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Tracking sinks of atmospheric methane using small world networks

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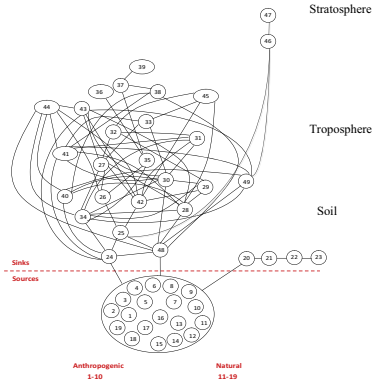
HIGHLIGHTS

- Use of small world network for analyzing atmospheric CH_4 sinks and sources.
- Analysis without considering rate constant as well as species concentration.
- $\cdot OH$ and $HO_2\cdot$ radicals, chlorine atoms and NO as key elements for CH_4 sinks.
- Applied to other environmental issues, e.g., eutrophication.

GRAPHICAL ABSTRACT

Major reactions: $CH_4 + \cdot OH \rightarrow CH_3\cdot + H_2O$; $HO_2\cdot + NO \rightarrow NO_2 + \cdot OH$; $CH_3O_2H \rightarrow CH_3O\cdot + \cdot OH$; and $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$. Major elements: $OH/HO_2\cdot$radicals, chlorine atoms and NO.



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ABSTRACT

The present study uses small world network to highlight the key hubs for CH_4 atmospheric pathways without considering rate constant of each reaction and concentrations of each species. The atmospheric methane sources and sinks were formulated into a well-organized network of 49 nodes and 302 links. In the network, reactions (including substrates and products) are considered as *nodes* and their pathways as *links*. Using a small world model, we analyzed the weighted and directed network of methane sources and sinks. By analyzing the characteristic path length, clustering coefficient, and degree distribution, we obtained insights into the methane network. The results indicate that only a few key nodes serve as hubs or limiting reactions, such as $CH_4 + \cdot OH \rightarrow CH_3 + H_2O$; $HO_2 + NO \rightarrow NO_2 + \cdot OH$; $CH_3O_2H \rightarrow CH_3O\cdot + \cdot OH$; and $CH_4 + Cl\cdot \rightarrow CH_3 + HCl$. The network is highly efficient; when key hub reactions experience interruptions, pathways to other nodes can be accessed to complete the methane degradation process. Additionally, our directed network keeps sources and sinks independent of each other such that changes in the number or type of methane sources does not affect the findings related to sinks. Tracking the structure of methane sources and sinks not only provides valuable, and perhaps universal, information about the network structure, but also can lead to a better understanding of the dynamic processes that generate the network. Finally, this is the first attempt of the network model in analyzing environmental issues and may represent a common blueprint for the interconnected reactions (sources and sinks) of other greenhouse gases.

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1. Introduction

Atmospheric methane (CH_4) accounts for about 15–20% of overall global warming, second only to carbon dioxide, and has a global warming potential of 20–30 times greater than that of CO_2 (IPCC, 2007). As the most abundant reactive trace gas in the troposphere, CH_4 is involved in both tropospheric and stratospheric chemistry (Wuebbles and Hayhoe, 2002) and has an atmospheric life of 8–12 years (Hütsch, 2001; Houghton, 2005). Of the approximately 600 million metric tons (MMT) of CH_4 emitted each year (Keppler and Röckmann, 2007), about 40% comes from natural sources and about 60% from anthropogenic sources (Wuebbles and Hayhoe, 2002; Lowe, 2006). Methane fate can be classified into three broad pathways: tropospheric oxidation, stratospheric loss, and soil microbial reactions.

There are hundreds of photoreactions involving CH_4 for its disappearance. Shallcross et al. (2007) have summarized the key reactions responsible for CH_4 sinks with OH radical as the major sink for CH_4, and chlorine atoms and possibly nitrate radicals as minor sinks in the troposphere. However, the rate constants of reactions and concentrations of species are uncertain considering their spatial and temporal variation. Moreover, reactions of the entire CH_4 sinks are interconnected (some may have feedback reactions) that form a complete and structured network.

To better understand overall atmospheric CH_4 reactions and its eventual sink, many questions should be addressed. These include: Which reaction limits the overall CH_4 sinks? Which reaction is the most subject to perturbation resulting in termination of certain reactions? Which is major hub of the network? Which reactions are most closely related? Which contributes to the accumulation of CH_4? All questions essentially indicate one thing: which nodes/reactions are important and why? The current approach for estimating CH_4 sinks may not fully address the above mentioned concerns. To examine parts of these questions and understand the behavior of the linked reactions, this study was undertaken by using a small world network (SWN) to provide a functional model.

SWNs are originally associated with the phrase of "six degrees of separation," which indicates how each individual is connected directly or indirectly to all other individuals by about six links (Milgram, 1967). Later, parameters such as path length and clustering were introduced and applied to diverse networks such as electric power grids (Sachtjen et al., 2000), neural networks (Latora and Marchiori, 2001), and connections among film actors (Watts and Strogatz, 1998). The "scale free network" concept was further introduced to refer to SWNs whose degree distribution typically follows a power law (Barabási and Albert, 1999). Not surprisingly, the SWN model with its complex connections and links has also been applied to biochemical reactions (Jeong et al., 2000, 2001; Wagner and Fell, 2001; Vendruscolo et al., 2002).

Certain parameters identified in SWN analysis (e.g., path lengths, clustering coefficients, and degree distributions) can help rationalize and explain the complex reactions among and within methane sinks. Since SWN analysis has not been applied to environmental issues, this study aims to: (1) formulate the architecture of the atmospheric methane sources and sinks network; (2) understand the reaction pattern of methane sinks through a directed and weighted SWN analysis; (3) evaluate the important/relevant parameters of SWN analysis for methane network; (4) evaluate the roles of the complex reactions of which the links are perturbated for methane sinks; and (5) highlight the hubs and limiting reactions that govern the overall network.

2. Methodology

2.1. SWNs

The SWN concept was developed to explain observed behaviors that failed to fit within the previous network models (Watts and Strogatz, 1998). A SWN lies between the two extreme categories of regular and random networks (see Fig. SM-1 in Supplementary material (SM)), having some characteristics of both networks, i.e., not completely random, but not having well-defined rules (Watts and Strogatz, 1998).

Three important characteristics of SWNs are: (1) path lengths; (2) clustering coefficients; and (3) degree distribution among all nodes (Watts and Strogatz, 1998; Barabási and Albert, 1999). These parameters will be briefly discussed below.

2.1.1. Characteristic path length

A network can have many paths (links) between any two nodes. The minimum path length (L_{min}) is the path with the smallest number of links from any two nodes (Montoya and Sole, 2002). For example, in Fig. 1a one potential path from node i to node j is via node a (i–a–j); the path length, L, for this route is 2. Other paths between i and j nodes include i–b–k–j ($L = 3$) and i–c–l–m–j ($L = 4$). In this example, $L_{min,i,j} = 2$.

The L_{min} from node i to any other node, m, can be determined in a similar manner. Once all the L_{min} associated with node i are known, the equivalent path length (L_{eq}) with respect to node i can be calculated by averaging all L_{min} for the node i:

$$L_{eq,i} = \frac{1}{N-1}\sum_{j=1}^{N-1} L_{\min,i,j} \tag{1}$$

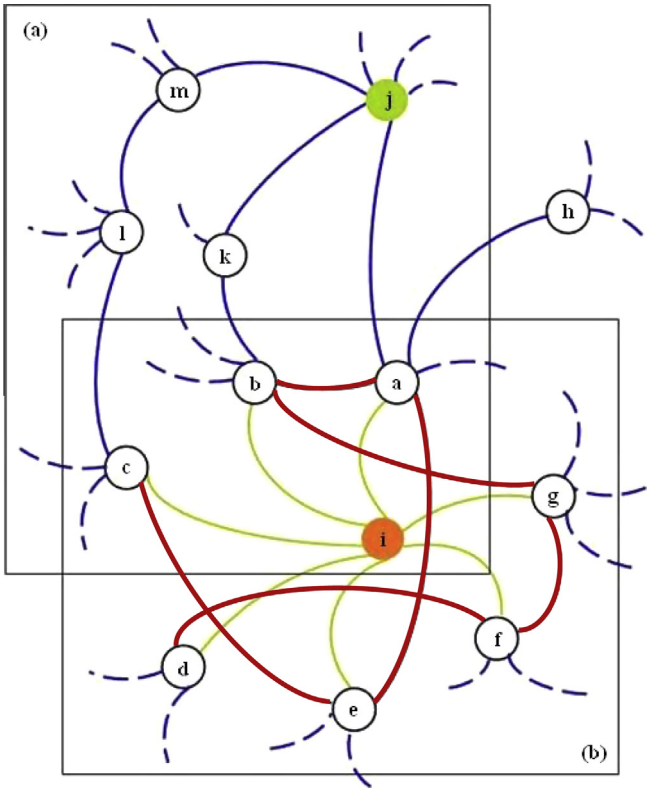

Fig. 1. Example of path lengths and clustering: (a) paths from node i to j; (b) clustering coefficient for node i.