

ADAPTATION OF A MULTIMEDIA MODEL TO ASSESS THE ENVIRONMENTAL BEHAVIOUR OF α -HEXACHLOROCYCLOHEXANE IN ITALIAN ALPS

Tair Teran-Guerrero^{1,2}, Lara Lamon^{1,2}, John N. Westgate³, Edoardo Bucchignani^{1,4}, Myriam Montesarchio^{1,4}, Frank Wania³, Antonio Marcomini^{1,2,*}

¹ Centro Euro-Mediterraneo per i Cambiamenti Climatici (CMCC), Divisione Impatti sul Suolo e sulle Coste (ISC), Via Augusto Imperatore 16, 73100 Lecce, Italy. ² Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari Venice, Calle Larga Santa Marta 2137, 30123 Venice, Italy. ³ Department of Physical and Environmental Sciences and Department of Chemistry, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, M1C 1A4, Canada. ⁴ Centro Italiano Ricerche Aerospaziali (CIRA), Capua, Italy. *Corresponding Author: telephone number: +39 041 234 8548 email: marcom@unive.it

Introduction

High-altitude mountainous ecosystems are important areas used for recreational, extensive agricultural purposes and as energy resources¹. In the last 25 years, studies have revealed that alpine environments, similar to the polar regions, are also affected by the transport of persistent organic pollutants (POPs)². Several studies have reported the presence of elevated concentrations of POPs in mountainous regions in both biotic and abiotic media compared with those found near of source's sites at mountains' bottom or valley^{1,3-5}. They noted a wide variety of concentration patterns due to changes in climatological patterns linked with geographical and seasonality of primary and secondary emissions and chemical properties, for a wide range of POPs, such mountain cold condensation patterns in mountainous regions^{1,6}. In order to explain the different patterns, several multimedia fate and transport models (MMMs) have been developed, as function of climate variables (e.g. temperature, atmospheric circulation, and precipitation), in order to analyse the effect of mountainous regime on POPs' environmental distribution due to changes in climatological patterns⁷⁻¹⁰.

Mountain cold condensation⁸ or cold-trapping^{5,10} was explored using the global dynamic model CliMoChem representing alpine conditions with lower temperatures and higher precipitations in the top of a generic mountain. The first results from this attempt found that wet atmospheric deposition, dependent of temperature and precipitation gradients, is mainly responsible for the mountain top and polar cold condensation effect⁸. These findings were strengthened by the MountainPOP model^{5,7,10}. Simulations performed with such model showed that POPs that are not efficiently scavenged by precipitation were found in higher concentrations at top elevations⁵. Moreover, the use of MountainPOP reveals which environmental factors are the key factors that explain this mountain cold-trapping behaviour: 1) a high atmospheric organic particle load; 2) a strong gradient of precipitation increasing upslope; 3) and a large temperature gradient from the valley to the mountain-top¹⁰. Westgate et al. (2013) proposed that European Alps exhibit a high mountain cold trapping due to their great height which produces strong gradients of precipitation and temperature¹⁰.

The aim of the present study is the adaptation and application of the MountainPOP model to a specific case study, in order to predict the environmental behaviour of alpha-HCH in Valtellina Valley in Northern Italian Alps at an altitudinal gradient. The model was evaluated considering climatic data related to a recent past period, obtained with the regional climate model COSMO-CLM²³ and then compared with alpha-HCH monitored concentration's data. The simulation has been focused in identifying the effect of climatological and environmental variables on POPs' environmental behaviour in the case in hand. Alpha-HCH was chosen because of the availability of real data observations, measured in mountainous regions of Valtellina Valley in more than one environmental compartment.

Materials and methods

MountainPOP is a fugacity based dynamic fate and transport box model^{5,10}, that have been used to hypothetical case studies^{5,7,10}. Our present version, MountainPOP3.0, is to our knowledge, the first attempt that considers real conditions and observations. MountainPOP3.0 describes a mountain as a sequence of five different altitudinal zones. Each zone contains three compartments: soil, fresh water stream and atmosphere. Zones can differ in their depth of soil, fraction of surface covered by the water stream, height of atmosphere, and fraction of soil organic matter¹⁰. Each zone is parameterized by its length and has its own temperature, precipitation, wind speed, water stream velocity and concentrations of contaminant in its compartments. Contaminants can move between zones in the atmosphere and in the water stream. Wind, and thus contaminants, are free to move out of the mountain by advecting down from the lowest compartment, or up from the top compartment¹⁰. Down-slope flux advects the contaminants between zones in water stream. The volume of water stream is dictated by a mass balance constructed from precipitation, evaporation and Horton's overland flow, considering the maximum rain and infiltration capacity of soils, in order to calculate the runoff that moves from saturated soil to water stream^{11,12}. This approach is feasible for scarce vegetation regions such as high elevated regions.

The interaction between the mountain and its surroundings is through a fraction of background concentrations (C_{back}), where C_{back} has been computed by the Global fugacity model BETR-Research^{13,14}. The C_{back} are presented as existing material during the first time-step in soil, and during all period for water stream and atmosphere.

The alpha-HCH chemical is emitted from the lowest zone into air and soil, supporting the approach that the greater human impact in this pristine mountainous zone occurs in the valley (bottom zone)¹⁰. The chemical is described by their temperature-dependent partitioning properties and their degradation rates¹⁰.

1. Model Set-up

Figure 1 shows the model domain and the five altitudinal zones. The model domain is the upper-Adda river basin scale (2580km²) in the north-eastern of Italian Alps, in Lombardy region located at latitude coordinates 46,12 and 46,55 and longitude coordinates 9,50 and 10,55.



Figure 1. Case study area. Adda River basin and location in the North-eastern of Italy, Lombardy Region¹⁵.

The mountain has been constructed taking into account the altitudinal and morphological characteristics. The five zones are described as follows: Zone 1 describes an altitudinal range of 200 to 1600m a.s.l and covers a surface area up to 796 km². Zone 2 contains an altitudinal range of 1601 to 2200 m a.s.l and a surface area of 700 km². Zone 3 describes an altitudinal range of 2701 to 3400m a.s.l and covers a surface area of 690km². Zone 4 describes an altitudinal range of 2701 to 3400m a.s.l and contains a surface area of 371km². Finally Zone 5 that contains the mountain top over 3041m a.s.l and has a surface area of 20km². The Adda River springs in zone 5 is modelled as a straight form with proportional dimensions through all the other zones. The alpha-HCH inputs come from the settlements found in the vicinity of Como municipality at zone 1. The atmosphere height is the same for all zones: 763,65km. The depth of soil varies for each zone in the range of 1,3 for the bottom zones and up to 0,02m for the top zones. The surface covered by water stream and the water current velocity were calculated for each zone taking the method of hydrological mass-balance^{16,17}.

2. Physical chemical data and environmental parameters

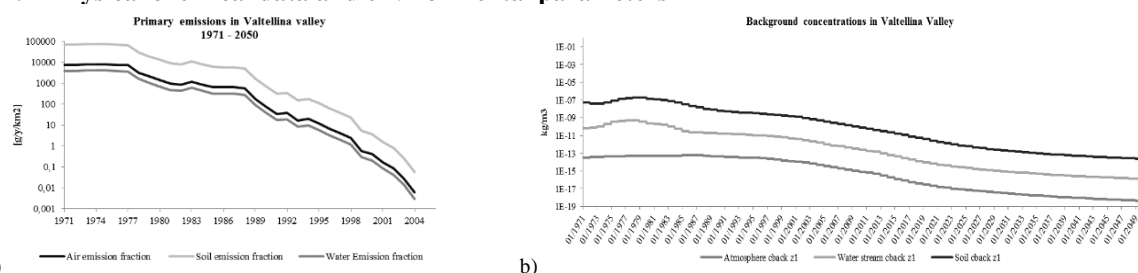


Figure 2. Input inflow emissions (a) and background concentrations (b) for Zone 1. Background concentrations were taken into account only for the first year of our simulation. These values were re-calculated from other works¹⁴.

The input physical chemical data for our simulations were taken from similar works¹⁸⁻²⁰. The input environmental parameters were: fraction of soil solids which are organic matter calculated from previous studies¹⁵; air-soil dry deposition velocity, volume fraction of aerosols in air; rain scavenging ratio; water to air mass transfer coefficient and air to water mass transfer coefficient took from past taken from other works^{5,10,21}.

Figure 2 shows the input inflow air and soil emissions and concentrations for the present scenario. These inputs were obtained from the calculations performed in Wöhrnschimmel et al (2012). The background concentrations and emissions were taken for region 61 of the BETR-Research model. In our model, Alpha-HCH background concentrations are expected to reduce under the present scenario (20CE). On the other hand, alpha-HCH has been banned during the last decade and the emissions have been null for Central Europe up to 2003.

3. Climate variables

Climate variables are defined by the simulations performed with COSMO-CLM²² to the Italian Alps at a about 8km²³ of spatial resolution. One simulation was performed assuming the present climate conditions. Temperature, precipitation and wind speed data were statistically treated in order to obtain the geometrical average values of each of zone. For the period of 1971 to 2005, the data are derived from reanalysis, while for constructing the period between 2006 and 2050 we used monthly averages from 1995 to 2005, in order to represent generic average conditions. Figure 3 shows the curves of the obtained results.

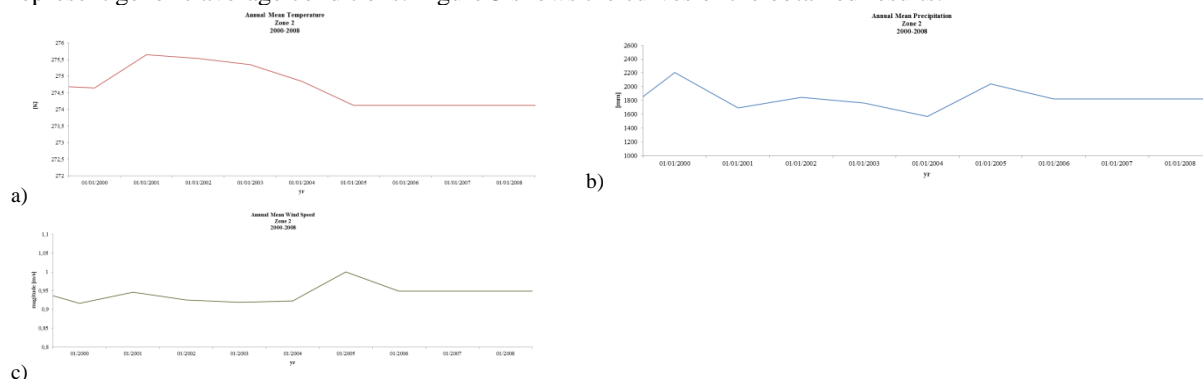


Figure 3. Climatological variables recalculated^{24,25} for Zone 2 of Valtellina mountain (a) Recalculated temperature data from 20CE scenario; (b) Precipitation data from 20CE scenario; (c) Wind speed magnitude data from 20CE scenario. The time period (2000 – 2008) corresponds to the monitoring period of alpha-HCH concentrations.

4. Results and discussion

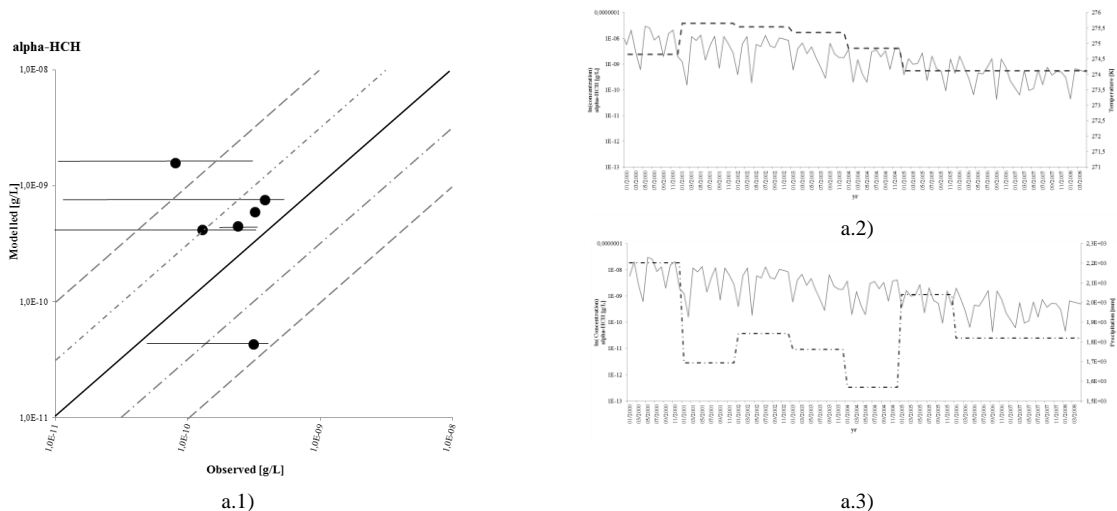


Figure 4. Experiments results for alpha-HCH with monthly time step. (a.1) Comparison between modelled and monitored concentrations in water stream compartment at 1600-2200m a.s.l. Horizontal lines shown the range of measurement concentration values taken in the same date. Sloping lines represent perfect agreement (10^0) and agreement within factors of $10^{1/5}$, $10^{1/3}$ and $10^{1/2}$. (a.2) Modelled concentrations data during the period 2000 to 2008, and temperature trend during the same period for zone 2. (a.3) Modelled concentrations data and precipitation trend for the same time period in zone 2.

In order to evaluate the accuracy of MountainPOP3.0, the alpha-HCH modelled concentrations were compared with alpha-HCH monitored data^{26–28} that were carried out during the period from 2005 to 2007. We chose monitored data in water stream from 1660 to 2200m a.s.l. of altitude, in order to compare the obtained results of Zone 2, in water stream compartment at the corresponding same altitude. The comparison was made only for water stream, given that for the other compartments, monitoring alpha-HCH values were scarce or unavailable. Figure 4 shows the comparison from the monitored and modelled data concentrations and the comparison between concentrations trend and climatological variables. The agreement between the observed and modelled results is within one order of magnitude, and 67% of the results lay within a factor of 3.

The model presents a tendency to underestimate the concentrations in water stream compartment. This may occur due to the model does not take into account the contribution of smelting glaciers as a secondary source of contaminants materials that reaches the water stream. Another explanation is that the contribution of precipitation to the water stream does not follow the exact real conditions, overestimating the mass contribution in stream recharging. At this point, it is important to note that precipitation data for each zone do not follow the expected trend¹⁰: precipitation increasing with altitude. In particular, Zone 2 features the higher precipitation than others mountains zones, during time.

By comparing the modelled concentrations and climatic trends, we found similarities in both trends. We assume that the variation in the modelled concentrations is due to (1) the climatic variables that affect directly the calculations. (2) The primary emission of alpha-HCH completely stopped in 2005 for Central Europe, so we may expect that concentrations decrease over time. (3) Alpha-HCH emissions were mainly in 5% air, 92.5% soil and 2.5% fresh water, and this distribution affects the modelled concentrations underestimating them. Finally, (4) alpha-HCH was emitted during April and May of each year, giving a possible seasonal trend in our modelled values. When temperature and precipitations become constants (from 2006) the modelled concentrations fluctuate less.

Conclusions

Valtellina valley in Italian Alps turns into ideal site to study HCH behaviour along gradients of climate variables^{8,29}. These specific meteorological conditions may increase the persistence, because degradation is slower at lower temperatures and the degradability of many substances is lower in surface media than in air³⁰, favouring these regions as secondary emitters for POPs. The modelled concentrations exhibit their presence into environmental compartment (water stream) during all period (1971 - 2050) even when others^{13,14} have been noted the HCH primary emissions were stopped in 2006 in Central Europe. Further research must be conducted for testing the presented findings, including an uncertainty analysis of the model application.

References

- (1) Daly, G.; Wania, F. *Environ. Sci. Technol.* **2005**, *39*, 385–398.
- (2) Kallenborn, R.; Christensen, G.; Evenset, A.; Schlabach, M.; Stohl, A. *J. Env. Monit* **2007**, *9*, 1082–1091.
- (3) Carrera, G.; Fernández, P.; Vilanova, R. M.; Grimalt, J. O. *Atmos. Environ.* **2001**, *35*, 245–254.
- (4) Fernández, P.; Carrera, G.; Grimalt, J. O. *Aquat. Sci.* **2005**, *67*, 263–273.
- (5) Wania, F.; Westgate, J. N. *Environ. Sci. Technol.* **2008**, *42*, 9092–9098.
- (6) Mackay, D. *Multimedia Environmental Models: The Fugacity Approach, Second Edition*; CRC Press, 2001.
- (7) Daly, G. L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Castillo, L. E.; Wania, F. *Environ. Sci. Technol.* **2007**, *41*, 1118–1123.
- (8) Wegmann, F.; Scheringer, M.; Hungerbühler, K. *Ecotoxicol. Environ. Saf.* **2006**, *63*, 42–51.
- (9) Shunthirasingham, C.; Wania, F.; MacLeod, M.; Lei, Y. D.; Quinn, C. L.; Zhang, X.; Scheringer, M.; Wegmann, F.; Hungerbühler, K.; Ivemeyer, S.; Heil, F.; Klocke, P.; Pacepavicius, G.; Alae, M. *Environ. Sci. Technol.* **2013**, *47*, 9175–9181.
- (10) Westgate, J. N.; Wania, F. *Environ. Sci. Process. Impacts* **2013**.
- (11) Brown, T. N. 6.1.4 Water Balance, University of Toronto: Toronto, Ontario, Canada, 2011.
- (12) Thomas Dunne; Luna Leopold. *Water in environmental planning*; W. H. Freeman & Co.: San Francisco, 1979.
- (13) Li, Y. F.; Scholtz, M. T.; van Heyst, B. J. J. *Geophys. Res. Atmospheres* **2000**, *105*, 6621–6632.
- (14) Wöhrschimmel, H.; Tay, P.; von Waldow, H.; Hung, H.; Li, Y.-F.; MacLeod, M.; Hungerbuhler, K. *Environ. Sci. Technol.* **2012**, *46*, 2047–2054.
- (15) Sturani, E. I suoli del fondovalle valtellinese. Progetto “carta pedologica,” 1992.
- (16) Regione Lombardia. Programma di tutela e uso delle acque, 2006.
- (17) Grassi, L. Definizione e analisi del bilancio idrologico di un fiume alpino: caso di studio del bacino valtellinese del fiume Adda. master degree, Ca Foscari Univeristy of Venice: Venice, Italy, 2014.
- (18) Armitage, J. M.; Wania, F. *Environ. Sci. Process. Impacts* **2013**, *15*, 2263–2272.
- (19) Xiao, H.; Li, N.; Wania, F. *J. Chem. Eng. Data* **2004**, *49*, 173–185.
- (20) Breivik, K.; Wania, F. *Environ. Sci. Technol.* **2002**, *36*, 1014–1023.
- (21) Lamon, L.; MacLeod, M.; Marcomini, A.; Hungerbühler, K. *Chemosphere* **2012**, *87*, 1045–1051.
- (22) COSMO-CLM - www.clm-community.eu <http://www.clm-community.eu/index.php?menuid=17> (accessed May 6, 2013).
- (23) Bucchignani, E.; Mercogliano, P.; Montesarchio, M.; Manzi, M.; Zollo, A. In *Climate change and its implications on ecosystem and society*; Lecce, Italy, 2013; pp. 78–89.
- (24) Montesarchio, M.; Zollo, A. L.; Bucchignani, E.; Mercogliano, P.; Castellari, S. *J. Geophys. Res. Atmospheres* **2014**, *119*, 2013JD021105.
- (25) Bucchignani, E.; Castellari, S.; Gualdi, S.; Schiano, P. *Climate Projections for the Greater Alpine Region with a new high resolution Regional Climate Model*; WP 5 Water regime; AdaptAlp: Italy, 2011.
- (26) Tremolada, P.; Villa, S.; Bazzarin, P.; Bizzotto, E.; Comolli, R.; Vighi, M. *Water. Air. Soil Pollut.* **2008**, *188*, 93–109.
- (27) Chiara Bizzotto. Environmental fate and ecotoxicological risk of persistent organic pollutants (POPs) in alpine environment [Tesi di dottorato]. PhD thesis, Università degli Studi di Milano-Bicocca: Milano, 2008.
- (28) Bizzotto, E. C.; Villa, S.; Vaj, C.; Vighi, M. *Chemosphere* **2009**, *74*, 924–930.
- (29) Gewurtz, S. B.; Laposa, R.; Gandhi, N.; Christensen, G. N.; Evenset, A.; Gregor, D.; Diamond, M. L. *Chemosphere* **2006**, *63*, 1328–1341.
- (30) Wegmann, F.; Cavin, L.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. *Environ. Model. Softw.* **2009**, *24*, 228–237.