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Global Mercury Footprint Evaluation using a Geographical Pollutant Propagation Model

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This work presents a method for the accurate evaluation of the footprint of chemical pollutants on a global scale. An extension of the standard pollution propagation models is proposed to calculate the chemical footprint efficiently. The proposed improvements overcome the current modelling and enable the evaluation of the directed transport of chemicals with water or air flows. The current research introduces several model modifications to account for the directed pollutant transport with global water flows and selects the Jacobi solution method for the resulting large-scale system of mass transfer equations. The model was combined with geographic information system data to account for the geographical propagation of the pollutants. The proposed method is implemented in Microsoft Excel using the built-in Visual Basic for Applications programming language. The method is tested on the example of evaluating the Global Mercury Footprint. As a result of the work, a tool was obtained that allows estimating the chemical load for the entire World, taking into account the transfer of chemicals with water flows. In the future, this tool can also be used to support regulatory decisions, for example, to assess the effect of mercury immobilization in solid waste on the mercury footprint.

1. Introduction

Prediction of the environmental impact of anthropogenic chemicals is a critical component of decision-making when choosing chemicals for use in production and everyday life. This is especially important when assessing the potential risks to human health and the environment when introducing new products/substances. Chemical load modelling is one of the main forecasting tools. In particular, an acute example of a chemical component in need of a global and accurate evaluation is mercury. This has been widely recognized by the scientific community, as can be witnessed by the review of mercury emissions from energy generation (Charvát et al., 2020). This is a global pollutant (Tauqeer et al., 2015). By 2020, according to the provisions of the Minamata Convention on Mercury (IPEN, 2018), the countries that have ratified the Convention, must phase out mercury-containing products: batteries, switches and relays, mercury lamps, thermometers etc. It should be noted that according to Tarasova et al. (2018), such products and their waste are among the most significant sources of mercury pollution (UN Environment, 2017). Takaoka (2015) confirms this for the case of Japan. Mercury can also be released from the incineration of mercury-containing household waste, such as e-waste, medical waste, and consumer products (compact fluorescent lamps, cosmetics, switches, thermometers) (IPEN, 2018). It has been estimated that up to 10 % of the current anthropogenic mercury emissions are released by open burning of such waste materials (Wiedinmyer et al., 2014). The global inventory of atmospheric mercury emissions from anthropogenic sources amounts to 2,000 - 3,000 t/y. Mercury emissions associated with the disposal of mercury-added product waste is 7 % of this (UN Environment, 2019).
Models describing the behavior (including transformation) of chemicals and their propagation into various natural media have been developed. Such are the models CalTOX (2020) – updated but not actively developed, BETR (2020) – partitioning the World map into 15 ° cells, USEtox (2020) – referred to as the "scientific consensus

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model", with its implementation (MacLeon et al., 2005). Of these, the USEtox model has several advantages. One is the database containing information on the ecotoxicological characteristics of approximately 2,500 chemicals – including mercury and other heavy metals (Rosenbaum et al., 2008). In the standard USEtox model, natural media are represented as compartments that contain a pollutant.
The environment is described in the USEtox model (Figure 1) in the form of a 2-tier system comprising regional and global levels, each of which includes compartments describing atmospheric air (urban and rural), agricultural soil, and soils of other types, freshwater, and coastal seawater or ocean. Depending on the processes taking place in a compartment, the pollutant may remain within the chamber where it was initially released, may be transformed into other chemicals via, e.g., hydrolysis or oxidation, or may migrate to another compartment (Fantke et al., 2017).

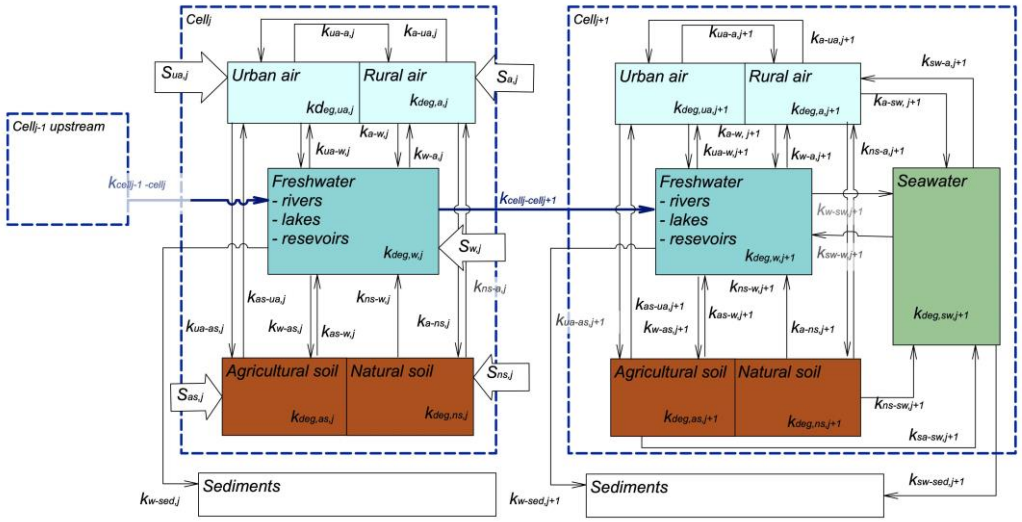

Figure 1: The model of mass transfer between cells (S - sources of hazardous chemicals, k - rate constants for the transfer/degradation/removed of chemicals)

Another model is Pangea (2020), developed by Australian scientists in 2017. It has been designed to estimate the content of chemicals in water, soil, and air, taking into account their propagation with water flows (Wannaz et al., 2018). The environmental process models in Pangea are currently based on the IMPACT (Pennington et al., 2005) and USEtox models, adapted for taking spatial data into account, aided by the use of Geographic Information Systems. The mode is of hierarchical nature, containing several levels. It lumps cells with similar properties into more massive clusters. This modelling technique greatly simplifies the solution but also leads to loss of accuracy and fidelity due to the lumping the measurement errors.
An alternative way of solving the large-scale matrix of mass balances is to use the original maps, avoiding data aggregation. The standard USEtox model was used as the basis for formulating the mass transfer equations, which is constitute the central part of the model for chemical footprint analysis. To take into account the transfer of chemicals with water flows, the USEtox model was adapted (Makarova et al., 2018). Instead of one local level as in the USEtox model, that work introduced a set of local levels (cells) (Figure 1). That allowed the model to take into account the interaction between the local levels, e.g., directed transfer of chemicals with water or air flows. The model was combined with GIS (Geographical Information System) data to solve this task, partitioning the studied area for the entire World on a 0.5 ° by 0.5 ° grid. In the model construction, the ocean and the atmospheric air above it remain at the global level. However, unlike the Pangea model, the cell scale was not enlarged. Instead, the model used the scale of the GIS data directly, avoiding additional interference to the initial data due to lumping. This chemical footprint model of the entire World results in a very large-scale underlying matrix of mass balance equations – of the size 1.5×10^6 (equations × variables) (Makarova et al., 2019).
In summary, the two main approaches to modelling the transfer and propagation of chemicals for estimating their impacts and footprints, resort to either highly lumped models or to the use of a finer map mesh. The issue with the lumped models lies in the amplification of the inaccuracies of the processed data, to the point that the model may be no longer representative of the problem. On the other hand, the finer-grained models result in a very large-scale matrix of equations, which takes an extremely long time to solve or does not converge at all.
The current paper presents an approach to solving the natural-scale system of equations in a reasonable time

and with the desired accuracy. The proposed method solves the equations of the USETox model in the variant of one global level and many local ones. The novel element is the introduction of additional degrees of freedom in the model, which allows accounting also for the mass transfer between the model compartments for air and ocean. The resulting system of equations is solved directly using the original GIS data on maps of 0.5 to 0.5 degrees without introducing intermediate aggregated levels and, without averaging the original GIS data, and without the errors associated with this averaging.

2. Evaluation method and computational results

The chemicals in the cell mainly come from stationary technogenic sources ($S_{p,n}$ = const (kg/s)). Assuming steady-state conditions, the following system of equations is obtained for the cells n = (1, N):

$$S_{p,n} = \sum_{j=1}^{N}\sum_{i=1}^{6} k_{p,n\to i,j,} m_{p,n} - \sum_{j=1}^{N}\sum_{i=1}^{6} k_{i,j\to p,n} m_{i,j} + k_{deg,p,n} m_{p,n} + k_{sed,p} m_{p,n}, \quad (1)$$

Where: n, i = {*a, as, ns, sw, ua, w*} compartments in a cell denoting natural media; j,p = {1.. 259, 200}: cells on the map; $S_{p,n}$ – chemical intake flow in the current compartment n in cell p (kg/s); $m_{p,n}$ – the mass of the chemical in the current compartment n in cell p (kg); $m_{i,j}$ – the mass of the chemical in the compartment i in cell j (kg).
The model expressed in Eq(1) takes as specifications:

- The migration rate $k_{p,n\to i,j}$ (s^{-1}) - between compartment n of the cell p and compartment i of the cell j, denoted as $k_{a\text{-}wj}$ (s^{-1}) in Figure 1 for the case of mass transfer from rural air of the cell$_j$ to the freshwater of the cell$_j$;
- The degradation rate $k_{deg,p,n}$ (s^{-1}) compartment n of the cell p, - denoted as $k_{deg.wj}$ (s^{-1}) in Figure 1 for the case of the chemical degradation in freshwater in cell$_j$;
- The rate of removal $k_{sed,n}$ (s^{-1}) from cell p to sediment - denoted as $k_{w\text{-}sed,j}$ (s^{-1}) in Figure 1 in case cell$_j$.

In Eq(1), the terms have the following meaning:

- $k_{p,n\to i,j} m_{p,n}$ – migration rate of the chemical from compartment n of cell p to compartment I, cell j (kg/s);
- $k_{i,j\to p,n} m_{i,j}$ – migration rate of the chemical from compartment i of cell j to compartment n of cell p (kg/s);
- $k_{deg,p,n} m_{p,n}$ – degradation rate of the chemical in the investigated compartment n of the cell p (kg/s);
- $k_{sed,n} m_{p,n}$ – chemical removal rate in sediments in the investigated compartment n of the cell p (kg/s).

An additional modelling element proposed in this study, at the stage of compiling the matrix of transfer coefficients, is to take into account the mass exchanges between the compartments for global air and the ocean due to the chemicals transfer. In a previous work (Makarova et al., 2019), which did not account for mass contaminant transfer concerning the ocean and atmospheric air components, this system of linear equations could not be solved by iterative methods.
Specifying more accurate values for the migration coefficients in global air and the ocean makes it possible to successfully use both direct and iterative methods for solving the system of contaminant mass balances.
The following approaches (Saad, 2007) to solve the model have been tested: Bistabilized Gradient Method, Linear Solver restarted GMRES (Generalised Minimum RESidual) and the MINRES (MINimum RESidual) iteration methods, the Jacobi method, the LGMRES method with a preconditioner – all supplied with the Python library (SciPy, 2020),

The first method evaluated for solving the model was the Bistabilized Gradient Method, in which initial guess m_n = 0 kg/s was taken. This method showed low efficiency, and after more than 10,000 iterations (Figure 2), no convergence was achieved. The merging was estimated using the residual norm equal to the square root of the sum of the squared deviations.

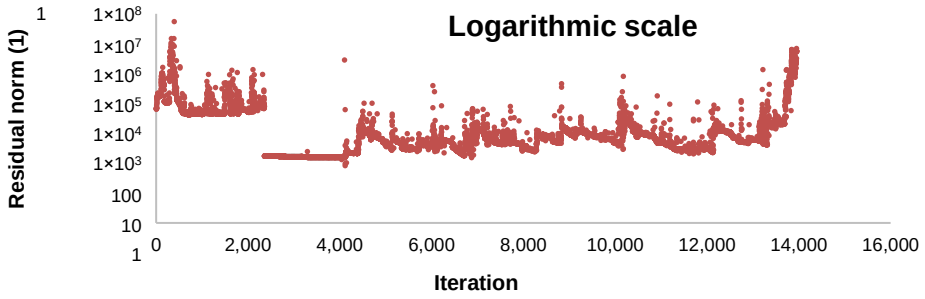

Figure 2: The residual norm for the Bistabilised Gradient Method

The next to solve this system were the iterative methods LGMRES (Linear Solver restarted GMRES), MINRES (MINimum RESidual iteration) and LSMR (Iterative solver for least-squares problems) (SciPy, 2020) from the linear algebra module for sparse matrices (scipy.sparse.linalg) in Python Figure 3a shows the dependence of the residual norm for the LGMRES method. The residual norm starts from 137 (1) and stabilises at 55.7 (1). When solving using the MINRES method (Figure 3b), the residual norm also starts from 137 (1). and then stabilises at 20.4 (1). These results are better, but the achieved convergence was poor.

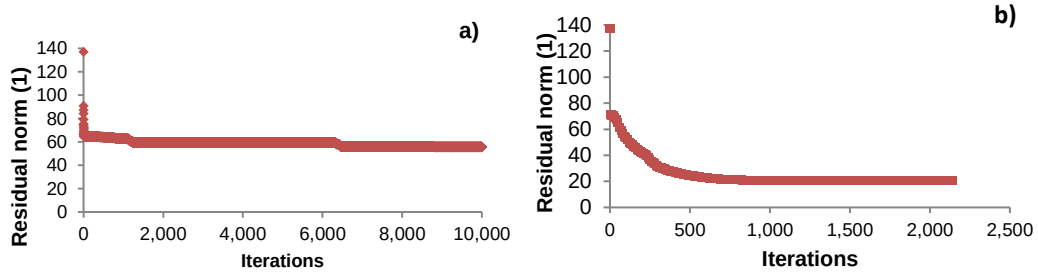

Figure 3: The residual norm in linear scale: a) for the LGMRES method, b) for the MINRES method

The Jacobi method, which previously worked only on a partitioned matrix, after the proposed model changes, converges relatively quickly for 394 (1) to a solution with an accuracy of 9.8×10^{-10} (1), demonstrating excellent final convergence. The graph of the error in the usual and logarithmic coordinates is presented in Figure 4.

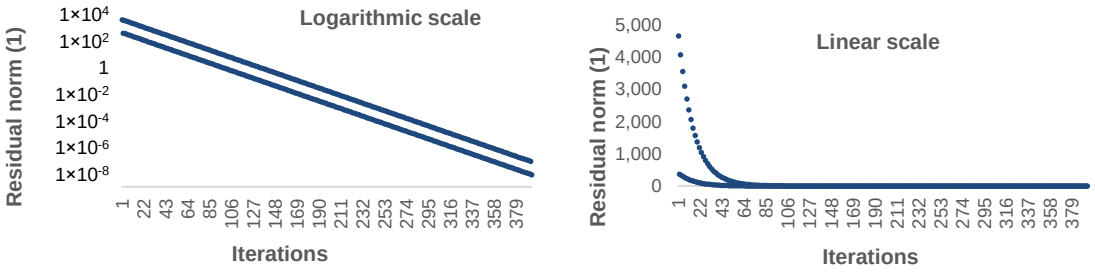

Figure 4: The residual norm for the Jacobi method in logarithmic and linear scale

The solution of the System of Linear Algebraic Equations using the LGMRES method with a preconditioner was also considered. The preconditioner was obtained using the scipy.sparse.linalg.spilu function (based on the Supernodal sparse direct solver). This resulted in a significant convergence acceleration. The sufficiently low residual norm at 6×10^{-10} (1) was already at the 3-rd iteration (Figure 5).

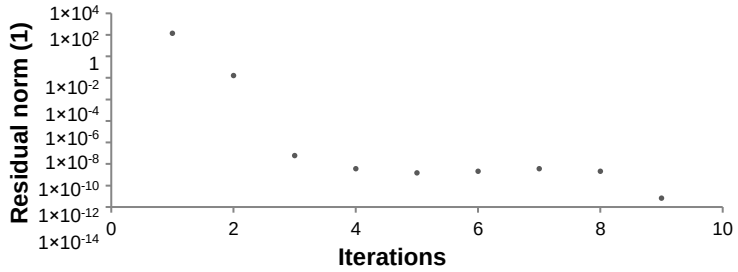

Figure 5: The residual norm for the LGMRES method with a preconditioner in logarithmic scale

For all considered iterative methods, a vector consisting of only 0 was taken as the initial approximation of the solution. Using the direct solution method **spsolve** from the **scipy.sparse.linalg** module (based on the UMFPACK package), it was possible to obtain a solution with a residual norm of 6.48×10^{-10} (1).
For quantifying the Global Mercury Footprint, the proposed model uses data on mercury emissions from anthropogenic sources. They were taken from the Arctic Monitoring and Assessment Program (AMAP/UNEP, 2013), which provides datasets on a 0.5 ° x 0.5 ° grid. These include emissions in kg/"grid cell", and the grid cell

area (km^2). The 2010 global mercury intake flows ($S_{p,n}$ in Eq(1)) into the atmosphere, coming from anthropogenic sources, were determined for:(a) Stationary combustion sources: power plants, distributed heating, and energy use (excluding industry); (b) Industrial sources; (c) Sectors related to intentional use and product waste.

3. Analysis and discussion

The case study model has been solved using the Jacobi method as the best-performing one. This method, as also the LGMRES method with a precondition, allows us to quickly find a solution (Figure 4) tor the created matrix. However, the Jacobi method, unlike the LGMRES method with a precondition, is much simpler to implement and does not require additional software. The Jacobi method produced six maps of Global Mercury Footprint by environmental compartments – urban air, rural air, freshwater, seawater, agricultural soil, other soil. Figure 6 shows the Mercury Footprint for freshwater bodies calculated by the proposed model. The green color indicates areas in which the mercury concentration lower than the maximum permissible for the fishery. Yellow denotes areas where the maximum concentration limit for drinking water is exceeded (moderate heath risk), and red indicates extremely high levels posing a very serious danger to humans and biota. The map clearly shows the spread of mercury contamination in highly populated regions or regions of sourcing food, indicating the high level of threat to human health. These results correlate very much with the measured data of mercury concentrations in aquatic species (Evers et al., 2018), as well as with a map of global mercury-related worker disability (Steckling et al., 2017).

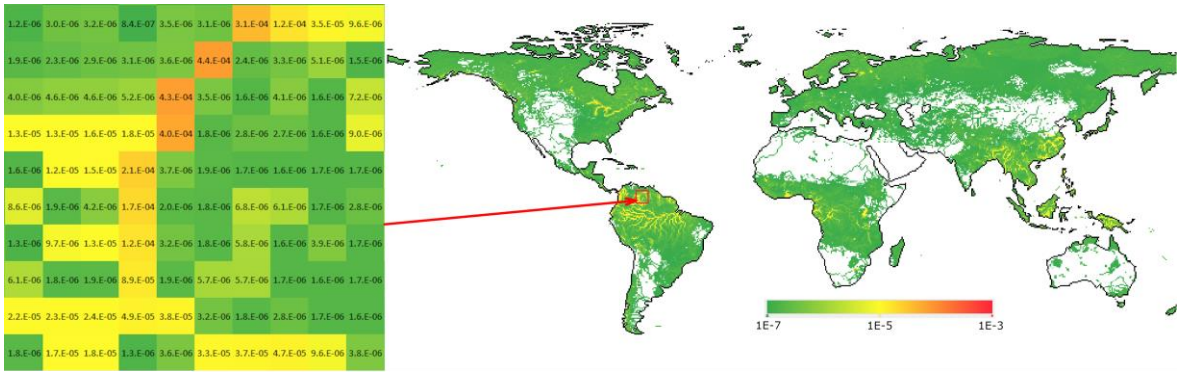

Figure 6: Mercury footprint for freshwater bodies calculated by the proposed model

4. Conclusions

The current work presents a model extension and a solution method for the evaluation of Global Chemical Footprints. Its efficiency and achievable accuracy have been demonstrated on the example of Global Mercury Footprint evaluation. The Jacobi method proved as the most efficient in obtaining the solution in several hundred iterations, compared with the slow convergence or the lack of that in previous chemical footprint evaluation models. The achieved convergence can be characterised quantitatively by the reduction of the residual norm from the order of 10^3 down to 10^{-10}. The results confirm the ability of the proposed model to evaluate the chemical footprints of any pollutants subject to data availability. The produced maps of Global Mercury Footprint provide better accuracy than the general maps lumping deceases by countries. The current model can be further extended to include a modelling component accounting for atmospheric transport of the pollutants, which presents an excellent avenue for future research.

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