Matriculation number: A01514157E Assignment: #1 for GE4212

Title: Measuring Atmospheric OCS in the Environment

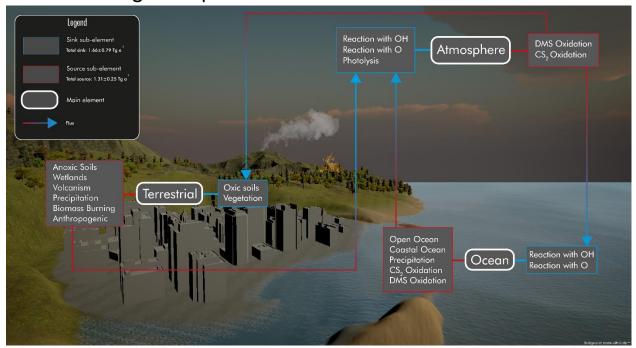


Fig.1 Final Conceptual model of Global Mass Budget of Carbonyl Sulfide (OCS)

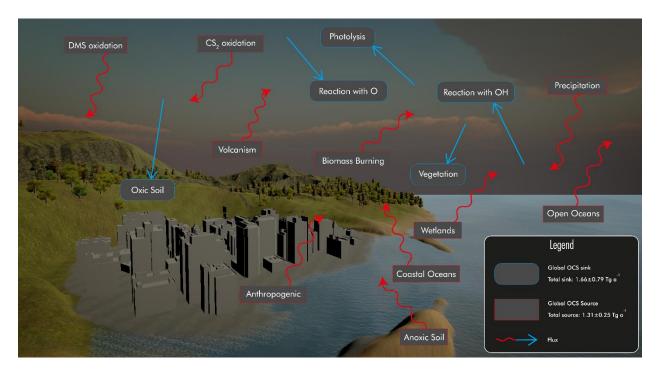


Fig 2. Initial Conceptual Model of Global Mass Budget of Carbonyl Sulfide (OCS)

Background

Atmospheric chemistry is a branch of atmospheric science in which studies the composition of the Earth's atmosphere. The composition and chemistry of the Earth's atmosphere is significance for several reasons. One of the main reason for its importance is the interactions between the atmosphere and living organisms. Changes in the composition of the atmosphere is the result of natural process such as volcanism or solar radiation. In recent years, the dawn of Anthropocene, human activities have proven to significantly impact the earth's environment. Industrialization of the human race have created many global environmental issues which negatively affected the various "spheres" of the Earth and their respective ecosystems. For example, there is a need for atmospheric chemistry research to address environmental problems such as ozone depletion, acid rain, increased GHGs, photochemical smog etc. Atmospheric chemists aim to investigate the causes of these issues, and by having a theoretical understanding of them, allow possible mitigation measures to be tested and implemented via government policies. One of the ways in understanding atmospheric chemistry is to derive conceptual models for the chemical compounds to study their interaction with the environment.

This conceptual model above investigates the mass budget, global distribution, and transport of carbonyl sulfide (OCS). OCS is the most abundant naturally occurring and long-lived sulfur compound in the atmosphere (Watts, 2000). It is a significant chemical compound in world's sulfur circulation (sulfur cycle). OCS can be transported into the stratospheric sulfate layer is oxidized to sulfuric acid which is then precipitated as acid rain (Belviso, Mihalopoulos, & Nguyen, 1967). Wohlfahrt et al. (2012) reports that tracing OCS distribution and transport can track of global photosynthesis rate. According to Watts (2000), OCS is reported to be superior compound compared to CO₂ in measuring global photosynthesis activity in the world due many arising complications of CO2 emissions. Furthermore, OCS is a chemical compound that can affect the formation of SO₂ in the stratosphere or the troposphere. Mian & Davis (1993) postulated the lack of studies with the focus on tracing distribution of OCS. The mixing ratio of naturally occurring OCS in the atmosphere has increased from about 300-400 ppt in the preindustrial era to about 500 ppt in the present (U.S Nation Library of Medicine, 2008). About a third of the worldwide emission of OCS is a result of anthropogenic activities (American Chemical Society, n.d.). Meaningful studies of transport and distribution of OCS would allow climatology scientists to understand global climate change and advise policy makers on mitigation measures to tackle this problem. Besides transport, it is also important to understand the relative importance anthropogenic and non-anthropogenic sources/sinks of this gas to the atmosphere. Hence, there is a need to conceptualize and model the global circulation system of OCS in the environment.

Model description

The conceptual model is heavily based on a study (Watts, 2000) which aims to review to main points: (1) bring all four main components of the atmospheric reduced sulfur budget together in one place, and (2) to draw attention to the main problem areas in the mass budgets of these species. From the texts and data presented in the paper, I was able to derive an initial conceptual model (Figure 2). However, the initial conceptual model does not provide a comprehensive picture of OCS flux in the environment. OCS flux needed to be mapped and conceptualized in greater detail to in order to simulate real world environment. Based on further research, a secondary model (Figure 1) is created to paint a better picture of the global mass budget of OCS. This conceptual model (to be graded on) will be referred as the final model in this paper. The final model is created with the help of two software, Unity3D and Adobe Illustrator (Figure 3 & 4).

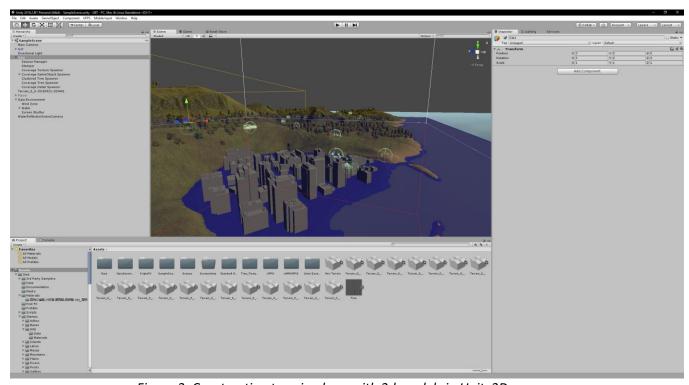


Figure 3. Constructing terrain along with 3d models in Unity3D

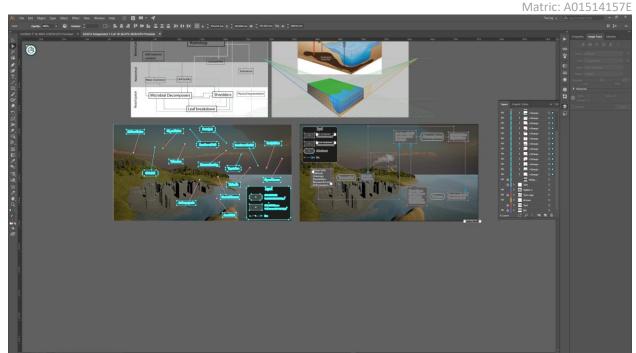


Figure 4. Final composite of the model in Adobe Illustrator

Initial Model Elements

The initial conceptual model (Figure 2) consists of two main elements. First, global OCS sources which is depicted by rectangular boxes with red outlines. Second element of the model is global OCS sinks which is represented by rounded rectangular boxes with blue outlines. For OCS sinks, the paper noted 5 main global sinks which are oxic soils, vegetation, reaction with OH⁻, reaction with O²⁻ and photolysis. The total annual flux intake of OCS is reported to be $1.66 \pm 0.79 \, \text{Tg a}^{-1}$. There are 5 more OCS sources than sinks in the paper consisting of open ocean, coastal ocean, anoxic soils, wetlands, volcanism, precipitation, dimethyl sulfide (DMS) oxidation, carbon disulfide (CS₂) oxidation, biomass burning, and anthropogenic source. The total annual flux output of OCS is reported to be $1.31 \pm 0.25 \, \text{Tg a}^{-1}$. Process of fluxes is denoted by arrows which are either blue orS red. Blue straight arrows means the storage or breakdown of OCS into sinks. Red wavy arrows signify outgoing OCS from their respective sources. Although there is sufficient data for the author of the paper to present the data in table form. It is difficult to recreate an illustration of the model purely based on the table figures. A reconstruction is needed to help readers better visualize the spatial significance of each flux.

Final Model Elements

The final model (Figure 1) is a simplified version of the initial model where by OCS sinks and sources is grouped and classified spatially rather than sources or sinks. This is so show gas transfer (flux, represented by arrows) from one main element to another. In this stocks-and-flow diagram, there are 3 basic elements with their respective sub-elements: (1) Terrestrial (2) Atmosphere and (3) Oceans. The elements are classified by locality and is connected via arrows to show OCS exchange between each other. For each of the arrows, there is a gradual color change (color gradient) to show flow from an element's source to another element's sink. These three elements form a feedback loop. Within each main element there would be sub-elements depicting the sources/sinks mentioned in the paper. Each individual sub-element would have varying magnitudes affecting the gas exchanges (arrows) between main systems. The magnitudes affecting the flux needs further data which would be further elaborated

in the last section. Another slight change from the initial model is that volcanism and biomass burning is now represented by smoke particles and flame particles respectively.

Assumptions

What assumptions are made? Why? Are there processes & feedbacks that have been omitted or simplified? Why? You should provide argumentation for all the choices you have made. There are 4 main adjustments made for the conceptual model for mass budget of OCS:

- 1. Generalized ecosystem (assumption)
- 2. Methodology differences (assumption)
- 3. Limited soil types in the conceptual model (assumption)
- 4. Omitted Terrestrial-Ocean OCS exchange (omission)

Generalized environment and ecosystem

As pointed out by Watts (2000), it is difficult to accurately conduct measurements to trace OCS quantities for all the world's biomes. In order to do so would require detailed knowledge of the biome itself. For example, measurements concerning bogs, fens, swamps and marshes revealed very great variability (K.A. & J.F., 1985). In the conceptual model the sub-element wetlands encompasses very different types of environments which might not be so in reality. Each biome has very different behaviors and process which can affect OCS emissions or intake. For example, a peat bog has very different ecosystem processes as compared to a swamp. Hence the simplified sub-element could be problematic to monitor and measure OCS on a global scale.

Methodology differences

After reviewing literature regarding OCS budget, there very different approaches for data collection to derive flux estimates. With focus on different determinants of the flux OCS would affect the magnitude and sensitivity of feedbacks in the model. According to Watts (2000), for measuring ocean to atmosphere OCS fluxes, researcher investigating similar OCS emissions have focused their attention on the solar radiation and wind speed as the main determinants of the OCS while the paper asserts that dissolved organic matter (DOM) and dissolved amino acids are more significant in emitting OCS. The divergence in methodology can be also observed from measurements of OCS emissions from soils. Mian & Davis (1993) noted the ambiguity in measuring OCS emissions from soils as dynamic enclosures using either ambient or sulfur free air are used to estimate fluxes of volatile sulfur fluxes from soils.

Limited soil types in conceptual model

In addition to the measurement problems mentioned above, uncertainty of OCS measurements in soil is increased when soil types are generalized or simplified. According to Lehmann & Conrad (1996), OCS emission or intake for soil is largely based on soil type. In the model, there are only two main soil classes, "anoxic" or "oxic". "Anoxica soils include altisols, ultisols, spodsols, mollisols (especially aquents of these) which appear to be net sources of OCS to the atmosphere (Kanda, Tsuruta, & Minami, 1995). Having limited knowledge on soil types can limit the model's capabilities as it can create complications in the measurements for OCS emissions.

Omitted Terrestrial-Ocean OCS exchange

The conceptual model did not include OCS exchange processes between terrestrial and ocean due to the lack of research to show direct interaction between them. In the paper, OCS is directly emitted either from ocean or from terrestrial. There is insufficient research to show a direction relation of OCS between terrestrial and ocean. Hence there are no arrows linking terrestrial main element and oceanic element.

Inputs and parameters

In order for the conceptual model to be developed into an environmental model. There are two main components in the model to be defined, parameters and input data.

Parameters

The key parameters to consider in my conceptual model which affect its performance is spatial considerations.

One possible suggestion for parametrization would be to use systems-thinking whereby elements are separate but interconnected systems. Each element in the model is inherently different and unique with their own sub-systems and process (i.e. wind systems and patterns in the atmosphere). This concept is because it aids the explanation of the interactions of the atmospheric chemicals on Earth. In the context of the conceptual model, by grouping source and sinks of OCS into elements and systems, OCS formation, transport and distribution can be visualized and explained much clearer. Hence, in my conceptual model, I try to reference it to the concept of Earth systems (Jacobson, Charlson, Rodhe, & Orians, 2000). The main elements are akin to the "spheres" of the earth. This gives scope to the model which ease the process of data collection and analysis. Dataset for numerical input would need the amount of OCS produced and taken.

Another possible parameter for the conceptual model can be the processes of gas exchange. As of now, the it is difficult to pinpoint exactly the flux of OCS to each main element in the model. Further studies may be needed to supplement data for the model.

Input Data

The main data to be collected would be OCS concentration from each different parameter. Input data will need to be collection from different region (oceans, soils, vegetation, anthropogenic emitter CS_2 and DMS oxidation rates will also need to be collected as they directly affect OCS levels in the atmosphere. CS_2 and DMS data would be require dataset available from similar atmospheric research.

In order for the model to replicate a global OCS circulation, a large amount of data would be required to feed the model to test its performance. This is not realistic due to the cost and manpower needed for data collection. Hence only samples will be collected which then can be extrapolated to simulate the entire system.

For terrestrial OCS data, data would need to be collected at three different sub-systems. Firstly, the two main types of soils would need to be sampled to obtain OCS concentration. Next, anthropogenic emissions of OCS would also need to be recorded. Lastly, gas exchange between vegetation and the environment need to be measured.

For oceanic and atmospheric OCS data, samples of water at different regions (coastal or open ocean) need to be collected and analyzed to reveal their respective OCS concentrations. (Rasmussen, Hoyt, & Khalil, 1982) proposed using cryogenic sampling to measure OCS concentrations in water and air.

Word count: 2024

Bibliography

- American Chemical Society. (n.d.). *American Chemical Society*. Retrieved September 28, 2018, from https://www.acs.org/content/acs/en/molecule-of-the-week/archive/c/carbonyl-sulfide.html
- Belviso, S., Mihalopoulos, N., & Nguyen, B. C. (1967). The supersaturation of carbonyl sulfide (OCS) in rain waters. *Atmospheric Environment*, *21*(6), 1363-1367. doi:https://doi.org/10.1016/0004-6981(67)90083-2
- Jacobson, M., Charlson, R. J., Rodhe, H., & Orians, G. H. (2000). Earth System Science. In M. Jacobson, & G. Orians (Ed.), *Earth System Science: From Biogeochemical Cycles to Global Changes* (Vol. 72). Academic Press.
- K.A., B., & J.F., M. (1985). Sulfate uptake from surface water by peat. *Soil Biology and Biochemistry,* 17(4), 411- 420. doi:10.1016/0038-0717(85)90002-1
- Kanda, K.-i., Tsuruta, H., & Minami, K. (1995). Emissions of biogenic sulfur gases from maize and wheat fields. *Soil Science and Plant Nutrition*, *41*(1), 1-8. doi:10.1080/00380768.1995.10419553
- Lehmann, S., & Conrad, R. (1996). Characteristics of turnover of carbonyl sulfide in four different soils. *Journal of Atmospheric Chemistry*, *23*(2), 193-207. doi:10.1007/bf00048260
- Mian, C., & Davis, D. (1993). Global sources and sinks of OCS and and CS2 and their distribution. *Global Biogeochemical Cycles*, 7(2), 321-337. doi:10.1029/93gb00568
- Rasmussen, R., Hoyt, S., & Khalil, M. (1982). Atmospheric carbonyl sulfide (OCS): Techniques for measurement in air and water. *Chemosphere*, *11*(9), 869-875. doi:10.1016/0045-6535(82)90133-3
- U.S Nation Library of Medicine. (2008, June 04). *TOXNET, Toxicology Data Network*. Retrieved September 28, 2018, from https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/r?dbs+hsdb:@term+@DOCNO+6127
- Watts, S. F. (2000). The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide. *Atmospheric Environment*, 761-779.
- Wohlfahrt, G., Brilli, F., Hortnagl, L., Xu, X., Bingemer, H., Hansel, A., & Loreto, F. (2012, April). Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: potential and limitations. *Plant, Cell and Environment, 35*(4), 657-668. doi:https://doi.org/10.1111/j.1365-3040.2011.02451.x