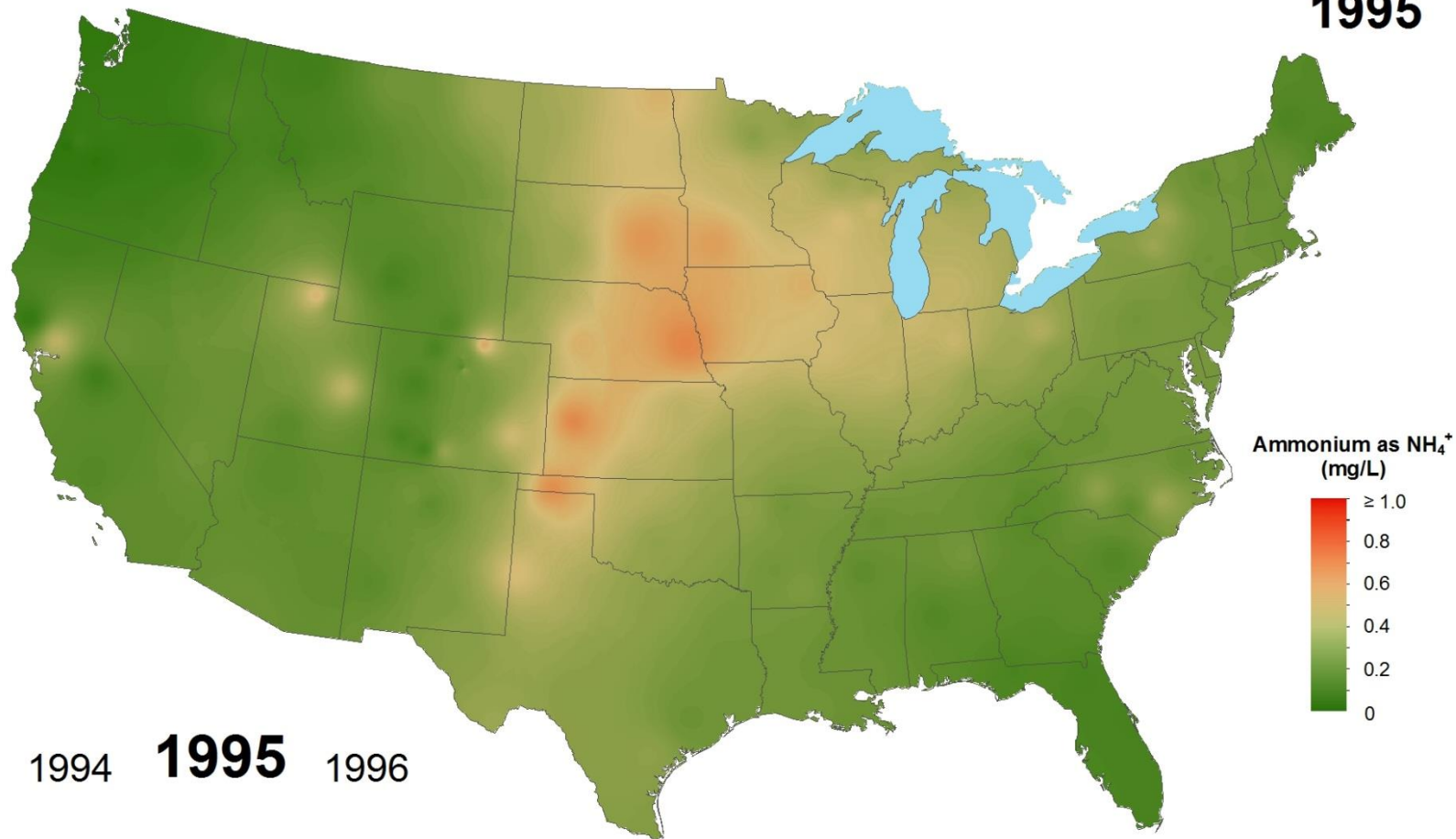
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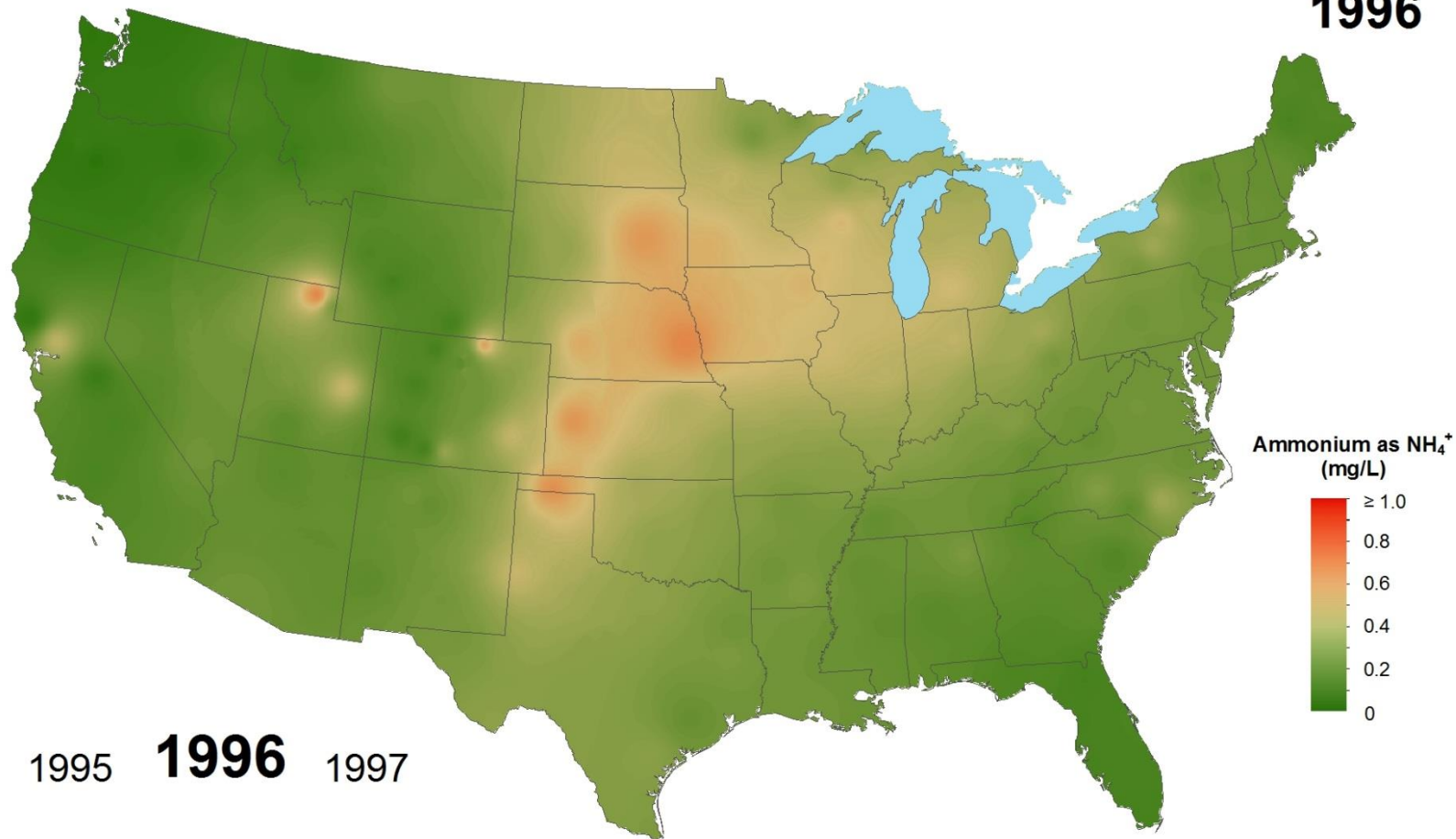
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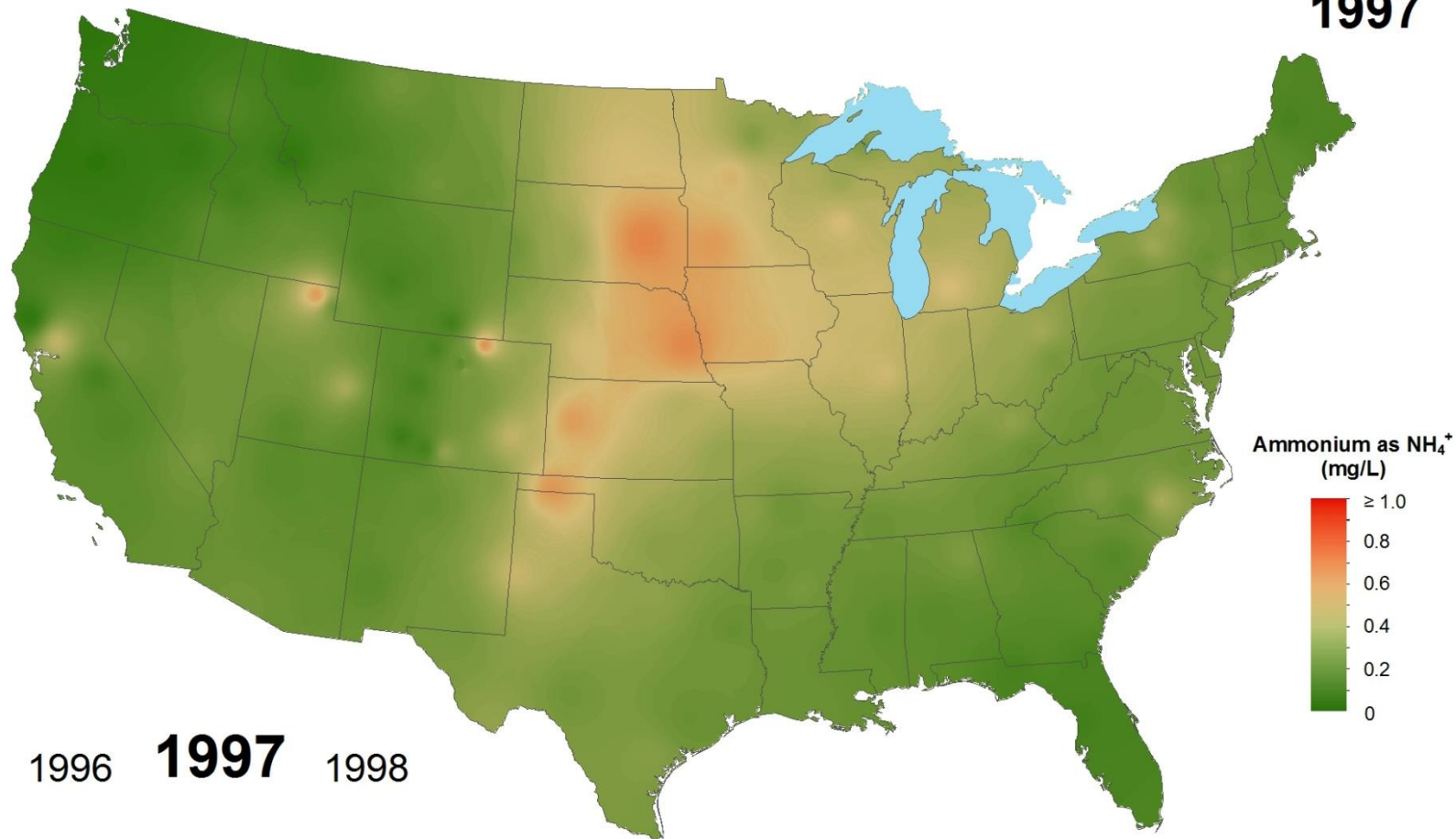
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# Ammonium ion concentration 1996



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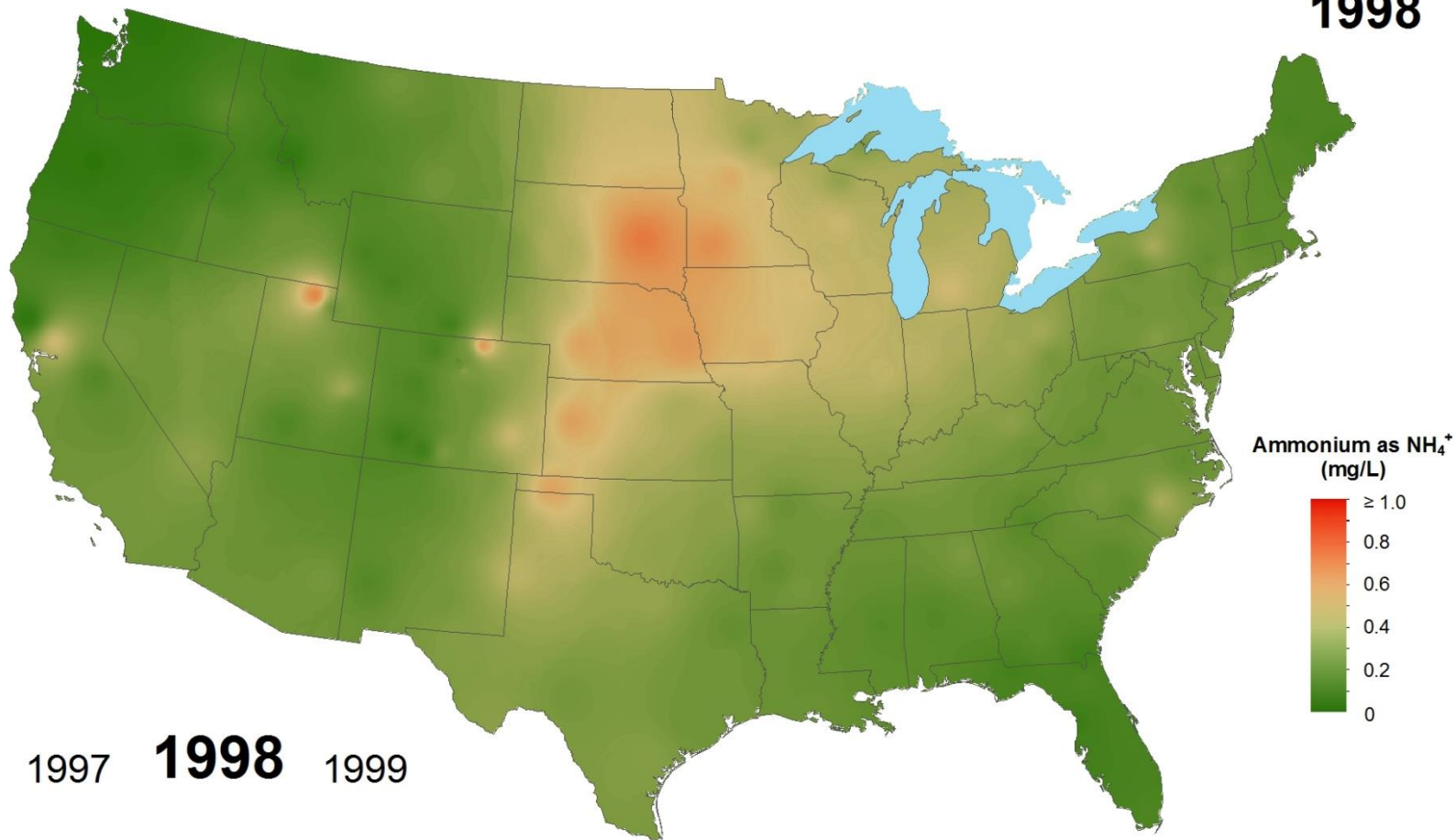
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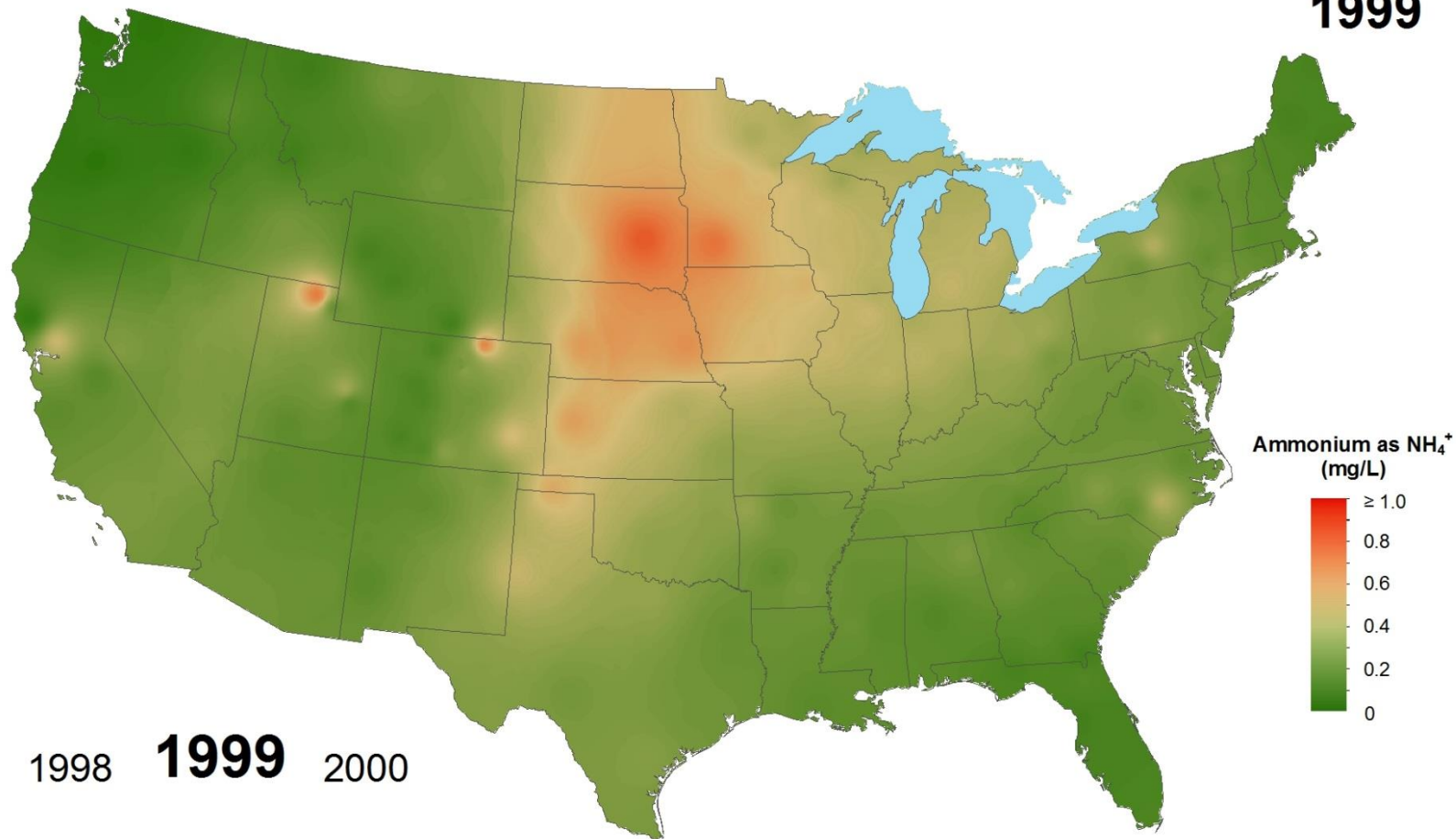


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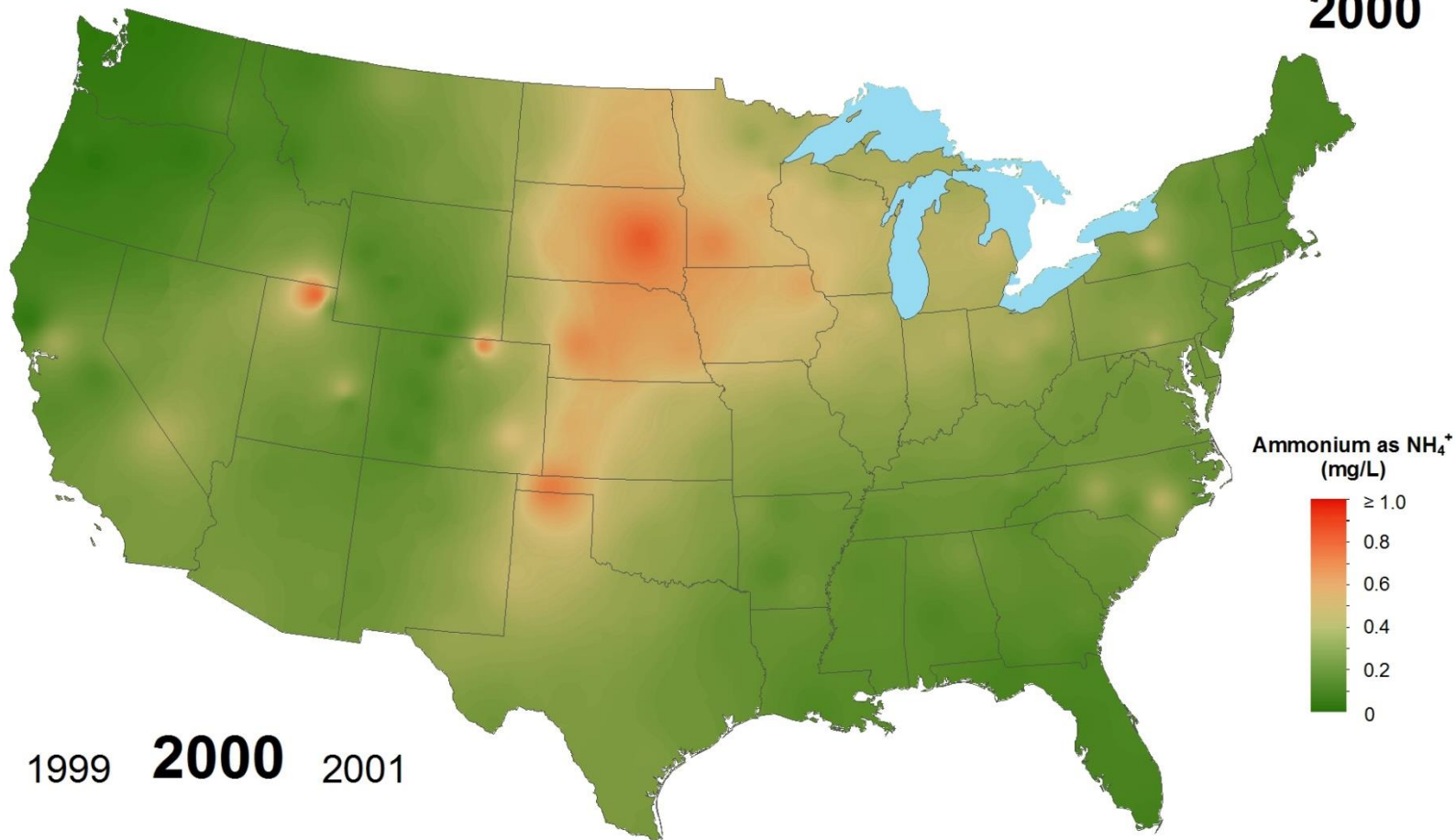
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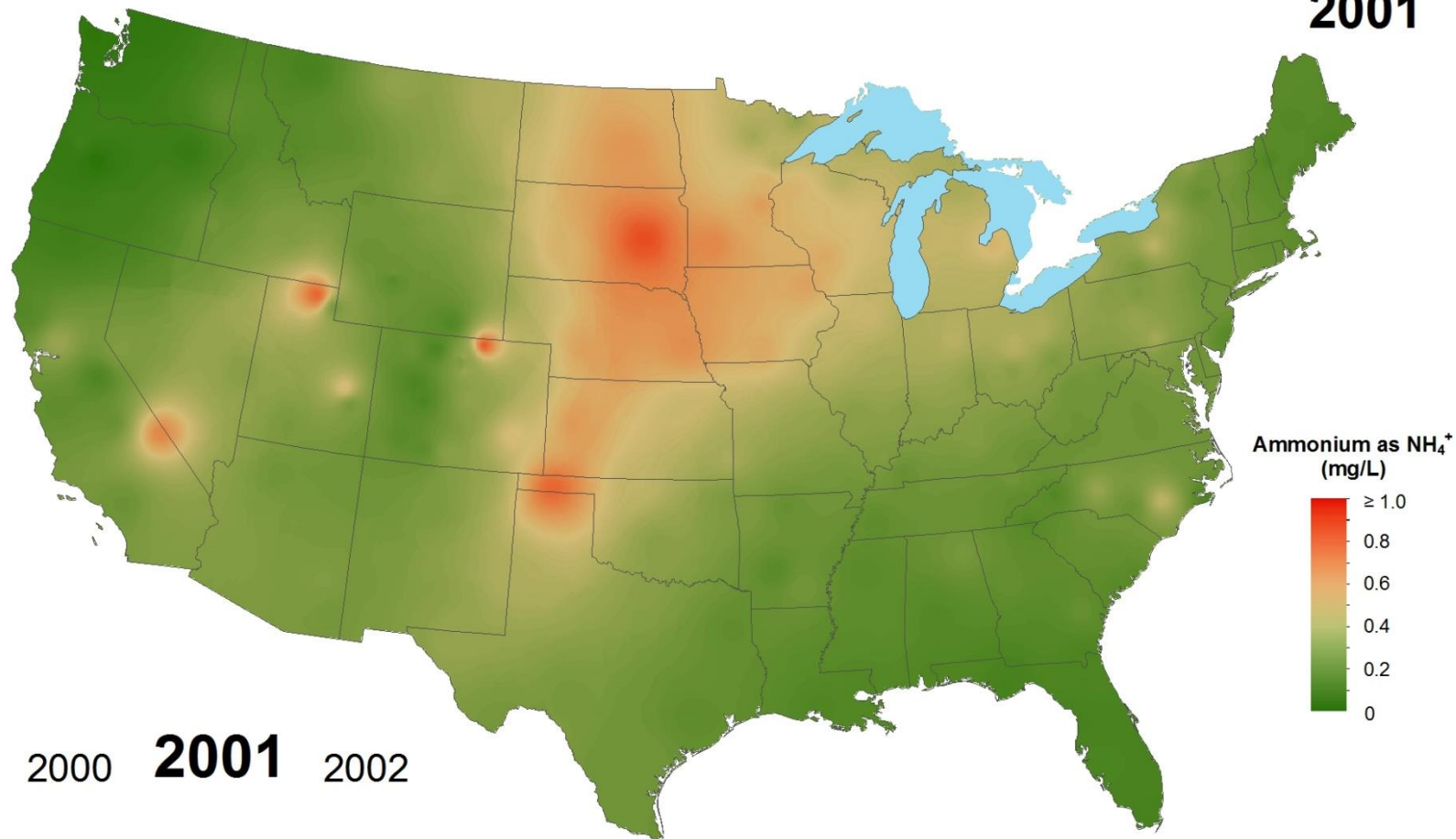
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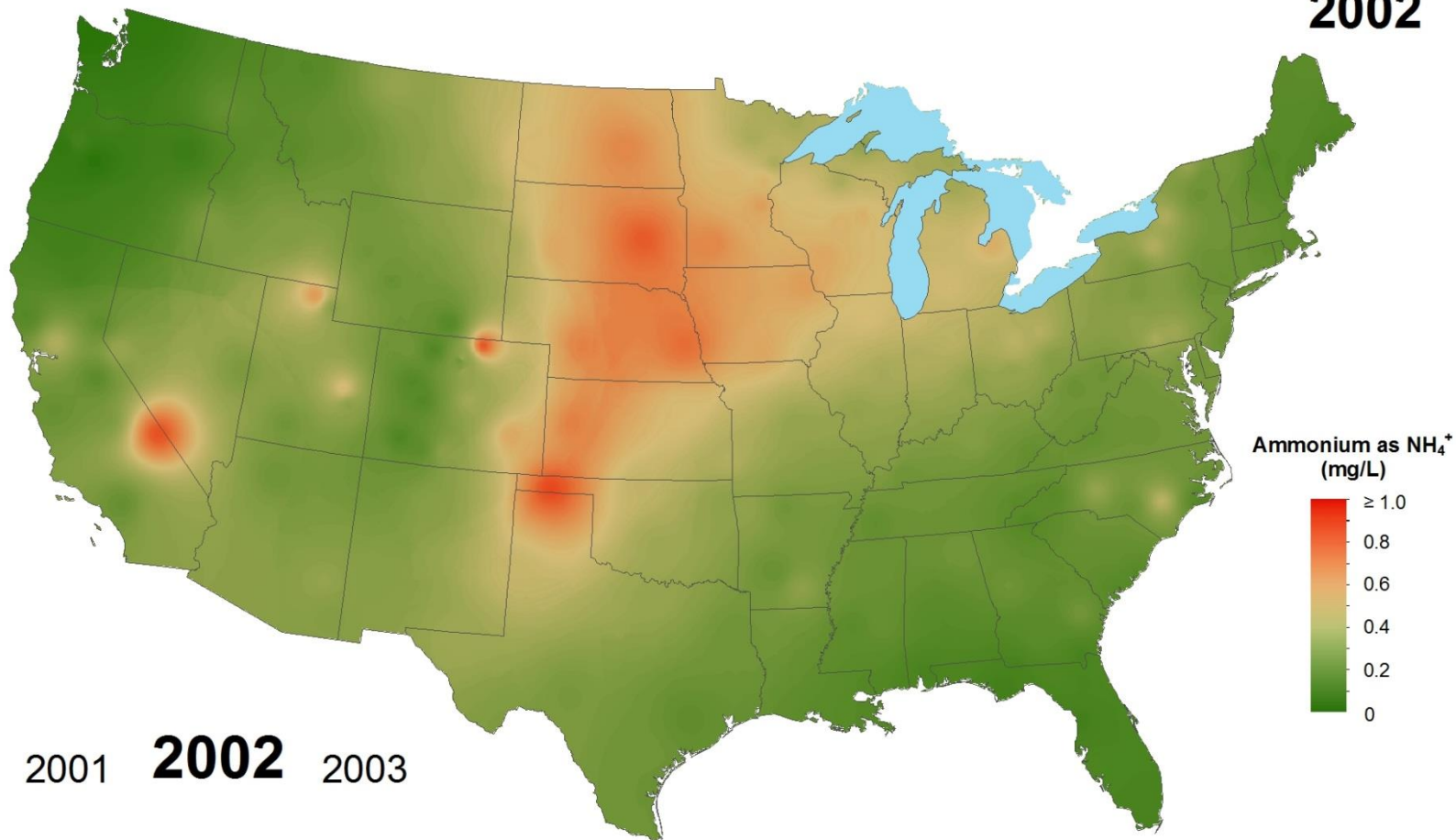
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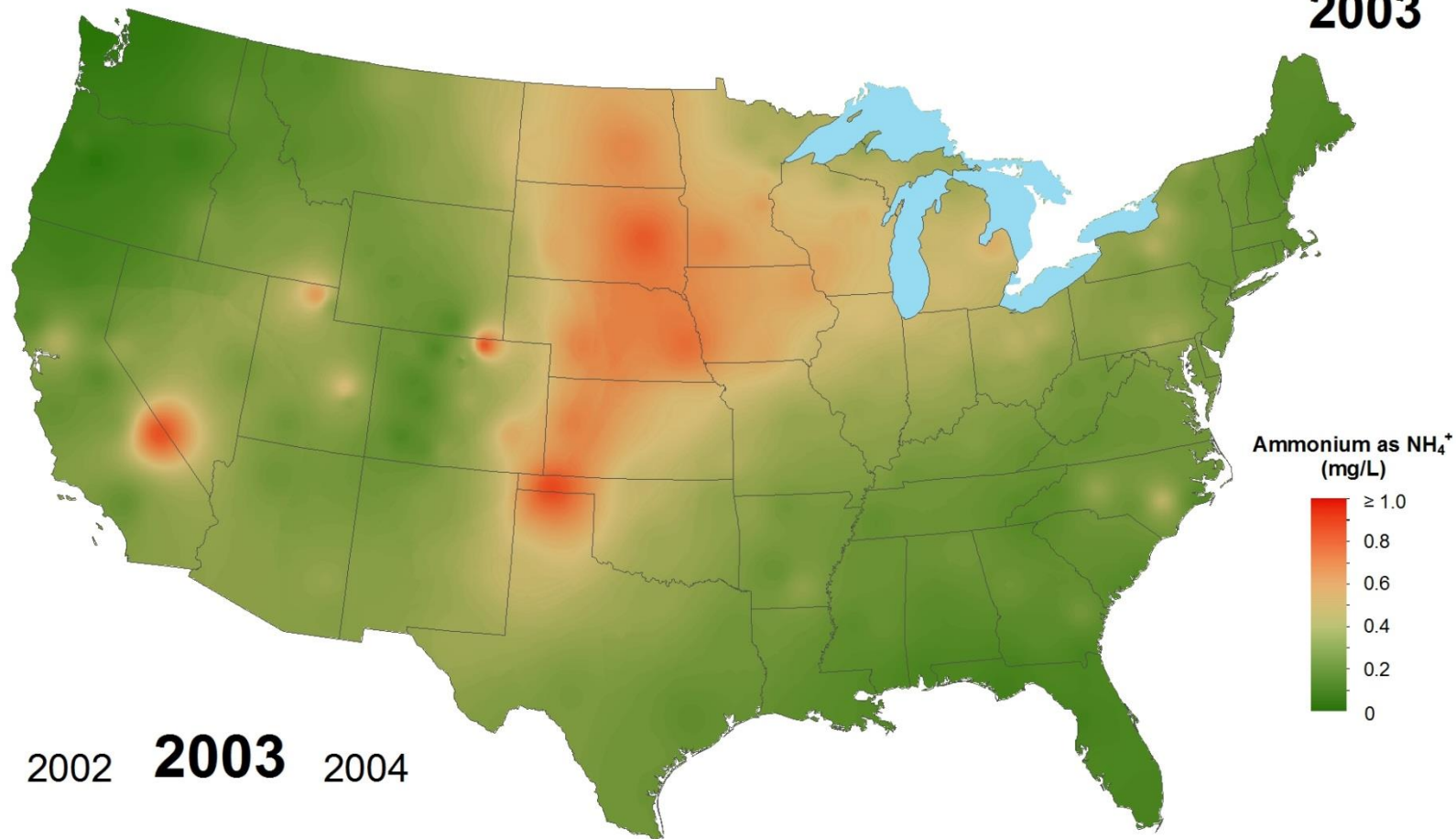
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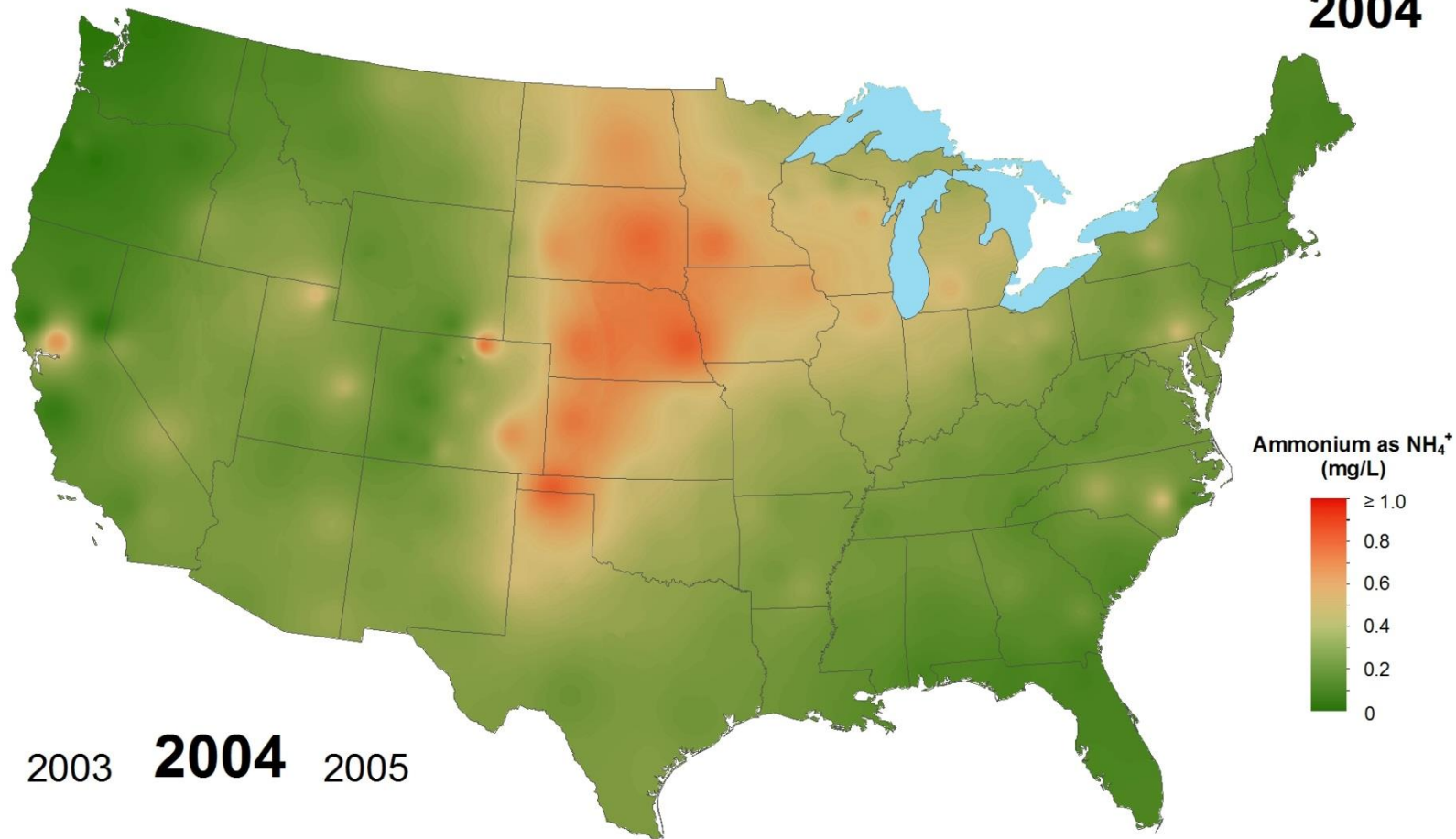
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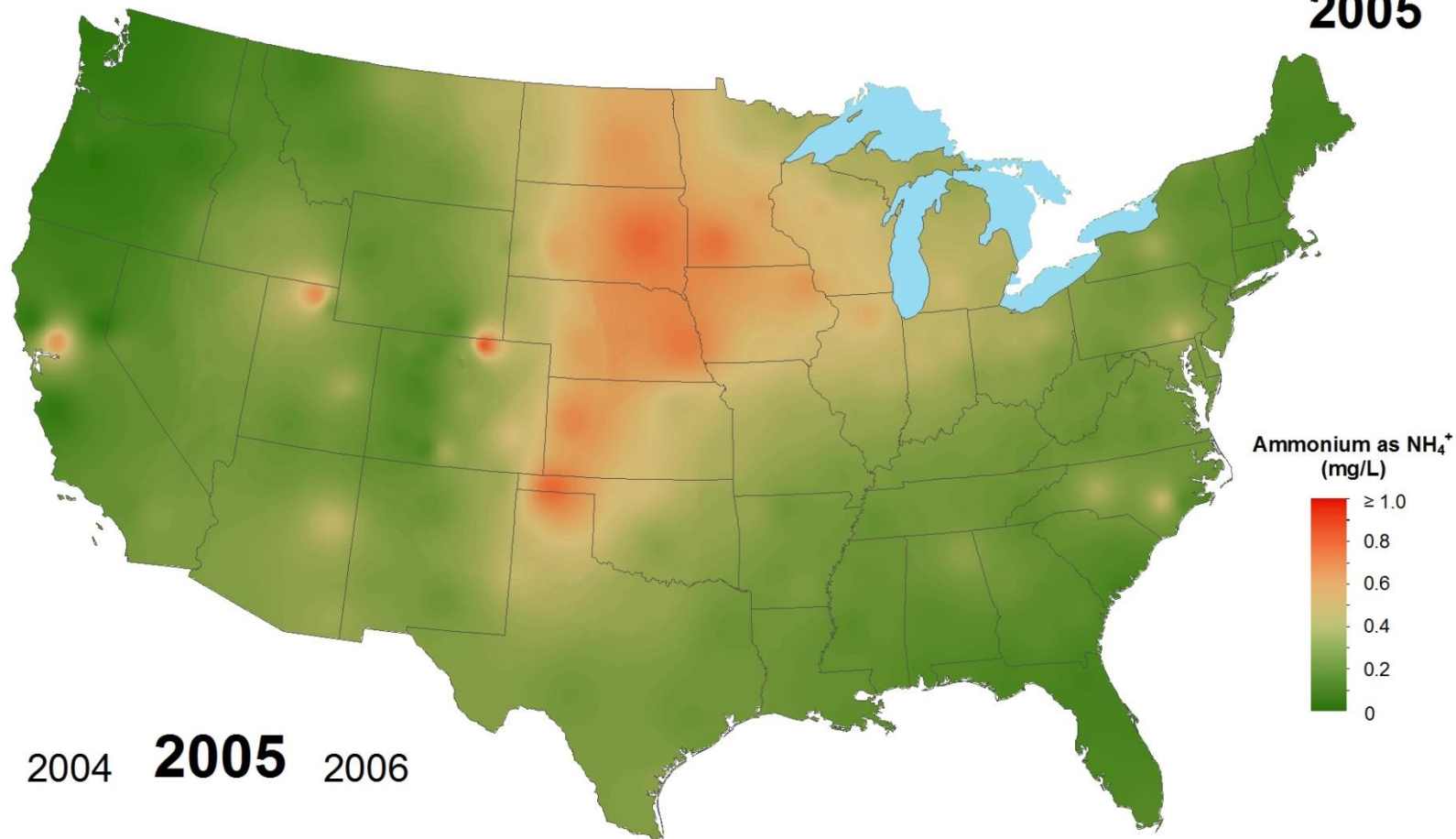
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National Atmospheric Deposition Program/National Trends Network  
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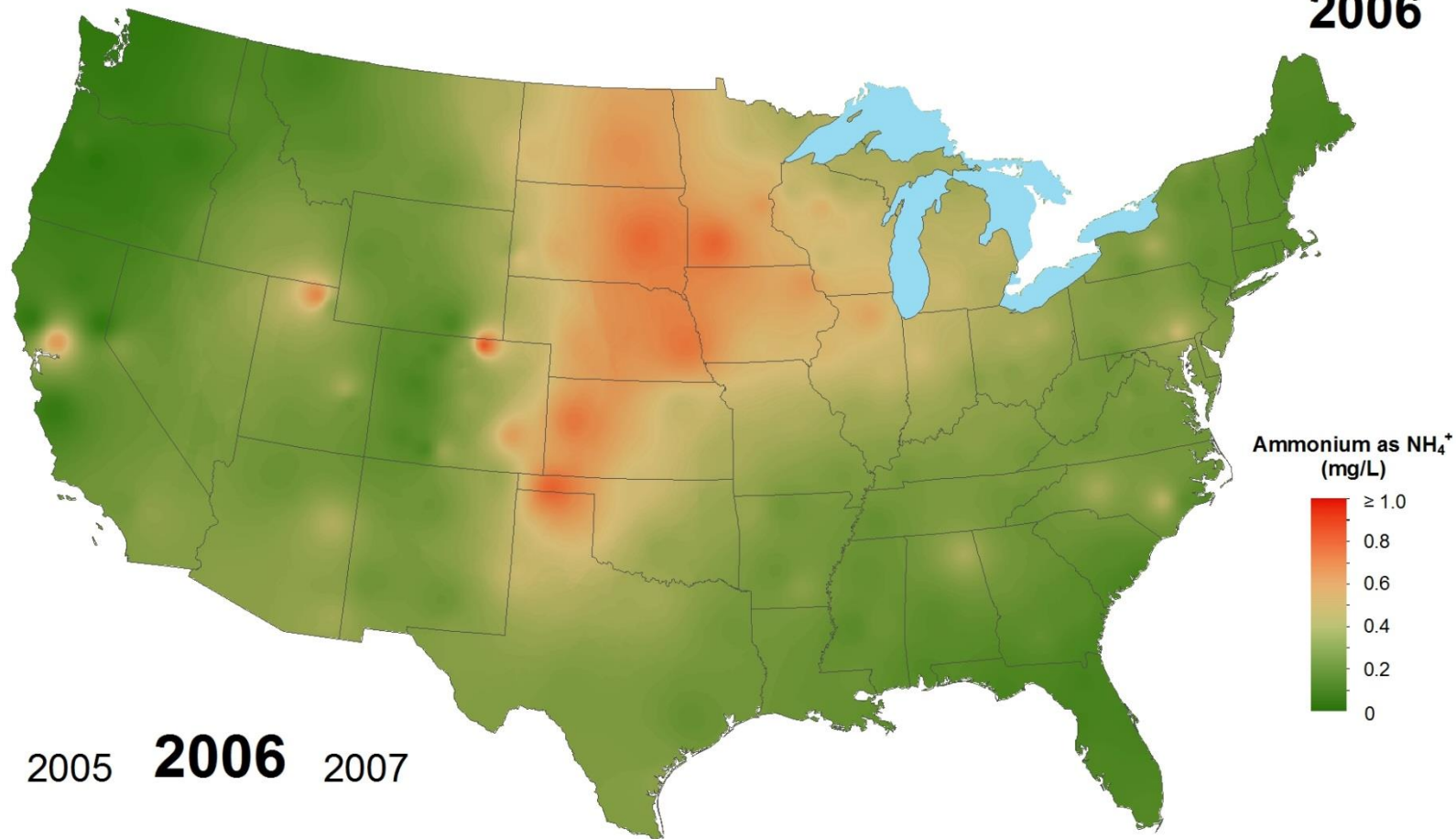
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National Atmospheric Deposition Program/National Trends Network  
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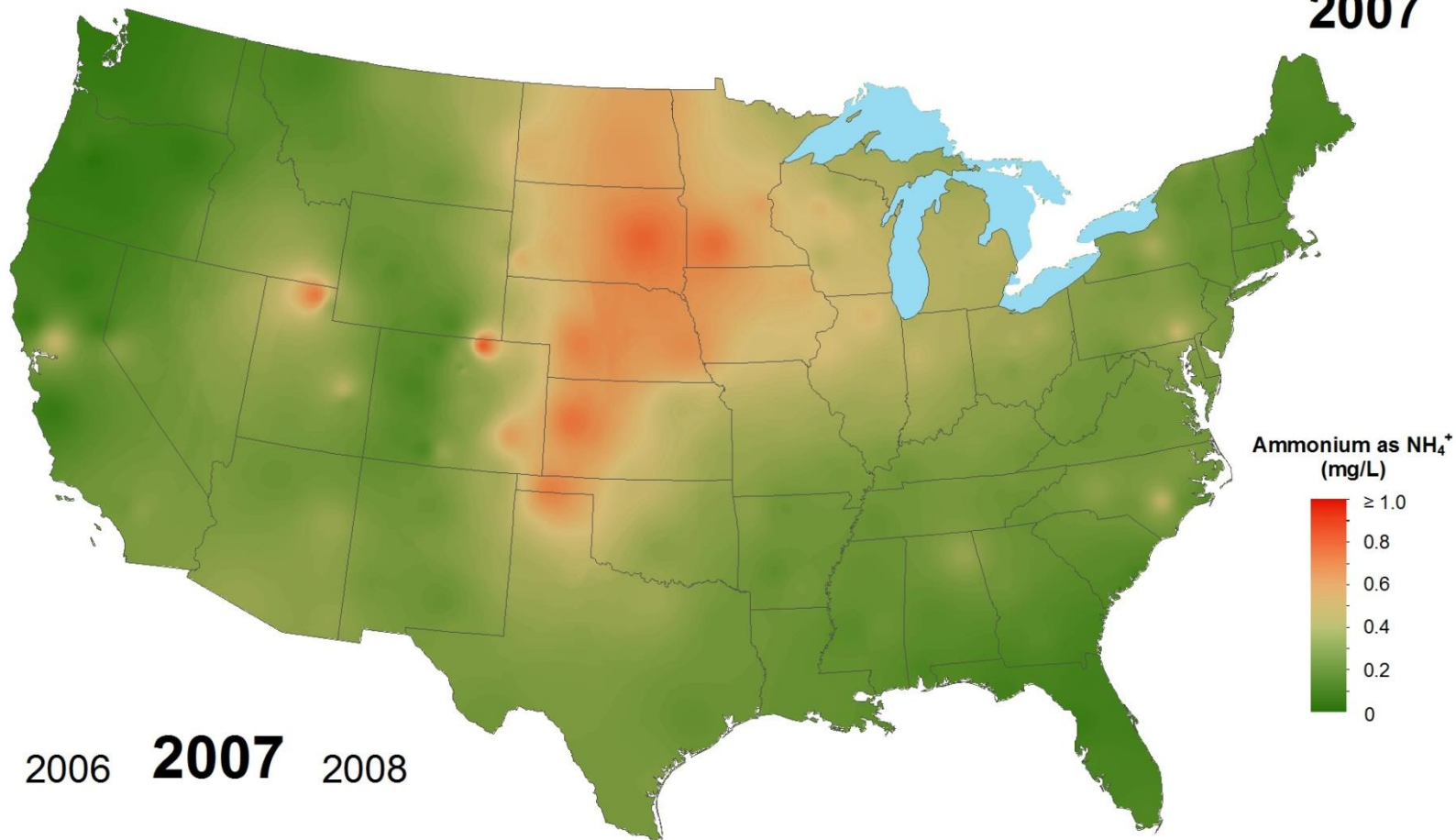


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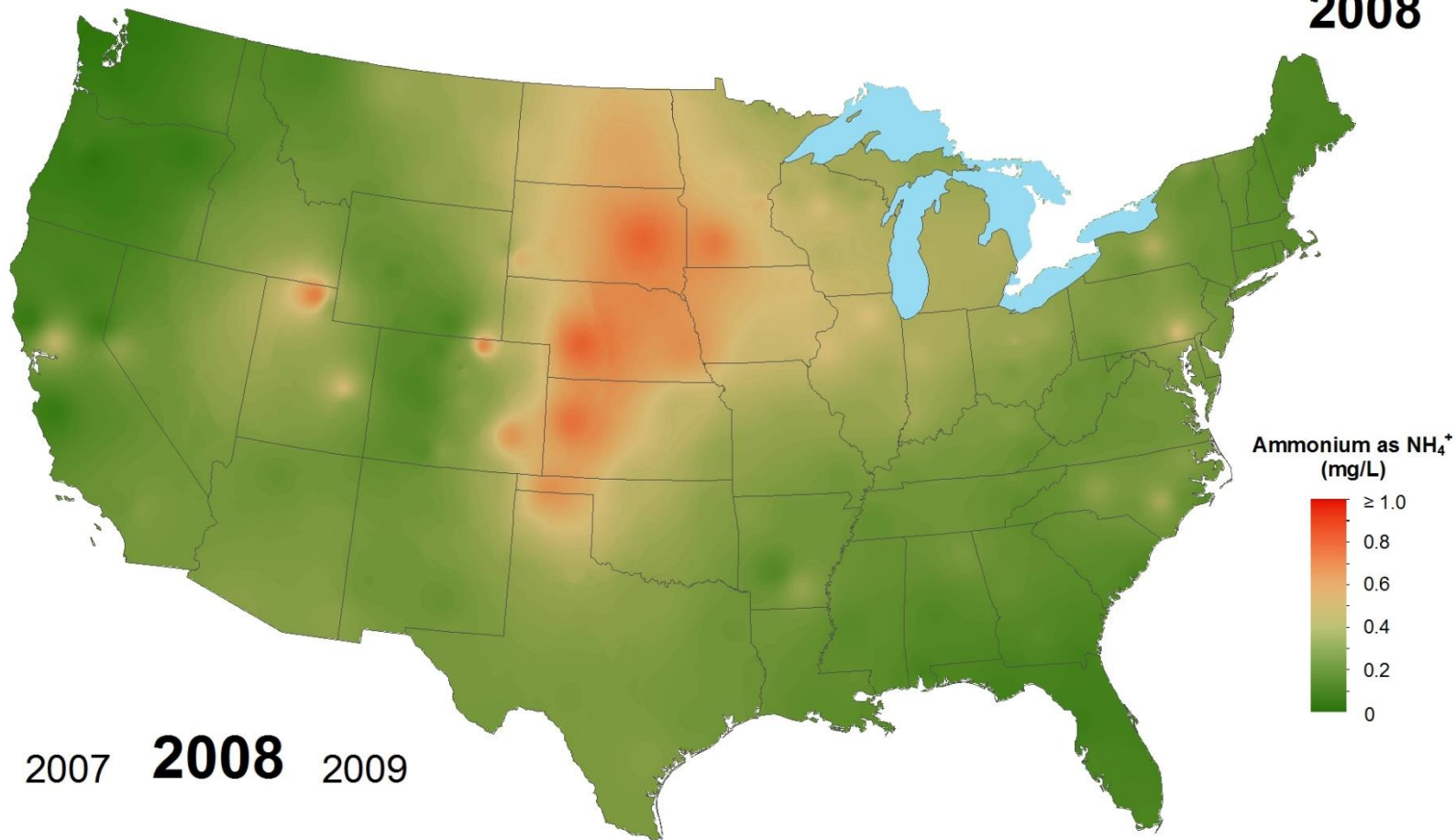
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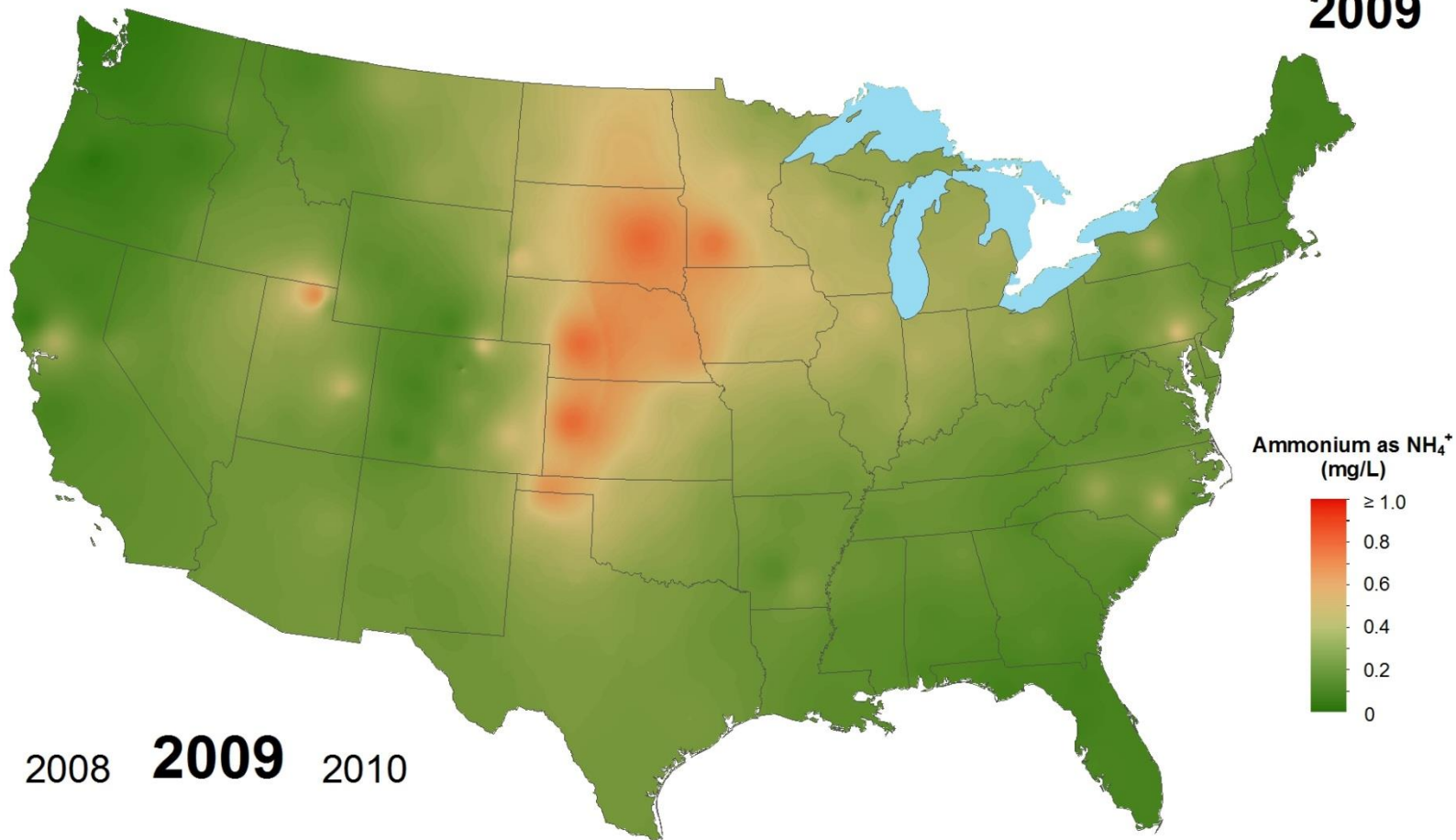
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# Ammonium ion concentration 2008



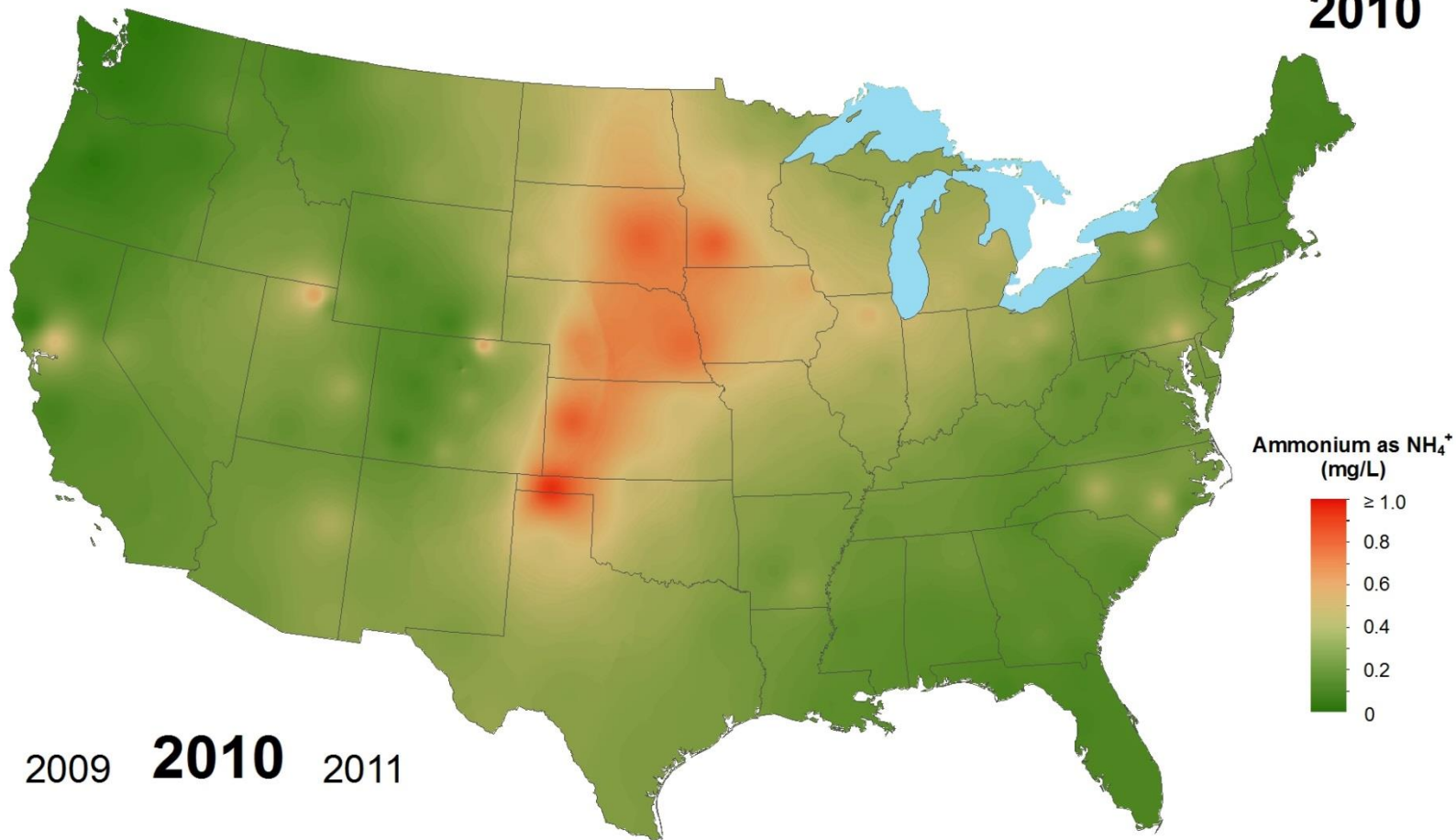
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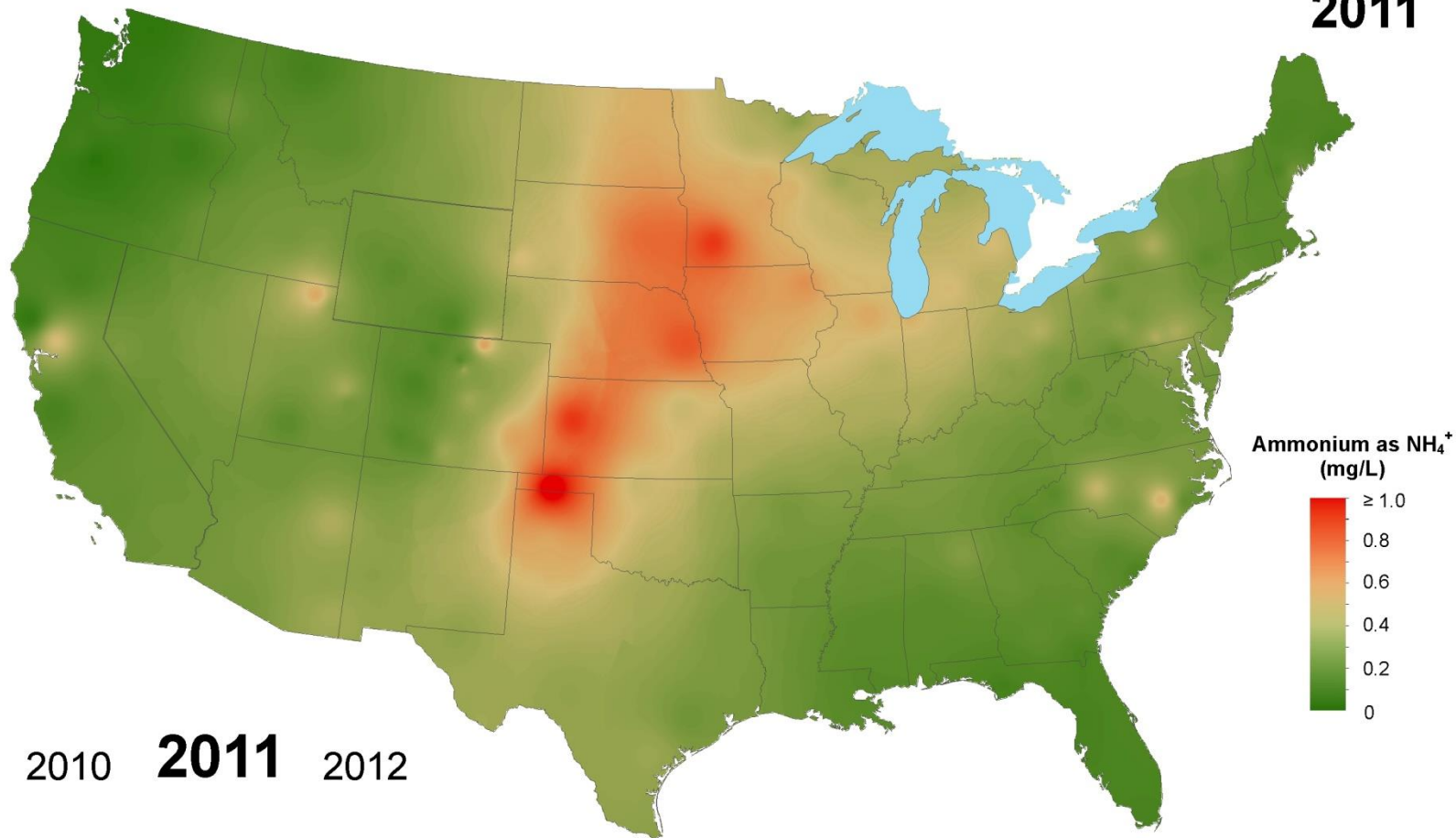
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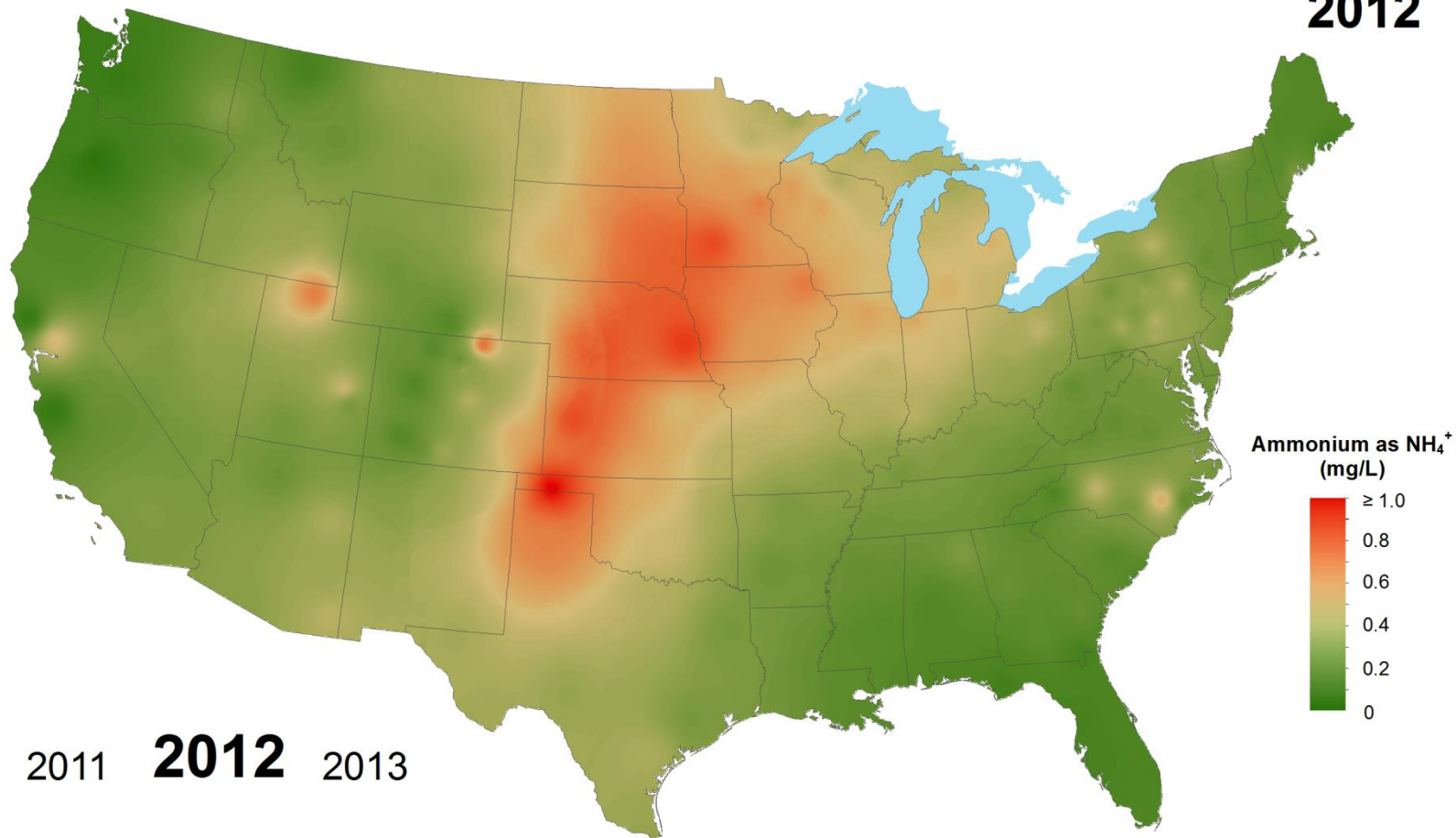
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# Ammonium ion concentration 2011



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# Ammonium ion concentration 2012



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## Types of Environmental Damage

- Focus today on plants and animals.
- First signs of acid-related damage came as "fish kills" in Scandinavian lakes.
- Many regions show forest deaths (Germany, NE US), but hard to separate conclusively from other pollutant causes.





## Trees and other plants

### Affected in two ways:

- Direct (primary) deposition – burning of leaves, etc.
- Secondary effects – related to reactions in soil and forest litter; alters nutrients

### Possible Mechanisms

1. Reacts with minerals to leach out some metals, such as Al, which can be toxic to plants.
2. Changes nutrients available to plants
3. Affects decomposition of humus and subsequent organic material
4. Otherwise disturbs plant physiology

## Aquatic Life

- Acid or acid-created byproduct arrives by direct deposition or via runoff
- pH changes in many lakes have been observed
- Fish are very sensitive to acidity, particularly in the egg and larval stages.
- Some fish lose reproductive capacities under acidic conditions (salmon, trout at pH < 5.5; most others at pH < 4.2; "dead lakes" at pH ~ 3.5)
- Mountain lakes and rivers often have seasonally-varying losses due to melting of acidic snows in the spring – gives rise to a "burst" of highly acidic water.

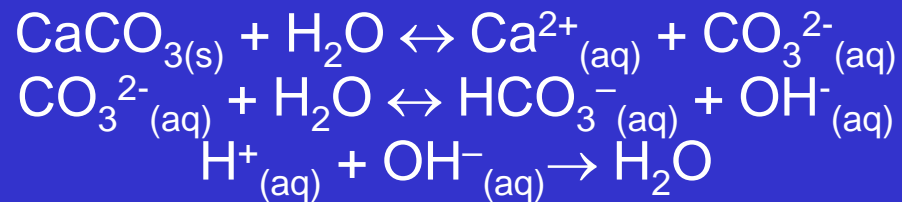
# Susceptibility to acidity

|             | pH 6.5 | pH 6.0 | pH 5.5 | pH 5.0 | pH 4.5 | pH 4.0 |
|-------------|--------|--------|--------|--------|--------|--------|
| TROUT       | ✓      | ✓      | ✓      | ✓      |        |        |
| BASS        | ✓      | ✓      | ✓      |        |        |        |
| PERCH       | ✓      | ✓      | ✓      | ✓      | ✓      |        |
| FROGS       | ✓      | ✓      | ✓      | ✓      | ✓      | ✓      |
| SALAMANDERS | ✓      | ✓      | ✓      | ✓      |        |        |
| CLAMS       | ✓      | ✓      |        |        |        |        |
| CRAYFISH    | ✓      | ✓      | ✓      |        |        |        |
| SNAILS      | ✓      | ✓      |        |        |        |        |
| MAYFLY      | ✓      | ✓      | ✓      |        |        |        |

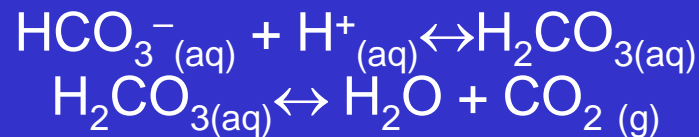
# The Role of Soils

## What is a buffer?

Something that acts to mitigate the effects on pH of acid or base addition  
In the laboratory, usually a solution of a weak acid and its conjugate base (or vice versa). In natural systems, the buffering capacity comes from minerals in the soils, to varying degrees. Of particular importance are carbonates ( $\text{CO}_3^{2-}$ ), such as limestone ( $\text{CaCO}_3$ ).



If enough  $\text{H}^+$  is added,  $\text{CO}_2$  can be released:

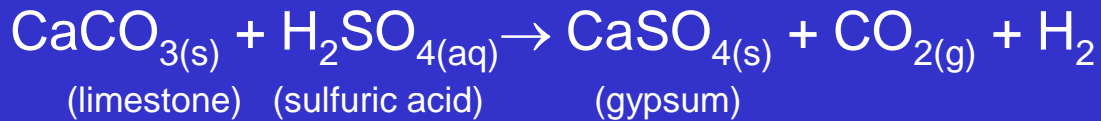
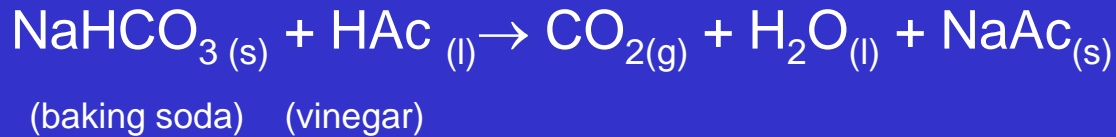


This set of reactions can effectively buffer pH's from the mid-5's to about 8.3. At lower pH's other mineral systems are involved – silicates, aluminum ions, iron ions.

# Effects on Structures

## Stonework and statuary

- Many buildings and monuments are made of limestone ( $\text{CaCO}_3$ ) or marble, which is the metamorphic version of limestone.
- Add acidic precipitation. Result? Similar to the kid's volcano made of baking soda and vinegar



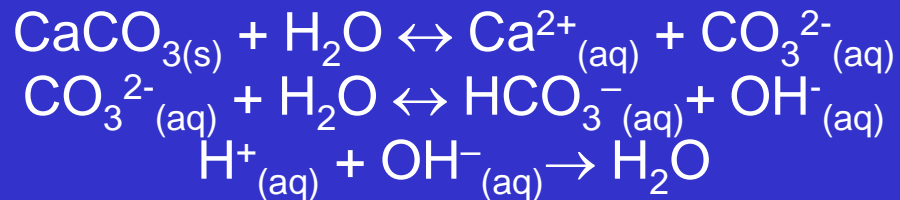
- Gypsum is the mineral used to make dry-wall materials and plasters; it is a white powdery substance.
- These chemical processes cause degradation of statues, building facades, gravestones, etc. Average rate of degradation for marble is about  $10 \mu\text{m}/\text{m}$  rainfall.

## Other Materials

- Metals: Zinc, copper and steel all susceptible to dissolution by acids, mainly by sulfuric acid.
- Paints: Easily etched by acids; car finishes especially vulnerable

## Strategies for Remediation

- Reducing emissions that lead to acid precipitation
- Use low-sulfur fuels in sensitive areas
- Remove sulfur from high-sulfur fuels before burning them
- "Scrub" the emissions from fuel-burning plants
- Disperse emissions using higher smokestacks
- Develop alternative energy sources
- Site power plants to minimize local impact
- Try to counteract effects of acidification by adding limestone to bodies of water



## Note

There are other species that are acidic. We will see next that when methane oxidizes, short-lived (~hours to days) intermediates form. These compounds are often acidic (as oxygen atoms are added to the chain), the molecules become more soluble in water. In the presence of wet particles they will partition into the aqueous phase. This changes the oxidation process, shifting the role of oxidant from gas-phase OH to strong acid species (like  $\text{SO}_4^-$  or  $\text{NO}_3^-$ ) that are found in particles)