Evaluating the temporal variability of concentrations of POPs in a glacier-fed stream food chain using a combined modeling approach

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Evaluating the temporal variability of POP concentrations in a glacier-fed stream food chain using a combined modelling approach

Melissa Morselli[1], Matteo Semplice[2], Sara Villa[3] and Antonio Di Guardo[1*]

[1]Department of Science and High Technology - University of Insubria, Via Valleggio 11, 22100 Como CO, Italy

[2]Dipartimento di Matematica - Università degli Studi di Torino, Via C. Alberto 10, 10123 Torino TO, Italy

[3]Department of Earth and Environmental Sciences - University of Milano-Bicocca, Piazza della Scienza 1, 20126 Milano MI, Italy

[*]Corresponding author

Abstract

Falling snow is known to act as an efficient scavenger of contaminants from the atmosphere and, accumulating on the ground surface, behaves as a temporary storage reservoir; during snow ageing and metamorphosis, contaminants may concentrate and be subject to pulsed release during intense snow melt events. In high-mountain areas, firn and ice play a similar role. The consequent concentration peaks in surface waters can pose a risk to high-altitude ecosystems, since snow and ice melt often coincides with periods of intense biological activity. In such situations, the role of dynamic models can be crucial when assessing environmental behavior of contaminants and their accumulation patterns in aquatic organisms. In the present work, a dynamic fate modelling approach was combined with a hydrological module capable of estimating water discharge and snow/ice melt contributions on an hourly basis starting from hourly air temperatures. The model was applied to the case study of the Frodolfo glacier-fed stream (Italian Alps), for which concentrations of a number of POPs in stream water and four macroinvertebrate groups were available. Considering the uncertainties in input data, results showed a satisfying agreement for both water and organism concentrations. This study demonstrated the model adequacy for the estimation of pollutant concentrations in surface waters and consequent bioaccumulation in aquatic organisms, as well as its possible role in assessing the consequences of climate change on POP cycle.

Keywords: EcoDyna model, glacier-fed stream, POPs, macroinvertebrates, PCBs, DDE, snow, exposure

1. Introduction

Snow scavenging efficiently removes contaminants from the atmosphere (Franz and Eisenreich, 1998; Herbert et al., 2006); such process is of particular importance in the Northern hemisphere, where snow covers up to 50% of the land and most of the contaminants are emitted (Meyer and Wania, 2008). Snow, accumulating on the ground surface, acts as a temporary storage reservoir of contaminants (Daly and Wania, 2004). During snowpack ageing and metamorphosis, contaminants may undergo several fate processes: for example, they may be degraded, released with melt water to aquatic and terrestrial ecosystems, or volatilize back to the atmosphere (Wania, 1997; Daly and Wania, 2004). Depending on their physical-chemical characteristics and on snow properties, contaminants may also concentrate in the snowpack, and be rapidly released to surface waters during a short melt period. This can result in spring peak concentrations, which have been measured in a number of studies (e.g., Quémerais et al., 1994; Lafrenière et al., 2006; Bizzotto et al., 2009a). Moreover, in high-mountain areas, where snowfall rates are high and low temperatures allow snow accumulation, a fraction of the chemical burden contained in snow is incorporated into firn and ice. Similarly to the snowpack, glaciers can be important sources of pollutants to surface waters: for example, Blais et al. (2001) showed that melting glaciers supply 50 to 97% of the organochlorine pesticide input to the sub-alpine Bow Lake (Alberta, Canada).

The timing of contaminant release from snow and ice with respect to the seasonal cycle of ecosystems is crucial: in high-altitude areas, snow and ice melt often coincides with periods of intense biological activity, when organisms are at a vulnerable stage of development (Meyer and Wania, 2008). Moreover, such ecosystems experience extremely harsh conditions such as daily and seasonal extremes in temperature, wind speed and water discharge; for this reason, the growing season is limited and survival, development and reproduction of organisms is difficult (Füreder et al., 2005). However, only few comprehensive studies were conducted on the occurrence and fate of POPs in organisms living at high altitudes (e.g., Grimalt et al., 2001; Blais et al., 2003; Vives et al., 2004a, 2004b, 2004c; Bartrons et al., 2007).

In such context, in which pulsed pollutant loadings and fast biological cycles regulate water contamination and bioaccumulation, dynamic models could play a vital role in the understanding of POP fate and transfer to ecosystems. This has been underlined in a recent opinion of the three scientific committees of the European Commission (EC, 2013). Additionally, the lack of temporally and spatially resolved concentrations in water and sediment does not allow to evaluate realistic concentrations of exposure (Di Guardo and Hermens, 2014). The prediction of the potential for snowmelt to cause spring concentration peaks in water, air and soil has been the object of a number of publications: for example, Daly and Wania (2004) incorporated a snow compartment into a dynamic model to investigate the effect of snow on the temporal variability of the concentrations of some organic contaminants. Despite the inclusion of a snow or ice compartment could substantially improve fate predictions, model parameterization (e.g., snow and ice melting rates) could be extremely difficult. Moreover, also a spatial variability exists in snow and ice accumulation and melting patterns, and such heterogeneity could be hard to assess given the low accessibility typical of high-altitude areas. In hydrological models, snow and ice melt contributions are generally computed using either energy balance approaches, which attempt to quantify melt as residual in the heat balance equation, or temperature-index approaches, which assume an empirical relationship between air temperatures and melt rates (Hock, 2003). While the former can provide a more accurate picture of runoff deriving from snow and ice melt, they require data which are generally not available in cold, remote regions (Mou et al., 2008); in contrast, temperature-index models rely on temperature, which correlates well with melt, and are the most widely used approaches for runoff computations from glacierized basins (Singh et al., 2008).

In this work, the concentrations of three POPs (PCB 70, PCB 101 and p,p'-DDE) measured in the Frodolfo stream (Italian Alps) (Bizzotto et al., 2009a) were selected and used as model compounds to reconstruct water concentration profiles deriving from ice and snow melt during the year 2006 and to investigate the subsequent accumulation patterns in four macroinvertebrate trophic groups for which POP concentrations were measured in the same year (Bizzotto et al., 2009b); this was done by means of a dynamic organism-water-sediment model, in which the organism compartment was parameterized to simulate individuals belonging to the macroinvertebrate groups sampled in the Frodolfo stream. The model was provided with a hydrological module which permitted the estimation of water discharge and snow/ice melt contributions on an hourly basis. This allowed to: (I) observe the influence of the high variability of environmental characteristics (e.g., water discharge) and organism properties (e.g., organism volume and lipid fraction) on pollutant concentrations in water and on the consequent accumulation in aquatic organisms and (II) preliminarily calculate chemical loadings to the Frodolfo stream determined by the melting of the glacier and of the snowpack.

2 Materials and methods

2.1 Case study description

During the year 2006, water, sediment and macroinvertebrate sampling campaigns were performed on the Frodolfo stream, a glacial stream fed by the Forni glacier (Ortles-Cevedale group, Italian Alps) and on a nearby spring-fed river, in order to investigate the concentrations of a number of POPs and their relationship with glacier and snow melt (Bizzotto et al., 2009a,b). Investigated chemicals included DDTs (all isomers and metabolites), HCB, α-, β- and γ-HCH, and a selection of PCB congeners (from trichloro- to octachloro-biphenyls). The sampling campaigns were performed on May 31st, June 18-19th, July 18-19th, September 12th, and October 11th. Frodolfo stream water and sediment were collected in four sites located at different distances from the glacier lobe, while organisms were sampled in one of the four sites, located at a distance of about 2.5 km from the glacier lobe, where environmental characteristics allow benthic community to reach a relatively high level of biodiversity. Details concerning the sampling and analytical results can be found in Bizzotto et al. (2009a,b).

Figure 1 shows the location of the study area in the Italian Alps, together with a map of the Frodolfo stream course from its source (the Forni glacier) and the site investigated in the present work (i.e., the site in which macroinvertebrates were collected).

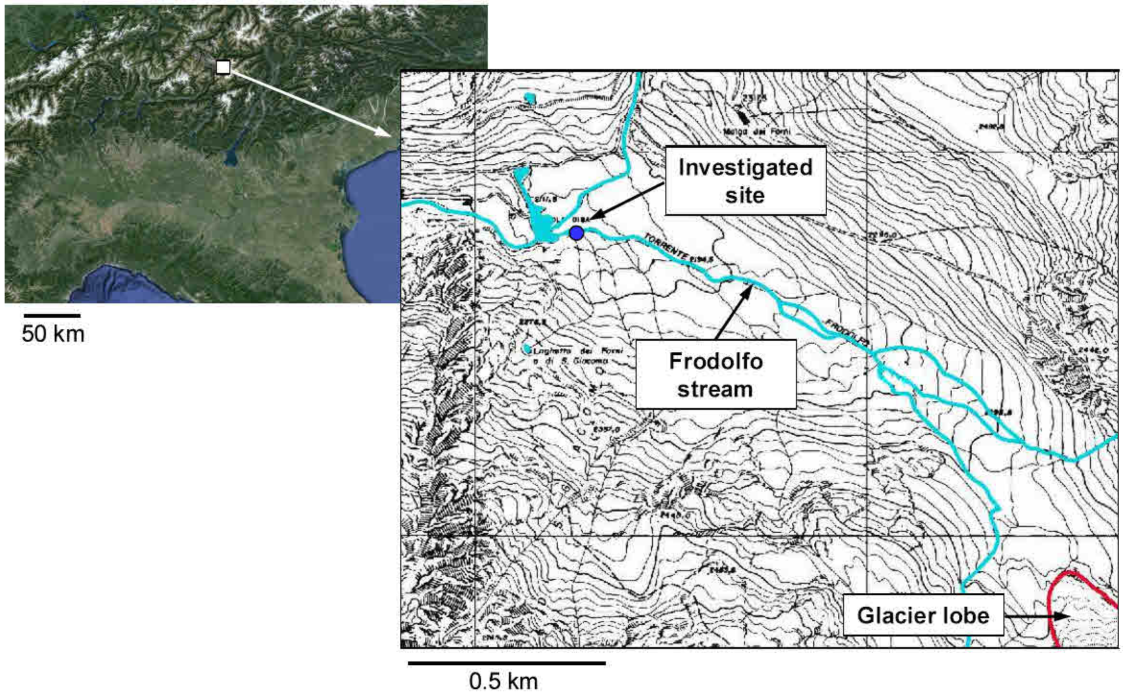

Figure 1. Location of the study area in the Italian Alps and of the investigated site on the Frodolfo stream with respect to the Forni glacier frontal lobe. Satellite image from Google Maps (2014).

2.2 Modelling approach

EcoDynA (Infantino et al., 2013), a fugacity-based model (Mackay, 2001) developed to investigate the fate of organic chemicals in a dynamic organism-water-sediment system, was used for the simulations. In EcoDynA, chemical fate in the three compartments (organism, water and sediment) is described by a system of 1st-order ordinary differential equations (ODEs), one for each compartment, which is solved using a 5th-order adaptive, diagonally implicit Runge-Kutta numerical method (Semplice et al., 2012).

Model dynamics concern not only chemical emission (which can be varied on an hourly basis) but also environmental and organism properties. More specifically, model input include hourly values of parameters such as water temperature, water inflow and outflow and suspended solids concentration in water. In the current version of EcoDynA, suspended solids are modelled as a water sub-compartment, and the presence of particulate organic carbon (POC) is simulated by specifying the organic fraction of suspended solids. Organism properties can also be input on an hourly basis and include organism volume and lipid fraction, feeding rate, gut absorption efficiency, digestion factor, metabolism half-life and lipid fraction in food.

In the present work, the organism compartment was parameterized to simulate single macroinvertebrates belonging to different trophic groups (see 2.4). Uptake from food was modelled considering food in equilibrium with water. More details on model formulation can be found in Infantino et al. (2013), which also illustrates an application of EcoDynA to a case of bioaccumulation of DDTs in fish.

2.3 Environmental scenario

The EcoDynA model was parameterized to simulate a 50-m segment of the Frodolfo stream (Figure SI 1). Daily averages of water discharge measured at a dam located about a hundred meters downstream from the investigated site were obtained by A2A Company. (Bondiolotti, personal communication). However, (I) measured discharge includes different contributions (snow and ice melt, precipitation) and provides no information on how such contributions could be distinguished and (II) since glacier-fed rivers are characterized by high diel fluctuations in discharge (Cuffey and Paterson, 2010), the use of daily averages as model input can be misleading. For these reasons, in the present work, an effort was made to calculate hourly values of water discharge from estimates of snow and ice melt on an hourly basis.

For a period of *n* time intervals, temperature-index models can be described as follows (Hock, 2003):

$$\sum_{i=1}^{n} M_i = DDF \sum_{i=1}^{n} T_i^{+} \Delta T \quad (1)$$

where M_i (mm) is the amount of ice or snow melt in the time interval *i*, *DDF* (mm d^{-1} $°C^{-1}$) is a proportionality factor known as "degree-day factor", T_i^{+} (°C) is the sum of positive air temperatures in *i*, and ΔT (d) is the duration of *i*. Given the need for hourly values of discharge, for the calculations presented here Equation 1 was modified as follows:

$$M_h = \frac{DDF}{dTh} T \quad (2)$$

where M_h (mm) is the amount of ice or snow melt in the time interval of 1 h, *dTh* (= 24 h d^{-1}) is a unit conversion factor, and *T* (°C) is a positive air temperature. No melt was assumed to for $T \leq 0$ °C. Since DDF depends on a number of factors (e.g., solar radiation, albedo, snow/ice physical properties) which considerably vary in space and time (e.g., seasonally), DDF also is subject to such variability (Singh et al., 2008; Hock, 2005). However, for simplicity, in the present work fixed values of DDF for snow and ice were adopted. Hourly air temperatures for the year 2006 were acquired for the "Valfurva - Forni" meteorological station (2118 m a.m.s.l.) (ARPA Lombardia, 2014). Hourly observations of precipitations were also collected, in order to calculate runoff deriving from rain.

For computations, the total watershed area (29 km^2) was divided into 9 elevation zones (Figure SI 2) (altitude interval = 200 m), in which the glacierized and non-glacierized areas were distinguished. In order to calculate snow cover, temporal profiles of the snow line for both ice-covered and ice-free areas throughout 2006 were defined (SGL, 2006). This allowed the estimation, for each elevation zone, of the temporal variation of the areas covered by snow. Ice melt was assumed to occur in case of free ice-surface only. For each elevation zone, temperature records were corrected using a lapse rate of 0.6 °C every 100 m (Singh et al., 2008). In case of precipitation, rain contribution to runoff was calculated in case of $T \geq 1$ °C only. Infiltration and sub-surface runoff were neglected, but for all contributions (from snow/ice melt and rain) a delay of 2 days was adopted to account for water transport from its source in the watershed to the investigated site; furthermore, for rain contribution, a "retention factor" was applied (see 3.1).

The hourly values of M_h (mm) computed using Equation 2 for snow and ice were converted into meters and multiplied by the corresponding areas covered by snow or ice, in order to obtain runoff fluxes (m^3 h^{-1}). By adding the rain contribution, hourly discharge estimates were obtained. Such values were used as inflow and outflow rates from the 50-m stream segment; hourly values of water volume were then calculated assuming a rectangular section and establishing the relationships "discharge-stream width" and "discharge-water level" in order to derive hourly values of such parameters. Details are reported in Text SI 1.

Since suspended solids concentrations (SSC) also vary during the day, and variations are often related to discharge (Lenzi et al., 2003; Singh et al., 2005; Haritashya et al., 2010; Iida et al., 2012; Wulf et al., 2012), a relationship was built in order to derive hourly values of SSC (see 3.1); such relationship was grounded on SSC values measured in Frodolfo stream water sampled during summer campaigns in 2011 and 2013, as described in Text SI 2.

For the simulations presented here, basing on field observations, sediment depth was set to 5 mm; this value was obtained from a weighted average, considering that 1/10 of the riverbed was occupied by 5-cm deep sediment, while the remainder by cobbles and boulders with no sediment on them. Since measurements conducted in the Frodolfo stream from May to October, 2006 revealed an almost constant temperature of approximately 5 °C (Bizzotto et al., 2009b), such value was adopted for the simulations. In Table SI 3 the values selected for static environmental parameters and mass-transfer coefficients (MTCs) are reported.

2.4 Organism compartment

Information concerning the typical macroinvertebrate community structure in glacier-fed Alpine streams can be found in Text SI 3. Such picture is confirmed by the organism sampling performed in 2006 in the Frodolfo stream (Bizzotto et al., 2009b). Starting from such knowledge, 4 keystone species, classified according to their trophic role (Vannote et al., 1980), were selected for the simulations: *Baetis alpinus* (Baetidae) and *Diamesa nivoriunda* (Chironomidae) for collectors, *Rhithrogena nivata* (Heptageniidae) for scrapers and a stonefly of the family Perlodidae (*Dictyogenus fontium*) for predators.

For the simulations presented here, temporal profiles of organism volume (Figure SI 9) were built for all the modelled macroinvertebrates; such profiles were derived from growth rates and relationships between body length and mass available in the literature (Berg and Hellenthal, 1991; Ritter, 1990; Cereghino and Lavandier, 1998). Despite lipid fraction in macroinvertebrates is known to vary with time and is generally maximum in summer (Meier et al., 2000), in the present work fixed values of organism lipid fraction were adopted to match the ones measured in the macroinvertebrates sampled in the Frodolfo stream in 2006 (Bizzotto et al., 2009b). More details can be found in Text SI 3. Given the lack of data, the other organism properties were kept constant throughout the simulation period: values for digestion factor (4), gut absorption efficiency (63%), and feeding rate (4% body weight d^{-1}) were taken from Campfens and Mackay (1997). A high chemical metabolic half-life (i.e., 10000 d) was adopted as typical of non-metabolizing substances. Collectors and scrapers were assumed to feed on periphyton, to which a lipid content of 0.3% was assigned (Walters et al., 2008). Predators were assumed to feed on Chironomidae (70%), Baetidae (10%), Heptageniidae (10%) and Perlodidae themselves (10%) (Silveri et al., 2008, 2009; Fenoglio et al., 2007), with their corresponding lipid fraction; the feeding preferences of predators were adapted according to prey availability (see Figure SI 9).

2.5 Chemicals

Two PCB congeners (PCB 70 and 101) and p,p'-DDE were selected for the simulations as model substances; this allowed to investigate the fate of chemicals which, during the 2006 campaign on the Frodolfo stream, had shown different behavior (Bizzotto et al., 2009a). Among DDT isomers and metabolites, p,p'-DDE only was always found; its water bulk concentrations were similar in May and June (~ 60 pg L^{-1}), peaked in July (1323 pg L^{-1}) and decreased to about 80 pg L^{-1} in September and October. In contrast, all the analyzed PCBs occurred in highest levels in June. PCB 70 concentrations were of 30 pg L^{-1} in May, 2526 pg L^{-1} in June, again 30 pg L^{-1} in July, and not detectable in September and October; similarly, PCB 101, which was not detected in May, peaked in June (5091 pg L^{-1}), decreased to 76 pg L^{-1} in July and to lower levels (near the method detection limit) in the following months. In Table SI 4 the physical-chemical properties adopted for the three chemicals are listed.

3 Results and discussion

3.1 Water discharge

The first effort was devoted to estimate the contributions of snow and ice melt to total discharge on an hourly basis. In order to do so, DDF values for snow and ice were calibrated in order to obtain the best fit between predicted and measured average daily discharges, which were the only experimental data available concerning stream flow. Figure 2 reports the results of the comparison. The adopted DDF values (3.7 mm d^{-1} $°C^{-1}$ for snow and 7.1 mm d^{-1} $°C^{-1}$ for ice) were in line with those found in the literature (e.g., Hock, 2005; Pellicciotti et al., 2005). In order to account for the loss of water due to infiltration and evaporation, precipitation contribution to runoff was scaled using a "retention factor", which was also calibrated in order to improve the fit; the optimal value was found to be 0.45.

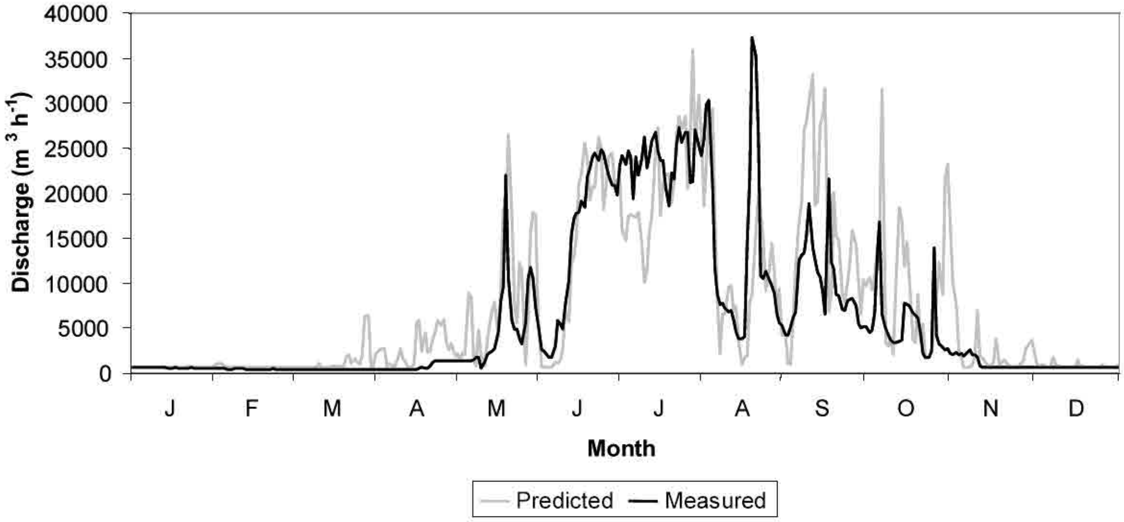

Figure 2. Comparison between predicted and measured discharge (m^3 h^{-1}). For comparison purposes, hourly predictions were averaged on a daily basis.

Generally, a good agreement was obtained (R^2 = 0.66, Figure SI 13). The best fit was observed for the central part of the year, from May to August; an exception was the underestimation in the first half of July. Poorer fit, mostly due to an overestimation of the snow contribution, was observed in spring, especially in April, and from September to November. On a yearly basis, a total discharge of $6.46 \cdot 10^7$ was predicted, while from measured data a value of $5.54 \cdot 10^7$ can be obtained. Such discrepancies can be ascribed to the assumptions made for runoff calculations, in particular to the use of fixed values of DDF, of a "retention factor" for liquid precipitations instead of accounting for infiltration, and to the adoption of a 2-day lag instead of accounting for sub-surface runoff. Moreover, it must be remarked that predictions were compared to measured values computed assuming Frodolfo discharge equal to 2/3 the discharge provided by A2A (Bondiolotti, personal communication), since in the original values the contribution of a relatively important stream (coming from the Cedèc Valley) was included; this factor was selected on the grounds of field observations, but it is unlikely to be constant during the year. A picture of the temporal variation of the different contributions to total discharge is provided in Figure 3, where the different sources (minimum flow, snow melt, ice melt and rain) are distinguished. Ice melt mainly occurred in July, August and September; snow melt was always dominant, except in some occasions during the month of August, when ice melt prevailed. The first relevant episode of snow melt occurred in late June, when most of the winter snow pack over terrain in the Frodolfo watershed melted. Finally, the contribution of liquid precipitation was limited, in some cases comparable to minimum stream flow. Given the number of assumptions and the lack of data which would have been necessary in order to apply a more accurate melt model, the obtained agreement was considered satisfying; this allowed the computed hourly discharges and relative contributions from the different sources to be used for chemical loading calculations (see 3.3).

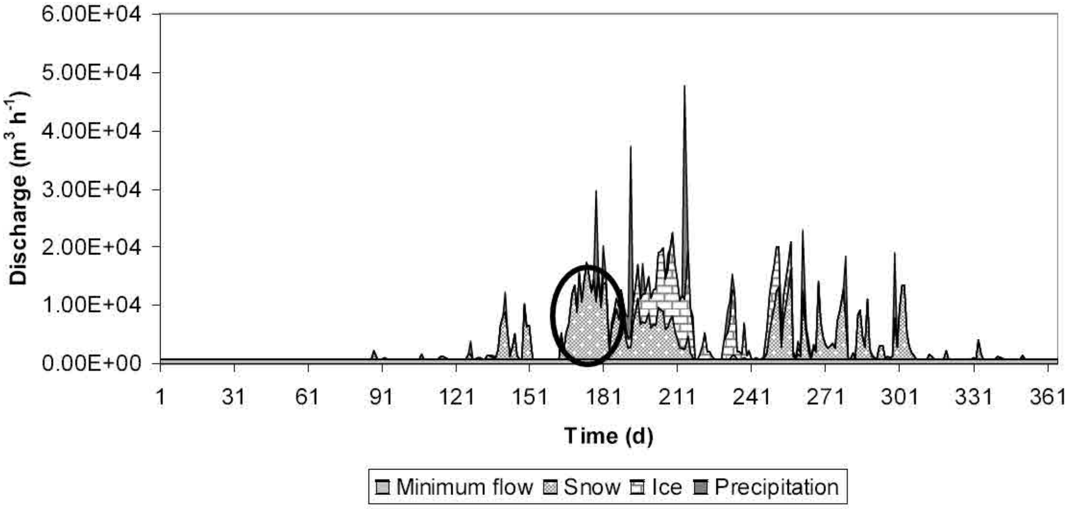

Figure 3. Temporal profile of computed discharge (daily averages, m^3 h^{-1}) divided according to the different contributions. The circle indicates the late-spring flush due to sudden snow melt.

3.2 Suspended solids

A positive correlation between discharge and suspended solids concentration (SSC) generally exists (e.g., Lenzi et al., 2003; Iida et al., 2012; Wulf et al., 2012); such relationship is strong at the beginning and at the end of the ablation period and poorer in the peak melt season, when some events may occur in which the increase in SSC can be much higher than the one in discharge (Singh et al., 2005). Since no data concerning suspended solids were available from the 2006 campaigns on the Frodolfo stream, field investigations were conducted in 2011 and 2013, in order to obtain an estimate of SSC. Sampling and analysis are discussed in detail in Text SI 2. In 2011, Frodolfo stream water at the investigated site was collected twice, on July 31st and August 28th, at the same time of the day (3 PM), when discharge was estimated to be the highest; in 2013, water was sampled at different times of the same day (9.30 AM and 3 PM, September 1st), in order to take a picture of the SSC variability. Results (Figure SI 7) showed concentrations in the range of 1000 to 2000 mg L^{-1} in all the three afternoon samples, while water sampled in the morning revealed SSCs which were lower of more than one order of magnitude with respect to the afternoon ones. All the measured values were in line with those find in the literature for glacial streams (e.g., Haritashya et al., 2010). Starting from the obtained data, a linear relationship between the hypothesized discharge at the sampling times and the measured SSCs was built, which allowed the calculation of hourly values which were used as model input (Figure SI 8). The solids obtained from the filtration of the water samples collected in 2013 were also analyzed for organic carbon content (see Text SI 2); results indicated a very low organic carbon content, of 0.74% (S.D. = 0.03) in the morning water and 0.38% (S.D. = 0.01) in the afternoon one. Given the lack of other information, the latter value was adopted as static organic carbon fraction of suspended solids.

3.3 Chemical concentrations in water

For the investigated chemicals, temporal profiles of bulk water concentrations were derived assigning time-varying concentrations to melting snow and ice; this allowed the calculation of hourly chemical loadings to the water compartment. Although some evidence of increased background air concentrations around contaminated sites close to two former production plants in northern Italy exists for DDT, (Di Guardo et al., 2003; 2008) and PCBs (Colombo et al., 2013), their influence in terms of potential secondary sources of POPs to the Alps is still to be properly quantified. However, some data seem to confirm higher PCB level in the snow of the Alps (Carrera et al., 2001). Given the total lack of data concerning local soil and snow characteristics, no chemical loadings were assumed to derive from rainfall and subsequent runoff. A fit with the contaminant concentrations measured in the Frodolfo stream in 2006 (Bizzotto et al., 2009a) was pursued; this was performed with the only aim of investigating the potential exposure levels (and thus accumulation in organisms) when measures were not available. The obtained temporal profiles of bulk water concentrations (pg L^{-1}) for the selected contaminants are reported in Figure 4. PCB 70 and 101, as all the other measured PCB congeners, peaked in June (see 2.5 and Bizzotto et al., 2009a). From Figure 3 it is evident that, starting from the second half of June, snow melt represented the main contribution, accounting from 65 to 95% of the total discharge. Since in July, when snow melt contribution was still important (5-85%) and ice melt occurred at high rates (5-75%), PCB concentrations decreased, it was hypothesized that the first snow melt water reaching the stream was highly concentrated. The observed PCB levels also suggested that the contribution from ice melt was relatively unimportant. According to these considerations, during all the simulation year with the exception of the second half of June, snow concentrations of 15 pg L^{-1} for PCB 70 and 20 pg L^{-1} for PCB 101 were assigned, within the range of the ones measured in nearby locations (data, presented for the first time in this work, are reported in Text SI 4). Fixed concentrations were assigned to ice (60 pg L^{-1} for PCB 70, 100 pg L^{-1} for PCB 101); such values were similar to the ones measured in a 300-km far Alpine glacier (Villa et al., 2001). In order to match the PCB levels measured in June, concentration of 5 ng L^{-1} for PCB 70 and 15 ng L^{-1} for PCB 101 were necessary; these values are more than two orders of magnitude higher than the ones measured in the snow sampled in nearby locations (Text SI 4) and other Alpine sites (Herbert et al., 2004; Finizio et al., 2006) and would indicate the concentration occurred in the winter snowpack before late-spring sudden melt. It is known that, if the snowpack is relatively warm, the wet snow metamorphism preceding the melt period may concentrate chemicals (Meyer and Wania, 2008); in the subsequent melt phase, which can be extremely rapid (few days or weeks), chemicals may be rapidly released to surface waters in two distinct flushes (water-dissolved and particle-bound). Given the high log K_{OW} values of both PCB 70 and 101 (6 and 6.4, respectively), the two chemicals are expected to be eluted from the snowpack with a certain time delay with respect to the first melt water formation, due to their affinity to organic particles (Daly and Wania, 2004; Meyer and Wania, 2008). However, Lafrenière et al. (2006) measured very high concentrations even of the most hydrophobic compounds (e.g., DDTs, PCBs) in the first snowmelt samples taken from an alpine snowfield. This was ascribed to a low content of particulate organic matter in the snowmelt water, which would have kept even the more hydrophobic substances in the dissolved phase. A similar situation, confirmed by a low organic carbon content of the suspended solids in the Frodolfo stream (see 3.2), could concern this case study. It was observed that, even during high-SSC episodes (i.e., in case of elevated discharges), the low organic carbon content resulted in a negligible influence of suspended solids in determining reduced water-dissolved contaminant concentrations.

In contrast, p,p'-DDE peaked in July (see 2.5 and Bizzotto et al., 2009a), and the same behavior was described in a previous study on the Frodolfo stream (Villa et al., 2006a). A fixed snow concentration of 70 pg L^{-1} was adopted, equal to the minimum concentration measured in the snow sampled in 2008 (Text SI 4); since no late-spring peak was observed for this chemical, no chemical enrichment in snow was assumed to occur. In ice, a fixed chemical concentration of 1000 pg L^{-1} was assumed, except for the month of July: it was observed that, in order to match the concentration value measured in the Frodolfo stream, a concentration in ice of 3000 pg L^{-1} was necessary. No data concerning p,p'-DDE concentration in Alpine glaciers were available for a comparison, but the adopted values were one order of magnitude higher than the concentrations measured in firn at a 300-km far Alpine site (Villa et al., 2006b).

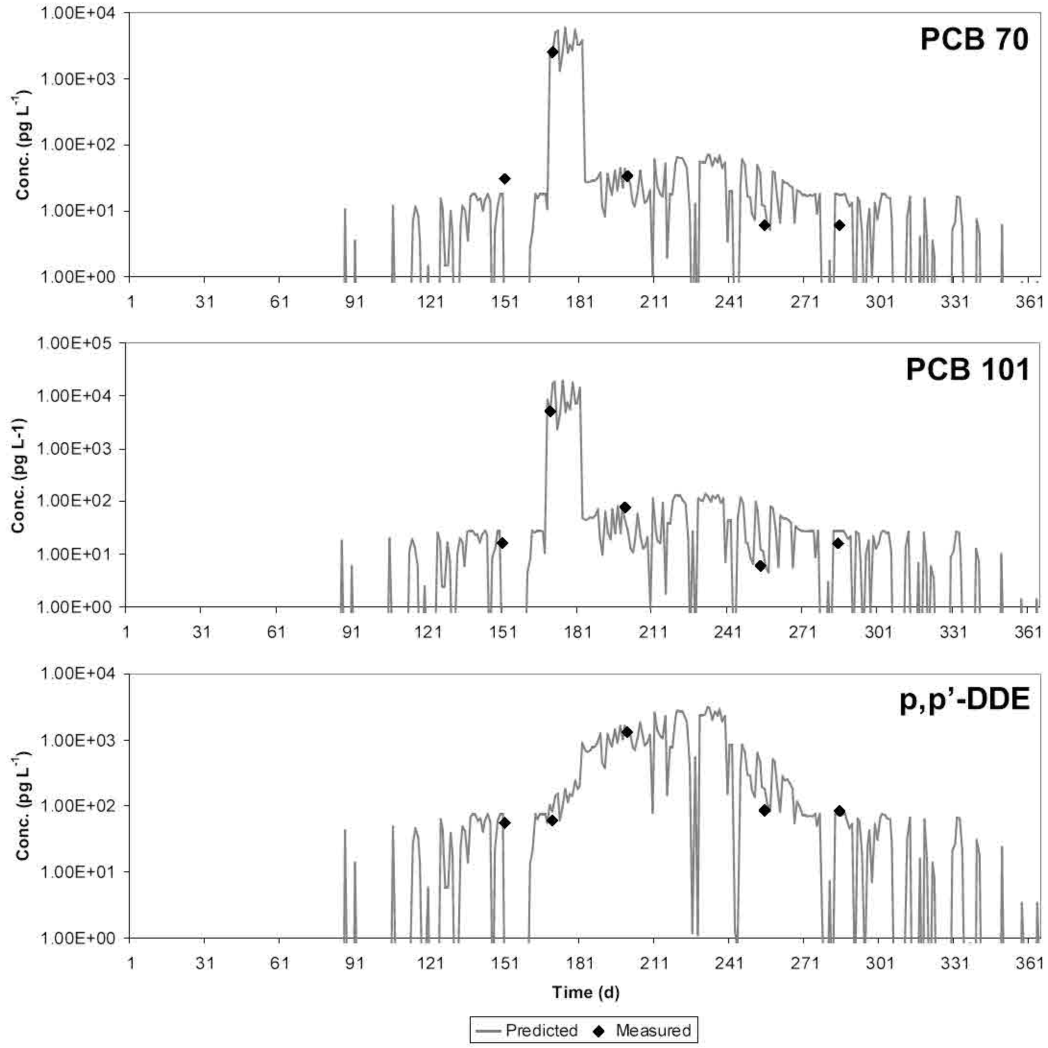

Figure 4. Temporal profiles of the bulk water concentrations (pg L^{-1}) obtained for the modelled chemicals. Grey lines depict model results, while markers represent measured concentrations. The y-axis is in log-scale.

3.4 Bioaccumulation in organisms

In Figures 5, 6 and 7 the results of the comparison between predicted and measured concentrations (ng g^{-1} d.w.) of the investigate chemicals in the four modelled macroinvertebrates are reported.

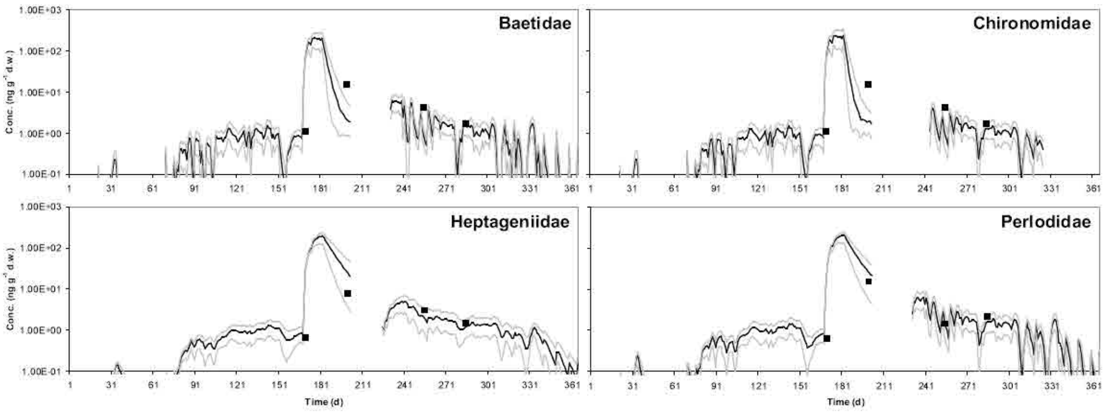

Figure 5. Comparison between PCB 70 measured and predicted concentrations (ng g^{-1} d.w.) in the modelled organisms. Black lines represent model predictions obtained using the organism lipid fractions described in Text SI 3, while grey lines represent model predictions obtained increasing (upper line) or decreasing (lower line) organism lipid fraction of 50%. Markers indicate measured values. The y-axis is in log-scale.

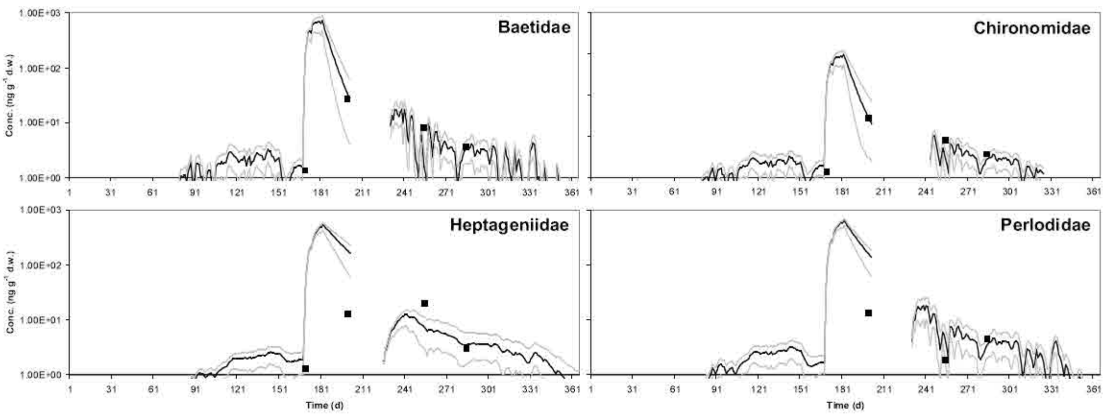

Figure 6. Comparison between PCB 101 measured and predicted concentrations (ng g^{-1} d.w.) in the modelled organisms. Black lines represent model predictions obtained using the organism lipid fractions described in Text SI 3, while grey lines represent model predictions obtained increasing (upper line) or decreasing (lower line) organism lipid fraction of 50%. Markers indicate measured values. The y-axis is in log-scale.

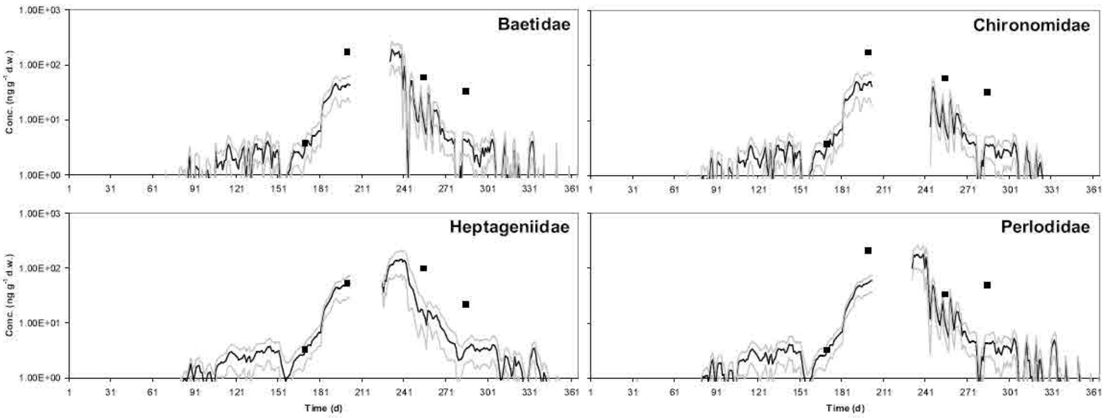

Figure 7. Comparison between p,p'-DDE measured and predicted concentrations (ng g^{-1} d.w.) in the modelled organisms. Black lines represent model predictions obtained using the organism lipid fractions described in Text SI 3, while grey lines represent model predictions obtained increasing (upper line) or decreasing (lower line) organism lipid fraction of 50%. Markers indicate measured values. The y-axis is in log-scale.

A preliminary sensitivity analysis conducted on the EcoDynA model revealed that the parameters which mostly affect organism concentrations are organism lipid fraction, gut absorption efficiency, feeding rate and lipid fraction in food (Infantino et al., 2013). Given the high uncertainty associated to such parameters, it was chosen to perform additional simulations increasing and decreasing the most influential one (i.e., organism lipid fraction) of 50% (grey lines in the figures). A different fresh to dry weight ratio for each macroinvertebrate group was used to convert concentration of a dry weight basis; these values, measured in the organism sampled in the Frodolfo stream in 2006, were 4.2 for collectors, 3.5 for scrapers, 3.55 for predators.

Considering all uncertainties in model input, for PCB 70 a satisfying agreement between predictions and observations was generally observed; the best model performance concerned scrapers (Heptageniidae) and predators (Perlodidae), while for Baetidae and Chironomodae the model underestimated July and September concentrations of a factor of 2 to 7. A similar good model performance was observed for PCB 101, for which the only underestimated concentration was the September one for collectors and scrapers (factor of 2 to 4). Less satisfying was the comparison between predicted and measured p,p'-DDE concentrations, since the model generally underestimated chemical levels in all macroinvertebrates, in some cases even of one order of magnitude. As for PCB 70, the best agreement was observed for scrapers and predators. Despite uptake from food is usually one of the most important bioaccumulation pathways by which hydrophobic and persistent organic chemicals may accumulate in aquatic organism such as fish or macroinvertebrates, for collectors and scrapers it was substantially negligible; in contrast, it was relatively important for predators, responsible for 15% of the accumulation of PCB 70, 30% of PCB 101, and 12% of p,p'-DDE.

The observed discrepancies could be attributed, for example, to the use of static values of organism lipid fraction and other organism parameters (e.g., absorption efficiency and feeding rate) instead of temporal profiles. More accurate data on the modelled organisms could dramatically improve model performance. Moreover, considering food in equilibrium with water could also be misleading; this could be overcome by simulating a food web.

3.5 Considerations on chemical loadings to surface water

The modelling effort presented in this work allowed a very preliminary and rough estimation of the total amounts of the investigated pollutants which were released to

Frodolfo stream water from ice and snow during 2006. According to our calculations, the total released amounts were $2.86 \cdot 10^{-2}$ kg for PCB 70, $8.64 \cdot 10^{-2}$ kg for PCB 101, and $4.09 \cdot 10^{-2}$ kg for p,p'-DDE. While for PCB 70 and 101 the most important contribution was snow melt, accounting for about 98% of the total chemical burden, for p,p'-DDE ice was the main chemical source (92%). These results highlight the possible valuable role of dynamic modelling approaches such as the one presented here in the estimation of the consequences of changing climate regimes on exposure levels and environmental fate of POPs stored in cold archives such as glaciers.

4. Conclusions

In the present work, a dynamic organism-water-sediment modelling approach was combined with a hydrological module capable of estimating water discharge and snow/ice melt contributions on an hourly basis starting from hourly air temperatures. The application of the model to the Frodolfo case study showed its adequacy for the estimation of pollutant concentrations in surface waters and consequent bioaccumulation in aquatic organisms, and the possible role of the model in assessing the consequences of climate change on POP cycle was also highlighted.

For a more thorough calibration and validation of the modelling approach presented here, which will be object of future work, more information will be needed: for example, higher-temporal resolution water and organisms samplings, as well as more detailed information on organism parameters (especially the most influential ones). More complete sensitivity and uncertainty analyses need also be performed. However, the results presented here show the potential benefits of a dynamic predictive tool in the calculation of exposure variation in time of macroinvertebrates and, potentially, further levels in the food web for an alpine stream.

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