

BAE 820 Physical Principles of Environmental Systems

Combustion smoke Fundamentals

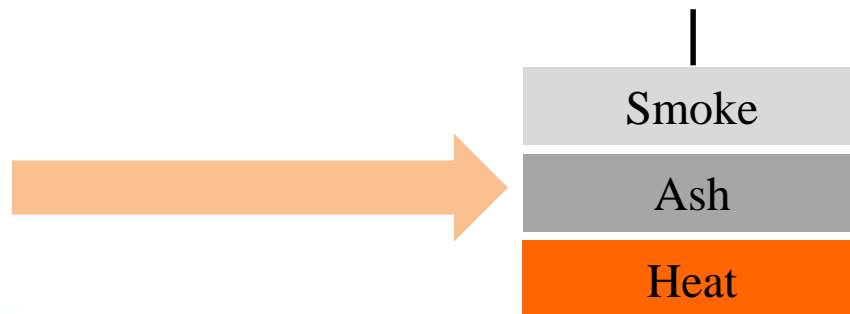
Dr. Zifei Liu

Combustion and smoke

- Combustion (fire) is the first controlled chemical reaction discovered by humans, and is widely used
 - to produce energy.
 - to destroy (incinerate) waste.
- It is a high-temperature chemical reaction between a fuel and an oxidant.
 - It releases heat (exothermic).
 - It produces smoke and ash.

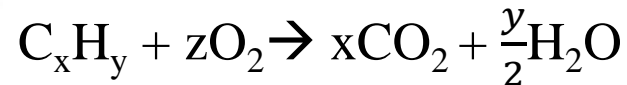


A complex mixture of oxidized products including gases and particles



Stoichiometric combustion

- Stoichiometry is the calculation of relative quantities of reactants and products in chemical reactions. In stoichiometric combustion, there is no remaining fuel and no remaining oxidant.
- Complete combustion is stoichiometric, and it produces primarily the most common oxides (maximum degree of oxidation).
 - E.g. Carbon will yield CO₂, sulfur will yield SO₂.
- A simple chemical equation for combustion of a hydrocarbon in O₂ is



For stoichiometric combustion, $z = x + \frac{1}{4}y$.

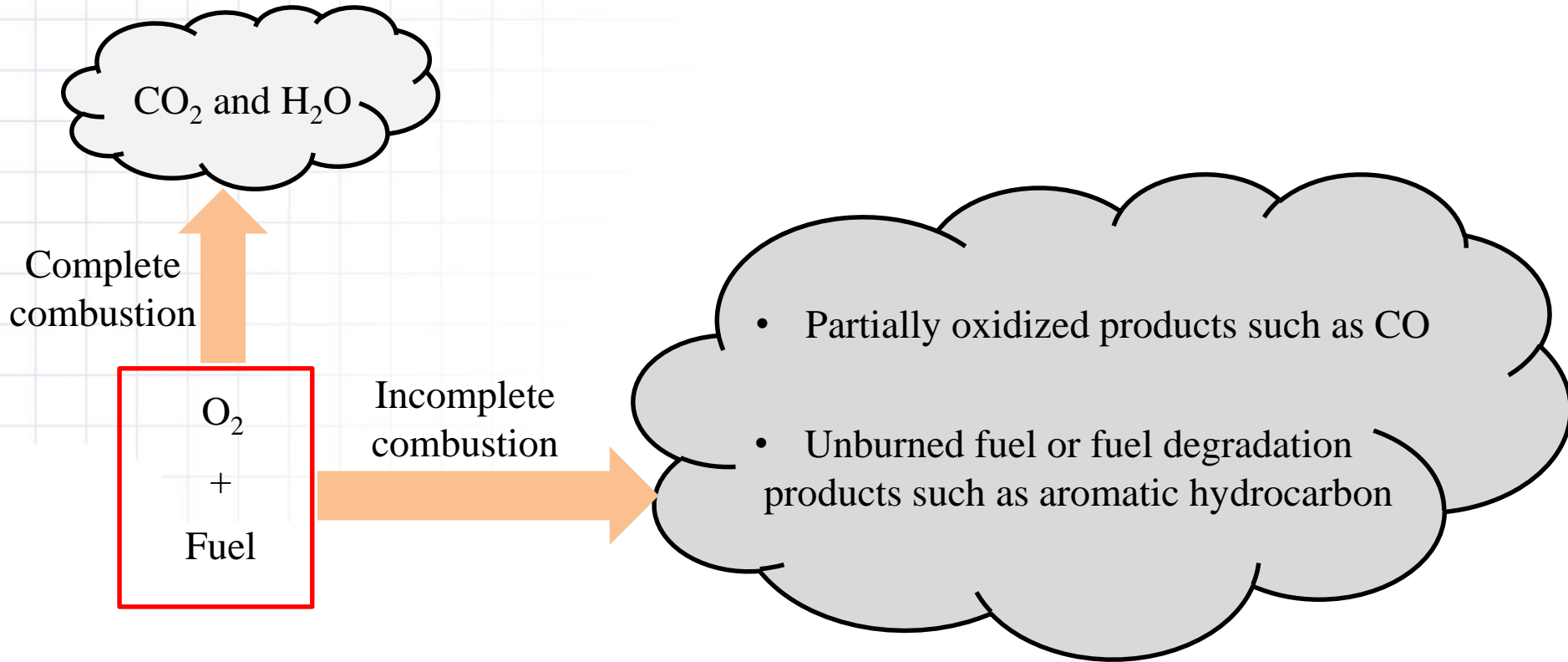
In the above equation, when z falls below roughly 50% of the stoichiometric value, CH₄ can become an important combustion product; when z falls below roughly 35% of the stoichiometric value, elemental carbon may become stable.

Incomplete combustion

In reality,

- Combustion typically involve hundreds of chemical species reacting according to thousands of reactions. It is a chain reaction in which many distinct radical intermediates participate.
 - For any C-H-O system, combustion products mainly include CO_2 and H_2O and their dissociated products, including CO , H_2 , O_2 , OH , H , O , O_3 , C , CH_4 . For a C-H-O-N system, N_2 , N , NO , NH_3 , and NO^+ could be added.
 - Any combustion at high temperatures in atmospheric air, which is 78% N_2 , will also create small amounts of NO_x .
 - It is not necessarily favorable to the maximum degree of oxidation, and it can be temperature-dependent.
- Complete combustion is almost impossible to achieve.
 - In a typical fire, substantial temperature and concentration gradient exist in the buoyancy-induced turbulent flow. Incomplete combustion will occur when there is no enough O_2 or when there is a heat sink causing low temperature.
 - Incomplete combustion results in unburnt or partially oxidized compounds.

Smoke is mainly a product of incomplete combustion



Smoke compounds depend on both the fuel properties (especially the elemental composition) and the combustion conditions.

Air-to-fuel ratio

- Air–fuel ratio is the mass ratio of air to fuel present in a combustion process. If exactly enough air is provided to completely burn all of the fuel, the ratio is known as the stoichiometric ratio. Different hydrocarbon fuels have a different contents of carbon, hydrogen and other elements, thus their stoichiometry varies.

Stoichiometric air-to-fuel ratios of common fuels

Fuel	Ratio by mass
Gasoline	14.7 : 1
Diesel	14.5 : 1
Natural gas	17.2 : 1
Propane (LP)	15.67 : 1
Ethanol	9 : 1
Hydrogen	34.3 : 1

Fuel-air equivalence ratio

- Fuel-air equivalence ratio Φ is defined as

$$\Phi = \frac{\text{actual fuel to air ratio}}{\text{stoichiometric fuel to air ratio}}$$

Typical CO/CO₂
ratio (v/v)

$\Phi < 1$	Well-ventilated flames	<0.05
$\Phi = 1$	Stoichiometric flames	~0.05
$\Phi > 1$	Under-ventilated flames	0.2-0.4

ISO classification of fire stages

Fire stages	Smoke Temp (°C)	Fuel-air equivalence ratio	Typical CO/CO ₂ ratio (v/v)	Combustion efficiency (%)
1. Non-flaming				
1a. Self-sustained smouldering	25-85	-	0.1-1	50-90
1b. External radiation (pyrolysis)	-	-	-	-
2. Well-ventilated flaming	50-500	<1	<0.05	>95
3. Under-ventilated flaming (post-flashover)	>600	>1	0.1-0.4	70-90

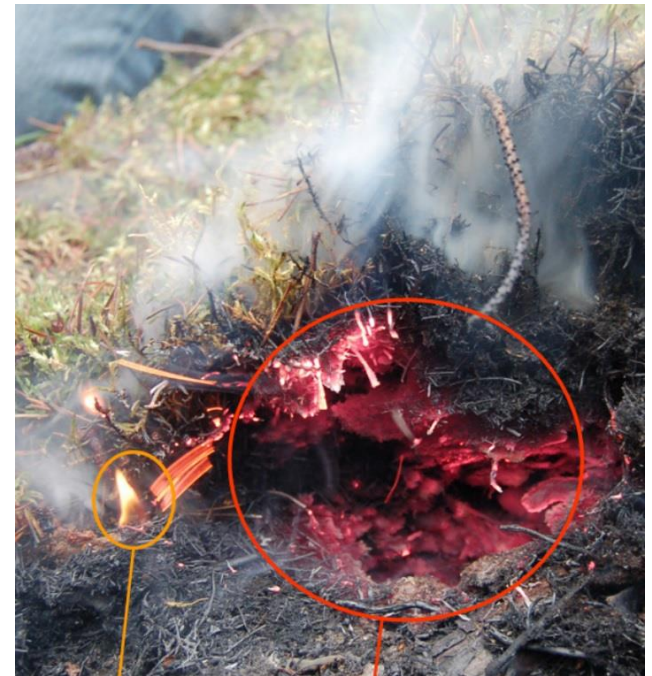
(Adapted from ISO 19706 and fire toxicity)

- Combustion of solid fuels first need to undergo pyrolysis (chemical decomposition) to produce more easily oxidized gaseous fuels, and then they volatilize from the surface and enter the flame.
- Self-sustained smouldering can only occur to porous material. Smouldering of biomass can exist after flaming has ceased for days or weeks.

Smouldering

- Smouldering is the slow, low-temperature, flameless form of combustion, sustained by the heat evolved when oxygen directly attacks the surface of a condensed-phase fuel.
 - A typically incomplete combustion.
 - Low temperature.
 - A surface phenomenon (occurs on the surface of solid rather than in gas phase).
 - Slow but persistent (about ten times slower than flames spread over a solid).
 - A significant fire hazard.
 - Emits much more toxic smoke than flaming fires.
- A burning cigarette is a familiar example of smoldering combustion.

Many solid materials can sustain a smouldering reaction, including cellulose and wood.

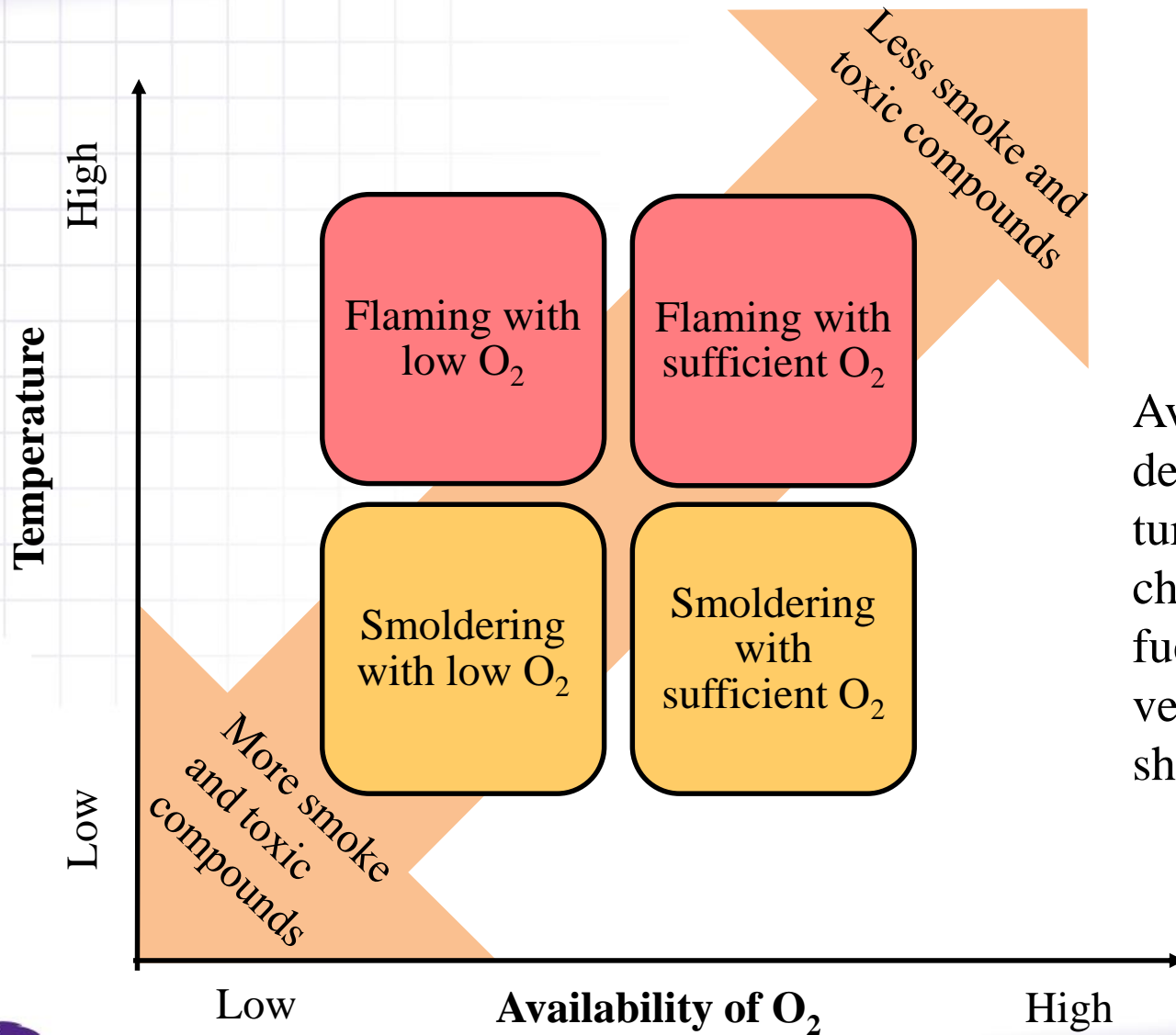


Flaming

Smouldering

(Photo credit: Rein, 2009)

Smoke and combustion conditions



Availability of O_2 depends on wind, turbulence, and characteristics of the fuel, such as vegetation density, shape, and structure.

Combustion temperature

Fuel properties

- The heating value and the specific heat capacity.
- Moisture content: water vaporization lowers temperature.

Air and fuel temperature

Combustion temperature

The equivalence ratio

- $\Phi < 1$, overoxidized, the excess O_2 must be heated to the product temperature and thus the temperature drops.
- $\Phi > 1$, underoxidized, no enough O_2 to burn fuel to the most oxidized state, so energy released is less and temperature drops as well.

Open vegetation fires

- In open vegetation fires, a moving fire front passes through a fuel bed, such as a grassland or forest. Different combustion conditions may occur simultaneously at different locations within the fire environment. Their proportions and the prevalent conditions vary over time, typically with more flaming in the earlier part of the fire and more smoldering during the latter part.



Not all smoke is equal

- Fuel characteristics
- Combustion conditions
 - Weather conditions
 - Fuel conditions
- **The overall mixture of combustion products is usually determined by the amount of smoldering combustion.**
- Nature thick fuel and organic soil prone to smouldering combustion. Natural thick fuels include stumps, snags, downed logs, large branches and roots. Organic soils include hummus, duff, peat, coal seams and others.

Effect of moisture content of vegetation fuel

Vegetation with lower moisture content burns faster, eventually causing O₂-limited conditions that also lead to increased smoke formation.

Smoke
production

An appreciable amount of energy is necessary to vaporize the water. Water vaporization lowers temperature, which favors smoldering and increased smoke formation.

Lower moisture
content

Higher moisture
content

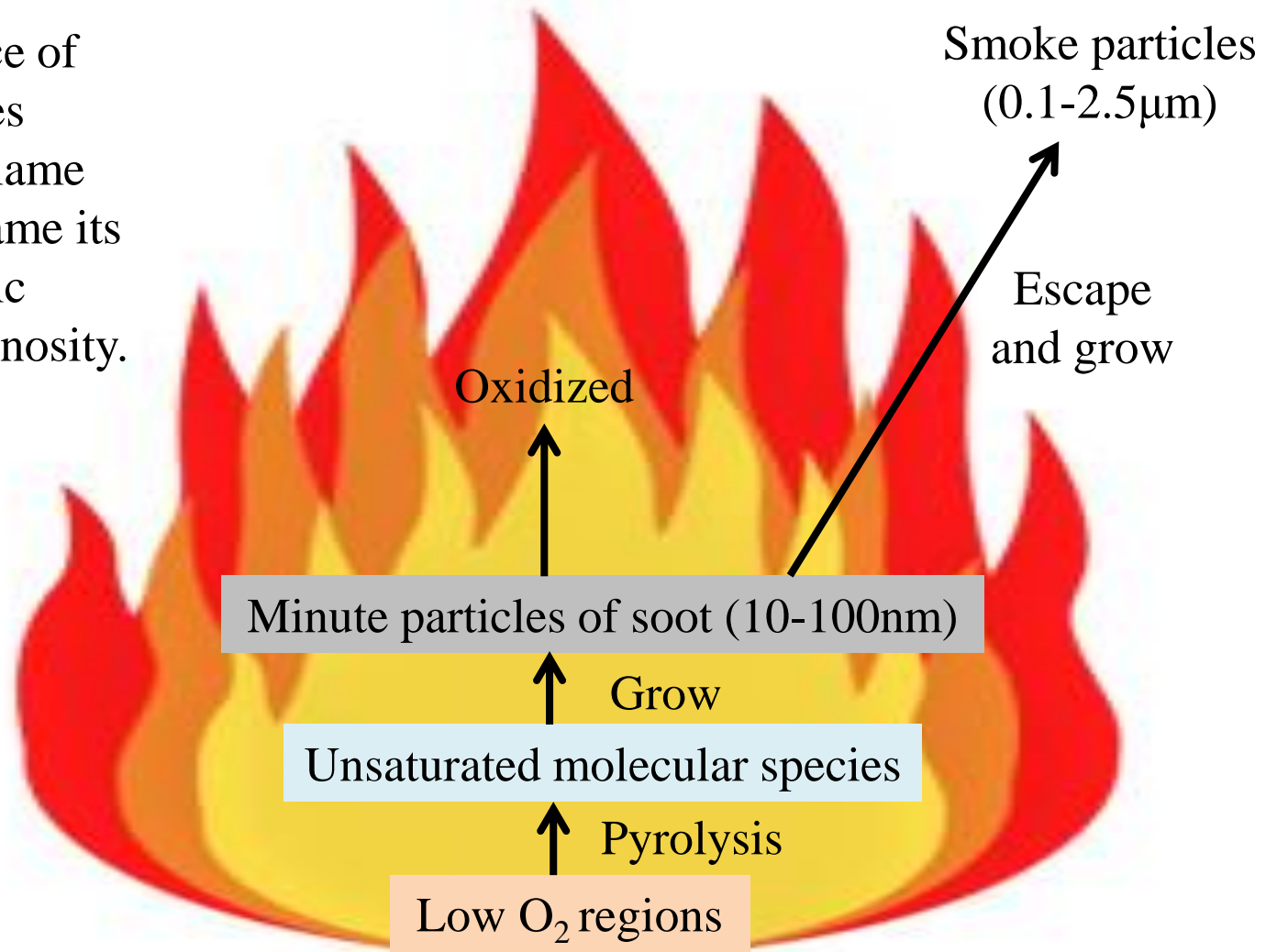
The optimal moisture content in terms of minimizing PM emissions is 20–30% for wood combustion.

Main components of vegetation fire smoke

Particulate matter	Complex mixtures of EC, OC and inorganic ash; 70–90% of PM is PM _{2.5}
VOCs	Acrolein, formaldehyde, isocyanic acid, ...
SVOCs	Polycyclic aromatic hydrocarbons (PAHs), ...
Permanent gases	CO ₂ , CO, CH ₄ , NO _x , ...
Water vapor	Reduce visibility
O ₃	Secondary product of NO _x , VOCs and CO

Generation of particulates in smoke

The presence of soot particles within the flame gives the flame its characteristic yellow luminosity.



Generation of particulates in smoke

PM is the solid or liquid component of smoke, which is highly visible and is the principal public health concern from smoke exposure.

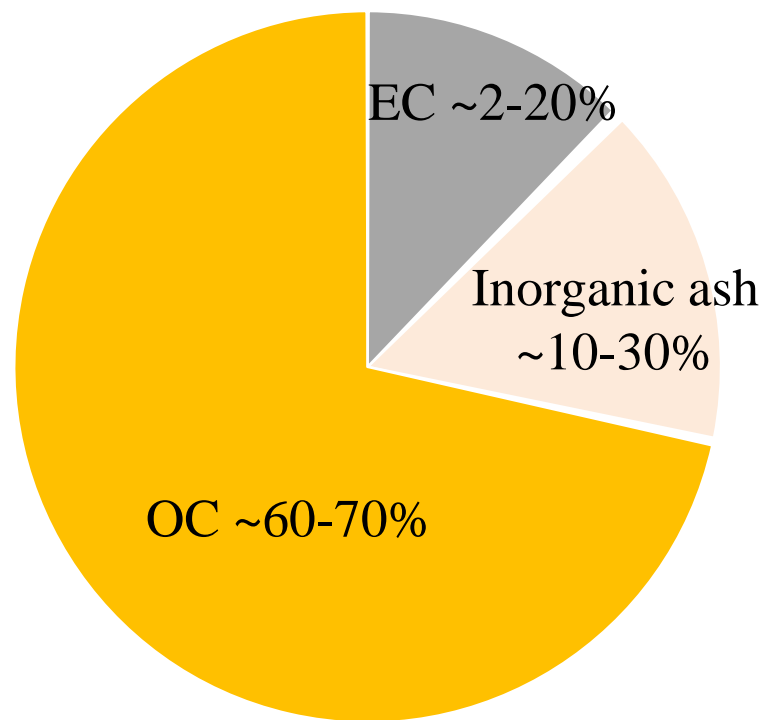


(Photo credit: S. O'Neill)

Particulate matter (PM) in smoke

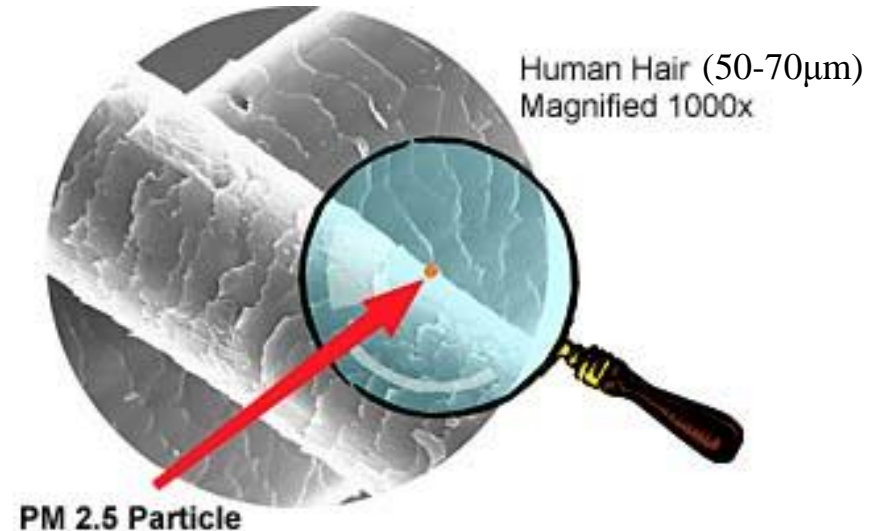
- Smoke PM acts as a vehicle to carry absorbed hazardous compounds into the respiratory tract. The adsorbed hazardous compounds may include VOCs such as formaldehyde and acrolein, SVOCs such as PAHs and dioxin, gases such as NO_2 , and toxic metal elements such as lead and mercury.
- PM from air in an urban area and that near a wildfire induced different inflammatory, oxidative stress, and xenobiotic responses in human bronchial epithelial cells.

Composition of smoke PM



Size of smoke PM

- ~90% of PM in biomass smoke is PM₁₀
~70–90 % of PM is PM_{2.5}
- Particles of this size range are not easily removed by gravitational settling and therefore can be transported over long distances.
- The depth of particle penetration into the lungs and the likelihood of them being exhaled depend on their size. Coarse particles affect nasopharyngeal region, whereas fine particles can penetrate the large airways of the trachea, bronchi, and bronchioles, and even reach the alveoli.
- Smoke PM has a size range near the wavelength of visible light (0.4–0.7 μ m) and therefore can efficiently scatter light and reduce visibility.



Volatile organic compounds (VOCs)

- Organic irritants
 - Aldehydes:
 - Combustion of cellulose-based material such as wood has been demonstrated to evolve significant quantities of formaldehyde and acrolein.
 - Isocyanic acid:
 - Recently identified in outdoor air under the influence of wild fires, a potentially toxic compound found in both cigarette smoke and vegetation fire smoke.
- Precursor of O₃

Semi-volatile organic compounds (SVOCs)

- Complex molecules such as polycyclic aromatic hydrocarbons (PAHs).
 - Benzo(a)pyrene (BaP), naphthalene, and anthracene, ...
 - Specific species varies with composition of vegetation.
 - Condense or adsorbed onto fine particles or as volatiles in the vapor phase.
 - Carcinogenic and mutagenic.
- PAHs emissions were more strongly influenced by burning conditions than by the type of fuel
 - For low-intensity backing fires, the ratio of BaP to PM is higher by almost 2 orders of magnitude over that for heading fires

Permanent gases

- CO_2 , CH_4
 - Greenhouse gases
- CO
 - Toxic
- NO_x (NO and NO_2)
 - Due to the low combustion temperatures in vegetation fires, the nitrogen species emissions are mainly based only on fuel nitrogen.
 - Precursor of O_3

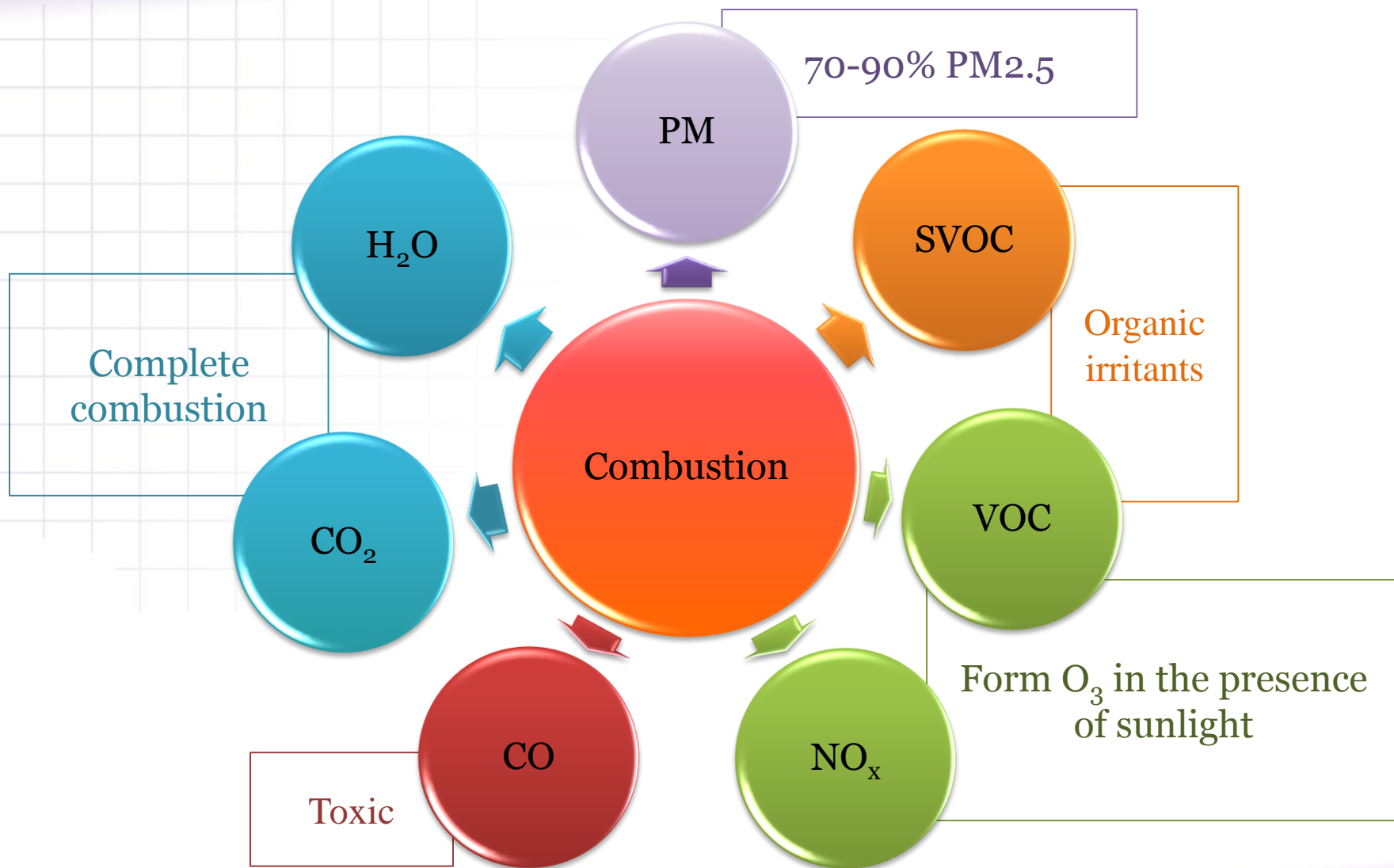
Secondary products of the smoke plume

- Secondary products can be produced in the smoke plume through photochemical reactions under solar radiation.
- The production of O_3 occurs either in the original plume or as a result of the smoke plume interacting with existing pollutants in the atmosphere.
- Precursors in smoke: VOCs, NO_x , and CO.

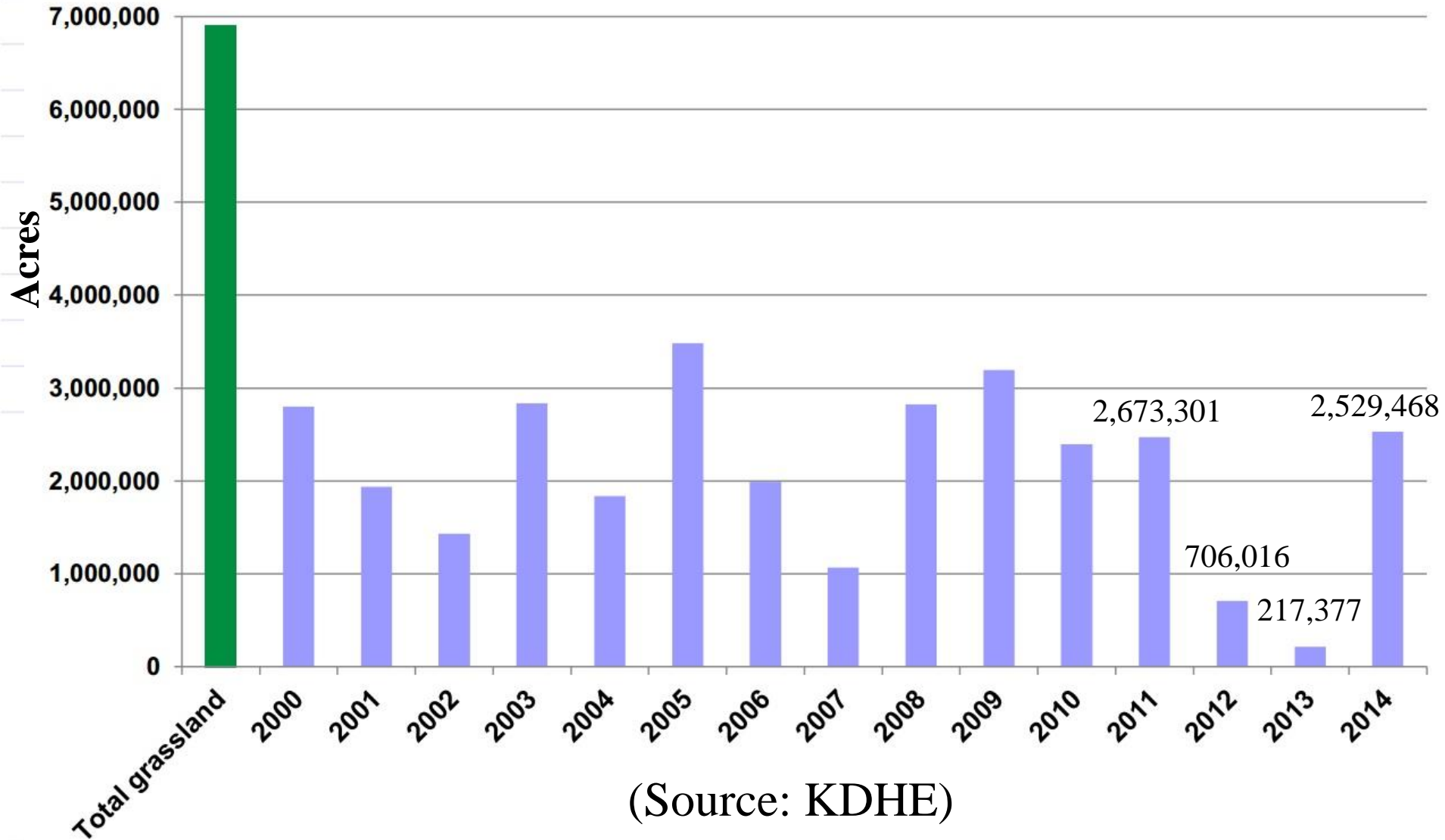
Other trace combustion products

- Herbicides and insecticides
 - may become re-suspended in the air.
- Dioxins
 - are found in soils in remote areas and are sometimes present in vegetation fire smoke
- Sulfur-based compounds
 - can be produced when sulfur-rich vegetation or soil are burned.
- Free radicals
 - may persist up to 20 min following formation and may be of concern to people exposed to them because free radicals may react with human tissues

Summary of smoke composition

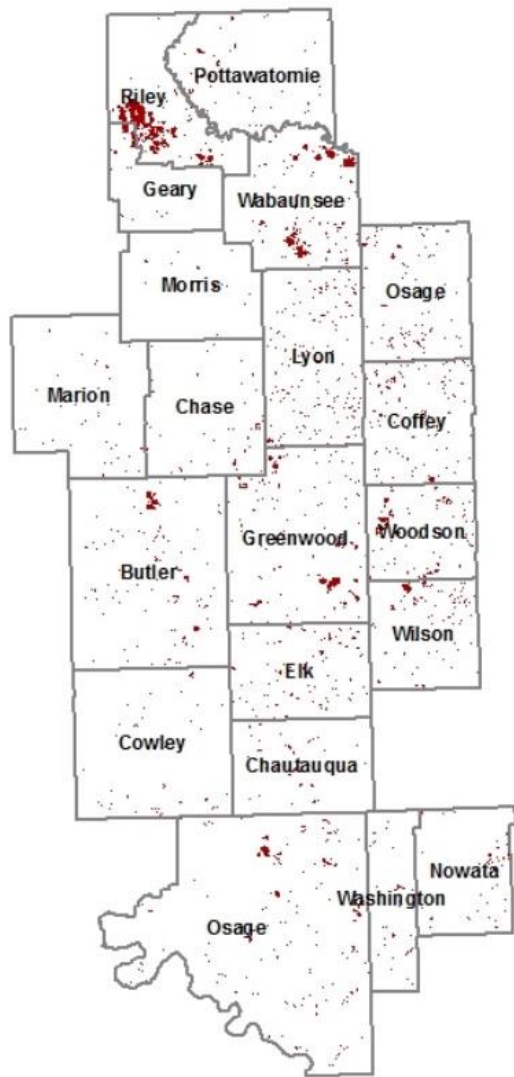


Flint Hills acres burned 2000-2014



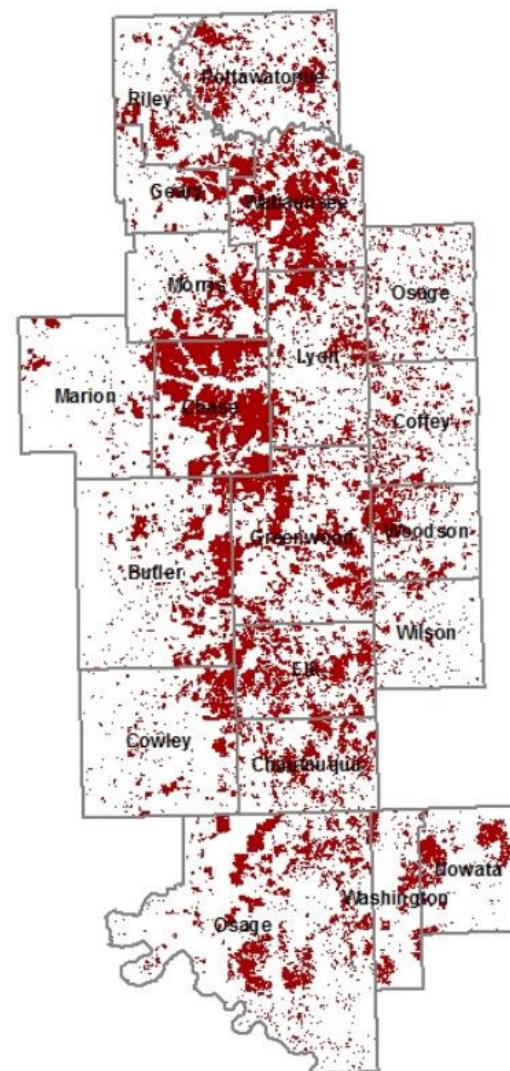
(Source: KDHE)

2013 Flint Hills Burning

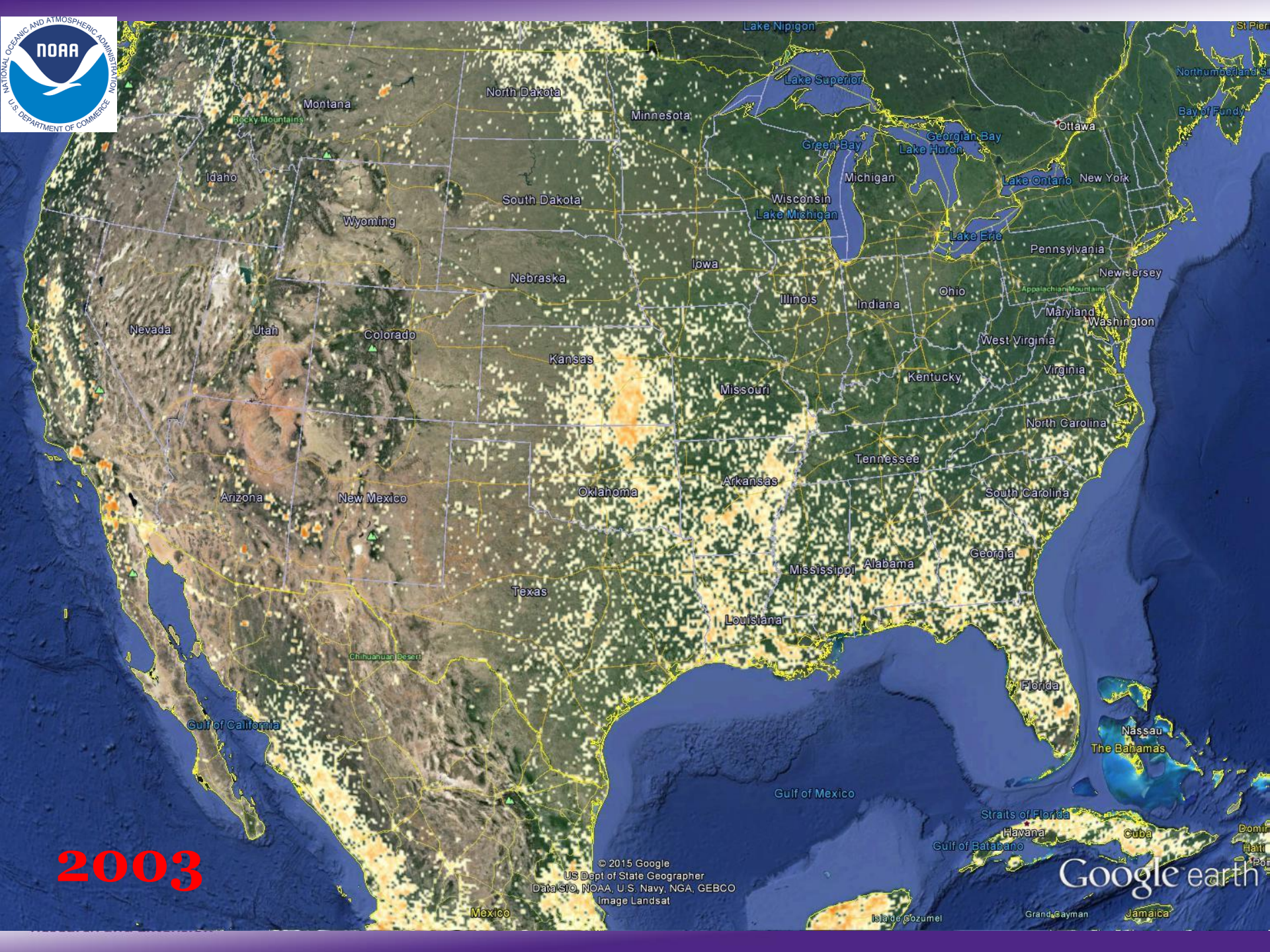


217,377 burned acres

2014 Flint Hills Burning



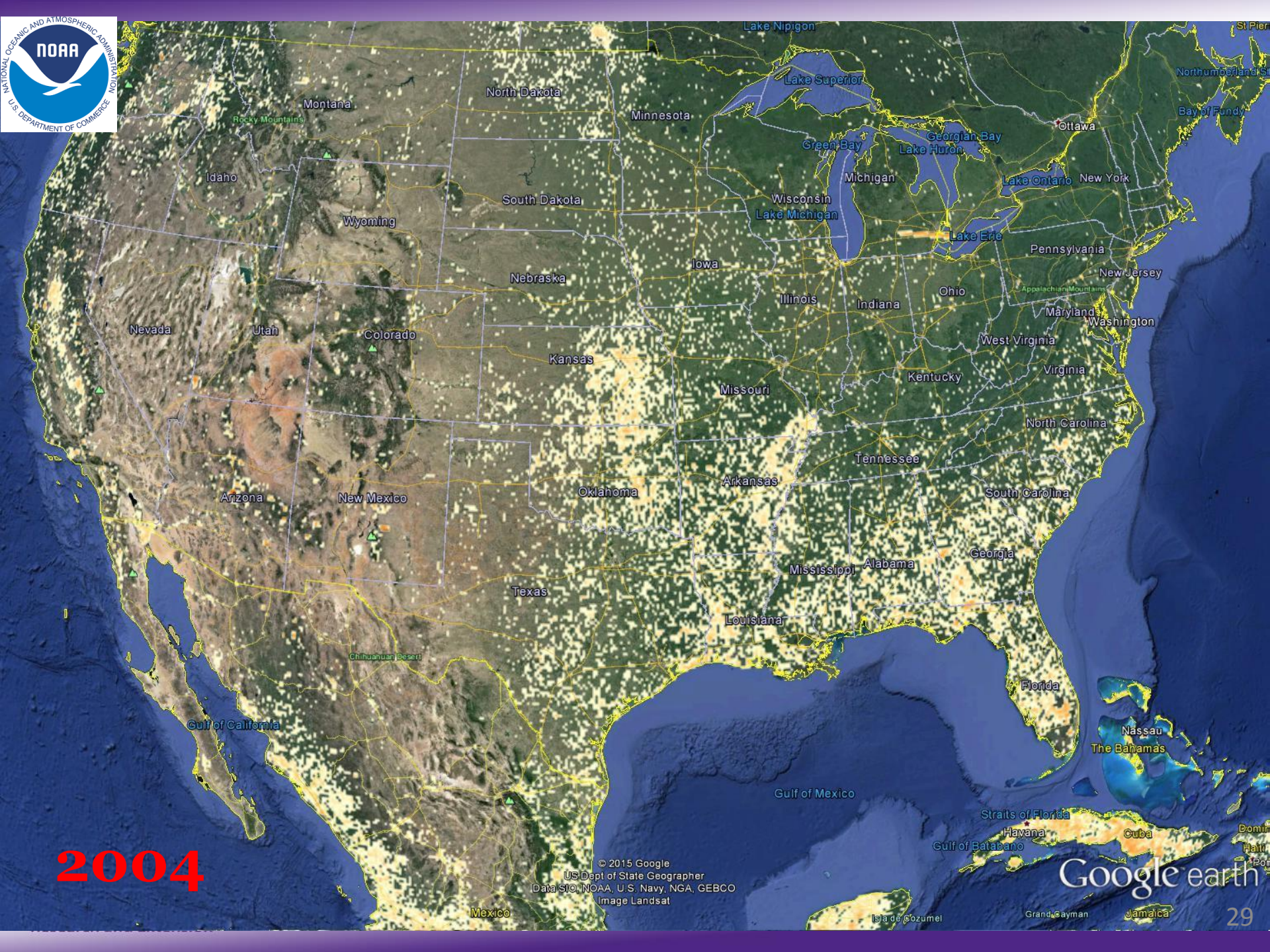
2,529,468 burned acres



2003

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Image Landsat

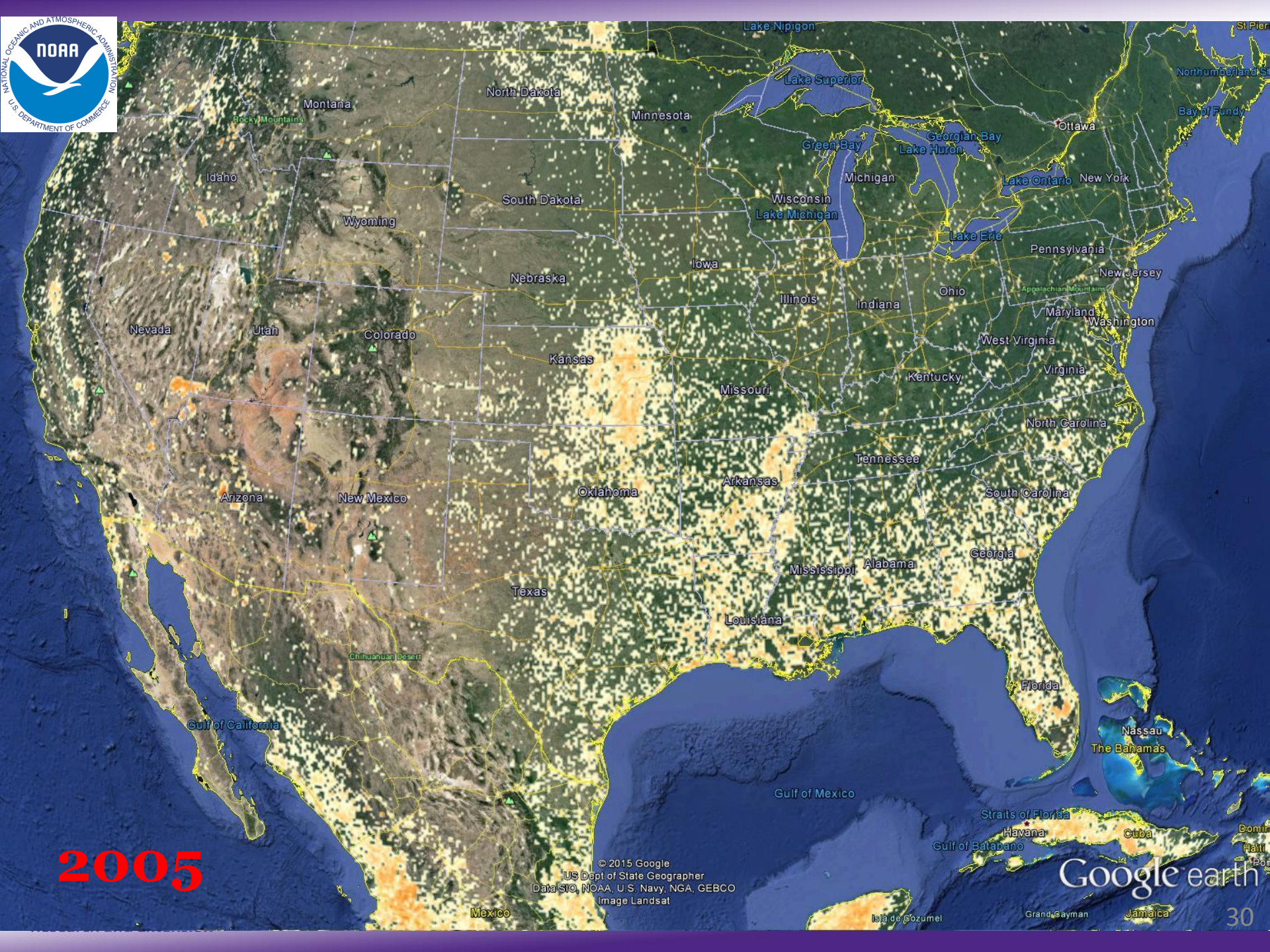
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2004

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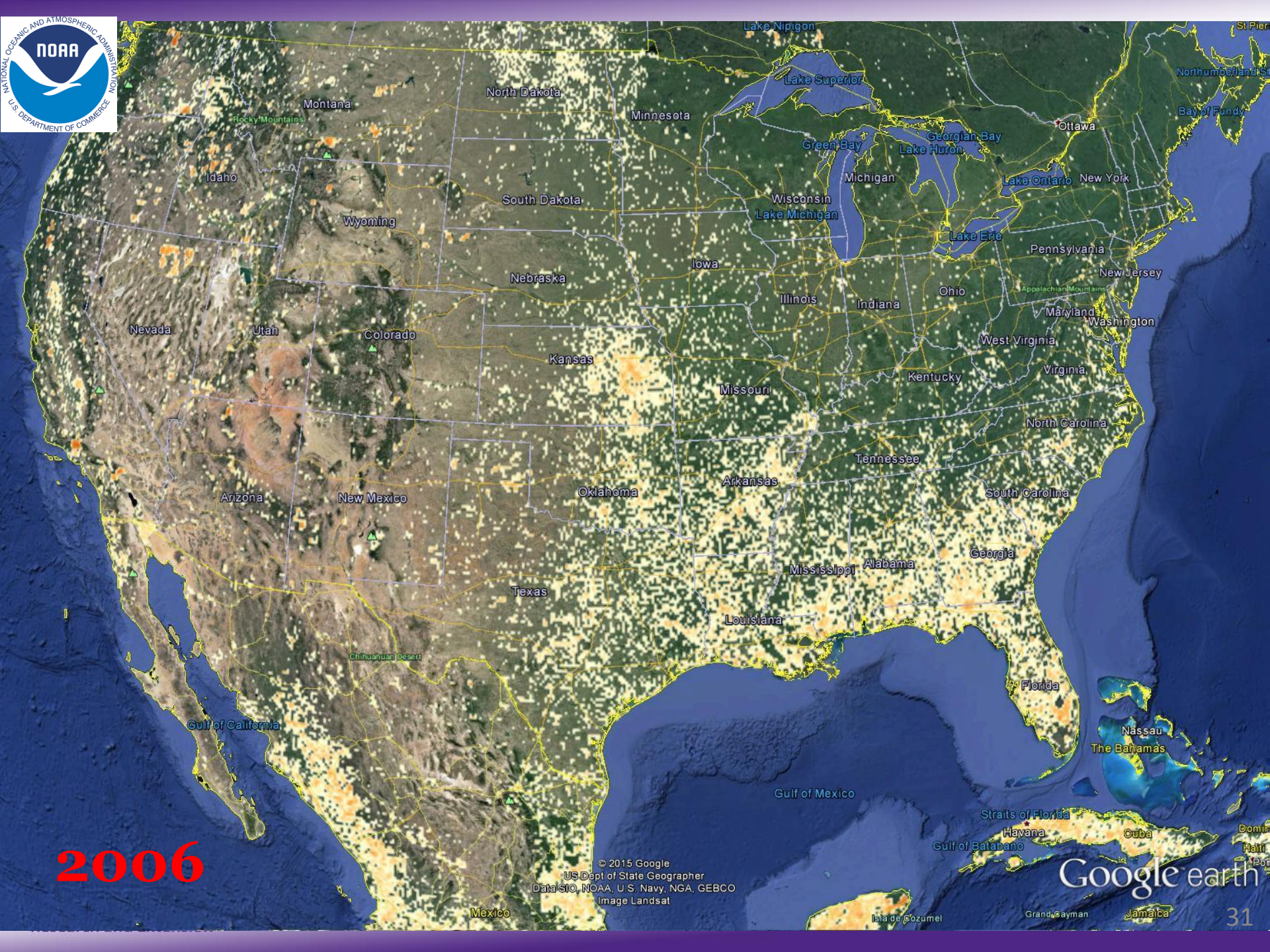
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2005

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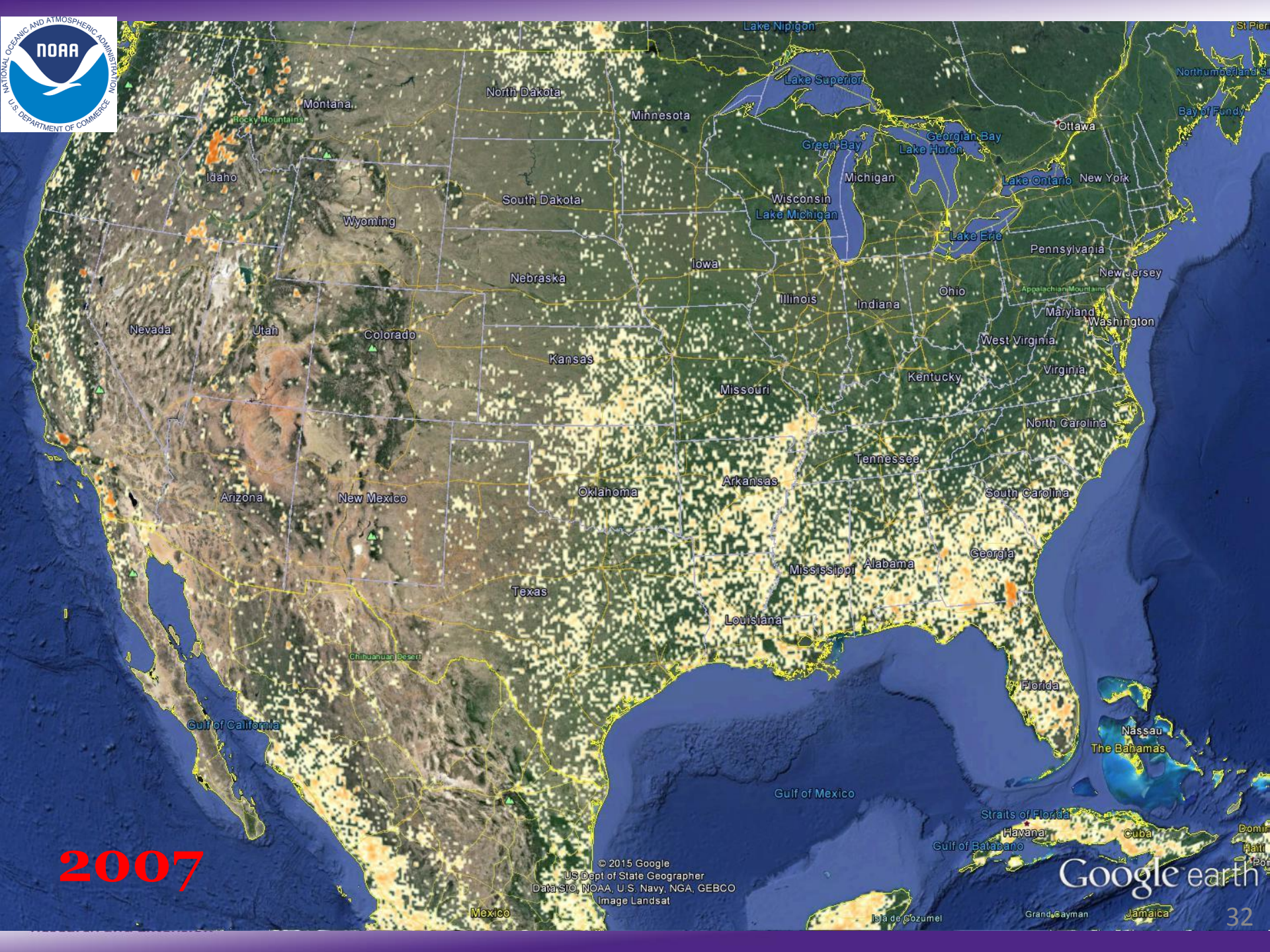
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2006

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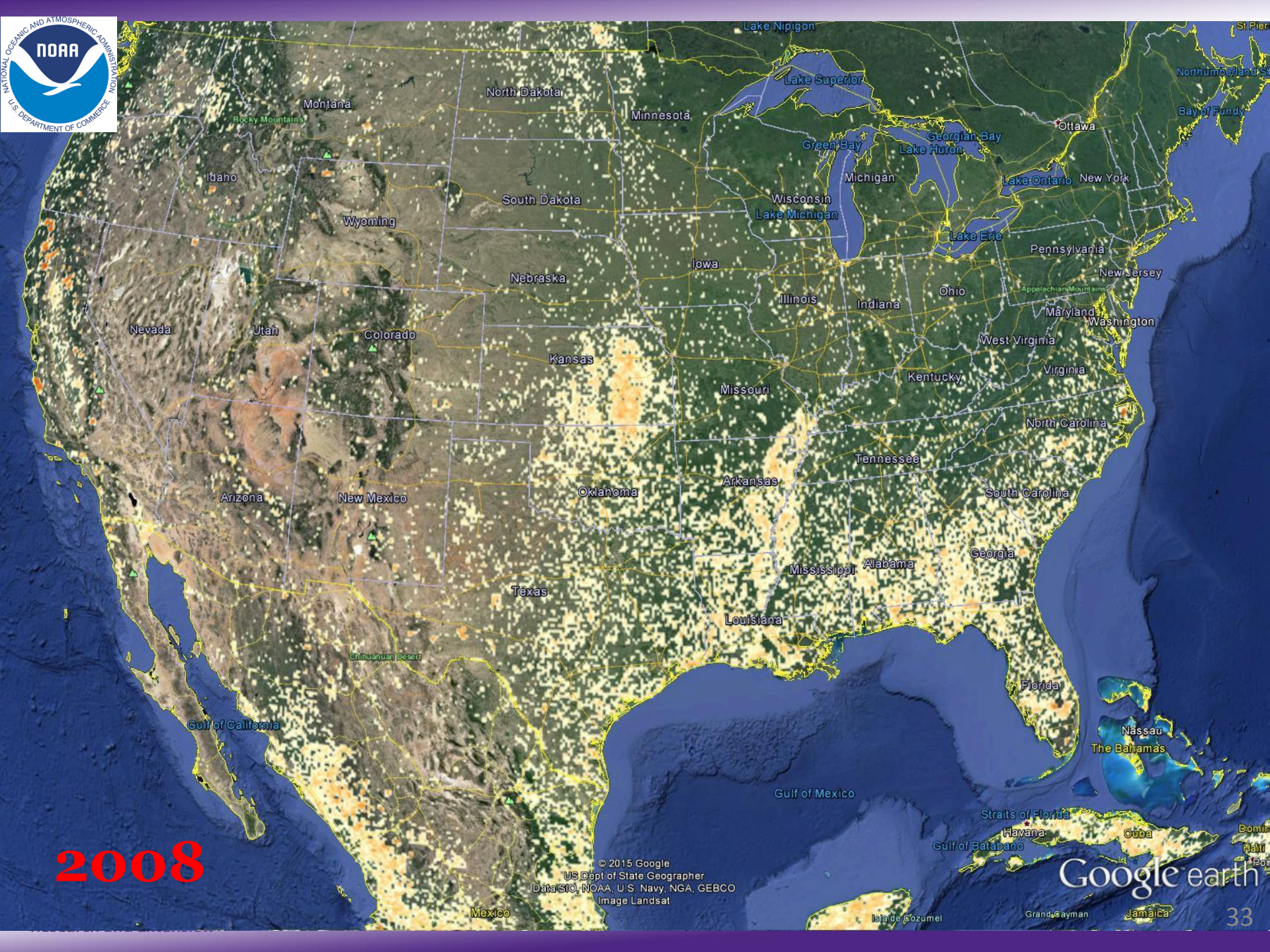
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2007

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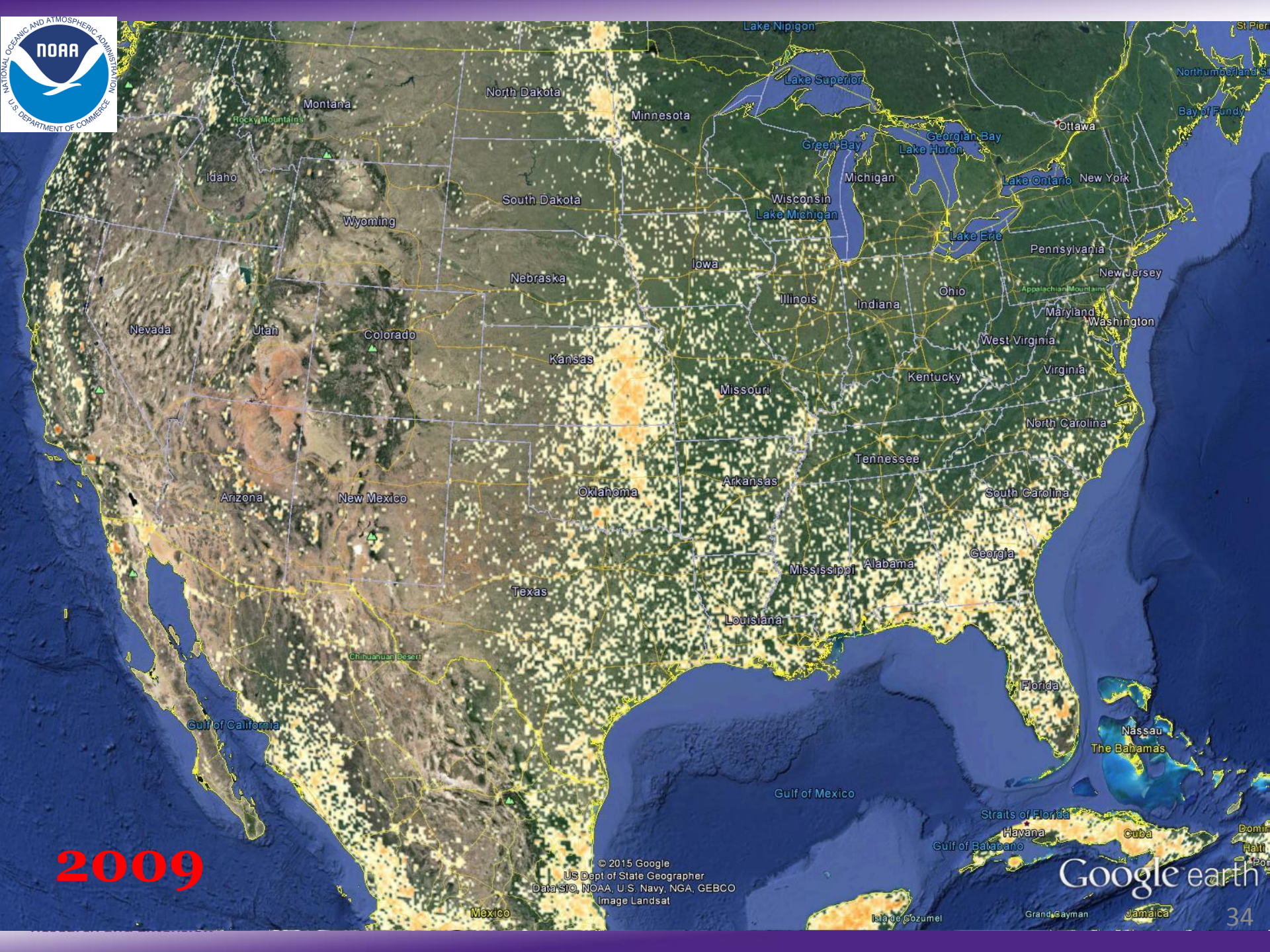
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2008

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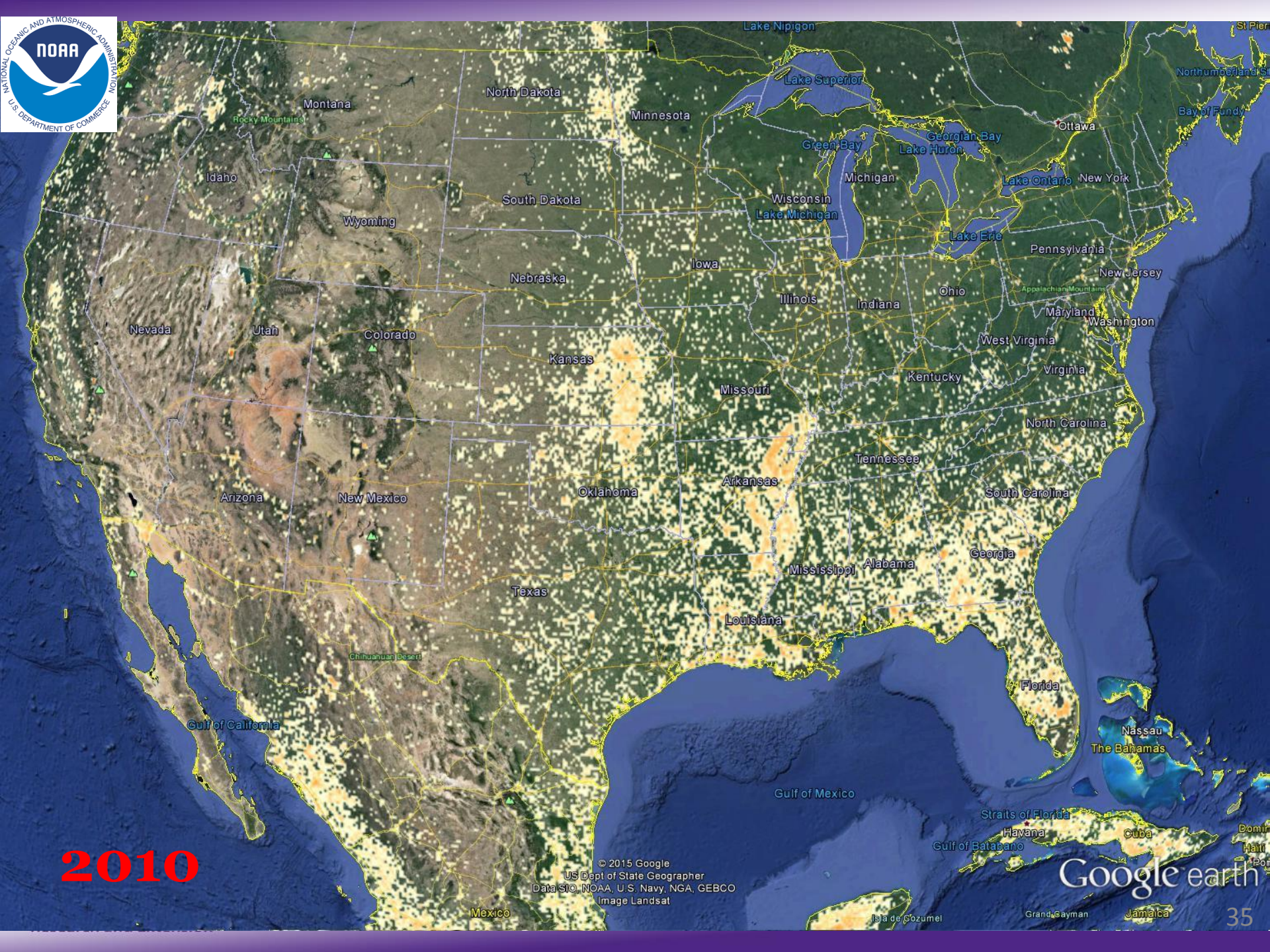
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2009

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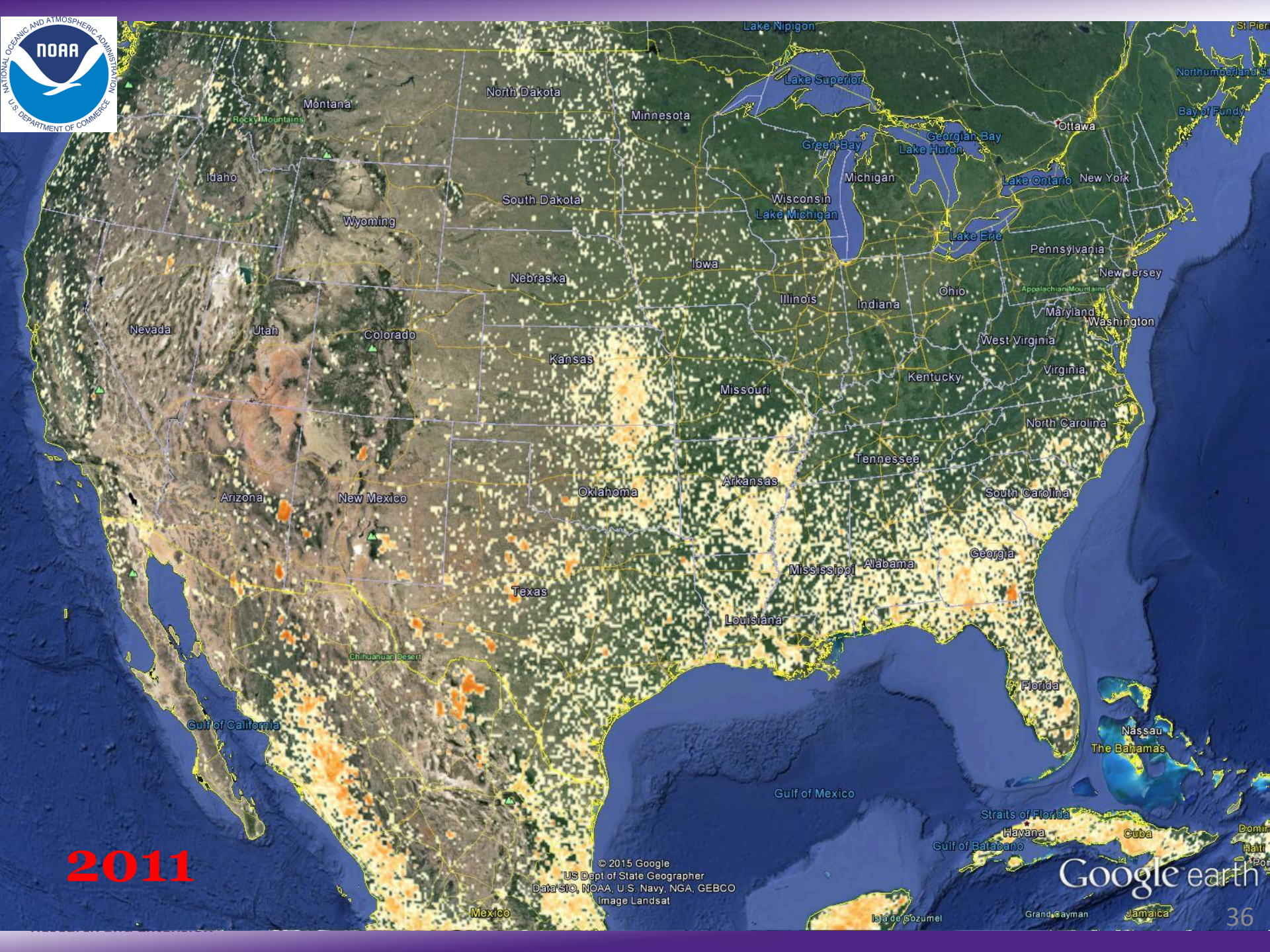
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2010

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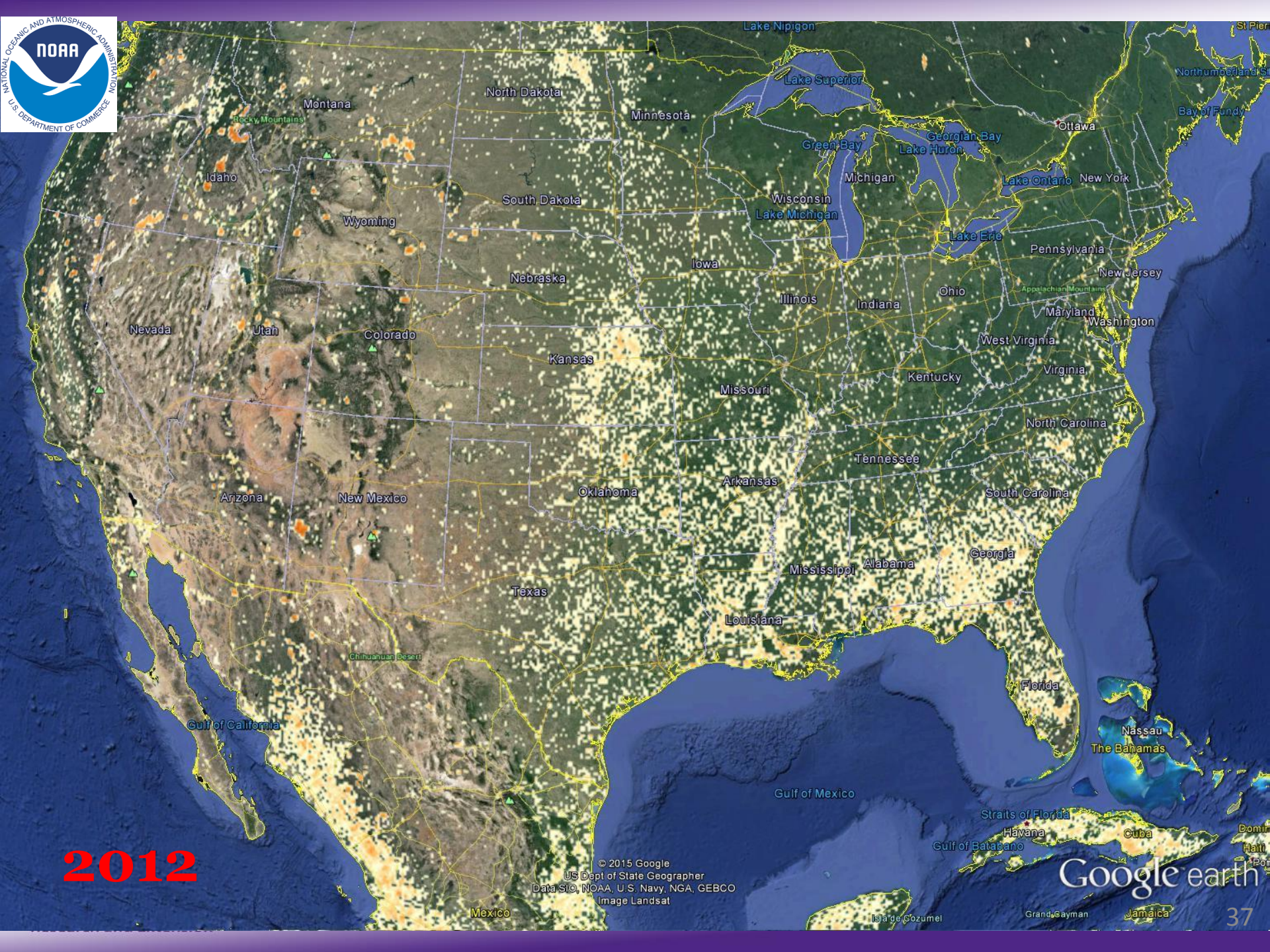
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2011

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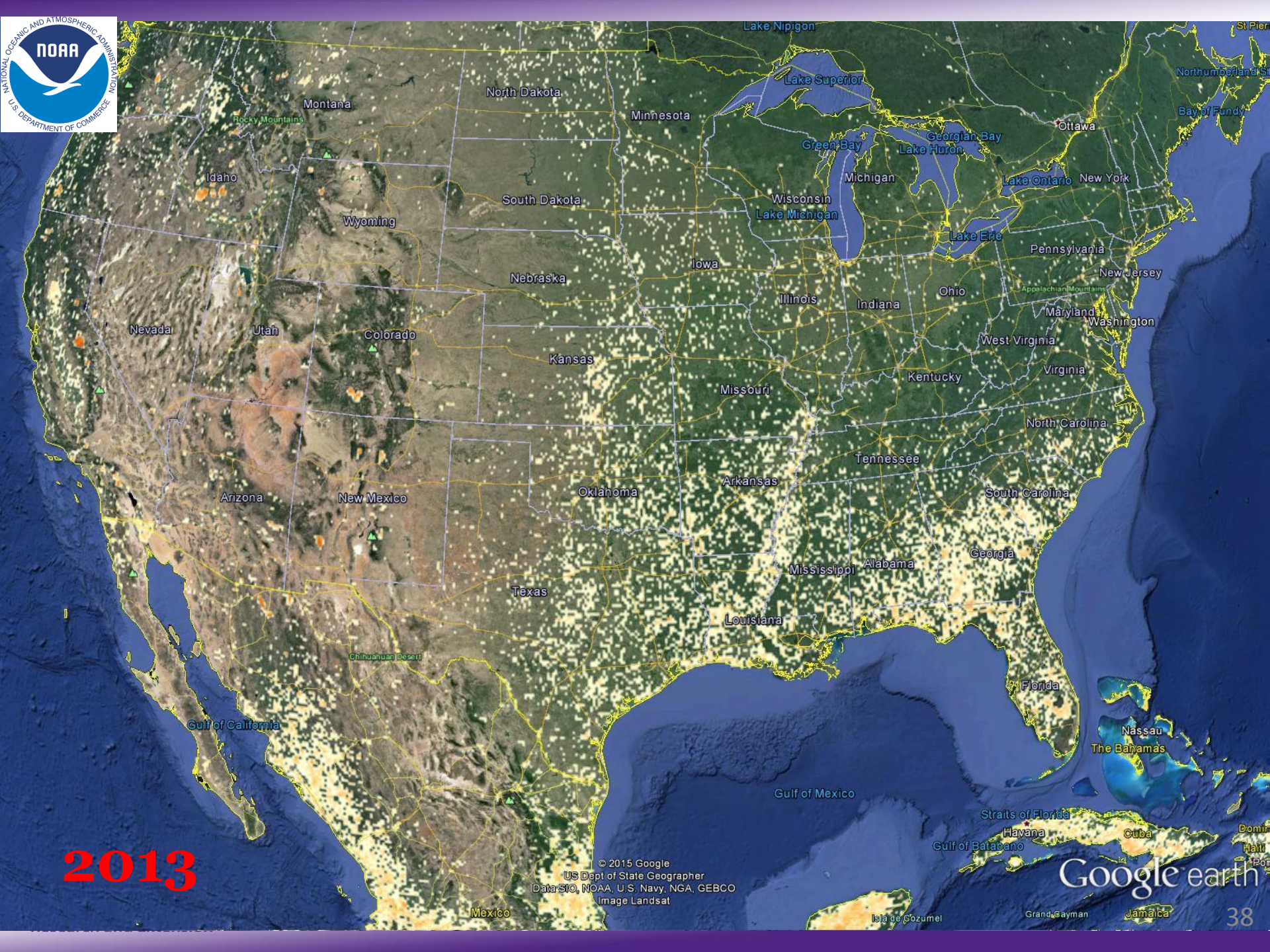
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2012

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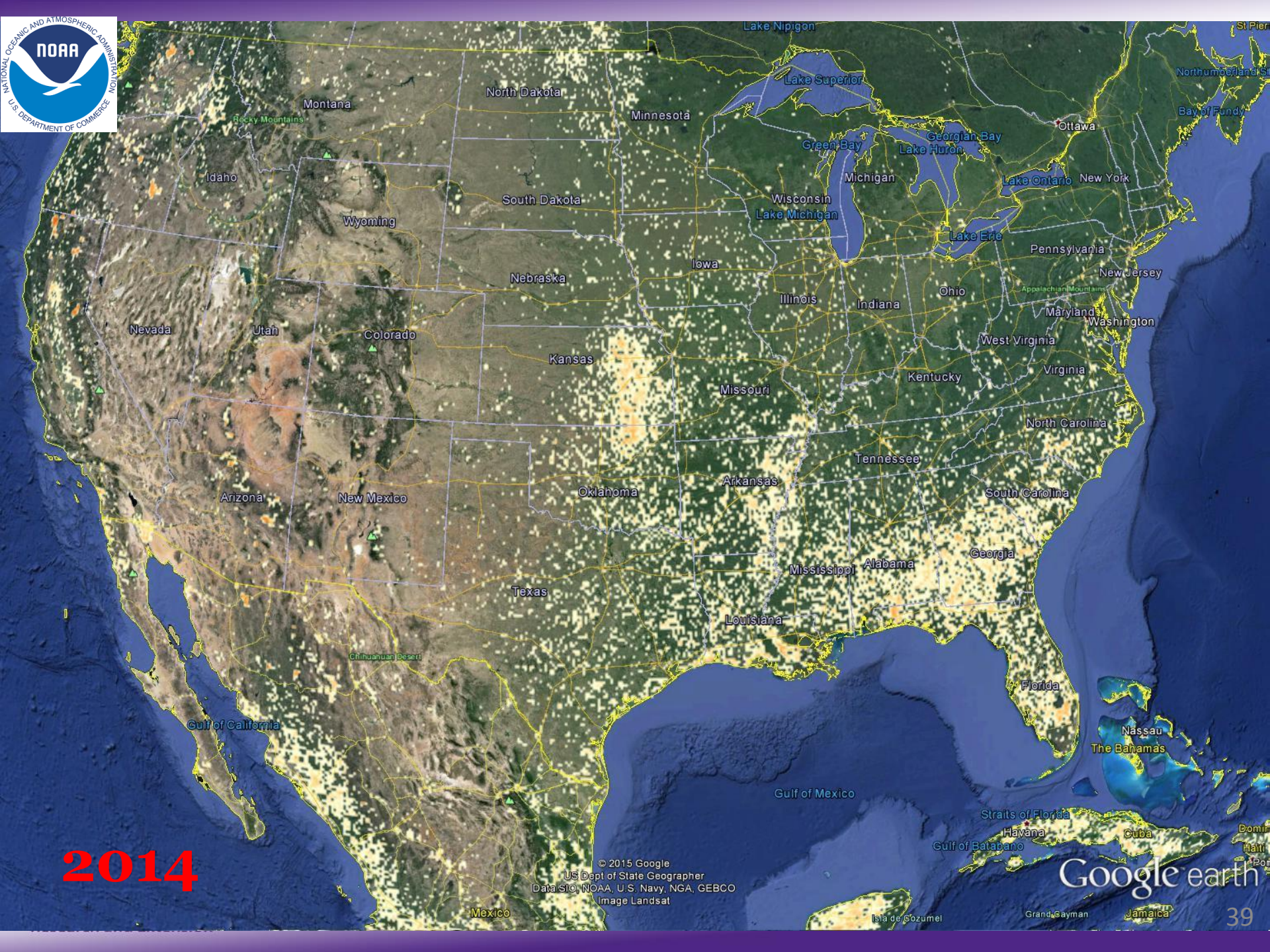
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2013

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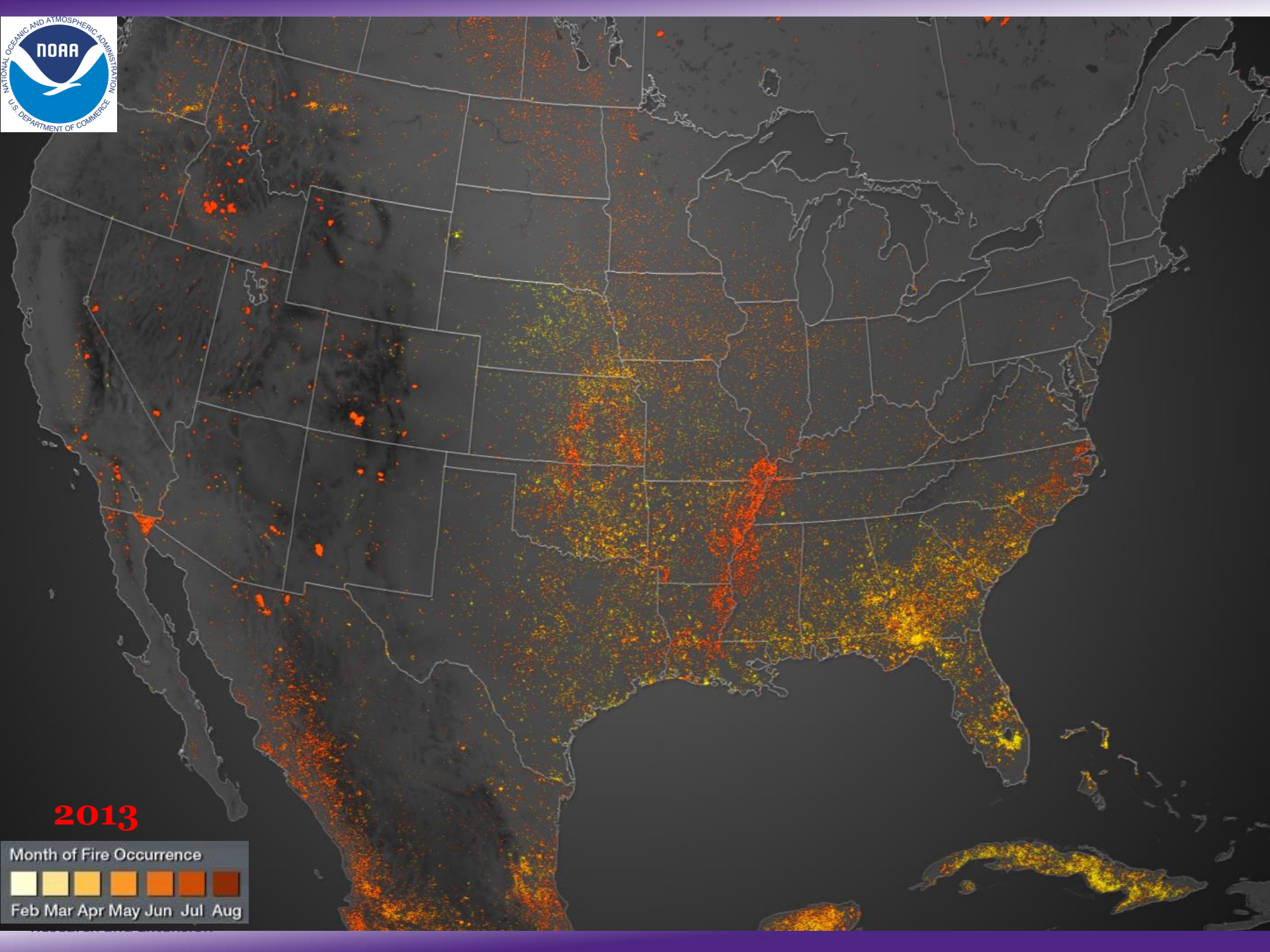
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2014

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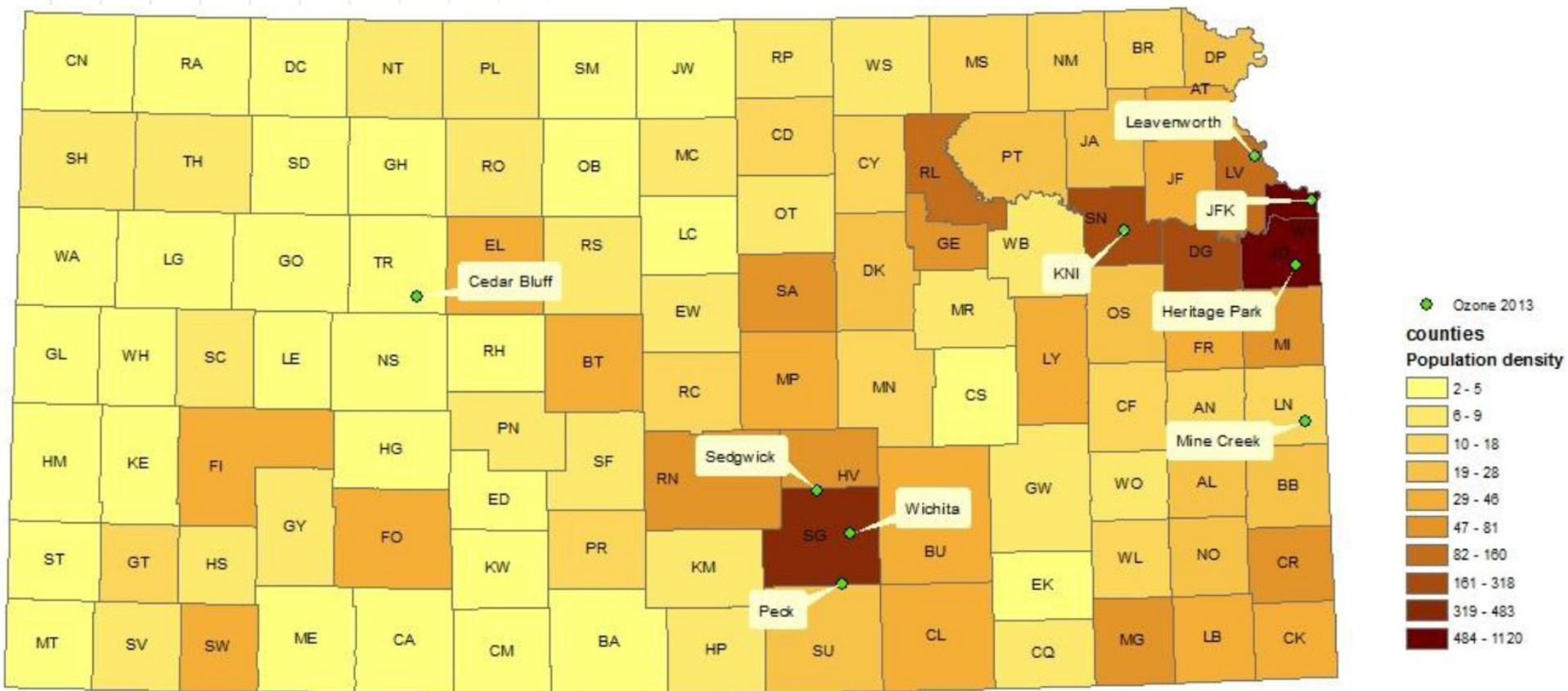
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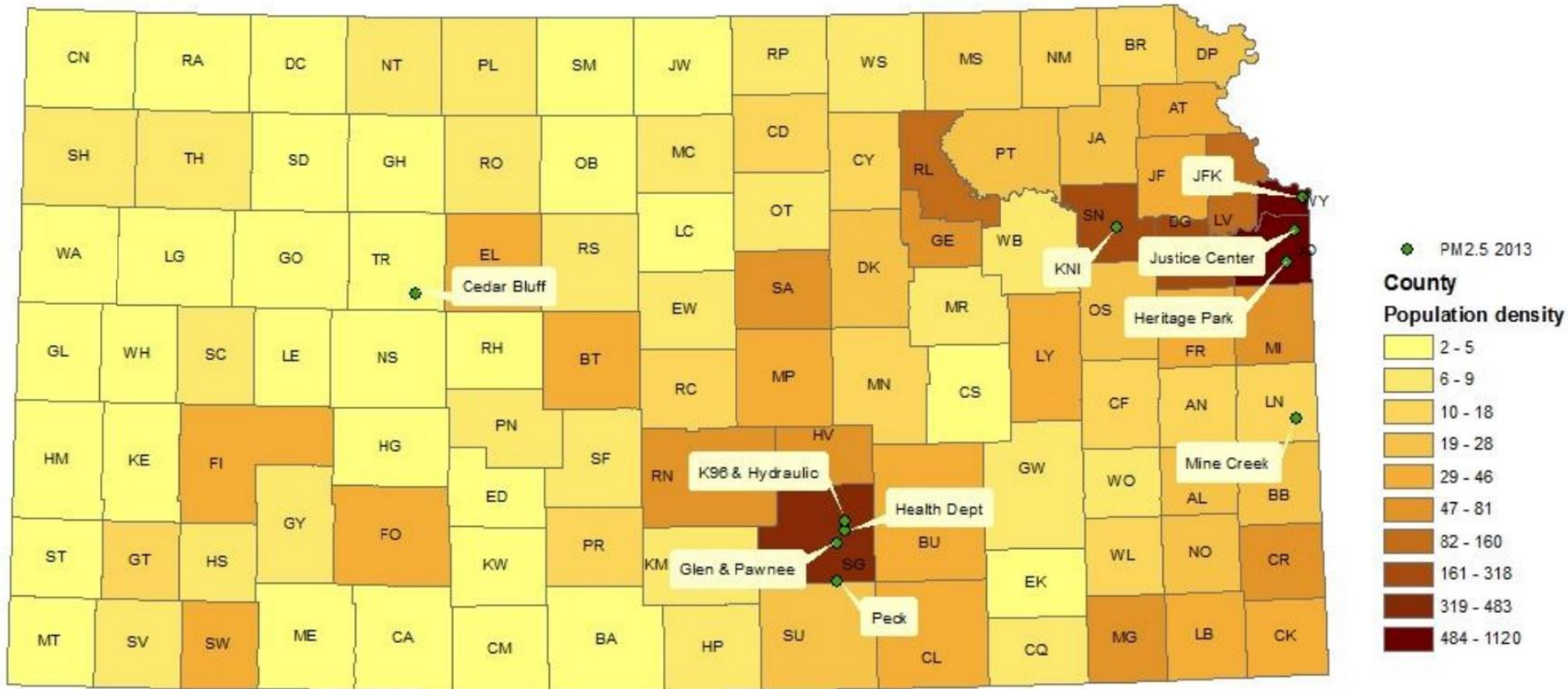
2013



Population density map and location of the 9 O₃ monitoring sites run by KDHE



Population density map and location of the 10 PM_{2.5} monitoring sites run by KDHE

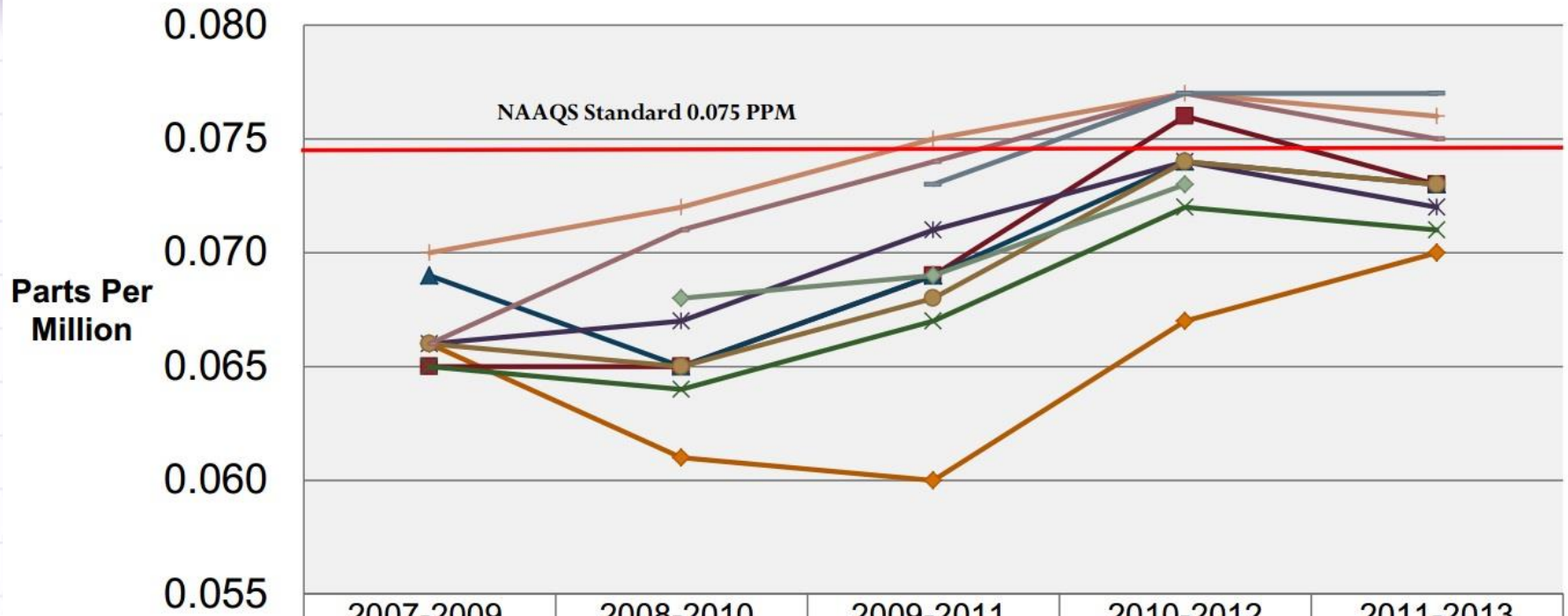


- The Clean Air Status and Trends Network (CASTNET) is a national network designed to provide long-term monitoring of air quality in rural areas.
- Data is available at <http://epa.gov/castnet/>

The two CASNET sites run by EPA

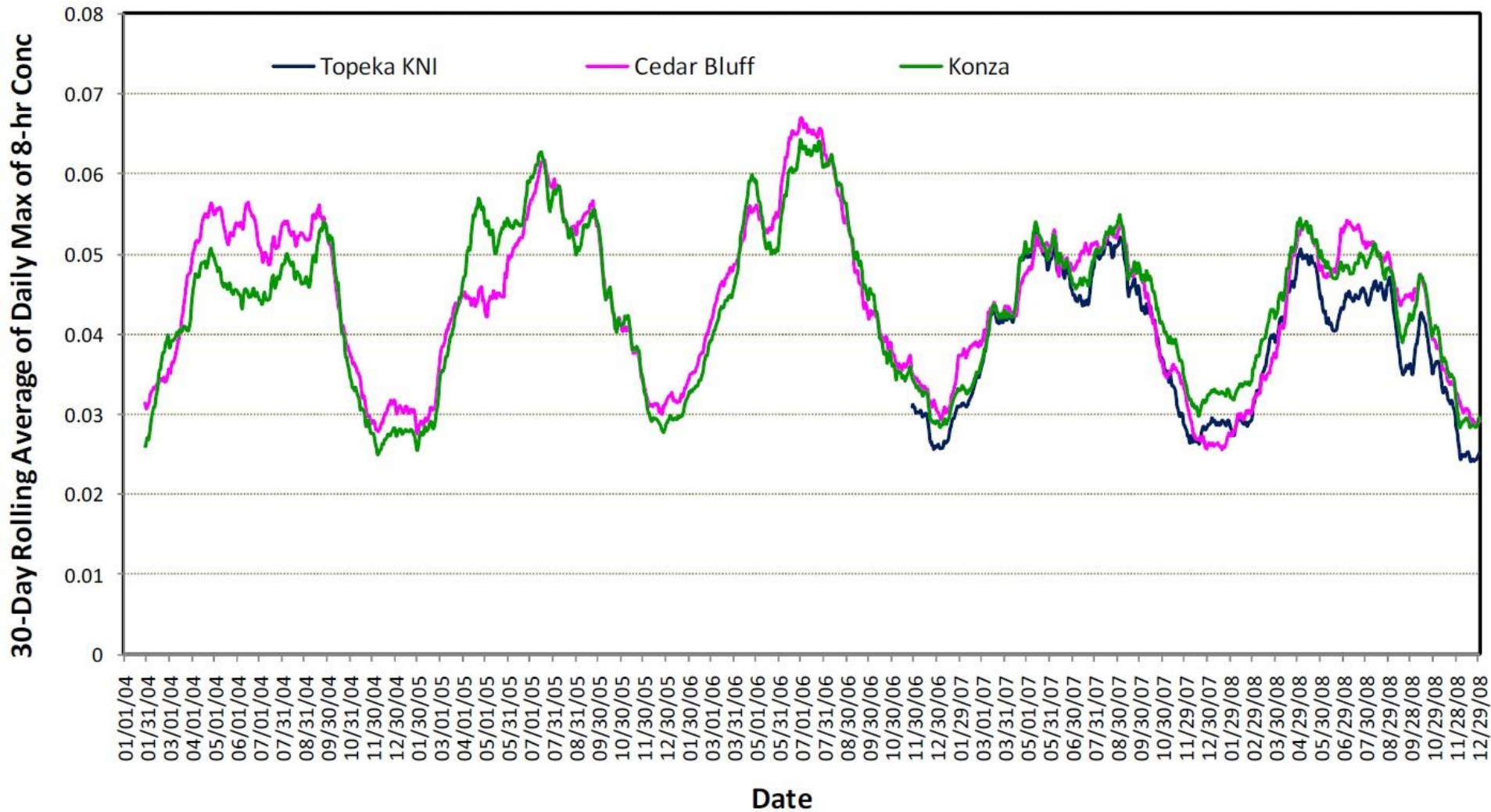


Kansas 8 Hour Ozone Design Values



	2007-2009	2008-2010	2009-2011	2010-2012	2011-2013
◆ JFK	0.066	0.061	0.060	0.067	0.070
■ Heritage Park	0.065	0.065	0.069	0.076	0.073
▲ Leavenworth	0.069	0.065	0.069	0.074	0.073
× Mine Creek	0.065	0.064	0.067	0.072	0.071
* Cedar Bluff	0.066	0.067	0.071	0.074	0.072
● KNI/Topeka	0.066	0.065	0.068	0.074	0.073
+ Peck	0.070	0.072	0.075	0.077	0.076
— Wichita HD	0.066	0.071	0.074	0.077	0.075
— Sedgwick			0.073	0.077	0.077
◆ Konza Casnet		0.068	0.069	0.073	

30-day Rolling Average of Daily Maximum 8-hour O₃ Concentration at three sites



(Reference: Kansas 5-year monitoring network assessment, KDHE)