



UNIVERSITY OF INSUBRIA

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Ph.D. Course in Chemical and Environmental Sciences

**Improving ecosystem exposure assessment of
organic chemicals: evaluating their mobility and
bioavailability with novel chemical measurements
and modelling approaches**

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Ph.D. Thesis

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“Per aspera ad astra”

Marcus Tullius Cicero, *De natura deorum*

To my family,
with love

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Summary of the thesis

Exposure assessment of chemicals released in terrestrial and aquatic ecosystems by anthropic activities (e.g. industrial processes, agricultural practices, waste treatment, etc.) is a fundamental step to evaluate the potential risk for human and wildlife health, derived from the discharge of these chemicals in the environment. The characterization of the exposure scenario involves the evaluation of the chemical exchange and fluxes among different environmental media (air, soil, water, sediment, and biomass) (namely the mobility assessment) in order to understand the potential for a chemical application/release to reach other non-target compartments as well as the estimation of the actual and/or potential chemical concentration available for uptake into organisms (namely the bioavailability assessment).

Evaluating the mobility and bioavailability of chemicals released in terrestrial and aquatic environments is a complex task that needs to be better refined in the environmental risk assessment framework. To perform a more realistic exposure assessment of contaminated sites, the temporal and spatial variability of the environmental conditions and factors affecting chemical mobility and bioavailability (e.g. water fluxes, dissolved organic carbon fluxes) need to be accounted for. Environmental fate models are the *de facto* standard for assessing chemical exposure but, to retain model simplicity, many crucial dynamics controlling chemical mobility and bioavailability are typically overlooked by the approaches implemented so far. This Ph.D. thesis aims to deal with some of the new challenges in exposure assessment of organic chemicals concerning the improvement of modelling tools for evaluating chemical mobility and bioavailability in the soil/sediment-water systems through laboratory experiments and the development of measurement methods.

First, a new multimedia fate model is presented, and then the focus is moved on the improvement of model features and predictive equations to simulate more realistic conditions and obtain reliable predictions of chemical fluxes and on the development of novel laboratory measurement techniques to assess chemical bioavailability. The model proposed is a new spatially explicit air-soil-water model with high temporal resolution (hourly) suitable to predict short-term peak of contamination in surface waters and better describe exposure scenarios where the temporal and spatial heterogeneity is fundamental in estimating chemical fluxes. This model implements a dissolved organic carbon sub-compartment in the soil porewater that can enhance the chemical movement from soil towards the water bodies (e.g. during runoff events).

Some of the aspects related to the reliability of the model predictions of the soil mobility of hydrophobic organic chemicals under variable environmental scenarios are questioned and suggestions for improving modelling approaches are proposed. More specifically, the influence of dissolved organic carbon and fine particles/colloids on vertical and horizontal movement of organic chemicals from soil to surface and groundwaters as well as the environmental variables potentially affecting transport associated to these phases (e.g. temperature, saturation conditions, soil organic carbon degradation) were investigated. This goal was pursued by performing *ad hoc* experiments and running model simulations to compare predicted and measured data and discuss the paradigms that need to be revisited in environmental fate models.

Predictive equations for estimating the association between organic chemicals and dissolved organic carbon were reviewed and new relationships were proposed for non-polar and polar chemicals. Finally, new time and cost-efficient approaches for measuring bioavailable freely dissolved concentrations of poorly soluble hydrophobic organic chemicals in soil/sediment porewater are presented.

Publication list

This Ph.D. thesis is based on the following papers:

- **Paper I.** Morselli M., Vitale C.M., Ippolito A., Villa S., Giacchini R., Vighi M., Di Guardo A. Predicting pesticide fate in small cultivated mountain watersheds using the DynAPlus model: Toward improved assessment of peak exposure. *Science of The Total Environment* 615 (2018), 307-318.
- **Paper II.** Vitale C.M., Terzaghi E., Zati D., Di Guardo A. How good are the predictions of mobility of aged polychlorinated biphenyls (PCBs) in soil? Insights from a soil column experiment. *Science of The Total Environment* 645 (2018), 865-875.
- **Paper III.** Vitale C.M., Di Guardo A. A review of the predictive models estimating association of neutral and ionizable organic chemicals with dissolved organic carbon. *Science of The Total Environment* 666 (2019), 1022-1032.
- **Paper IV.** Vitale C.M., Di Guardo A. Predicting dissolved organic carbon partition and distribution coefficients of neutral and ionizable organic chemicals. *Science of The Total Environment* 658 (2019), 1056-1063.
- **Paper V.** Vitale C.M., Knudsmark Sjøholm K., Di Guardo A., Mayer P. Accelerated equilibrium sampling of hydrophobic organic chemicals in solid matrices – automated SPME with reduced equilibration times. Draft to be submitted to *Environmental Science & Technology*.

1. Introduction and aims

1.1. Environmental risk assessment of chemicals

Environmental risk assessment (ERA) is one of the main frameworks in the decision-making process for chemical regulation. ERA bases on the assumption that risk can be quantified by evaluating the concentration of a target chemical in the main environmental media where a specific organism lives (air, soil, water, sediment) and possibly in its preys, representing a potential source of secondary poisoning, towards the adverse effects associated to that exposure (EC (European Commission), 2003). ERA encompasses the following steps: 1) effect assessment, 2) exposure assessment and 3) risk characterisation (EC, 2003).

The effect assessment includes 1) the hazard identification and 2) the dose (concentration)/response (effect) assessment (EC, 2003). The hazard identification consists in the individuation of the inherent capability of a chemical to affect organisms (e.g. type and extent of toxicity). The dose (concentration)/response (effects) assessment consists in the determination of the relationship between the magnitude of exposure (i.e. concentration level) and the probability of incidence and severity of the effect. This step should end up in determining a threshold of predicted no effect concentration (PNEC) by dividing specific endpoints from toxicological assays such as LC_{50} (lethal concentration that kills 50% of the population), EC_{50} (effective concentration that induces a response in 50% of the population) or NOEC (no observed effect concentration), for an appropriate assessment factor (e.g. 1000) to account for the uncertainty derived by extrapolating the data from few target species to the entire ecosystem (EC, 2003).

The exposure assessment is generally performed obtaining predictions (e.g. by using modelling approaches) of the chemical concentrations in various environmental compartments (EC, 2003).

Measurements are crucial at later stages of the assessment when predicted contamination levels need to be verified in order to assure the correctness of the assessment; measurements of contamination evolution should also be monitored with time, e.g. during remediation of contaminated areas. However, monitoring is *a posteriori* measure after contamination already occurred without, of course, any possibility for prevention (EC, 2013). Monitoring is useful to capture an overview of contamination levels in real time but does not provide any information about chemical fate and future contamination scenarios. Modelling approaches instead can be employed as *a priori* predictive tool to estimate chemical distribution and fate in a multimedia environment, before authorization for production, use and emission but need to be coupled with measured data for their development, improvement, calibration and validation (EC, 2013). Models, furthermore, can be used to 1) interpret monitoring data (e.g. in chemical management to evaluate the efficacy of regulatory measures), 2) planning new monitoring campaigns (e.g. focusing on the phases where the chemical preferably associate). In exposure assessment, the use of both multimedia fate models and measured data if available and suitable is encouraged whenever possible (EC, 2003; EC, 2013). The most commonly used multimedia fate models are “box models”, developed on the grounds of the Mackay fugacity approach where the fugacity concept, introduced by G. N. Lewis in 1901 as a thermodynamic equilibrium criterion, is adopted to calculate chemical mass balance (Mackay, 1979; Mackay and Paterson, 1981). In these models each environmental compartment is represented as a “well mixed” box with homogenous properties and chemical distribution. Simulations can be run in a static “steady-state” scenario, meaning that chemical discharge and environmental characteristics (e.g. compartment size, temperature, organic carbon content and water fluxes) are constant with time or in a dynamic “unsteady-state” scenario, allowing for temporal and spatial modulation of the environmental

characteristics and pulse discharges (EC, 2013). Most multimedia fate models developed in the last 30 years are steady state models (Di Guardo and Hermens, 2013; Di Guardo *et al.*, 2018) such as EQC (Mackay *et al.*, 1996a), ChemCAN (Mackay *et al.*, 1996b) and the reference tool adopted in the European regulatory framework EUSES (European Union System for the Evaluation of Substances) (EC, 2004). By using physico-chemical properties of the target substances, emission rates and standardized scenarios at local, regional or continental scale, model simulations are finalized to PEC (predicted environmental concentration) calculations in various environmental media.

PECs together with the PNECs are used to quantify the risk in the final step of the risk characterisation and to establish if the substance presents a treat for organisms. If the PEC/PNEC ratio is substantially < 1 there is no immediate concern about the substance and the risk is considered acceptable; otherwise (PEC/PNEC ratio ≥ 1) the regulator should take measures to reduce the risk.

1.2. Challenges in exposure assessment of organic chemicals for terrestrial and aquatic ecosystems

The recent scientific opinion “Addressing the New Challenges for Risk Assessment” (EC, 2013) of the former three scientific committees of the European Commission (SCHER, Commission Scientific Committee on Health and Environmental Risks; SCENIHR, Scientific Committee on Emerging and Newly Identified Health Risks; SCCS, Scientific Committee on Consumer Safety) focused on a number of issues in the evaluation of the ecosystem and human exposure and effects. Some of the most urgent challenges related to the exposure assessment were reviewed by Di Guardo and Hermens (2013) and by Di Guardo *et al.* (2018) and concern:

- Accounting for bioavailability;
- Improving modelling approaches;
- Improving quality and accessibility of experimental and monitoring data.

Bioavailability is a critical issue in defining chemical exposure in terrestrial and aquatic ecosystems that should be accounted for in exposure assessment (EC, 2013). In soils/sediments contaminated by hydrophobic organic chemicals (HOCs) ($K_{ow} > 10^4$), for example, it is well recognized that total concentrations, (including both the fraction of molecules associated to the solid matrix and dissolved in the water phase) are poorly representative of to the actual exposure of the organisms to the chemicals and risk (Di Toro *et al.*, 1991; Ortega-Calvo *et al.*, 2015; Reichenberg and Mayer, 2006) since the marked affinity of such hydrophobic chemicals for the particulate (POC) and dissolved (DOC) organic carbon, the aging processes (e.g. formation of bound residues) and the slow desorption kinetics, dramatically reduce the fraction of freely dissolved chemicals in the water phase bioavailable for organism uptake (Enell *et al.*, 2016; Luthy *et al.*, 1997; Pignatello and Xing, 1995; Xing and Pignatello, 1997). For freshwater ecosystems assessing bioavailability is a crucial task in evaluating the impact of micropollutants (Schwarzenbach, 2006) as well also understanding variations of the bioavailable concentrations in response to biomass dynamics and POC/DOC fluxes (Morselli *et al.*, 2015).

However, nowadays bioavailability is not clearly incorporated in risk assessment procedures yet (EC, 2013). ERA of contaminated soils/sediments, for example, based on measurements of total concentrations and the attempts to include the bioavailability in regulatory programs are still rare (Ortega-Calvo *et al.*, 2015). Not accounting for bioavailability in risk assessment and management of contaminated sites can lead to unrealistic goals for remediation purposes and useless costs in cleanup actions. The reluctance to include bioavailability in ERA framework is also due to the lack

of a univocal definition of bioavailability and time/cost efficient methods for its measurement (Reichenberg and Mayer, 2006). As recently reviewed by Ortega-Calvo *et al.* (2015), three main schools of thought have different opinion about the meaning of bioavailability and the closely linked concept of bioaccessibility. Ehlers and Luthy (2003) defined “bioavailability processes” as all the steps that take place starting from the contaminant being sorbed to the soil/sediment matrix to the contaminant be incorporated into a living organism. Semple *et al.* (2004), instead, defined the term bioavailability referring to the fraction of chemical readily available for organism uptake which crosses cell membranes and bioaccessibility as the fraction of chemical that can become available for organism uptake with time since reversibly bound to labile contaminant pools. Finally, Reichenberg and Mayer (2006) proposed that bioavailability could be defined by the two complementary sides of the accessibility and the chemical activity. If the (bio)accessibility refers to the “quantity of a chemical that is or can become available within a given time span”, the chemical activity describes the “potential for spontaneous physicochemical processes, such as diffusion and partitioning” and is strictly linked to the concept of freely dissolved concentrations (C_{free}) since C_{free} can be derived by chemical activity by using appropriated conversion factors and *vice versa* (Reichenberg and Mayer, 2006).

Freely dissolved concentrations are the effective water concentrations available for many spontaneous processes including the diffusive exchange and the uptake into organisms and are therefore better connected to the toxicity and potential for bioaccumulation and biomagnification (Di Toro *et al.*, 1991; Ortega-Calvo *et al.*, 2015; Reichenberg and Mayer, 2006). Bioavailable freely dissolved concentrations can be accurately measured by using passive sampling devices (Booij *et al.*, 2016; Cui *et al.*, 2013; Lang *et al.*, 2015; Lydy *et al.*, 2014; Mäenpää *et al.*, 2011; Mayer *et al.*, 2014, 2003, 2000; Schäfer *et al.*, 2015). Accessibility is instead operationally defined

basing on the determination methods (e.g. mild solvent extraction, cyclodextrin extraction, tenax extraction) (Cui *et al.*, 2013). If freely dissolved concentrations refer to the chemical concentrations available for organism uptake *hic et nunc* and is therefore a key value in assessing the real organism exposure, (bio)accessibility also includes the fraction of chemical that can become available over time and is crucial to evaluate long-term risk and chemical removal potential (e.g. by bioremediation).

In soil and sediments, chemical residues can be distinguished in four different classes: 1) non-extractable (not measurable), 2) very slowly/slowly desorbing (measurable with solvent extraction), 3) rapidly desorbing (measurable with bioaccessibility measurement approaches) and 4) dissolved in the water phase (composed by the fraction associated to DOC and freely dissolved concentrations, measurable with total aqueous extraction and passive sampling respectively) (Ortega-Calvo *et al.*, 2015). Considering bioavailability as expressed by rapidly desorbing and water dissolved concentrations, they proposed a tiered approach to include bioavailability in risk assessment and management by starting from a generic ERA based on total extractable concentration measurements (including the very slowly/slowly desorbing and the bioavailable fractions) and estimation of the pore water concentrations by using partition coefficients (tier 1), proceeding with the consecutive step of the bioavailability assessment if needed (e.g. when the quality criteria are not satisfied) (tier 2) to eventually conclude with a site-specific ERA to obtain detailed information about the area by monitoring biodiversity and by using fate modelling embedding bioavailability (tier 3). However, regardless the lack of specific guidelines to account for bioavailability in ERA, evaluating bioavailable concentrations is currently a tricky task with formidable challenges for both measurements and modelling aspects. In terms of measurements, more research is needed on the development of passive sampling techniques (EC, 2013).

Measuring equilibrium freely dissolved concentrations of HOCs by using passive sampling devices, for example, requires very long sampling time (Lydy *et al.*, 2014; Mayer *et al.*, 2014) with a consequent need of new time and cost efficient approaches. Modelling tools to account for the temporal and spatial variation of the bioavailable concentrations are also urgently needed to capture the ecological heterogeneity of the terrestrial and aquatic ecosystems and perform a realistic exposure assessment by including, for example, additional compartments and/or sub-compartments in dynamic models, influential in determining chemical bioavailability (e.g. primary producers, DOC and POC) (Di Guardo *et al.*, 2018). The latter is more generally included among the new challenges in improving modelling approaches for exposure assessment of contaminated sites, addressing the increasing of the ecological realism to simulate conditions that may be representative of variable environmental scenarios (EC, 2013). The assumption of steady scenarios, for example, is scarcely realistic and not representative of the spatial and temporal variability of the natural dynamic conditions and may therefore lead to misleading results in modelling attempts (Di Guardo and Hermens, 2013). To deal with such complexity, the implementation of modelling tools able to catch the heterogeneity of the environmental compartments and their evolution with time is crucial as well as collecting temporally and spatially resolved data to investigate the actual relevance of the variability of the environmental factors (e.g. temperature, soil saturation, meteorological conditions, organic carbon dynamics) on concentrations measured in different media that can be used to validate and calibrate dynamic models.

Temporally and spatially explicit fate models can be used to pursue this goal. Spatial variability, for example, can be better captured by introducing horizontal discretization of the different media (e.g. by using GIS (Geographic Information System) tools) and/or through vertical discretization

of model compartments (e.g. by using layered soil, air, water compartments) rather than using boxes with homogenous properties (Ghirardello *et al.*, 2010, 2014; Hansen *et al.*, 2004; Lindim *et al.*, 2016; Warren *et al.*, 2005). Models with high temporal resolution (e.g. hours, minutes, seconds) are able to catch short-term variation and peaks of contamination that can pose a severe risk for terrestrial and aquatic ecosystems otherwise ignored when considering average concentrations in longer time span (Camenzuli *et al.*, 2012; Morselli *et al.*, 2011, 2012). To calibrate/validate such dynamic models, quality data with high temporal and spatial resolution need to be collected and made available (open data) (Di Guardo and Hermens, 2013).

There is a large variability about the temporal and spatial evolution of the soil/sediment organic matter that need to be explored by providing new data (Di Guardo and Hermens, 2013). Various forms of organic carbon (e.g. black carbon, coal and kerogen) may influence the sorption capacity of contaminated soils/sediments meaning that not just the differences in organic carbon content but also its quality and variation with time are determining to assess the actual risk derived by the exposure to such contaminated matrices (Arp *et al.*, 2009; Cornelissen *et al.*, 2005; Pignatello, 2012). DOC affects horizontal and vertical transport of organic chemicals (e.g. from soil to surface and groundwaters) (McCarthy and Zachara, 1989; Moeckel *et al.*, 2008), their bioavailability (Suffet *et al.*, 1994) and (bio)remediation potential (Terzaghi *et al.*, 2018) at an extent not completely understood yet. Environmental variables (e.g. temperature, meteorological conditions) and microbiological communities influence organic carbon mineralization and DOC fluxes (Kalbitz *et al.*, 2000). DOC heterogeneity (e.g. molecular size, hydrophobicity, aromaticity) can be a large source of uncertain for modelling transport of contaminants associated to this phase. For hydrophobic chemicals, for example, structure and composition of DOC may determine variation of DOC-water partition coefficients up to 2-3 orders of magnitude (Burkhard, 2000; Gauthier *et*

al., 1987; Krop *et al.*, 2001). The variability of particulate and dissolved organic carbon and the environmental factors influencing their fluxes have a relevant impact on chemical mobility that should be therefore interpreted under a dynamic point of view. Defining chemical mobility (e.g. from soil to surface and groundwaters) in a dynamic view requires a better understanding of the impact of many relevant environmental factors (e.g. temperature, water balance, time evolution) on chemical sorption/desorption processes, DOC and particle/colloid movement and related chemical transport.

Finally, the applicability domain of fate models, generally suitable to predict environmental distribution of non-polar organic chemicals, need to be extended to include polar and ionizable chemicals and simulate environmental behaviour of new emerging contaminants, such as pharmaceuticals, veterinary products and other active substances (EC, 2013). If equilibrium partition coefficients of non-polar chemicals (e.g. soil organic carbon/water partition coefficient, K_{OC} ; DOC/water partition coefficient, K_{DOC}) can be satisfyingly estimated from their hydrophobic properties (e.g. K_{OW}), the chemical distribution of polar/ionizable chemicals among different phases is much more complex to predict because of different and variable interactions mechanisms with the environmental matrices other than hydrophobic partition (e.g. electrostatic interactions), the dissociation/speciation behaviour varying with pH and chemistry of the solutions (Franco *et al.*, 2009; Franco and Trapp, 2008; Haftka *et al.*, 2010; ter Laak *et al.*, 2006). This implies the urgent need to fulfil the substantial lack of predictive equations to estimate distribution coefficient of polar and ionizable chemicals among different phases to build predictive models also for polar/ionized chemicals.

1.3. Aims of the thesis

This Ph.D. thesis aims to deal with some of the challenges underlined in the debate on how to improve the exposure assessment of organic chemicals for terrestrial and aquatic ecosystems. The focus was on evaluating chemical mobility and bioavailability with a special concern on both measurement and modelling issues. More specifically, the goals of this Ph.D. thesis were to:

- Develop and apply a new dynamic spatially-explicit air-soil-water model with elevated temporal resolution (hourly) to predict short-term peaks of contamination, suitable for evaluating ecosystem exposure in conditions when an elevated temporal and spatial resolution is needed (e.g. mountain basins), accounting for DOC influence on chemical availability and movement (Paper I).
- Investigate the influence of some relevant environmental factors on mobility of some hydrophobic organic chemicals in soil and evaluate model predictions in comparison to such dynamics to gain insights on model paradigms to be updated/reviewed (Paper II).
- Review the currently available models for estimating DOC/water partition and distribution coefficients of neutral and ionizable chemicals (Paper III).
- Propose new predictive equations for estimating DOC/water partition and distribution coefficients of neutral and ionizable chemicals (Paper IV).
- Point out new passive sampling methods to achieve a fast equilibrium sampling of hydrophobic organic chemicals and obtain simultaneously measurements of freely dissolved and total concentrations in soil/sediment systems to fulfil both the regulatory requirement of knowing total concentrations with the need to investigate bioavailable concentrations (Paper V).

2. Summary of the results

2.1. Paper I: Predicting pesticide fate in small cultivated mountain watersheds using the DynAPlus model: Toward improved assessment of peak exposure

The use of plant protection products (PPPs) in agricultural areas implies potential chemical loadings to surface waters, which can pose a risk to aquatic ecosystems and human health. Due to the spatio-temporal variability of PPP applications and of the processes regulating their transport to surface waters, aquatic organisms are typically exposed to pulses of contaminants. In small mountain watersheds, where runoff fluxes are more rapid due to the steep slopes, such exposure peaks are particularly likely to occur. In this work, a spatially explicit, dynamic model for predicting pesticide exposure in surface waters of cultivated mountain basins (DynAPlus) has been developed.

The model has been applied to a small mountain watershed (133 km²) located in the Italian Eastern Alps and characterized by intensive agriculture (apple orchards) around the main river and its tributaries. DynAPlus performance was evaluated for chlorpyrifos through experimental monitoring, using samples collected during the 2011 and 2012 productive seasons. The comparison between predictions and measurements resulted in a good agreement ($R^2=0.49$, efficiency factor 0.60), although a more accurate spatial information in the input scenario (e.g., field-specific applications, rainfall amount, soil properties) would dramatically improve model performance.

A set of illustrative simulations performed for three PPPs highlighted the potential role of DynAPlus in improving exposure predictions for ecological risk assessment and pesticide management practices (e.g., for active ingredient and application rate selection), as well as for

planning efficient monitoring campaigns and/or interpreting monitoring data. However, some model improvements (e.g., solid erosion and transport) and a more thorough model validation are desirable to enlarge the applicability domain.

2.2. Paper II: How good are the predictions of mobility of aged polychlorinated biphenyls (PCBs) in soil? Insights from a soil column experiment

A column leaching experiment was performed to evaluate the influence of some relevant environmental factors (soil/water contact time, temperature, saturation) on mobility of aged polychlorinated biphenyls (PCBs) in soil together with transport mediated by dissolved organic carbon (DOC) and mobile organic carbon (OC) coated fine particles/colloids. Consecutive fractions of leachates were collected after a variable pre-equilibration time (2, 5, 7, 48 days), using leaching solutions with different DOC content (tap water vs. Aldrich humic acid), in saturated vs. field capacity conditions and at different temperatures (25 °C vs. 15 °C). The data obtained were compared to the predicted values using a multimedia model (SoilPlusVeg) to evaluate model behaviour. Contact time and temperature determined a relevant effect on DOC and particle/colloid availability, with significant variations in leachate concentrations (up to 1 order of magnitude), typically overlooked by most environmental fate models. Results obtained at different temperatures show a modulation of the DOC/particles production with temperature and therefore the role of temperature changes in the environmental scenarios (e.g. seasonal variations). Transport of PCBs enhanced by Aldrich DOC was not linearly correlated to chemical hydrophobicity but revealed a threshold to $\sim \text{Log } K_{ow} 6.5$, likely because of the slow sorption kinetics of more hydrophobic chemicals. Additionally, variation of the saturation conditions (e.g. drying-wetting cycles) can determine contamination peaks at the beginning of an irrigation/rainfall event because of the soil/water equilibration. Model simulations, even when including DOC in the

water phase, but not accounting for the particle/colloidal transport and sorption/desorption kinetics, mismatched the ratio of dissolved vs. DOC-associated and particle-associated PCBs and substantially underpredicted concentrations, especially for the high chlorinated congeners. The results indicated that some of the common assumptions and paradigms in fate modelling of such hydrophobic compounds should be revisited and models updated.

2.3. Paper III: A review of the predictive models estimating association of neutral and ionizable organic chemicals with dissolved organic carbon

Dissolved organic carbon (DOC) plays a key role in environmental transport, fate and bioavailability of organic chemicals in terrestrial and aquatic ecosystems. Predicting the association of contaminants to DOC is therefore crucial in modelling chemical exposure and risk assessment. The models proposed so far to describe interaction mechanisms between chemicals and DOC and the most influential variables have been reviewed. The single parameter linear free energy relationships (sp-LFERs) and the poly-parameter linear free energy relationships (pp-LFERs) in the form of linear solvation energy relationships (LSERs) currently available in literature for estimating dissolved organic carbon/water partition (K_{DOC}) and distribution (D_{DOC}) coefficients for organic chemicals were discussed, and limits of the existing approaches explored. For neutral chemicals many predictive equations are currently available in literature, but the quality of the input data on which they are based is often questionable, due to the lack of an unequivocal definition of DOC among different references and to the different and often unreliable K_{DOC} measurement method. For ionizable chemicals instead there is a substantial lack of predictive approaches that need to be fulfilled since just few models are nowadays available to predict D_{DOC}

of ionized species. This paper reviews the current approaches for neutral and ionizable chemicals proposing guidelines to select conditions for obtaining reliable data and predictive equations for an improved estimation of K_{DOC} and D_{DOC} .

2.4. Paper IV: Predicting dissolved organic carbon partition and distribution coefficients of neutral and ionizable organic chemicals

Estimating K_{DOC} (dissolved organic carbon/water partition coefficient) and D_{DOC} (dissolved organic carbon/water distribution coefficient) of neutral and ionizable organic chemicals is a crucial task for assessing mobility, modelling transport, environmental fate of a variety of chemicals and for evaluating their bioavailability in terrestrial and aquatic environments. A critical literature search of reliability-selected K_{DOC} and D_{DOC} values was performed to setup novel predictive relationships for K_{DOC} and D_{DOC} of neutral and ionizable organic chemicals. This goal was pursued by using: 1) LSER (linear solvation energy relationship) models to predict K_{DOC} for neutral chemicals using Abraham solute parameters calculated for different DOC sources (all DOC sources together, soil porewater, surface water, wastewater and Aldrich humic acid); 2) linear regressions for predicting D_{DOC} of organic acids from the octanol/water partition coefficient ($\text{Log } K_{\text{OW}}$ or $\text{Log } P$) and the dissociation constant (pK_a), accounting separately for the contribution of the neutral and ionic fraction. The proposed models predicted $\text{Log } K_{\text{DOC}}$ and D_{DOC} values within a root mean square deviation (RMSD) generally smaller than 0.3 log units.

2.5. Paper V: Accelerated equilibrium sampling of hydrophobic organic chemicals in solid matrices – automated SPME with reduced equilibration times

Equilibrium sampling of hydrophobic organic chemicals (HOCs) is increasingly used to measure freely dissolved concentrations and chemical activities in sediments and soils. However, for the most hydrophobic chemicals ($\text{Log } K_{ow} > 6$) such equilibrium sampling requires very long sampling times in the order of weeks to months. The aim of the present study was to explore two strategies for markedly increasing the HOC mass transfer from matrix to sampler with the overall goal to shorten equilibration times down to a few hours. Two Solid Phase Microextraction (SPME) approaches were thus developed and tested in sediment and soil contaminated by polychlorinated biphenyls (PCBs). In the first method, the SPME fiber was immersed directly in the aqueous suspension of the sample under vigorous agitation. In the second method equilibration took place via the headspace and was accelerated by elevating the temperature. Both methods were calibrated by passive dosing from preloaded silicone rods and yielded similar results thereby cross-validating each other. Headspace-SPME at 80 °C provided fast equilibration within approximately two hours without contacting the sample and thus avoiding fiber fouling. Finally, by using ^{13}C labelled PCB standards, total concentrations were simultaneously measured, which in turn allowed calculation of matrix–water distribution coefficients.

3. Conclusive remarks

This Ph.D. thesis, “Improving ecosystem exposure assessment of organic chemicals: evaluating their mobility and bioavailability with novel chemical measurements and modelling approaches”, focused on the refinement of some aspects related to the mobility and bioavailability assessment of organic chemicals in terrestrial and aquatic ecosystems. The goal was investigating the

reliability of the existing paradigms and proposing novel approaches to perform a more realistic chemical exposure assessment, accounting for the actual mobility and bioavailability of chemicals under different scenarios. This objective was pursued dealing with both modelling and measurement issues.

In **Paper I**, “Predicting pesticide fate in small cultivated mountain watersheds using the DynAPlus model: Toward improved assessment of peak exposure”, some aspects related to the mobility assessment in time and space of heterogeneous environments were dealt with. The novel air/soil/water DynAPlus model was developed to allow predictions of pulses of contaminants in contexts where chemical loadings to surface waters are typically episodic events (e.g. related to spray drift and runoff events). Such peaks can be short in terms of duration but high in terms of contamination level, determining a serious risk for aquatic organisms. The model showed the importance of DOC in enhancing the mobility of hydrophobic contaminants in steep soils. However, some further improvements are needed to better define chemical loadings and distribution such as: 1) the inclusion of a DOC compartment in the water compartment to calculate the truly dissolved bioavailable chemical concentrations, 2) the simulation of the solid runoff and the transport associated to particles, 3) the DOC/particle turnover/mass balance modulation. Additionally, the sensitivity analysis showed the crucial role of the DOC in driving chemical movement from soil to surface water and connecting terrestrial and aquatic chemical exchanges, being DOC parametrization among the most influential factors in model outputs (chemical concentrations and fluxes), especially in enhancing mobility of the most hydrophobic chemicals. The relevance of these aspects to produce reliable prediction have been investigated in the Paper II.

In **Paper II**, “How good are the predictions of mobility of aged polychlorinated biphenyls (PCBs) in soil? Insights from a soil column experiment”, the theme of mobility was faced performing several column leaching experiments to evaluate the influence of many relevant environmental variables on chemical fluxes under different environmental scenarios and model performances (SoilPlusVeg; Terzaghi *et al.*, 2017) in capturing these dynamics. The results suggested that some relevant factors driving chemical mobility need to be embedded in fate models to obtain reliable predictions, especially concerning DOC and particle/colloidal dynamics and transport. DOC and particles, for example, showed a rather different affinity for chemicals since the contribution of the particle transport was much more relevant in affecting overall mobility, especially for most hydrophobic chemicals where their transport occurs mainly in association with this phase. DOC/particle quality, furthermore, varies significantly in time, depending on environmental conditions (e.g. “aged” DOC vs. “fresh” DOC; “winter” vs. “summer” DOC). Environmental fate models used in the regulatory framework typically ignore these aspects, potentially determining misleading results in chemical mobility evaluation. This paper therefore prompts to improve modelling features that could be objects of future research. The correct prediction of the chemical mobility associated to DOC and particle is fundamental in calculating the phase distribution (e.g. between the solid matrix and water) and therefore the fraction of chemical available for biological uptake. Such issues have been further investigated in Paper III, IV and V.

In **Paper III**, “A review of the predictive models estimating association of neutral and ionizable organic chemicals with dissolved organic carbon”, the models proposed so far to predict the association of chemicals to DOC were reviewed and their limits discussed. In particular, the need to extend the research on ionizable chemicals was emphasized as well as on DOC characterization since DOC from different sources shows rather different affinity for chemicals. Additionally,

different predictive equation for estimating K_{DOC} determine differences of orders of magnitude in the final predicted environmental concentration. Hence, it is crucial to apply reliable models to perform a correct assessment of the chemical mobility and bioavailability.

In the **Paper IV**, “Predicting dissolved organic carbon partition and distribution coefficients of neutral and ionizable organic chemicals”, based on the findings of the previous work, new predictive equations were proposed both for neutral and ionizable chemicals (organic acids), performing a literature search of reliable measurements. These equations can be implemented in environmental fate models to produce more accurate predictions of the chemical association to DOC and a more refined estimation of mobile and bioavailable chemical concentrations. However, few data were available for ionizable chemicals and therefore the models proposed for such chemicals can be considered less trustworthy.

Finally, in **Paper V**, “Accelerated equilibrium sampling of hydrophobic organic chemicals in solid matrices – automated SPME with reduced equilibration times”, the focus was on obtaining chemical bioavailability (e.g. C_{free}) of hydrophobic organic chemicals through passive sampling and dosing approaches. New time and cost-efficient methods have been proposed by using automated SPME in historically contaminated soil and sediment that however need to be tested in other matrices.

Overall, this PhD thesis addressed some recent findings and advances in chemical mobility and bioavailability assessment performing laboratory experiments, running model simulations, setting up new predictive models or equations and revisiting literature data. However, many aspects are not still completely understood and need to be analysed in future research:

- The characterisation of mobile phases, such as DOC and small particles/colloids to account for their variability depending on origin, evolution and composition and to gain insight in their environmental behaviour;
- The inclusion of more dynamics (e.g. transport mediated by particles, modulation of the DOC production and quality with temperature and time) in environmental fate model to determine more realistic predictions of chemical mobility and more accurate evaluation of their bioavailability;
- The production of new measurements (e.g. D_{DOC}) for ionizable chemicals, since data currently available are relatively scarce and environmental behaviour much more complex to predict.

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5. References

- Arp, H.P.H., Breedveld, G.D., Cornelissen, G., 2009. Estimating the *in situ* sediment–porewater distribution of PAHs and chlorinated aromatic hydrocarbons in anthropogenic impacted sediments. *Environ. Sci. Technol.* 43, 5576–5585. <https://doi.org/10.1021/es9012905>
- Booij, K., Robinson, C.D., Burgess, R.M., Mayer, P., Roberts, C.A., Ahrens, L., Allan, I.J., Brant, J., Jones, L., Kraus, U.R., Larsen, M.M., Lepom, P., Petersen, J., Pröfrock, D., Roose, P., Schäfer, S., Smedes, F., Tixier, C., Vorkamp, K., Whitehouse, P., 2016. Passive sampling in regulatory chemical monitoring of nonpolar organic compounds in the aquatic environment. *Environ. Sci. Technol.* 50, 3–17. <https://doi.org/10.1021/acs.est.5b04050>
- Burkhard, L.P., 2000. Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. *Environ. Sci. Technol.* 34, 4663–4668. <https://doi.org/10.1021/es0012691>
- Camenzuli, L., Scheringer, M., Gaus, C., Ng, C.A., Hungerbühler, K., 2012. Describing the environmental fate of diuron in a tropical river catchment. *Sci. Total Environ.* 440, 178–185. <https://doi.org/10.1016/j.scitotenv.2012.07.037>
- Cornelissen, G., Gustafsson, Ö., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., van Noort, P.C.M., 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* 39, 6881–6895. <https://doi.org/10.1021/es050191b>

- Cui, X., Mayer, P., Gan, J., 2013. Methods to assess bioavailability of hydrophobic organic contaminants: Principles, operations, and limitations. *Environ. Pollut.* 172, 223–234. <https://doi.org/10.1016/j.envpol.2012.09.013>
- Di Guardo, A., Gouin, T., MacLeod, M., Scheringer, M., 2018. Environmental fate and exposure models: advances and challenges in 21st century chemical risk assessment. *Environ. Sci. Process. Impacts* 20, 58–71. <https://doi.org/10.1039/C7EM00568G>
- Di Guardo, A., Hermens, J.L., 2013. Challenges for exposure prediction in ecological risk assessment: challenges in exposure prediction. *Integr. Environ. Assess. Manag.* 9, e4–e14. <https://doi.org/10.1002/ieam.1442>
- Di Toro, D.M., Zarba, C.S., Hansen, D.J., Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P., Allen, H.E., Thomas, N.A., Paquin, P.R., 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* 10, 1541–1583. <https://doi.org/10.1002/etc.5620101203>
- EC (European Commission), 2013. Addressing the new challenges for risk assessment. Opinion adopted in March 2013. SCHER (Scientific Committee on Health and Environmental Risks), SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks), SCCS (Scientific Committee on Consumer Safety). http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_131.pdf.
- EC (European Commission), 2004. European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). Background report 601900005/2004. <http://www.pbl.nl/sites/default/files/cms/publicaties/601900005.pdf>.

- EC (European Commission), 2003. Technical guidance document on risk assessment; 2nd ed; EUR 20418 EN/2.
http://echa.europa.eu/documents/10162/16960216/tgdpart2_2ed_en.pdf.
- Ehlers, L.J., Luthy, R.G., 2003. Peer reviewed: contaminant bioavailability in soil and sediment. Environ. Sci. Technol. 37, 295A-302A. <https://doi.org/10.1021/es032524f>
- Enell, A., Lundstedt, S., Arp, H.P.H., Josefsson, S., Cornelissen, G., Wik, O., Berggren Kleja, D., 2016. Combining leaching and passive sampling to measure the mobility and distribution between porewater, DOC, and colloids of native Oxy-PAHs, N-PACs, and PAHs in historically contaminated soil. Environ. Sci. Technol. 50, 11797–11805. <https://doi.org/10.1021/acs.est.6b02774>
- Franco, A., Fu, W., Trapp, S., 2009. Influence of soil pH on the sorption of ionizable chemicals: modeling advances. Environ. Toxicol. Chem. 28, 458. <https://doi.org/10.1897/08-178.1>
- Franco, A., Trapp, S., 2008. Estimation of the soil–water partition coefficient normalized to organic carbon for ionizable organic chemicals. Environ. Toxicol. Chem. 27, 1995–2004. <https://doi.org/10.1897/07-583.1>
- Gauthier, T.D., Seitz, W.R., Grant, C.L., 1987. Effects of structural and compositional variations of dissolved humic materials on pyrene Koc values. Environ. Sci. Technol. 21, 243–248. <https://doi.org/10.1021/es00157a003>
- Ghirardello, D., Morselli, M., Otto, S., Zanin, G., Di Guardo, A., 2014. Investigating the need for complex vs. simple scenarios to improve predictions of aquatic ecosystem exposure with the SoilPlus model. Environ. Pollut. 184, 502–510. <https://doi.org/10.1016/j.envpol.2013.10.002>

- Ghirardello, D., Morselli, M., Semplice, M., Di Guardo, A., 2010. A dynamic model of the fate of organic chemicals in a multilayered air/soil system: Development and illustrative application. *Environ. Sci. Technol.* 44, 9010–9017. <https://doi.org/10.1021/es1023866>
- Haftka, J.J.H., Govers, H.A.J., Parsons, J.R., 2010. Influence of temperature and origin of dissolved organic matter on the partitioning behavior of polycyclic aromatic hydrocarbons. *Environ. Sci. Pollut. Res.* 17, 1070–1079. <https://doi.org/10.1007/s11356-009-0263-9>
- Hansen, K.M., Christensen, J.H., Brandt, J., Frohn, L.M., Geels, C., 2004. Modelling atmospheric transport of α -hexachlorocyclohexane in the Northern Hemisphere with a 3-D dynamical model: DEHM-POP. *Atmospheric Chem. Phys.* 4, 1125–1137. <https://doi.org/10.5194/acp-4-1125-2004>
- Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. <https://doi.org/10.1097/00010694-200004000-00001>
- Krop, H.B., van Noort, P.C.M., Govers, H.A.J., 2001. Determination and theoretical aspects of the equilibrium between dissolved organic matter and hydrophobic organic micropollutants in water (Kdoc), in: Ware, G.W. (Ed.), *Rev. Environ. Contam. Toxicol.* Springer New York, New York, NY, pp. 1–122. https://doi.org/10.1007/978-1-4613-0107-3_1
- Lang, S.-C., Hursthouse, A., Mayer, P., Kötke, D., Hand, I., Schulz-Bull, D., Witt, G., 2015. Equilibrium passive sampling as a tool to study polycyclic aromatic hydrocarbons in Baltic Sea sediment pore-water systems. *Mar. Pollut. Bull.* 101, 296–303. <https://doi.org/10.1016/j.marpolbul.2015.10.069>

- Lindim, C., van Gils, J., Cousins, I.T., 2016. A large-scale model for simulating the fate & transport of organic contaminants in river basins. *Chemosphere* 144, 803–810. <https://doi.org/10.1016/j.chemosphere.2015.09.051>
- Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, J.J., Reinhard, M., Traina, S.J., Weber, W.J., Westall, J.C., 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* 31, 3341–3347. <https://doi.org/10.1021/es970512m>
- Lydy, M.J., Landrum, P.F., Oen, A.M., Allinson, M., Smedes, F., Harwood, A.D., Li, H., Maruya, K.A., Liu, J., 2014. Passive sampling methods for contaminated sediments: state of the science for organic contaminants. *Integr. Environ. Assess. Manag.* 10, 167–178. <https://doi.org/10.1002/ieam.1503>
- Mackay, D., 1979. Finding fugacity feasible. *Environ. Sci. Technol.* 13, 1218–1223. <https://doi.org/10.1021/es60158a003>
- Mackay, D., Di Guardo, A., Paterson, S., Cowan, C.E., 1996a. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. *Environ. Toxicol. Chem.* 15, 1627–1637. <https://doi.org/10.1002/etc.5620150929>
- Mackay, D., Di Guardo, A., Paterson, S., Kicsi, G., Cowan, C.E., Kane, D.M., 1996b. Assessment of chemical fate in the environment using evaluative, regional and local-scale models: illustrative application to chlorobenzene and linear alkylbenzene sulfonates. *Environ. Toxicol. Chem.* 15, 1638–1648. <https://doi.org/10.1002/etc.5620150930>
- Mackay, D., Paterson, S., 1981. Calculating fugacity. *Environ. Sci. Technol.* 15, 1006–1014. <https://doi.org/10.1021/es00091a001>

- Mäenpää, K., Leppänen, M.T., Reichenberg, F., Figueiredo, K., Mayer, P., 2011. Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment: comparison of two approaches to determine equilibrium partitioning concentrations in lipids. *Environ. Sci. Technol.* 45, 1041–1047. <https://doi.org/10.1021/es1029969>
- Mayer, P., Parkerton, T.F., Adams, R.G., Cargill, J.G., Gan, J., Gouin, T., Gschwend, P.M., Hawthorne, S.B., Helm, P., Witt, G., You, J., Escher, B.I., 2014. Passive sampling methods for contaminated sediments: scientific rationale supporting use of freely dissolved concentrations. *Integr. Environ. Assess. Manag.* 10, 197–209. <https://doi.org/10.1002/ieam.1508>
- Mayer, P., Tolls, J., Hermens, J.L., Mackay, D., 2003. Peer reviewed: equilibrium sampling devices. ACS Publications.
- Mayer, P., Vaes, W.H.J., Wijnker, F., Legierse, K.C.H.M., Kraaij, R.H., Tolls, J., Hermens, J.L.M., 2000. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ. Sci. Technol.* 34, 5177–5183. <https://doi.org/10.1021/es001179g>
- McCarthy, J.F., Zachara, J.M., 1989. Subsurface transport of contaminants. *Environ. Sci. Technol.* 23, 496–502. <https://doi.org/10.1021/es00063a001>
- Moeckel, C., Nizzetto, L., Di Guardo, A., Steinnes, E., Freppaz, M., Filippa, G., Camporini, P., Benner, J., Jones, K.C., 2008. Persistent organic pollutants in boreal and montane soil profiles: distribution, evidence of processes and implications for global cycling. *Environ. Sci. Technol.* 42, 8374–8380. <https://doi.org/10.1021/es801703k>

- Morselli, M., Ghirardello, D., Semplice, M., Di Guardo, A., 2011. Modeling short-term variability of semivolatile organic chemicals in air at a local scale: An integrated modeling approach. *Environ. Pollut.* 159, 1406–1412. <https://doi.org/10.1016/j.envpol.2010.12.034>
- Morselli, M., Ghirardello, D., Semplice, M., Raspa, G., Di Guardo, A., 2012. Integration of an atmospheric dispersion model with a dynamic multimedia fate model: development and illustration. *Environ. Pollut.* 164, 182–187. <https://doi.org/10.1016/j.envpol.2012.01.039>
- Morselli, M., Semplice, M., De Laender, F., Van den Brink, P.J., Di Guardo, A., 2015. Importance of environmental and biomass dynamics in predicting chemical exposure in ecological risk assessment. *Sci. Total Environ.* 526, 338–345. <https://doi.org/10.1016/j.scitotenv.2015.04.072>
- NRC (National Research Council), 1983. Risk assessment in the Federal Government: managing the process.
- Ortega-Calvo, J.J., Harmsen, J., Parsons, J.R., Semple, K.T., Aitken, M.D., Ajao, C., Eadsforth, C., Galay-Burgos, M., Naidu, R., Oliver, R., Peijnenburg, W.J.G.M., Römbke, J., Streck, G., Versonnen, B., 2015. From bioavailability science to regulation of organic chemicals. *Environ. Sci. Technol.* 49, 10255–10264. <https://doi.org/10.1021/acs.est.5b02412>
- Pignatello, J.J., 2012. Dynamic interactions of natural organic matter and organic compounds. *J. Soils Sediments* 12, 1241–1256. <https://doi.org/10.1007/s11368-012-0490-4>
- Pignatello, J.J., Xing, B., 1995. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ. Sci. Technol.* 30, 1–11. <https://doi.org/10.1021/es940683g>
- Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils. *Environ. Toxicol. Chem.* 25, 1239–1245. <https://doi.org/10.1897/05-458R.1>

- Schäfer, S., Antoni, C., Möhlenkamp, C., Claus, E., Reifferscheid, G., Heininger, P., Mayer, P., 2015. Equilibrium sampling of polychlorinated biphenyls in River Elbe sediments – Linking bioaccumulation in fish to sediment contamination. *Chemosphere* 138, 856–862. <https://doi.org/10.1016/j.chemosphere.2015.08.032>
- Schwarzenbach, R.P., 2006. The challenge of micropollutants in aquatic systems. *Science* 313, 1072–1077. <https://doi.org/10.1126/science.1127291>
- Suffet, I.H., Jafvert, C.T., Kukkonen, J., Servos, M.R., Spacie, A., Williams, L.L., Noblet, J.A., 1994. Synopsis of discussion session: influences of particulate and dissolved material on the bioavailability of organic compounds. *Bioavailab. Phys. Chem. Biol. Interact.* 93–108.
- ter Laak, T.L., Gebbink, W.A., Tolls, J., 2006. Estimation of soil sorption coefficients of veterinary pharmaceuticals from soil properties. *Environ. Toxicol. Chem.* 25, 933. <https://doi.org/10.1897/05-229R.1>
- Terzaghi, E., Morselli, M., Semplice, M., Cerabolini, B.E.L., Jones, K.C., Freppaz, M., Di Guardo, A., 2017. SoilPlusVeg: An integrated air-plant-litter-soil model to predict organic chemical fate and recycling in forests. *Sci. Total Environ.* 595, 169–177. <https://doi.org/10.1016/j.scitotenv.2017.03.252>
- Terzaghi, E., Zanardini, E., Morosini, C., Raspa, G., Borin, S., Mapelli, F., Vergani, L., Di Guardo, A., 2018. Rhizoremediation half-lives of PCBs: role of congener composition, organic carbon forms, bioavailability, microbial activity, plant species and soil conditions, on the prediction of fate and persistence in soil. *Sci. Total Environ.* 612, 544–560. <https://doi.org/10.1016/j.scitotenv.2017.08.189>

Warren, C., Mackay, D., Whelan, M., Fox, K., 2005. Mass balance modelling of contaminants in river basins: a flexible matrix approach. *Chemosphere* 61, 1458–1467.

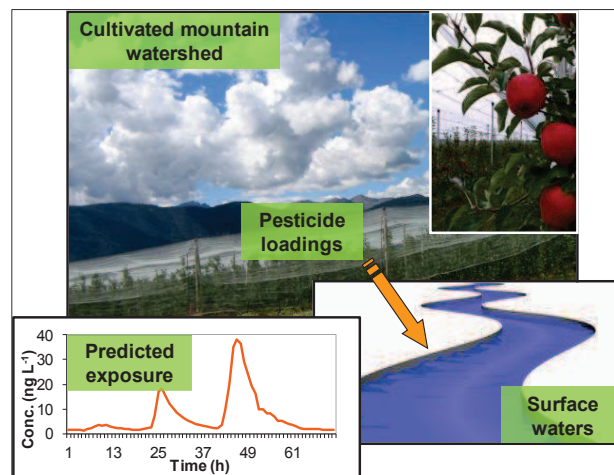
<https://doi.org/10.1016/j.chemosphere.2005.04.118>

Xing, B., Pignatello, J.J., 1997. Dual-mode sorption of low-polarity compounds in glassy poly (vinyl chloride) and soil organic matter. *Environ. Sci. Technol.* 31, 792–799.

<https://doi.org/10.1021/es960481f>

Individual studies

Paper I: Predicting pesticide fate in small cultivated mountain watersheds using the DynAPlus model: Toward improved assessment of peak exposure



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