Holocene Concentrations of Methane in the Atmosphere are in Part Proportional to Concentrations of Sulfur Dioxide and Inversely Proportional to the Oxidizing Capacity of the Atmosphere

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The atmosphere cleans itself by oxidizing pollutants. The primary oxidant is the hydroxyl radical (OH) formed by photodissociation of ozone in the near ultra-violet. Ozone and OH are in limited supply. Sulfur dioxide (SO_2) absorbs near ultraviolet light limiting production of OH and reacts immediately with any available OH, forming sulfuric acid. Methane reacts more slowly with OH and will typically not be oxidized until there is little SO_2. Thus a high concentration of methane indicates low oxidizing capacity. The rate at which SO_2 is injected into the atmosphere controls oxidizing capacity and climate change in four ways:

1. Moderate rate: Large volcanic eruptions (VEI >=6) lower global temperatures for a few years provided they are separated by years to decades so the oxidizing capacity of the atmosphere can fully recover. In 1991, Pinatubo volcano in the Philippines erupted 20 Mt SO_2 and 491 Mt H_2O, the largest volcanic eruption since 1912. The SO_2 was oxidized primarily by OH to form a 99% pure aerosol of sulfuric acid and water at an elevation of 20-23 km. This aerosol reflected sunlight, lowering the world's temperature on average 0.4^{o}C for three years. Ozone levels were reduced by 10\%. Methane increased by 15 ppb for a year. The e-folding time for SO_2 was 35 days.

2. High rate: When large eruptions occur once to several times per year, there is insufficient oxidizing capacity leading to increases in methane and other greenhouse gases and global warming. There were 15 times in the Holocene when large volcanoes erupted on average at least every year for 7 to 21 years. Man is now putting as much SO_2 from burning fossil fuels into the atmosphere every year as one large volcano, causing current global warming. The two previous times were from 818-838 AD, the onset of the Medieval Warming Period, and from 180-143 BC, the onset of the Roman Warm Period.

3. Low rate: When there are no large eruptions for decades, the oxidizing capacity can catch up, cleaning the atmosphere, removing most of the methane and other pollutants. A clean atmosphere leads to cooling and drought. The 8.2 ka event is a classic example, but similar decadal droughts around 6.2, 5.8, 5.4, 4.2, and 2.9 ka caused the demise of most major civilizations.

4. Extreme rate: Whereas large volcanic eruptions produce 10-1000 km^3 of andesitic and silicic tephra, flood basalt eruptions produce as much as 3,000,000 km^3 of basalt containing 10 to 100 times more SO_2 per km^3. The result is runaway global warming, widespread acid rain, and mass extinctions.

The link between SO_2 and global warming is good news because we have developed many efficient technologies that burn fossil fuels with less SO_2 emission and scrub SO_2 out of smoke stacks. Efforts to reduce acid rain have been successful in reducing manmade emissions of SO_2 by >20% since 1980 and thereby reducing methane concentrations.

Sudden increases in methane during the Pleistocene Dansgaard-Oeschger events follow sudden increases in volcanism. High rainfall especially in the Sahara and high methane concentrations in the early Holocene are clearly related to increased volcanism that brought about the end of the Ice

Age. Increases in global warming at 3170 BC, 161 BC, and 828 AD are contemporaneous with short-term increases in methane. The rapid increase in SO_2 from burning fossil fuels since 1850 can explain much of the corresponding rapid increase in methane. But during the last 5000 years, volcanism has been relatively constant and thus it can not explain the observed gradual increase in methane.