**User Instructions of Global 14-Box Model of Hg Isotopes (GBM-Hg-ISO-14box-v1)**

**Model name:** Global 14-Box Model of Hg Isotopes

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**Description:** In this @Matlab package, there are 9 normal code scripts, 3 function code scripts and 4 data text files (data input) and 1 @Excel workbook (result output). All the scripts and functions have a prefix ODE, meaning that the algorithm is based on ordinary differential equations. The prefix ODE is used to distinguish Amos et al. (2014)’s @Matlab code files. This package is triggered by *ODE\_main.m*, and it mainly consists of three scenarios of simulations (six files): natural (*ODE\_pre.m* + *ODE\_pre\_function.m*), pre-1850 anthropogenic (*ODE\_anthro\_pre\_1850.m* + *ODE\_anthro\_pre\_1850\_function.m*), and post-1850 anthropogenic (*ODE\_anthro\_post\_1850.m* + *ODE\_anthro\_post\_1850\_function.m*), corresponding to natural, pre-1850 anthropogenic and 1850-2010 anthropogenic Hg cycles. In these three scenarios of simulations, the variable *sign\_type* is used to defined the types of isotope simulation (**sign\_type=1 for MDF, default value; sign\_type=2 for MIF of odd or even isotopes**; the model runs either MDF or MIF, but not both at the same time). *ODE\_display\_output.m* is used to display numerically the simulation results (Hg mass and Hg isotope ratio in each box, various Hg fluxes between boxes). Other scripts are used to define the parameters in these three scenarios of simulations, which are described here in an order of their execution.

1. *ODE\_rate\_coeffs\_species.m*: first-order rate coefficient of Hg transfer between boxes (Figure 1).
2. *ODE\_makeA\_species.m*: assemble the first-order rate coefficient in a matrix
3. *ODE\_AnthroEmiss.m*: Primary anthropogenic Hg emissions into atmosphere from all sectors (a function of time, including ‘by-product’ and ‘intentional uses of liquid Hg’ sectors) ([Horowitz et al., 2014](#_ENREF_3); [Streets et al., 2011](#_ENREF_5)), and total Hgdischarges into river (a function of time, including the dumping of wastewater from the commercial liquid uses in industrial processes, i.e. primary anthropogenic riverine Hg and erosion/terrestrial runoff, i.e. background riverine Hg) ([Amos et al., 2014](#_ENREF_1)). Raw data for primary anthropogenic Hg emissions and total Hg discharges data are stored *in AnthroEmissAllTime\_20120112.txt* (THg: 2nd column, GEM: 3rd column, averaged GOM+PBM: 4th column) and *River\_flux.txt* (dissolved Hg: 2nd column, particle-bound Hg: 3rd column), respectively.
4. *ODE\_Epsilon.m*: Primary anthropogenic Hg isotope emissions into atmosphere from all sectors (a function of time, including ‘by-product’ and ‘intentional uses of liquid Hg’ sectors) ([Sun et al., 2016](#_ENREF_6)), and primary anthropogenic riverine Hg isotope discharges (constant, The MDF and odd isotope MIF values of dissolved Hg and particle-bound Hg are assumed to be identical to commercial liquid Hg); the ‘epsilon’ enrichment factors (per mil Hg isotope fractionation) for Hg isotope fractionation between boxes. Raw data for primary anthropogenic Hg isotope emission and primary anthropogenic riverine Hg isotope discharges are stored *in Anthro\_isotope.txt* (MDF of GEM: 2nd column, MDF of averaged GOM+PBM: 3rd column, odd isotope MIF of GEM: 4th column, odd isotope MIF of averaged GOM+PBM: 5th column) and *River\_isotope.txt* (MDF of dissolved Hg: 2nd column, MDF of particle-bound Hg: 3rd column, odd isotope MIF of dissolved Hg: 4th column, odd isotope MIF of particle-bound Hg: 5th column), respectively. The default enrichment factors values are for ‘standard MDF and odd-MIF isotope model’ described in the accompanying manuscript, which can be changed to optimized enrichment factors as needed.

Firstly, the model is run until steady-state for both Hg mass and Hg isotope ratios in each box using natural Hg flux and Hg isotope ratios (we use a nominal timespan of 1\*10^5 years) (*ODE\_pre.m* + *ODE\_pre\_function.m*). Note that Hg and Hg isotope ratios may need different times to reach steady-state (see Note 3 of SUPPLEMENTARY INFORMATION for details). Using the Hg and Hg isotope ratios in natural steady state as initial conditions, the model is run until 1850 (*ODE\_anthro\_pre\_1850.m* + *ODE\_anthro\_pre\_1850\_function.m*) to simulate the pre-1850 anthropogenic Hg cycle. Then, using the Hg and Hg isotope ratios in the ending year of the pre-1850 anthropogenic Hg cycle as initial conditions, the model is run until 2010 (*ODE\_anthro\_post\_1850.m* + *ODE\_anthro\_post\_1850\_function.m*) to simulate the post-1850 anthropogenic Hg cycle. Figures 1-7 show natural cycle; Figure 11-14 show anthropogenic cycle; Figure 5 is Hg mass distribution at steady-state; Figure 15 is Hg mass distribution at 1850; and Figure 25 is Hg mass distribution at 2010.

**IMPORTANT NOTE!**

* *River\_flux.txt* stores total Hgdischarges into river (‘primary anthropogenic riverine Hg’ + ‘background riverine Hg’); *River\_isotope.txt* stores‘primary anthropogenic riverine Hg’ isotope composition (i.e. commercial liquid Hg); ‘background riverine Hg’ isotope compositions are the same as fast/slow/armored soil pools
* If you want to switch from MDF to MIF simulation, please change the values of variable **sign\_type** in all six scripts (*ODE\_pre.m* + *ODE\_pre\_function.m*, *ODE\_anthro\_pre\_1850.m* + *ODE\_anthro\_pre\_1850\_function.m*, and *ODE\_anthro\_post\_1850.m* + *ODE\_anthro\_post\_1850\_function.m*) from 1 (default value) to 2. Then, please change the source MIF signatures and MIF enrichment factors in *ODE\_Epsilon.m* in order to simulate odd- or even-MIF.

**Further reading:** Before using this code, it is useful to read previously relevant work.

1. Anthropogenic Hg emission to atmosphere ([Horowitz et al., 2014](#_ENREF_3); [Streets et al., 2011](#_ENREF_5))

2. Anthropogenic riverine Hg discharges ([Amos et al., 2014](#_ENREF_1))

3. primary anthropogenic Hg isotope emissions into atmosphere ([Sun et al., 2016](#_ENREF_6));

4. Box model of THg ([Amos et al., 2014](#_ENREF_1); [Amos et al., 2013](#_ENREF_2)) (@Matlab codes can be found here: <http://bgc.seas.harvard.edu/models.html>)

5. Global Hg isotope odd-MIF box model ([Sonke, 2011](#_ENREF_4));

**SUPPLEMENTARY INFORMATION**

1. **Why separate anthropogenic emissions into pre-1850 and post-1850?**

Amos et al. (2014) gives an estimate of post-1850 total riverine Hgdischarges (‘primary anthropogenic riverine Hg’ + background riverine Hg’). We assume ‘primary anthropogenic riverine Hg’ and background riverine Hg’ have different Hg isotope compositions, the former is represented by commercial liquid Hg and the latter by fast/slow/armored soil pools. In order to obtain ‘primary anthropogenic riverine Hg’ discharges, we have to subtract ‘background riverine Hg’ discharges from total riverine Hgdischarges. This will lead to a small difference in the code syntax between *ODE\_anthro\_pre\_1850\_function.m* and *ODE\_anthro\_post\_1850\_function.m*.

1. **How to obtain the differential equations of Hg isotopes in the function scripts?**

First, write out the differential equation of Hg isotope ratio, here we use δ202Hg as an example:



Then, applying the product rule to the left hand of the differential term:



and writing out (the definition of the Hg mass ODE) and move to right hand side:



Last, this equation is arranged for each box as shown in the function script:

@Matlab’s ODE solver automatically solves all function’s ODE (*ODE \_pre\_1850\_function.m, ODE\_anthro\_pre\_1850\_function.m* and *ODE\_anthro\_post\_1850\_function.m*) for all boxes.

1. **How to check the steady-state of Hg and Hg isotope under steady-state?**

Under the steady-state, the Hg and Hg isotope ratios of the whole system (all the boxes) should be constant.

1. **For Hg masses of boxes under steady-state**



Which can be decomposed as:



The natural Hg emission flux E\_geo is S, and the output fluxes are HgP sedimentation onto ocean floor occurring at surface, intermediate and deep ocean, and riverine HgP removal via fast/slow/armored soil erosion at coastal areas. We use *variable SS\_Hg* to store the computed value of this equation. If Hg reaches the steady state, then the *variable SS\_Hg* should zero (see *ODE\_pre.m, Figure 6)*.

1. **For Hg isotope ratios of boxes under steady-state**



Does Hg mass reaches the steady-state before Hg isotope ratio reaches steady-state? If it does, (i.e. ), then



Which can be decomposed as:

 We use variable *SS\_iHg* to store the computed value of this equation.

If , then



We use variable *SS\_iHg\_t* to store the computed value of this equation, and. If Hg isotope ratios reaches the steady state, then the *variable SS\_iHg\_t* should be zero (see *ODE\_pre.m, Figure 7)*.

References

Amos, H.M. et al., 2014. Global Biogeochemical Implications of Mercury Discharges from Rivers and Sediment Burial. Environmental Science & Technology, 48(16): 9514-9522.

Amos, H.M., Jacob, D.J., Streets, D.G., Sunderland, E.M., 2013. Legacy impacts of all-time anthropogenic emissions on the global mercury cycle. Global Biogeochemical Cycles, 27(2): 410-421.

Horowitz, H.M., Jacob, D.J., Amos, H.M., Streets, D.G., Sunderland, E.M., 2014. Historical Mercury Releases from Commercial Products: Global Environmental Implications. Environmental Science & Technology, 48(17): 10242-10250.

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