FATE AND TRANSPORT OF DDT IN A TROPICAL FLOODPLAIN LAKE

Annelle Mendez[1*], Carla Ng[1], João Torres[2], Konrad Hungerbühler[1]

[1]Institute for Chemical and Bioengineering, ETH Zurich, CH-8093 Zurich, Switzerland; [2]Universidade Federal do Rio de Janeiro, 21941-902 Rio de Janeiro, Brazil

Introduction

A Northern bias has been identified in environmental science research, wherein monitoring and modeling of persistent organic pollutants (POPs) have mostly centered in temperate and cold regions[1]. In Latin America, limited data exist to establish temporal trends of POPs in core media, which would facilitate an assessment of the effectiveness of efforts to reduce or eliminate POP releases into the environment[2,3]. DDT is an organochlorine insecticide whose use is currently restricted to indoor residual spraying (IRS) for malaria vector control under the Stockholm Convention on POPs. In 2011, nearly 3.3 billion people worldwide were at risk of malaria, which is endemic to tropical countries, including Brazil [4]. According to law, DDT use for vector control in Brazil was reduced in the mid-90s and a final federal ban was issued in 2009. However, in a traditional Amazonian settlement around Lake Puruzinho, studies in 2005 and recent sampling campaigns in 2011 have found that DDT and its metabolites have accumulated in soils, sediments, and fish tissue[5]. Also, biomonitoring studies in 2004 detected ΣDDT concentrations in human breast milk that result in an infant daily intake four times above the WHO standard[6]. To gain an insight into the potential pathways leading to such high DDT levels, within the larger goal of contributing to a better understanding of POP dynamics in under-studied tropical ecosystems, a temporally resolved multimedia environmental model describing the fate and transport of DDT and its metabolites was developed. The model captured the highly variable environmental conditions, particularly the seasonality of the hydrological cycle, that characterize tropical floodplain lakes and their effects on pollutant distribution and mobilization.

Materials and methods

Multimedia mass-balance box models provide a comprehensive way to organize and link empirical and theoretical knowledge gained from studies of chemical properties, partitioning, mass transport, and transformation into a coherent overall picture and thus identify the processes that determine pollutant concentrations in the environment[7]. To apply the concepts of multimedia modeling to the Puruzinho environment using a fugacity approach, the lake was first divided into four sections to take into account discharge by tributaries and advection[8]. Each section was in turn divided into six well-mixed "boxes" or compartments: atmosphere, water, sediment, flooded floodplain soil, aerated floodplain soil, and upland terra-firme soil (Fig 1). Houses are located on terra-firme soils, which are never flooded. Chemicals are transported across boxes through several intermedia exchange processes such as diffusion and deposition, and are lost within each box as a result of advective processes such as soil burial and degradation (Fig. 1a). Mass balances for each compartment were solved through numerical integration to take into account variability in input parameters through time as a result of changing environmental conditions, particularly precipitation. Puruzinho Lake behaves like a lentic (still) aquatic system during extreme low water and high water levels and as a lotic (flowing) system in the transition times. The water level varies from 1m-12m, driven by regional precipitation. Seasonal changes in water levels, resulting in changes in flooded areas (Fig. 1b), were represented through different inflow and outflow scenarios included in a water mass balance.

DDT has been applied for malaria vector control on the inside house walls of Puruzinho houses as a water dispersible powder since 1960. Based on legislation and on observations from scientists engaged in public health research at Puruzinho, it was assumed that 2 g of active ingredient were applied per m^2 of house wall from 1960-1992, 1 g/m^2 from 1992-1997, and 0.5 g/m^2 from 1998 until the final federal ban in 2009. Spraying occurred twice per year, and it was assumed that the amount of DDT sprayed was continuously emitted from the walls until the next application. Two emissions scenarios describing the maximum amount of DDT that could have been emitted into the Puruzinho environment were set up.

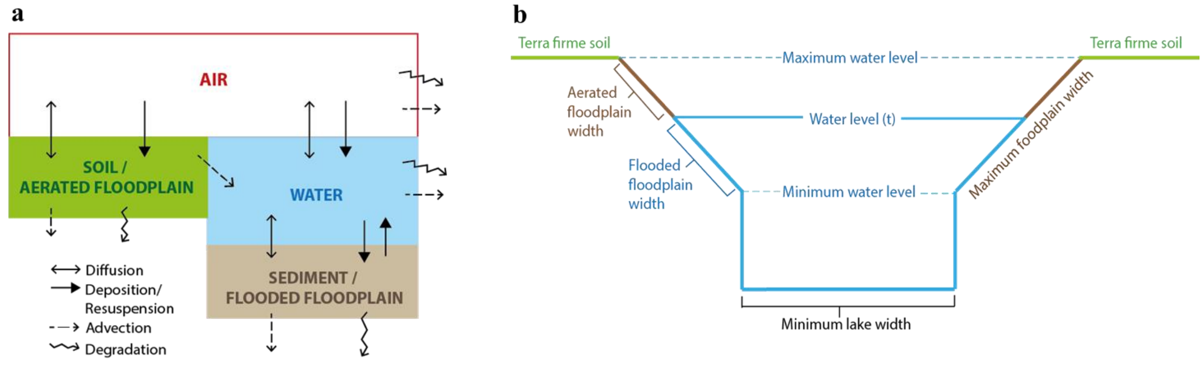

Figure 1. a) Diagram illustrating processes for the inter-compartment exchange and loss of DDT from each compartment in the environmental model. b) Cross-section of Lake Puruzinho

Scenario 1 assumed that 100% of the DDT applied is released into the air, based on a model for a South African hut[9]. Given that houses have a different structure in Brazil, with less absorbent wooden walls, scenario 2 assumes 10% emissions into soil, based on a WHO generic model for exposure during IRS[10].

The model was run from 1960-2013 and tracked the p,p'-DDT isomer, which constitutes 75% of the active ingredient, and its degradation products: p,p'-DDE and p,p'-DDD. A one-factor-at-a-time sensitivity analysis was carried out to identify the input parameters with the greatest influence on model results through time.

Results and discussion

Under both emissions scenarios, concentrations of DDT and its metabolites follow the decreasing trend of emissions throughout the model run, as shown in Fig. 2a for emissions scenario 1 from 1980-2013. DDT accumulates mostly in soils and sediments. In these compartments, the response of DDT concentrations to reductions in emissions is very slow. This behaviour is expected as DDT partitions preferentially into the organic carbon in soil and sediment solids due to its high octanol-water partition coefficient (K_{OW}). Furthermore, the degradation half-life of DDT in soils and sediments is estimated to be two orders of magnitude longer than that in air and nearly twice as long as that in water. Less DDT accumulated in the air and water compartments and emissions reductions resulted in a sharp decrease in DDT concentrations, particularly after emissions ceased in 2009. DDT is mainly associated with the particulate phase (suspended solids in water and aerosols in air). These particles represent only a minimal volume of the bulk air and water compartments, and they are deposited into the soils and sediments, so the water and air compartments do not represent long-term repositories for DDT.

DDT accumulation in the compartments followed a cyclical pattern in response to spatial and temporal environmental changes induced by the hydrological cycle (Fig. 2b). Lake Puruzinho is a highly dynamic floodplain lake whose volume changes continuously throughout the year, driven by regional rainfall. As rain increases, water level increases, so a larger volume and surface area of water can interact with the air and the flooded floodplain. Wet gaseous and aerosol deposition from the air to the surfaces and soil runoff also increase. Overall, DDT inputs into the water increase with increasing water levels and rainfall. Furthermore, DDT mass in the aerated floodplain is transferred to the flooded floodplain as water levels increase, and the opposite occurs as water levels decrease. The periodicity of DDT concentrations in the terra-firme soils and sediments is less pronounced as DDT has a long half-life and a high affinity for the organic carbon in these compartments, as explained above, and is thus less mobile. DDE and DDD exhibit a similar partitioning behaviour in the environment as their parent compound, as they have similar physico-chemical properties. These observations also hold for model results under emissions scenario 2.

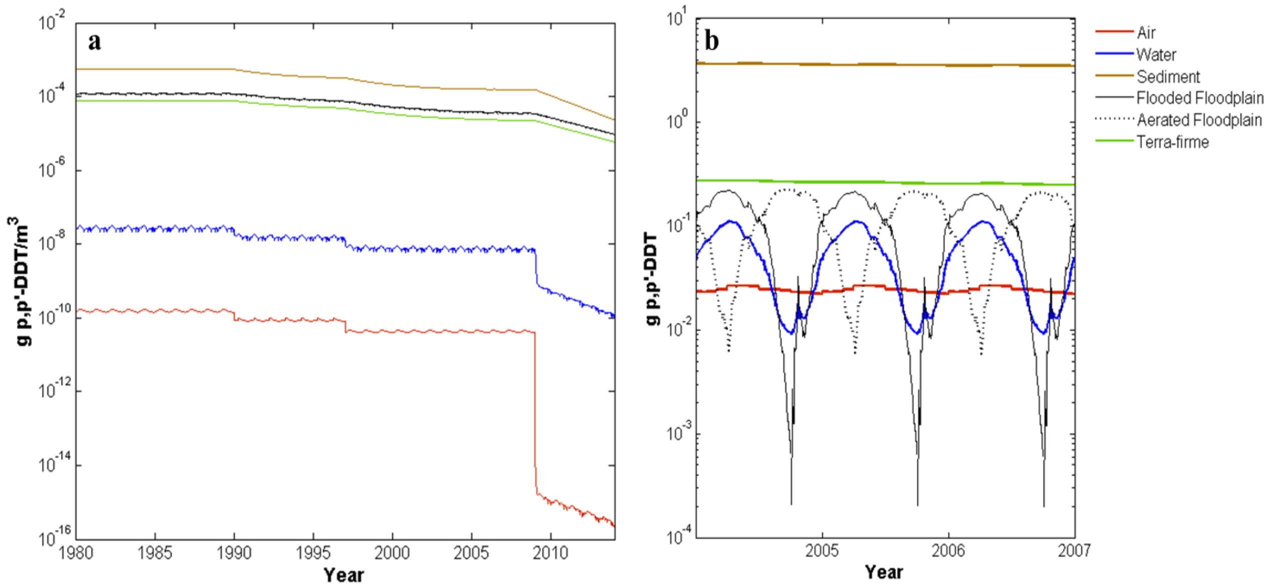

Figure 2. a) Concentration of p,p'-DDT in the different compartments predicted by the environmental model under emissions scenario 1. b) Periodicity in the mass of p,p'-DDT in the different compartments.

The following discussion for DDT also holds for its metabolites. As shown in Figure 3, only a few measurements for DDT, DDE and DDD are available for comparison with the model results, and these measurements vary substantially. In 2005 and 2011, higher DDT concentrations were measured in house soils than in background soils collected from nearby forests. DDT house soil concentrations in 2011 are 1-2 orders of magnitude higher than in 2005, which is unusual as DDT was expected to have been phased out by then. When 100% of the emissions occur into the air, the model predicts soil concentrations that are between the 2005 and 2011 house soil measurements and over-predicts DDT concentrations in the sediments (Fig. 3a). When 10% of the emissions occur into the soil (Fig. 3b), the model over-predicts DDT concentrations in all compartments, as expected given our high emissions scenarios. However, the model now shows that DDT accumulation in the terra-firme soils is higher than in the sediments, which is consistent with the 2011 measurements. Under both emissions scenarios, the model predicts a slow decrease in DDT concentrations in terra-firme soils as a result of ceased emissions. Elevated DDT levels detected in Puruzinho house soils in 2011 could be a result of measurements in hot-spots, as only a few measurements were taken, or due to new, unreported use of DDT. While DDT concentrations in breast milk samples from Puruzinho in 2004 are within the same order of magnitude as those measured in South African sites with a similar history of IRS[11,12] , 2011 soil concentrations measured in Puruzinho are unusually high compared to these sites, which raises concerns about recent DDT applications and higher human exposure.

A sensitivity analysis was carried out to investigate differences between model results and measurements that could arise from the model input parameters. This analysis showed that the model is sensitive to similar parameters throughout each year and only a few differences in sensitivity appear between pre and post-ban years. Throughout all years of the model run, DDT concentrations in different compartments are the most sensitive to input parameters associated with emissions, such as DDT application rates and residual efficacy, to chemical properties such as degradation half-lives and K_{OW}, and to the fractions of formation of DDE and DDD from their parent compound. In post-ban years, the model output becomes less sensitive to partition coefficients, and more sensitive to parameters associated with loss processes, particularly those involved in the sediment mass balance, such as the concentration of suspended particles, the organic carbon content and settling velocity of suspended particles, and the sediment burial rate.

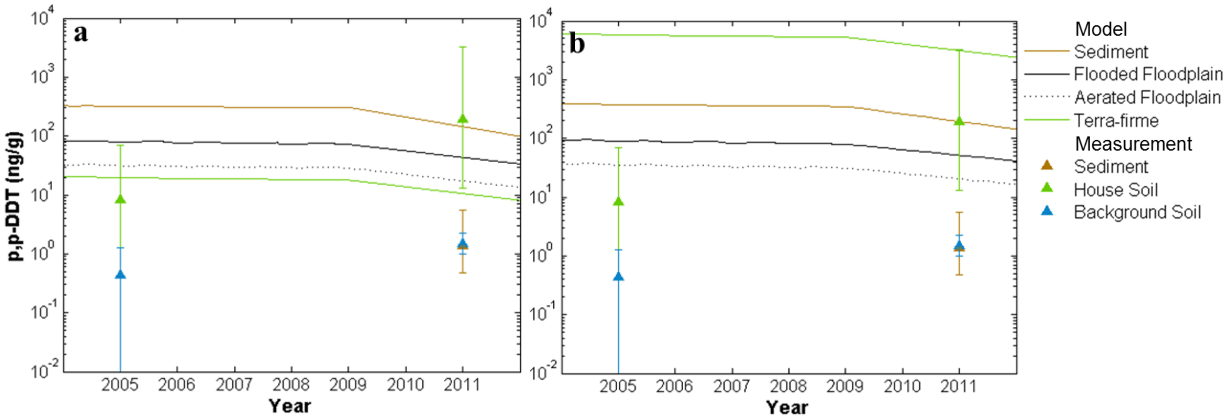

Figure 3. Comparison of model results under emissions scenario 1 (a) and emissions scenario 2 (b) with 2005 and 2011 data available for p,p'-DDT in Puruzinho.

Overall, through a multimedia environmental mass balance model, we explored how variable environmental conditions in a tropical floodplain, particularly seasonal rainfall patterns, as well as different emissions scenarios associated with IRS affect the movement and distribution of DDT and its degradation products. When the model results are compared with DDT measurements in soils and sediments, the scenario with 10% emissions into the soil best represents the pattern of DDT accumulation among the compartments. Nonetheless, this observation is based on only one existing set of sediment measurements. Therefore, we are currently analysing a second set of sediment and soil measurements to confirm this pattern and to shed light on the unexpectedly high DDT concentrations detected in soil samples from 2011. In addition, the emissions scenario must be fine-tuned, as the model output is very sensitive to input parameters associated with emissions and the two scenarios tested represent an upper-bound for the amount of DDT sprayed on the walls that reaches the environment. A multimedia model for a house will be created to better describe DDT transfer from the house interior into the outdoors, and will be coupled to the environmental model for Puruzinho. Once the differences between model results and measurements are bridged, this model can be used as a predictive platform to assess the effect of environmental changes, such as a different length of dry and wet seasons as a result of climate change, on pollutant mobilization, and to explore the fate and transport of other POPs in tropical floodplains.

References:

1. Karlsson S, Srebotnjak T, Gonzales P. (2007); *Environmental Science & Policy* 10(7–8): 668-684
2. UNEP. (2009) *Global Monitoring Plan for Persistent Organic Pollutants. First Regional Monitoring Report. Latin America and the Caribbean Region*
3. Barra, R.; Colombo, J.; Eguren, G.; Gamboa, N.; Jardim, W. F.; Mendoza, G. (2006); *Reviews of Environmental Contamination and Toxicology*, 185:1-33
4. WHO (2012); *World Malaria Report.* Available at: http://www.who.int/malaria/publications/world_malaria_report_2012/report/en/index.html.
5. Saldanha, G. C.; Bastos, W. R.; Torres, J. P. M.; Malm, O. (2010); *J. Braz. Chem. Soc.* 21: 306-311
6. Azeredo, A. (2007). Pesticidas organoclorados e HPAs: Estudo de dois grupos de poluentes organicos. DSc Thesis, Universidade Federal do Rio de Janeiro
7. MacLeod M, Scheringer M, McKone TE, Hungerbuhler K. (2010); *Environ Sci Technol.* 44(22): 8360-8364
8. Mackay D. (2001); *Multimedia environmental models: the fugacity approach*.
9. Niederman, N. (2012) Modeling the fate of DDT applied in Indoor Residual spraying in a South African Homestead. Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology Zurich
10. FAO/WHO JMPR (2001). *FAO Plant Production and Protection Paper 163*
11. Van Dyk, J. C.; Bouwman, H.; Barnhoorn, I. E. J.; Bornman, M. S. (2010); *Science of The Total Environment,* 408 (13): 2745-2752
12. Bornman, M.S.; Barnhoorn, I.E.J.; Genthe, B. (2010); DDT for Malaria Control: Effects in Indicators and Health Risk. *WRC Report No. 1674/1/09*